Nickel-Catalyzed Carbonylation of Secondary Trifluoromethylated, Difluoromethylated and Nonfluorinated Aliphatic Electrophiles with Arylboronic Acids under 1 atm of CO

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1. General Information

**General Information:** $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM400, AM500 and Agilent 400 spectrometer and are calibrated using residual undeuterated solvent (CHCl$_3$ at 7.26 ppm $^1$H NMR, 77.00 ppm $^{13}$C NMR). $^{19}$F NMR was recorded on a Bruker AM400 spectrometer (CFCl$_3$ as an external standard and low field is positive). Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by $^{19}$F NMR using fluorobenzene as an internal standard before working up the reaction.

**Materials:** All reagents were used as received from commercial sources without further purification, unless specified otherwise, or prepared as described in the literature. Super dry solvents were purchased from commercial sources. NiBr$_2$-DME was purchased from Strem and kept in glove box, 1,10-Phenanthroline was purchased from J & K Chemicals, K$_2$CO$_3$ was ground to a fine powder and kept in glove box. The following compounds were prepared according to the literature, and the characterization data was consistent with those reported in the literature.
2. Optimizations for the Nickel-Catalyzed Carbonylation of Secondary Aliphatic Electrophile 1a with Arylboronic Acid 2a (Tables S1-S7).

To a 25 mL of Schlenk tube were added ligand (3-12 mol%), arylboronic acid 2b (1.5 equiv), nickel catalyst (2.5-10 mol%) and base (3.0 equiv) in a glove box. The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). Secondary alkyl iodide 1a (0.3 or 0.5 mmol, 1.0 equiv) and dioxane (3 or 5 mL) were then added. The tube was screw capped and put into a preheated oil bath (rt to 80 °C). After stirring for 8 to 12 h, the reaction mixture was cooled to room temperature. The yield was determined by $^{19}$F NMR using fluorobenzene as an internal standard before working up. If necessary, the reaction mixture was diluted with ethyl acetate and H$_2$O. The resulting mixture was then extracted with ethyl acetate, the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified with silica gel chromatography to give product 3b.
Table S1. Ligand effect on Nickel-Catalyzed Carbonylation of Secondary Aliphatic Electrophile 1a with Arylboronic Acid 2b.\(^{[a]}\)

\[
\text{\textbf{Entry}} \quad \text{\textbf{Ligand}} \quad \text{\textbf{Yield [%]}^{[b]}}
\]

\begin{tabular}{llll}
1 & L1 & 1 & 12 & 69 \\
2 & L2 & 6 & 29 & 55 \\
3 & L3 & 5 & 16 & 62 \\
4 & L4 & 6 & ND & 93 \\
5 & L5 & 28 & ND & 66 \\
\end{tabular}

[a] Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), 2b (0.45 mmol, 1.5 equiv), dioxane (3 mL).

[b] Determined by \(^{19}\text{F}\) NMR using fluorobenzene as an internal standard. ND, not detected.
### Table S2. Screening of the Nickel Sources.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Ni]</th>
<th>Yield [%][b]</th>
<th>1a</th>
<th>3b</th>
<th>6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl₂·DME</td>
<td>6</td>
<td>29</td>
<td>ND</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>NiCl₂</td>
<td>98</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>NiBr₂</td>
<td>97</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>NiI₂</td>
<td>ND</td>
<td>67</td>
<td>23</td>
<td>107</td>
</tr>
<tr>
<td>5</td>
<td>NiBr₂·DME</td>
<td>ND</td>
<td>1</td>
<td>52</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>NiCl₂(PPh₃)₂</td>
<td>ND</td>
<td>52</td>
<td>33</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td>NiBr₂(PPh₃)₂</td>
<td>ND</td>
<td>40</td>
<td>28</td>
<td>28</td>
</tr>
</tbody>
</table>

[a] Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), 2b (0.45 mmol, 1.5 equiv), dioxane (3 mL).

[b] Determined by \(^{19}\text{F NMR}\) using fluorobenzene as an internal standard. ND, not detected.

### Table S3. Screening of the Solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield [%][b]</th>
<th>1a</th>
<th>3b</th>
<th>6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dioxane</td>
<td>ND</td>
<td>67</td>
<td>23</td>
<td>23</td>
</tr>
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<td>2</td>
<td>THF</td>
<td>ND</td>
<td>49</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>Triglyme</td>
<td>ND</td>
<td>98</td>
<td>ND</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>89</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>DCM</td>
<td>81</td>
<td>2</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

[a] Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), 2b (0.45 mmol, 1.5 equiv), solvent (3 mL).

[b] Determined by \(^{19}\text{F NMR}\) using fluorobenzene as an internal standard. ND, not detected.
**Table S4.** Screening of the Bases.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield [%](^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K₂CO₃</td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td>KOAc</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>K₃PO₄</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>Na₂CO₃</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>Cs₂CO₃</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>NaOCH₃</td>
<td>ND</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), 2b (0.45 mmol, 1.5 equiv), dioxane (3 mL).

\(^{[b]}\) Determined by \(^{19}\)F NMR using fluorobenzene as an internal standard. ND, not detected.

**Table S5.** Screening of the Reaction Temperature.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>Yield [%](^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rt</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>ND</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Reaction conditions (unless otherwise specified): 1a (0.3 mmol, 1.0 equiv), 2b (0.45 mmol, 1.5 equiv), dioxane (3 mL).

\(^{[b]}\) Determined by \(^{19}\)F NMR using fluorobenzene as an internal standard. ND, not detected.
Table S6. Optimization of the Reaction Parameters.\textsuperscript{[a]}

![Chemical structures](image1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>2b/1a</th>
<th>x</th>
<th>y</th>
<th>Time (h)</th>
<th>Yield [%]\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>10</td>
<td>12</td>
<td>8 h</td>
<td>ND 62 35</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>10</td>
<td>12</td>
<td>8 h</td>
<td>ND 67 23</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>10</td>
<td>12</td>
<td>8 h</td>
<td>ND 66 25</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>5</td>
<td>6</td>
<td>8 h</td>
<td>4 60 28</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>2.5</td>
<td>3</td>
<td>8 h</td>
<td>ND 33 52</td>
</tr>
<tr>
<td>6\textsuperscript{[c]}</td>
<td>1.5</td>
<td>5</td>
<td>6</td>
<td>12 h</td>
<td>ND 71 (70) 21</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Reaction conditions (unless otherwise specified): 1a (0.3 mmol), dioxane (3 mL). \textsuperscript{[b]} Determined by \textsuperscript{19}F NMR using fluorobenzene as an internal standard. The number given in parentheses is the isolated yield. \textsuperscript{[c]} 1a (0.5 mmol, 1.0 equiv), 2b (0.75 mmol, 1.5 equiv), dioxane (5 mL). ND, not detected.

Table S7. Control Experiments.\textsuperscript{[a]}

![Chemical structures](image2)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield [%]\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without [Ni]</td>
<td>96 ND ND</td>
</tr>
<tr>
<td>2</td>
<td>Without Ligand</td>
<td>94 ND ND</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Reaction conditions (unless otherwise specified): 1a (0.5 mmol, 1.0 equiv), 2b (0.75 mmol, 1.5 equiv), dioxane (5 mL). \textsuperscript{[b]} Determined by \textsuperscript{19}F NMR using fluorobenzene as an internal standard. ND, not detected.
3. Mechanistic Studies

a) Reaction of Nickel Complex A1 with CO (1 atm)

**Procedure:** To a 10 mL sealed tube was charged with nickel complex (A1)[6] (24 mg), fluorobenzene (0.01 mmol, used as an internal standard) and CD$_2$Cl$_2$ (0.75 mL) under Ar at room temperature. The NMR tube was evacuated and backfilled with CO balloon (1 atm). The reaction was monitored by $^{19}$F NMR and showed a 71% yield (determined by $^{19}$F NMR) of acyl nickel complex B1 was generated after consuming of A1. The $^{19}$F NMR data of B1 is consistent with the literature.[6] $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.85 (s, 1H), 8.62 (s, 2H), 7.86 (s, 2H), 7.69 (s, 1H), 7.51 (s, 1H), 7.20 (s, 1H), 7.11 (s, 2H), 1.40 (s, 9H), 1.34 (s, 9H) (Note: the signals at 3.68 ppm and 1.84 ppm are the protons of THF). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) $\delta$ -109.3 (m).

b) Reaction of B1 with 1a

**Procedure:** To a 25 mL of Schlenk tube were added nickel complex B1[6] (0.1 mmol, 1.0 equiv) and 1a (0.1 mmol, 1.0 equiv) in a glovebox. To the Schlenk tube was added dioxane (2 mL). The tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. $^{19}$F NMR showed a 52% yield of compound 3a was produced and no compound 4a was observed. Data for compound 3a: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85-7.81 (m, 2H), 7.30 – 7.08 (m, 3H), 7.15-7.07 (m, 4 H), 4.17 – 4.03 (m, 1H), 2.82 – 2.67 (m, 1H), 2.63 – 2.39 (m, 2H), 2.30 – 2.16 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.0 (d, $J = 8.3$ Hz, 3F), -103.3 – -103.4 (m, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.5 (m), 166.3 (d, $J = 257.1$ Hz), 139.7, 133.0, 128.6, 128.5,
126.6, 124.9 (q, \( J = 281.0 \text{ Hz} \)), 116.1, 115.9, 48.1 (q, \( J = 25.5 \text{ Hz} \)), 32.6, 28.0 (q, \( J = 2.1 \text{ Hz} \)). MS (EI): m/z (%) 310.1 (M⁺), 104 (100). HRMS: Calculated for C₁₇H₁₄F₄O: 310.0981; Found: 310.0977.

c) Preparation of Nickel Complex B2

![Chemical structure of B2]

**Procedure:** The preparation of nickel complex (B2) is a modification of the literature method.[⁶] To a Schlenk tube was charged with Ni(COD)₂ (550 mg, 2.0 mmol), 1,10-phenanthroline (360 mg, 2.0 mmol) and degassed dry THF (5 mL) under Ar. The resulting dark solution was stirred for 1 hour at room temperature. The corresponding benzoyl chloride (2.1 mmol, 1.05 equiv) was then added and the reaction mixture was stirred for 10 mins (Note: the color of solution turn to red immediately after the addition of benzoyl chloride). The resulting dark red solution was triturated with degassed dry pentane and the precipitate was collected on a frit immediately. And the complex was rinsed with pentane and dried under vacuum to give nickel complex B2 as a dark red powder (660 mg, 76% yield) (Note: Complex B2 is unstable in solution). ¹H NMR (400 MHz, CD₂Cl₂) δ 9.24 (d, \( J = 4.6 \text{ Hz} \), 1H), 8.72 (dd, \( J = 8.2, 5.6 \text{ Hz} \), 2H), 8.45 (t, \( J = 10.8 \text{ Hz} \), 2H), 8.16 (d, \( J = 4.7 \text{ Hz} \), 1H), 7.99 – 7.79 (m, 3H), 7.54 (s, 1H), 7.14 (t, \( J = 8.4 \text{ Hz} \), 2H) (Note: the signals at 3.68 ppm and 1.84 ppm are the protons of THF). ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -108.9 (m).

d) Reaction of B2 with 1a

![Chemical structures of reactions]

**Procedure:** To a 25 mL of Schlenk tube were added nickel complex B2 (0.1 mmol, 1.0 equiv), 1a (0.1 mmol, 1.0 equiv) and dioxane (2 mL) in a glovebox. The tube was screw capped and put into a
preheated oil bath (80°C). After stirring for 12 h, the reaction mixture was cooled to room temperature. $^{19}$F NMR showed an 83% yield of compound $3a$ was produced and no $4a$ was observed.

e) Reaction of Arylboronic Acid 2a or Secondary Aliphatic Electrophile 1a with MeOH under 1 atm of CO

![Chemical Reaction Diagram]

**Procedure:** To a 25 mL of Schlenk tube were added L2 (0.3 mmol, 60 mol%) and arylboronic acid 2a or 1a (0.5 mmol, 1 equiv) under air, followed by addition of NiBr$_2$-DME (0.25 mmol, 50 mol%) and K$_2$CO$_3$ (1.5 mmol, 3.0 equiv). The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). To the Schlenck tube was added MeOH (1.0 mmol, 2.0 equiv) and dioxane (5 mL). The tube was screw capped and put into a preheated oil bath (80°C). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and H$_2$O. The resulting mixture was then extracted with ethyl acetate, the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified with silica gel chromatography (PE:EA = 20:1) to give compound 12 (16 mg, 21% yield). While no compound 13 was detected. Data for compound 12: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 – 7.93 (m, 2H), 7.13 – 7.06 (m, 2H), 3.90 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -105.9 (m). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.1, 165.7 (d, $J = 253.7$ Hz), 132.1 (d, $J = 9.3$ Hz), 126.3 (d, $J = 3.0$ Hz), 115.5 (d, $J = 22.0$ Hz), 52.2.
f) Radical Inhibition Experiments

Reaction of B2 with 1a in the Presence of Radical Scavenger 14

Procedure: To a 25 mL of Schlenk tube were added nickel complex B2 (0.1 mmol, 1.0 equiv), 1a (0.1 mmol, 1.0 equiv), 14 (0.2 mmol, 1.0 equiv) and dioxane (2 mL) in a glovebox. The tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. $^{19}$F NMR showed a 32% yield of compound 3a was provided.

Reaction of 1a with 2a in the Presence of Radical Scavenger 14 and Catalytic Amount of B2 under 1 atm of CO

Procedure: To a 25 mL of Schlenk tube were added arylboronic acid 2a (0.75 mmol, 1.5 equiv), nickel complex B2 (0.05 mmol, 10 mol%) and K$_2$CO$_3$ (1.5 mmol, 3.0 equiv.) in a glove box. The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). To the Schlenck tube was added secondary alkyl iodide 1a (0.5 mmol, 1.0 equiv), α-phenyl styrene (0 or 2.0 equiv) and dioxane (5 mL). The tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction was monitored by $^{19}$F NMR (x = 2.0, 3a, 38% yield; x = 0, 3a, 72% yield).

g) Radical Clock Experiment

Procedure: To a 25 mL of Schlenk tube were added L2 (0.03 mmol, 6 mol%), arylboronic acid 2a (0.75 mmol, 1.5 equiv), NiBr$_2$-DME (0.025 mmol, 5 mol%) and K$_2$CO$_3$ (1.5 mmol, 3.0 equiv) in a
glove box. The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). To the
Schlenk tube was added secondary alkyl iodide 1a (0.5 mmol, 1.0 equiv), α-cyclopropyl styrene 15
(1.0 mmol, 2.0 equiv) and dioxane (5 mL). The tube was screw capped and put into a preheated oil
bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. The yield
was determined by 19F NMR using fluorobenzene as an internal standard before working up. The
product 16 was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50 / 1) as a
colorless oil (38 mg, 23%). Data for compound 16: 1H NMR (400 MHz, CDCl3) δ 7.24 – 7.08 (m, 7H),
7.03 (d, J = 7.0 Hz, 2H), 5.92 (t, J = 4.0 Hz, 1H), 3.10 – 2.94 (m, 2H), 2.80 – 2.65 (m, 3H), 2.64 – 2.53
(m, 1H), 2.47 – 2.32 (m, 2H), 2.32 – 2.20 (m, 2H), 1.97 – 1.73 (m, 2H). 19F NMR (376 MHz, CDCl3)
δ -70.2 (d, J = 8.4 Hz). 13C NMR (101 MHz, CDCl3) δ 141.2, 136.9, 133.5, 132.7, 128.6 (q, J = 280.5
Hz), 128.33, 128.32, 128.2, 127.9, 127.0, 126.5, 126.0, 122.4, 39.9 (q, J = 24.6 Hz), 33.0, 32.0 (q, J =
3.0 Hz), 29.4, 28.3, 23.1. MS (EI): m/z (%) 330.2 (M+), 129.1 (100). HRMS: Calculated for C21H21F3:
330.1595; Found: 330.1600.

4. General Procedure for the Preparation of Secondary Alkyl Iodides

General procedure A

![Chemical diagram]

Trifluoromethylation of the aldehyde:[1] A solution of TBAF (1.0 M in THF, 0.30 mmol, 0.01 equiv)
was added to a solution of the aldehyde (30 mmol) and TMSCF3 (36 mmol, 1.2 equiv) in THF (50 mL)
at 0 °C over 3 min. The reaction mixture was warmed to room temperature, and stirred for 2~3 h. The
reaction was quenched with an aqueous solution of HCl (2 M, 30 mL). The resulting mixture was
stirred at room temperature for another 2~3 h. Then, the reaction mixture was extracted with Et2O (3
× 50 mL), and the combined organic layers were dried over Na2SO4 and concentrated. The crude
product was purified by flash chromatography on silica gel to give alcohol 17.

Iodination of the alcohol 17:[2] A dry 250 mL flask was charged with alcohol 17 (5 mmol), PPh3 (20
mmol), imidazole (13.5 mmol), iodine (13.5 mmol) and toluene (50 mL). The resulting mixture was
stirred at 110 °C for 3 h. The reaction was quenched with water (50 mL). The aqueous phase was
extracted with petroleum ether (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel to give secondary aliphatic iodide 1.

**General procedure B**

![Chemical structure](image)

**Preparation of the ketone:**[¹] A solution of the Grignard reagent in THF (45 mmol) was added dropwise by a syringe to a solution of the ester (30 mmol) in THF (30 mL) at -78 °C. After stirring at -78 °C for 1 min, the reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched with saturated aqueous NH₄Cl solution at 0 °C. The organic solvent was removed, and the mixture was extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over Na₂SO₄, and concentrated. The crude product was purified by flash chromatography on silica gel to give ketone 18.

**Reduction of the ketone 18:**[¹] NaBH₄ (30 mmol, 1.5 equiv) was added in portions to a solution of the ketone 18 (20 mmol) in EtOH (20 mL) at 0 °C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C, and quenched with saturated aqueous NH₄Cl solution. The EtOH was removed, 50 mL H₂O was added. The resulting mixture was extracted with Et₂O (3 x 50 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel to give alcohol 17. The iodination step is the same with General Procedure A.

**(4,4,4-Trifluoro-3-iodobutyl)benzene (1a).** The reaction was carried out on 10 mmol scale. Compound 1a (1.97g, 63% yield) as a colorless oil was synthesized according to the General Procedure A, and was purified with silica gel chromatography (Hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.11 (m, 5H), 4.12 – 3.86 (m, 1H), 2.34 – 2.85 (m, 1H), 2.77 – 2.53 (m, 1H), 2.29 – 2.01 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -68.8 (d, J = 7.9 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 128.7, 128.5, 126.7, 124.6 (q, J = 276.5 Hz), 34.4, 34.2 (q, J = 1.8 Hz), 23.6 (q, J = 31.0 Hz).
1,1,1-Trifluoro-2-iodooctane (1b). Compound 1b (999.6 mg, 68% yield) as a colorless oil was synthesized according to the General Procedure A, and was purified with silica gel chromatography (Hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.20 – 4.08 (m, 1H), 1.84 (q, $J$ = 7.2 Hz, 2H), 1.67 – 1.55 (m, 1H), 1.47 – 1.22 (m, 7H), 0.97 – 0.81 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -67.0 (d, $J$ = 8.9 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 124.6 (q, $J$ = 276.5 Hz), 32.6 (q, $J$ = 30.9 Hz), 31.4, 28.9, 28.1, 24.6 (q, $J$ = 31.0 Hz), 22.5, 14.0. MS (EI): m/z (%) 294.0 (M$^+$), 57.1 (100). HRMS: Calculated for C$_8$H$_{14}$F$_3$I: 294.0092; Found: 294.0098.

(Z)-8,8,8-Trifluoro-7-iodooct-3-ene (1d). Compound 1d (949 mg, 65% yield) as a colorless oil was synthesized according to the General Procedure A, and was purified with silica gel chromatography (Hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.55 – 5.45 (m, 1H), 5.27 – 5.17 (m, 1H), 4.20 – 4.08 (m, 1H), 2.36 – 2.06 (m, 4H), 1.95 – 1.86 (m, 2H), 0.99 (t, $J$ = 7.5 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.9 (d, $J$ = 8.1 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.7, 125.4, 124.6 (q, $J$ = 276.4 Hz), 125.4, 124.6 (q, $J$ = 276.5 Hz), 32.7, 26.1, 23.8 (q, $J$ = 31.0 Hz), 20.9, 14.4. MS (EI): m/z (%) 292.0 (M$^+$), 69.1 (100). HRMS: Calculated for C$_8$H$_{13}$F$_3$: 291.9936; Found: 291.9937.

2-Methyl-5-(4,4,4-trifluoro-3-iodobutyl)furan (1e). Compound 1e (1.3 g, 81% yield) as a colorless oil was synthesized according to the General Procedure A, and was purified with silica gel chromatography (petroleum ether = 100%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.96 (d, $J$ = 3.0 Hz, 1H), 5.86 (d, $J$ = 3.0 Hz, 1H), 4.17 – 4.05 (m, 1H), 2.97 – 2.85 (m, 1H), 2.76 – 2.35 (m, 1H), 2.26 (s, 3 H), 2.30 – 2.17 (m, 1H), 2.16 – 2.04 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.9 (d, $J$ = 8.1 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.2, 150.8, 107.1, 106.0, 31.4, 27.3, 23.3 (q, $J$ = 31.3 Hz), 13.6. MS (EI): m/z (%) 318.0 (M$^+$), 95.1 (100). HRMS: Calculated for C$_9$H$_{11}$F$_3$OI: 317.9728; Found: 317.9734.

5,5,5-Trifluoro-4-iodopentyl benzoate (1f). Compound 1f (1.11 g, 60% yield) as a colorless oil was synthesized according to the General Procedure A, and was purified with silica gel chromatography (Hexane/DCM = 5/1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 7.7 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 4.45 – 4.32 (m, 2H), 4.31 – 4.18 (m,
1H), 2.19 – 1.81 (m, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -68.9 (d, J = 8.5 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.4, 133.1, 129.9, 129.5, 128.4, 124.4 (q, J = 276.7 Hz), 63.3, 29.7 (q, J = 1.9 Hz), 28.3, 23.3 (q, J = 31.2 Hz). MS (EI): m/z (%) 372.0 (M$^+$), 352.0 ([M-HF]$^+$), 105 (100). HRMS: Calculated for C$_{12}$H$_{12}$F$_3$IO$_2$: 371.9834; Found: 371.9831.

(4,4-Difluoro-3-iodobutyl)benzene (1k). Compound 1k (1.08g, 73% yield) as a colorless oil was synthesized according to the General Procedure B, and was purified with silica gel chromatography (Hexane = 100). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (t, J = 7.4 Hz, 2H), 7.28 – 7.17 (m, 3H), 5.70 (td, J = 56.6 Hz, 3.5 Hz, 1H), 4.00 – 3.86 (m, 1H), 3.02 – 2.91 (m, 1H), 2.78 – 2.65 (m, 1H), 2.21 – 2.05 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.63 (ddd, J = 271.8 Hz, 56.6 Hz, 13.9 Hz, 1F), -116.91 (ddd, J = 271.8 Hz, 56.6 Hz, 14.2 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.6, 128.6, 128.5, 126.5, 115.5 (t, J = 246.2 Hz), 34.6, 33.5 (t, J = 2.8 Hz), 29.2 (t, J = 22.2 Hz). MS (EI): m/z (%) 296.1 (M$^+$), 91.2 (100). HRMS: Calculated for C$_{10}$H$_{11}$F$_2$I: 295.9874; Found: 295.9871.

Preparation of 5,5,5-trifluoro-4-iodopentan-1-ol (1f$'$)

Procedure: Sodium carbonate (30 mmol, 3.0 equiv) was added to the solution of 5,5,5-trifluoro-4-iodopentyl benzoate (1f) (10.0 mmol, 1.0 equiv) in methanol (50 mL). The reaction was stirred at room temperature overnight. The resulting mixture was filtered. The filtrate was concentrated and the residue was purified with flash chromatography on silica gel (petroleum ether / ethyl acetate = 5/1) to give 1f$'$ (2.28 g, 85%) as a light-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.28 – 4.15 (m, 1H), 3.70 – 3.67 (m, 2H), 2.15 (s, 1H), 2.08 – 1.78 (m, 3H), 1.70 – 1.57 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -69.0 (d, J = 8.0 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 124.5 (q, J = 276.6 Hz), 61.4, 31.7, 29.6 (q, J = 1.8 Hz), 24.0 (q, J = 31.1 Hz). MS (EI): m/z (%) 267.9 (M$^+$), 248.0 ([M-H$_2$O]$^+$). HRMS: Calculated for C$_5$H$_8$F$_3$IO: 267.9572; Found: 267.9580.
Preparation of 5,5,5-trifluoro-4-iodopentyl cyclopropanecarboxylate (1h)

**Procedure:** To a DCM (20 mL) solution of 1f (536 mg, 2.0 mmol, 1.0 equiv) were added cyclopropanecarboxylic acid (258 mg, 3.0 mmol, 1.5 equiv) and 4-dimethylaminopyridine (24 mg, 0.2 mmol, 0.1 equiv) at 0 °C. Then, a solution of DCC (619 mg, 3.0 mmol, 1.5 equiv) in DCM (15 mL) was added to the reaction mixture over 10 min. The resulting mixture was stirred at room temperature for 8 hours. The reaction mixture was filtered. The filtrate was concentrated and the residue was purified with flash chromatography on silica gel (petroleum ether / ethyl acetate = 5/1) to give 1h (619 mg, 92% yield) as a colorless oil. 

1H NMR (400 MHz, CDCl3) δ 4.28 – 4.03 (m, 3H), 2.07 – 1.84 (m, 3H), 1.82 – 1.66 (m, 1H), 1.66 – 1.55 (m, 1H), 1.02 – 0.96 (m, 2H), 0.90 – 0.83 (m, 2H). 

19F NMR (376 MHz, CDCl3) δ -69.0 (d, J = 7.8 Hz). 

13C NMR (101 MHz, CDCl3) δ 174.8, 124.4 (q, J = 276.6 Hz), 62.8, 29.6 (d, J = 2.1 Hz), 28.2, 23.4 (q, J = 31.3 Hz), 12.7, 8.6. 

MS (EI): m/z (%) 229.9 (100), 336.0 (M+). 

HRMS: Calculated for C9H12F3IO2: 335.9834; Found: 335.9830.

1-(tert-Butyl) 2-(5,5,5-trifluoro-4-iodopentyl) (2S)-pyrrolidine-1,2-dicarboxylate (1j). Compound 1j was prepared according to the procedure of the preparation of compound 1h. The product as a colorless viscous oil (780 mg, 86% yield) was purified with silica gel column chromatography (petroleum ether / ethyl acetate = 5/1). 

1H NMR (400 MHz, CDCl3) δ 4.32 – 4.03 (m, 4H), 3.59 – 3.26 (m, 1H), 2.28 – 2.08 (m, 1H), 2.04 – 1.62 (m, 7H), [1.42 (s, rotamer), 1.37 (s, rotamer)] (9H). 

19F NMR (376 MHz, CDCl3) δ -68.96 (dd, J = 7.9 Hz, 3.2 Hz, 1F, rotamer), -69.01 (dd, J = 8.3 Hz, 3.0 Hz, rotamer). 

13C NMR (101 MHz, CDCl3) δ 173.0 (172.9), 154.3 (153.6), 124.34 (124.34) (q, J = 276.4 Hz) 79.79 (79.72), 63.2, 59.0 (58.8), 46.5 (46.2), 30.9, 29.90 (29.87), 29.56 (29.55), 28.31 (28.24), 28.19, 24.30 (24.28), 23.53. 

MS (EI): m/z (%) 114.1 (100), 364.0 ([M-Boc]+). 

HRMS: Calculated for C15H23NF3IO4: 465.0624; Found: 465.0614.
5,5,5-Trifluoro-4-iodopentyl 2-(2-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)acetate (1p). Compound 1p was prepared according to the procedure of the preparation of compound 1h, but 2 equiv. of Et$_3$N was used. The product as a colorless viscous oil (664 mg, 52% yield) was purified with silica gel column chromatography (ethyl acetate = 100%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.34 (m, 4H), 7.30 – 7.15 (m, 5H), 4.25 – 4.13 (m, 4H), 4.10 (s, 2H), 3.66 (t, $J$ = 5.6 Hz, 2H), 2.63 (t, $J$ = 5.6 Hz, 2H), 2.62 – 2.28 (br, 8H), 2.08 – 1.89 (m, 3H). 1.75 – 1.66 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.9 (d, $J$ = 7.8 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.3, 142.1, 141.4, 132.5, 129.2, 128.6, 128.5, 127.8, 127.0, 124.4 (q, $J$ = 277.0 Hz), 75.4, 69.0, 68.3, 63.2, 57.7, 53.7, 51.6, 29.7, 28.2, 23.1 (q, $J$ = 31.2 Hz). MS (ESI): m/z (%) 200.99 (100), 639.04 ([M+H]$^+$). HRMS (ESI): Calculated for C$_{26}$H$_{32}$ClF$_3$IN$_2$O$_3$: 639.1093 ([M+H]$^+$); Found: 639.1096.

5,5,5-Trifluoro-4-iodopentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (1q). Compound 1q was prepared according to the procedure of the preparation of compound 1h. The product as a yellow viscous oil (619 mg, 51% yield) was purified with silica gel column chromatography (petroleum ether / ethyl acetate = 5/1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J$ = 8.6 Hz, 2H), 7.45 (d, $J$ = 8.6 Hz, 2H), 6.95 (d, $J$ = 2.5 Hz, 1H), 6.85 (d, $J$ = 9.0 Hz, 1H), 6.65 (dd, $J$ = 9.0, 2.5 Hz, 1H), 4.23 – 4.02 (m, 3H), 3.81 (s, 3H), 3.67 (s, 2H), 2.39 (s, 3H), 2.00 – 1.63 (m, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.9 (d, $J$ = 7.8 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.5, 168.0, 156.0, 139.0, 135.8, 133.7, 131.0, 130.7, 130.4, 129.0, 124.3 (q, $J$ = 277.0 Hz), 114.9, 112.2, 111.4, 101.2, 63.3, 55.5, 30.2, 29.5, 28.1, 23.0 (q, $J$ = 31.2 Hz), 13.2. m/z (%) 608.53 ([M+H]$^+$). HRMS (ESI): Calculated for C$_{24}$H$_{23}$ClF$_3$INO$_4$: 608.0307 ([M+H]$^+$); Found: 608.0305.
5. General Procedure for the Nickel-Catalyzed Carbonylation of Secondary Aliphatic Electrophiles with Arylboronic Acids under 1 atm of CO

To a 25 mL of Schlenk tube were added phen \( L_2 \) (0.03 mmol, 6 mol%), aryloboronic acid \( 2 \) (0.75 mmol, 1.5 equiv), \( \text{NiBr}_2 \cdot \text{DME} \) (0.025 mmol, 5 mol%) and \( \text{K}_2\text{CO}_3 \) (1.5 mmol, 3.0 equiv) in a glove box (Note: \( \text{K}_2\text{CO}_3 \) was grinded into powder and kept in glove box). The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). Secondary alkyl iodide \( 1 \) (0.5 mmol, 1.0 equiv) and dioxane (5 mL) were then added. The tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and \( \text{H}_2\text{O} \). The resulting mixture was extracted with ethyl acetate, the combined organic layers were washed with brine, dried over \( \text{Na}_2\text{SO}_4 \), filtered, and concentrated. The residue was purified with silica gel chromatography to give the corresponding product.

6. Characterization data for compounds 3 and 7

**1-(4-Fluorophenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3a).** The product (98 mg, 63% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50:1) as a colorless oil.

**1-(4-(tert-Butyl)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3b).** The product (122 mg, 70% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 60:1) as a light-yellow oil. \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.79 \ (d, J = 8.2 \text{ Hz, 2H}), 7.48 \ (d, J = 8.2 \text{ Hz, 2H}), 7.32 – 7.17 \ (m, 3H), 7.09 \ (d, J = 7.1 \text{ Hz, 2H}), \delta 4.24 – 4.09 \ (m, 1H), 2.80 – 2.67 \ (m, 1H), 2.62 – 2.39 \ (m, 2H), 2.24 – 2.15 \ (m, 1H), 1.36 \ (s, 9H). \(^{19}\text{F} \text{NMR} \ (376 \text{ MHz, CDCl}_3) \delta -65.9 \ (d, J = 8.5 \text{ Hz}). \(^{13}\text{C} \text{NMR} \ (101 \text{ MHz, CDCl}_3) \delta 193.6 \ (m), 158.0, 140.0, 134.1, 128.6, 128.54, 128.46, 126.4, 125.8, 125.5 \ (q, J = 268.8 \text{ Hz}), 48.1 \ (q, J = 25.3 \text{ Hz}), 35.2, 32.7, 31.0, 28.2. \text{MS (EI): } m/z \ (%) 333.2 ([M-CH3]^+), 229.2 \ (100). \text{HRMS: Calculated for C}_{21}\text{H}_{23}\text{F}_3\text{O}: 348.1701; Found: 348.1697.}

**Gram-Scale Synthesis of Compound 3b.**

Procedure: To a 500 mL of Schlenk tube were added phen \( L_2 \) (0.36 mmol, 6 mol%), aryloboronic acid
[Note: $K_2CO_3$ was grinded into powder and kept in glove box]. The resulting mixture was evacuated and backfilled with CO (1 atm, balloon). Secondary alkyl iodide 1 (6 mmol, 1.0 equiv) and dioxane (60 mL) were then added. The tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and H$_2$O. The resulting mixture was extracted with ethyl acetate, the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified with silica gel chromatography to give the corresponding product (1.34 g, 64% yield).

1-((1,1'-Biphenyl)-4-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3c).

The product (144 mg, 78% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 60:1) as a white solid (m.p. 51.5 – 52.5 °C).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 7.1$ Hz, 2H), 7.52 – 7.52 (m, 3H), 7.31 – 7.18 (m, 3H), 7.14 – 7.05 (m, 2H), 4.28 – 4.13 (m, 1H), 2.82 – 2.68 (m, 1H), 2.64 – 2.42 (m, 2H), 2.30 – 2.16 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.5 (d, $J = 8.5$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.6 (q, $J = 2.2$ Hz), 146.7, 139.9, 139.4, 135.2, 129.3, 129.0, 128.6, 128.5, 127.4, 127.3, 126.5, 125.0 (d, $J = 280.9$ Hz), 48.0 (q, $J = 25.3$ Hz), 32.6, 28.2 (q, $J = 2.1$ Hz). MS (EI): m/z (%) 368 (M$^+$), 264 (100). HRMS (DART): Calculated for C$_{23}$H$_{20}$F$_3$O ([M+H]$^+$): 369.1461; Found: 369.1459.

1-(4-(Benzyloxy)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3d).

The product (159 mg, 80% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50:1) as a white solid (m.p. 57.7 – 58.2 °C).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.9$ Hz, 2H), 7.48 – 7.34 (m, 5H), 7.31 – 7.18 (m, 3H), 7.09 (d, $J = 6.8$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 2H), 5.16 (s, 2H), 4.16 – 4.05 (m, 1H), 2.77 – 2.67 (m, 1H), 2.60 – 2.41 (m, 2H), 2.26 – 2.15 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.0 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.3 (q, $J = 2.1$ Hz), 163.4, 139.9, 135.9, 131.1, 129.8, 128.7, 128.5, 128.5, 128.3, 127.4, 126.4, 125.1 (q, $J = 280.9$ Hz), 114.8, 70.2, 47.7 (q, $J = 25.2$ Hz), 32.6, 28.1 (d, $J$
= 2.2 Hz). MS (EI): m/z (%) 398 (M⁺), 91 (100). HRMS: Calculated for C₂₄H₂₁F₃O₂: 398.1494; Found: 398.1497.

1-(3,5-Dimethoxyphenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3e). The product (134 mg, 76% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a light-yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.18 (m, 3H), 7.09 (d, J = 7.2 Hz, 2H), 6.97 (s, 2H), 6.70 (s, 1H), 4.16 – 4.04 (m, 1H), 3.80 (s, 6H), 2.76 – 2.64 (m, 1H), 2.61 – 2.37 (m, 2H), 2.26 – 2.14 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.9 (q, J = 2.1 Hz), 161.0, 139.8, 138.5, 128.6, 128.4, 126.5, 124.9 (q, J = 280.9 Hz), 106.4, 106.3, 55.5, 48.4 (q, J = 25.5 Hz), 32.6, 28.3 (q, J = 2.3 Hz). MS (EI): m/z (%) 352.2 (M⁺), 228.1 (100). HRMS: Calculated for C₁₉H₁₉F₃O₂: 352.1286; Found: 352.1287.

1-(Benzo[d][1,3]dioxol-5-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3f). L₃ was used. The product (118 mg, 70% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50:1) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.18 (m, 3H), 7.08 (d, J = 6.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 1H), 6.06 (s, 2H), 4.11 – 3.98 (m, 1H), 2.76 – 2.65 (m, 1H), 2.58 – 2.38 (m, 2H), 2.25 – 2.14 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.0 (d, J = 9.0 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 193.9 (q, J = 2.1 Hz), 161.0, 139.8, 138.5, 128.6, 128.4, 126.5, 124.9 (q, J = 280.9 Hz), 106.4, 106.3, 55.5, 48.4 (q, J = 25.5 Hz), 32.6, 28.3 (q, J = 2.3 Hz). MS (EI): m/z (%) 336.2 (M⁺), 232.1 (100). HRMS: Calculated for C₁₈H₁₅F₃O₃: 336.0973; Found: 336.0968.

1-(4-(Diphenylamino)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3g). L₃ was used. The product (175 mg, 76% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.9 Hz, 2H), 7.40 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.22 – 7.13 (m, 7H), 7.11 (d, J = 7.2 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.12 – 3.96 (m, 1H), 2.79 – 2.62 (m, 1H), 2.58 – 2.36 (m, 2H), 2.22 – 2.09 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.1 (d, J = 8.2 Hz).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 191.7 (q, \(J = 2.1\) Hz), 152.9, 146.0, 140.2, 130.4, 129.7, 128.5, 128.5, 126.4, 126.3, 125.2 (q, \(J = 280.8\) Hz), 118.8, 47.6 (q, \(J = 25.2\) Hz), 32.7, 28.2 (q, \(J = 2.1\) Hz). MS (ESI): m/z (%) 460.0 ([M+H]\(^+\), 100), 482.0 ([M+Na]\(^+\)). HRMS (DART): Calculated for C\(_{29}\)H\(_{25}\)F\(_3\)NO ([M+H]\(^+\)): 460.1883; Found: 460.1880.

**1-(4-Morpholinophenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3h).** L3 was used. The product (140 mg, 74% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30:1) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, \(J = 8.8\) Hz, 2H), 7.33 – 7.18 (m, 3H), 7.11 (d, \(J = 7.2\) Hz, 2H), 6.86 (d, \(J = 8.8\) Hz, 2H), 4.17 – 4.02 (m, 1H), 3.87 (t, \(J = 4.8\) Hz, 4H), 3.36 (t, \(J = 4.8\) Hz, 4H), 2.79 – 2.65 (m, 1H), 2.60 – 2.42 (m, 2H), 2.26 – 2.12 (m, 1H).

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -66.1 (d, \(J = 8.3\) Hz).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 191.6 (q, \(J = 2.3\) Hz), 154.7, 140.2, 130.9, 128.5, 127.2, 126.3, 125.2 (q, \(J = 280.9\) Hz), 113.0, 66.5, 47.4 (q, \(J = 24.8\) Hz), 47.1, 32.7, 28.2 (q, \(J = 2.6\) Hz). MS (ESI): m/z (%) 378.0 ([M+H]\(^+\), 100), 400.0 ([M+Na]\(^+\)). HRMS (DART): Calculated for C\(_{21}\)H\(_{23}\)F\(_3\)NO\(_2\) ([M+H]\(^+\)): 378.1675; Found: 378.1674.

**1-(4-(Ethylthio)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3i).** The product (123 mg, 70% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a light-yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.6\) Hz, 2H), 7.30 – 7.15 (m, 5H), 7.09 – 7.05 (m, 2H), 4.17 – 4.03 (m, 1H), 3.02 (q, \(J = 7.4\) Hz, 2H), 2.80 – 2.65 (m, 1H), 2.59 – 2.39 (m, 2H), 2.25 – 2.14 (m, 1H), 1.38 (t, \(J = 7.4\) Hz, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -66.0 (d, \(J = 8.5\) Hz). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 192.9 (q, \(J = 1.9\) Hz), 146.5, 139.9, 132.9, 129.09, 128.59, 128.5, 126.4, 125.9, 125.0 (q, \(J = 281.0\) Hz), 47.7 (q, \(J = 25.6\) Hz), 32.5, 28.1, 25.7, 13.7. MS (EI): m/z (%) 352.1 (M\(^+\)), 248 (100). HRMS: Calculated for C\(_{19}\)H\(_{19}\)F\(_3\)OS: 352.1109; Found: 352.1103.

**Ethyl-(4-phenyl-2-(trifluoromethyl)butanoyl)benzoate (3j).** The product (115 mg, 63% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)
8.09 (d, \( J = 8.6 \) Hz, 2H), 7.82 (d, \( J = 8.6 \) Hz, 2H), 7.30 – 7.18 (m, 3H), 7.06 (d, \( J = 6.5 \) Hz, 2H), 4.42 (q, \( J = 7.1 \) Hz, 2H), 4.23 – 4.08 (m, 1H), 2.80 – 2.67 (m, 1H), 2.61 – 2.50 (m, 1H), 2.50 – 2.38 (m, 1H), 2.27 – 2.16 (m, 1H), 1.42 (t, \( J = 7.1 \) Hz, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta -65.9 \) (d, \( J = 8.2 \) Hz). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 193.8 \) (q, \( J = 2.2 \) Hz), 165.4, 139.6, 139.5, 135.0, 129.9, 128.7, 128.5, 128.4, 126.6, 124.8 (q, \( J = 280.9 \) Hz), 61.6, 48.5 (q, \( J = 25.5 \) Hz), 32.6, 28.0 (q, \( J = 2.2 \) Hz), 14.2. MS (EI): m/z (%) 319.2 ([M-OEt]+), 104 (100). HRMS: Calculated for C\(_{20}\)H\(_{19}\)F\(_3\)O\(_3\): 364.1286; Found: 364.1281.

**Ethyl 3-(4-phenyl-2-(trifluoromethyl)butanoyl)benzoate (3k).** The product (118 mg, 65% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a light-yellow oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.50 \) (s, 1H), 8.30 (d, \( J = 7.7 \) Hz, 1H), 7.99 (d, \( J = 7.8 \) Hz, 1H), 7.56 (t, \( J = 7.8 \) Hz, 1H), 7.32 – 7.16 (m, 3H), 7.07 (d, \( J = 7.2 \) Hz, 2H), 4.43 (q, \( J = 7.1 \) Hz, 2H), 4.28 – 4.14 (m, 1H), 2.77 – 2.65 (m, 1H), 2.63 – 2.42 (m, 2H), 2.30 – 2.16 (m, 1H), 1.43 (t, \( J = 7.1 \) Hz, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta -66.0 \) (d, \( J = 8.2 \) Hz). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 193.5 \) (q, \( J = 1.5 \) Hz), 165.4, 139.7, 136.9, 134.7, 132.5, 131.4, 129.6, 129.1, 128.6, 128.5, 126.6, 124.8 (q, \( J = 281.1 \) Hz) 61.5, 48.5 (q, \( J = 25.6 \) Hz), 32.7, 28.1, 14.3. MS (EI): m/z (%) 364.1 (M\(^+\)), 104 (100). HRMS: Calculated for C\(_{20}\)H\(_{19}\)F\(_3\)O\(_3\): 364.1286; Found: 364.1281.

**1-(4-Acetylphenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3l).** The product (119 mg, 71% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50:1) as a white solid (m.p. 63.5 – 64.5 °C). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.01 \) (d, \( J = 8.6 \) Hz, 2H), 7.86 (d, \( J = 8.6 \) Hz, 2H), 7.29 – 7.18 (m, 3H), 7.09 – 7.03 (m, 2H), 4.20 – 4.09 (m, 1H), 2.78 – 2.69 (m, 1H), 2.66 (s, 3H), 2.63 – 2.41 (m, 2H), 2.30 – 2.18 (m, 1H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta -65.8 \) (d, \( J = 8.2 \) Hz). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 197.1, 193.7 \) (q, \( J = 1.8 \) Hz), 140.7, 139.5, 139.5, 128.7, 128.7, 128.5, 128.5, 126.6, 124.5 (q, \( J = 281.0 \) Hz), 48.5 (q, \( J = 25.6 \) Hz), 32.5, 28.0 (q, \( J = 2.2 \) Hz), 26.8. MS (EI): m/z (%) 334.1 (M\(^+\)), 104 (100). HRMS: Calculated for C\(_{19}\)H\(_{17}\)F\(_3\)O\(_2\): 334.1181; Found: 334.1177.
4-Phenyl-2-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl) butan-1-one (3m). The product (113 mg, 63% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a light-yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.18 (m, 3H), 7.07 (d, $J = 7.1$ Hz, 2H), 4.20 – 4.06 (m, 1H), 2.81 – 2.68 (m, 1H), 2.65 – 2.40 (m, 2H), 2.32 – 2.20 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.3 (s, 3F), -65.9 (d, $J = 8.2$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.3, 139.5, 139.1, 135.2 (q, $J = 32.9$ Hz), 128.9, 128.7, 128.5, 126.7, 125.9 (q, $J = 3.8$ Hz), 124.77 (q, $J = 281.1$ Hz), 123.38 (q, $J = 272.9$ Hz), 48.5 (q, $J = 25.6$ Hz), 32.6, 27.9. MS (EI): m/z (%) 341.1 ([M-F$^+$]+, 104 (100). HRMS: Calculated for C$_{19}$H$_{17}$F$_3$O$_2$: 360.0949; Found: 360.0946.

4-Phenyl-1-(o-tolyl)-2-(trifluoromethyl)butan-1-one (3n). L3 was used. The product (98 mg, 58% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 60:1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.35 (m, 2H), 7.29 – 7.16 (m, 5H), 7.07 (d, $J = 7.3$ Hz, 2H), 4.10 – 3.97 (m, 1H), 2.77 – 2.66 (m, 1H), 2.64 – 2.53 (m, 1H), 2.49 (s, 3H), 2.47 – 2.35 (m, 1H), 2.26 – 2.13 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -65.9 (d, $J = 8.4$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.28 (q, $J = 2.1$ Hz), 139.9, 139.1, 137.4, 132.2, 132.1, 128.6, 128.6, 128.4, 126.5, 125.8, 125.0 (q, $J = 280.9$ Hz), 51.1 (q, $J = 25.0$ Hz), 32.7, 28.1 (q, $J = 1.9$ Hz), 21.1. MS (EI): m/z (%) 306.2 (M$^+$), 104.2 (100). HRMS: Calculated for C$_{18}$H$_{17}$F$_3$: 306.1232; Found: 306.1227.

4-Phenyl-2-(trifluoromethyl)-1-(4-(trimethylsilyl)phenyl)butan-1-one (3o). The product (107 mg, 59% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50:1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.31 – 7.19 (m, 3H), 7.09 (d, $J = 6.7$ Hz, 2H), 4.23 – 4.12 (m, 1H), 2.76 – 2.66 (m, 1H), 2.61 – 2.40 (m, 2H), 2.26 – 2.16 (m, 1H), 0.31 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -65.9 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.3 (q, $J = 2.3$ Hz), 148.6, 139.9, 136.6, 133.7, 128.6, 128.5, 127.5, 126.5, 125.0 (q, $J = 281.1$ Hz), 48.2 (q, $J = 25.3$ Hz), 32.7, 28.2 (q, $J = 2.2$ Hz), -1.4. MS (EI): m/z (%) 364.1 (M$^+$), 104 (100). HRMS: Calculated for C$_{20}$H$_{23}$F$_3$OSi: 364.1470; Found: 364.1464.
1-(Furan-3-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3p). The product (89 mg, 63% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.45 (s, 1H), 7.32 – 7.18 (m, 3H), 7.11 (d, $J$ = 7.2 Hz, 2H), 6.76 (s, 1H), 3.65 – 3.51 (m, 1H), 2.80 – 2.66 (m, 1H), 2.61 – 2.50 (m, 1H), 2.50 – 2.36 (m, 1H), 2.24 – 2.10 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -66.4 (d, $J$ = 8.4 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 187.8 (q, $J$ = 2.1 Hz), 148.4, 144.7, 139.8, 128.6, 128.5, 126.6, 124.7 (q, $J$ = 280.8 Hz), 108.7, 51.5 (q, $J$ = 25.6 Hz), 32.5, 27.5 (q, $J$ = 2.2 Hz). MS (EI): m/z (%) 282.2 (M$^+$), 104.2 (100). HRMS: Calculated for C$_{15}$H$_{13}$F$_3$O$_2$: 282.0868; Found: 282.0871.

4-Phenyl-1-(thiophen-3-yl)-2-(trifluoromethyl)butan-1-one (3q). L3 was used. The product (91 mg, 61% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40:1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (dd, $J$ = 2.8, 1.3 Hz, 1H), 7.50 (dd, $J$ = 5.1, 1.3 Hz, 1H), 7.33 (dd, $J$ = 5.1, 2.8 Hz, 1H), 7.30 – 7.18 (m, 3H), 7.09 (d, $J$ = 6.9 Hz, 2H), 3.98 – 3.83 (m, 1H), 2.78 – 2.68 (m, 1H), 2.62 – 2.50 (m, 1H), 2.50 – 2.38 (dm, 1H), 2.24 – 2.13 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -66.2 (d, $J$ = 8.5 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 187.7 (q, $J$ = 2.5 Hz), 142.1, 139.8, 133.7, 128.6, 128.5, 128.3, 127.1, 126.9, 126.5, 124.9 (q, $J$ = 280.9 Hz), 50.3 (q, $J$ = 25.4 Hz), 32.6, 27.8 (q, $J$ = 2.2 Hz). MS (EI): m/z (%) 298.1 (M$^+$), 104.1 (100). HRMS: Calculated for C$_{15}$H$_{13}$F$_3$OS: 298.0639; Found: 298.0631.

1-(Dibenzo[b,d]furan-2-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3r). L3 was used. The product (109 mg, 57% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30:1) as a white solid (m.p. 110.6 – 111.3 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, $J$ = 2.0 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.43 – 7.39 (m, 1H), 7.33 – 7.17 (m, 3H), 7.14 – 7.03 (m, 2H), 4.35 – 4.21 (m, 1H), 2.84 – 2.72 (m, 1H), 2.66 – 2.47 (m, 2H), 2.38 – 2.19 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -65.9 (d, $J$ = 8.2 Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 193.3 (q, $J$ = 2.1 Hz), 159.4, 156.9, 139.8, 131.9, 128.62, 128.58, 128.3, 128.2, 126.5, 125.1 (q, $J$ = 280.8 Hz), 124.8, 123.5, 123.4, 122.1, 121.0, 111.98, 111.96, 48.0 (q, $J$ = 25.4 Hz), 32.5, 28.2. MS (EI): m/z (%) 382 (M$^+$), 278 (100). HRMS: Calculated for C$_{23}$H$_{17}$F$_3$O$_2$: 382.1181; Found: 382.117.
Ethyl 4-(8-(4-phenyl-2-(trifluoromethyl)butanoyl)-5,6-dihydro-11H-
benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-
carboxylate (3s). L3 was used. The product (109 mg, 52% yield) was
purified with silica gel chromatography (petroleum ether / ethyl acetate = 1:3) as a white solid (m.p. 51.6 – 52.4 °C). 1H NMR (400 MHz, CDCl3) δ 8.43 (d, J = 4.4 Hz, 1H), 7.70 – 7.52 (m, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.32 – 7.16 (m, 4H), 7.13 (ddd, J = 7.7 Hz, 4.8 Hz, 1.3 Hz, 1H), 7.07 (d, J = 7.1 Hz, 2H), 4.18 – 4.07 (m, 4H), 3.83 (br, 2H), 3.52 – 3.33 (m, 2H), 3.22 – 3.10 (m, 2H), 2.94 – 2.80 (m, 2H), 2.75 – 2.64 (m, 1H), 2.62 – 2.14 (m, 7H), 1.25 (t, J = 7.1 Hz, 3H, rotamer). 19F NMR (376 MHz, CDCl3) δ [-65.88 (d, J = 8.1 Hz), -65.91 (d, J = 8.2 Hz), rotamer]. 13C NMR (126 MHz, CDCl3) δ 193.7, 156.3 (156.1), 155.4, 146.8, 145.5 (145.4), 139.84 (139.80), 138.55, 138.31 (138.26), 137.68 (137.64), 135.58 (135.49), 134.3, 133.41 (133.36), 129.65, 129.33 (129.28), 128.55, 128.51 (128.48), 126.5 (q, J = 6.8 Hz). 126.51, 126.45, 122.5, 61.3, 47.9 (q, J = 25.5 Hz), 44.7, 32.6, 31.71 (31.68), 31.5, 31.4, 30.8, 30.5, 28.2, 14.6. MS (ESI): m/z (%) 563.0 ([M+H]+, 100). HRMS (DART): Calculated for C33H34F3N2O3 ([M+H]+): 563.2516; Found: 563.2511.

1-((1,1'-Biphenyl)-4-yl)-2-(trifluoromethyl)octan-1-one (7a). The product (118 mg, 68% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50/1) as a colorless viscous oil. 1H NMR (400 MHz, CDCl3) δ 8.07 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 7.52 – 7.48 (m, 2H), δ 7.45 – 7.42 (m, 1H), 4.33 – 4.21 (m, 1H), 2.25 – 2.09 (m, 1H), 2.00 – 1.87 (m, 1H), 1.43 – 1.18 (m, 8H), 0.87 (t, J = 6.6 Hz, 3H). 19F NMR (376 MHz, CDCl3) δ -66.2 (d, J = 9.0 Hz). 13C NMR (101 MHz, CDCl3) δ 194.1 (q, J = 2.2 Hz), 146.6, 139.4, 135.5, 129.1, 129.0, 128.5, 127.5, 127.2, 125.1 (q, J = 280.8 Hz), 49.2 (q, J = 25.3 Hz), 31.3, 29.1, 26.9 (q, J = 2.5 Hz), 26.93, 22.4, 13.9. MS (EI): m/z (%) 348.2 (M+), 181.1 (100). HRMS: Calculated for C21H23F3O: 348.1701; Found: 348.1697.

1-Phenyl-2-(trifluoromethyl)octan-1-one (7b). The product (80 mg, 59% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50/1) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 8.0 – 7.9 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 – 7.46 (m, 2H), 4.25 – 4.10 (m, 1H), 2.16 – 2.00 (m, 1H), 1.95 – 1.79 (m, 1H), 1.35 – 1.10 (m, 8H), 0.83 (t, J =
6.6 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.3 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.6 (q, $J = 2.3$ Hz), 134.0, 133.9, 128.9, 128.5, 125.03(q, $J = 280.8$ Hz), 49.3 (q, $J = 25.4$ Hz), 31.3, 29.1, 26.9, 22.4, 13.9. MS (EI): m/z (%) 272.2 (M$^+$), 105.1 (100). HRMS: Calculated for C$_{15}$H$_{19}$F$_3$O: 272.1388; Found: 272.1386.

1-(4-Acetylphenyl)-2-(trifluoromethyl)octan-1-one (7c). The product (79 mg, 50% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.8$ Hz, 2H, AB), 8.03 (d, $J = 8.8$ Hz, 2H, AB), 4.24 – 4.10 (m, 1H), 2.65 (s, 3H), 2.16 – 2.02 (m, 1H), 1.93 – 1.82 (m, 1H), 1.33 – 1.14 (m, 8H), 0.82 (t, $J = 6.8$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.2 (d, $J = 7.9$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.2, 194.3 (q, $J = 2.3$ Hz), 140.7, 139.9, 128.70, 128.68, 124.8 (q, $J = 281.0$ Hz), 49.8 (q, $J = 25.5$ Hz), 31.3, 29.0, 26.92, 26.87, 22.4. MS (EI): m/z (%) 314.2 (M$^+$), 147.1 (100). HRMS: Calculated for C$_{17}$H$_{21}$F$_3$O$_2$: 314.1494; Found: 314.1487.

(Z)-1-(4-(tert-Butyl)phenyl)-2-(trifluoromethyl)oct-5-en-1-one (7d). The product (70 mg, 43% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50/1) as a colorless viscous oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 2H), 5.51 – 5.15 (m, 2H), 4.33 – 4.09 (m, 1H), 2.28 – 1.71 (m, 6H), 1.35 (s, 9H), 0.81 (t, $J = 7.5$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.2 (d, $J = 9.1$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.9, 157.9, 134.2, 133.9, 128.6, 126.7, 125.8, 125.1 (q, $J = 280.9$ Hz), 48.2 (q, $J = 25.3$ Hz), 35.2, 31.0, 26.7 (q, $J = 2.0$ Hz), 24.2, 20.4, 14.0. MS (EI): m/z (%) 311.1 ([M-CH$_3$]$^+$), 229.1 (100). HRMS: Calculated for C$_{19}$H$_{25}$F$_3$O$_2$: 326.18 58; Found: 326.1863.

Ethyl 3-(4-(5-methylfuran-2-yl)-2-(trifluoromethyl)butanoyl)benzoate (7e). The product (114 mg, 62% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.54 (s, 1H), 8.28 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H), 8.04 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 5.79 – 5.77 (m, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 4.34 – 4.21 (m, 1H), 2.75 – 2.39 (m, 3H), 2.27 – 2.16 (m, 1H), 2.15 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.1 (d, $J$
= 8.3 Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.4 (q, $J = 2.2$ Hz), 165.4, 151.3, 151.1, 136.8, 134.6, 132.5, 131.3, 129.6, 129.0, 124.8 (q, $J = 281.0$ Hz), 107.2, 105.9, 61.5, 48.1 (q, $J = 25.6$ Hz), 25.4 (q, $J = 2.3$ Hz), 25.0, 14.3, 13.3. MS (EI): m/z (%) 368.1 (M$^+$), 108.1 (100). HRMS: Calculated for C$_{19}$H$_{19}$F$_3$O$_4$: 368.1235; Found: 368.1225.

4-[[1,1'-Biphenyl]-4-carbonyl]-5,5,5-trifluoropentyl benzoate (7f). The product (149 mg, 70% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40/1) as a white solid (m.p. 79.3 – 80.1 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.46 – 7.38 (m, 3H), 4.43 – 4.28 (m, 3H), 2.40 – 2.26 (m, 1H), 2.18 – 2.04 (m, 1H), 1.90 – 1.80 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.0 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.4, 166.4, 146.8, 139.3, 135.1, 133.0, 130.0, 129.5, 129.2, 129.0, 128.5, 128.3, 127.5, 127.2, 124.9 (q, $J = 281.0$ Hz), 63.8, 48.7 (q, $J = 25.5$ Hz), 26.0, 23.5. MS (ESI): m/z (%) 449.0 ([M+Na]$^+$). HRMS (ESI): Calculated for C$_{25}$H$_{21}$F$_3$O$_3$ ([M+H]$^+$): 427.1516; Found: 427.1520.

5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl benzoate (7g). The product (118 mg, 62% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 20/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.93 (m, 4H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 4.41 – 4.16 (m, 3H), 3.86 (s, 3H), 2.34 – 2.21 (m, 1H), 2.11 – 1.98 (m, 1H), 1.83 – 1.72 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.2 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.1, 166.4, 164.3, 133.0, 131.0, 129.9, 129.5, 128.3, 124.9 (q, $J = 281.0$ Hz), 114.1, 63.9, 55.5, 48.3 (q, $J = 25.4$ Hz), 26.0, 23.4. MS (EI): m/z (%) 368.1 (M$^+$), 108.1 (100). HRMS: Calculated for C$_{19}$H$_{19}$F$_3$O$_4$: 368.1235; Found: 368.1225. MS (EI): m/z (%) 380.2 (M$^+$), 135.0 (100). HRMS: Calculated for C$_{20}$H$_{19}$F$_3$O$_4$: 380.1235; Found: 380.1230.

4-([4-(Benzyloxy)benzoyl]-5,5,5-trifluoropentyl cyclopropanecarboxylate (7h). The product (134 mg, 64% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40/1) as a white solid (m.p. 187.3 – 188.6 °C). $^1$H
NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 8.8$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.27 – 7.20 (m, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 4.27 – 4.13 (m, 1H), 4.13 – 3.94 (m, 2H), 2.28 – 2.10 (m, 1H), 2.04 – 1.87 (m, 1H), 1.74 – 1.45 (m, 5H), 1.00 – 0.93 (m, 2H), 0.88 – 0.81 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.8 (d, $J = 8.6$ Hz).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.3, 174.9, 163.1, 154.9, 131.1, 131.0, 130.2, 125.1, 124.8 (q, $J = 281.2$ Hz), 120.5, 117.2, 63.4, 48.4 (q, $J = 25.5$ Hz), 26.0, 23.4, 12.8, 8.5. MS (ESI): m/z (%) 420.2 (M$^+$).

HRMS (ESI): Calculated for C$_{23}$H$_{24}$F$_3$O$_4$: 426.1627 ([M+H]$^+$), found: 426.1631.

5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl cyclopropanecarboxylate (7i). The product (90 mg, 52% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 9.0$ Hz, 2H), 6.97 (d, $J = 9.0$ Hz, 2H), 4.27 – 4.13 (m, 1H), 4.10 – 3.98 (m, 2H), 3.88 (s, 3H), 2.24 – 2.10 (m, 1H), 2.00 – 1.87 (m, 1H), 1.68 – 1.50 (m, 3H), 0.98 – 0.92 (m, 2H), 0.87 – 0.78 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.3 (d, $J = 8.2$ Hz).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.1 (q, $J = 2.3$ Hz), 174.8, 164.4, 131.1, 129.7, 124.9 (q, $J = 280.8$ Hz), 114.1, 63.4, 55.6, 48.3 (q, $J = 25.3$ Hz), 26.0, 23.4 (q, $J = 2.3$ Hz), 12.7, 8.4. MS (EI): m/z (%) 344.1 (M$^+$), 135.0 (100). HRMS: Calculated for C$_{17}$H$_{19}$F$_3$O$_4$: 344.1235; Found: 344.1237.

2-(4-([1,1'-Biphenyl]-4-carbonyl)-5,5,5-trifluropentyl) 1-(tert-butyl)pyrroolidine-1,2-dicarboxylate (7j). The product (179 mg, 69% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40/1) as a viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.4$ Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 2H), 7.42 – 7.35 (m, 1H), 4.38 – 4.01 (m, 4H), 3.58 – 3.28 (m, 2H), 2.27 – 2.06 (m, 2H), 1.99 – 1.74 (m, 4H), 1.67 (p, $J = 7.0$ Hz, 2H), 1.47 – 1.32 (m, 9H), isomer]. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.03 – -66.23 (m, isomer). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.4 (193.2), 173.0 (172.9), 154.3 (153.6), 146.9 (146.7), 139.3 (139.2), 129.20 (129.16), 128.94 (128.91), 128.49 (128.41), 135.1, 127.5, 127.2, 124.82 (124.73) (q, $J = 280.0$ Hz), 79.68 (79.63), 63.7 (m), 58.9 (58.7), 48.63 (48.54) (q, $J = 25.8$ Hz). 46.4 (46.2), 30.8, 29.8, 28.25 (28.15), 25.9 (m), 23.5 (23.3). MS (ESI): m/z (%) 542.2 ([M+Na]$^+$, 100). HRMS (ESI): Calculated for C$_{28}$H$_{33}$F$_3$O$_3$N ([M+H]$^+$): 520.2305;
**1-(1,1'-Biphenyl-4-yl)-2-(difluoromethyl)-4-phenylbutan-1-one (7k).** The product (88 mg, 50% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 40/1) as a white solid (m.p. 64.3 – 64.9 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.49 – 7.46 (m, 2H), 7.42 (d, $J = 7.2$ Hz, 1H), 7.31 – 7.17 (m, 3H), 7.42 (d, $J = 7.2$ Hz, 1H), 7.31 – 7.17 (m, 3H), 7.11 (d, $J = 7.3$ Hz, 2H), 6.09 (td, $J = 56.4$ Hz, 6.5 Hz, 1H), 4.02 – 3.88 (m, 1H), 2.78 – 2.55 (m, 2H), 2.33 – 2.06 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.9 (ddd, $J = 285.0$ Hz, 56.4 Hz, 11.4 Hz, 1F), -122.8 (ddd, $J = 285.0$ Hz, 56.4 Hz, 11.4 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.7, 146.5, 140.4, 139.5, 135.1, 129.1, 129.0, 128.523, 128.515, 128.4, 127.4, 127.3, 126.3, 117.5 (dd, $J = 245.3$ Hz, 245.1 Hz), 49.2 (t, $J = 20.5$ Hz), 32.7, 29.19 (dd, $J = 3.0$ Hz, 1.5 Hz). MS (EI): m/z (%) 350.2 (M$^+$), 246.1 (100). HRMS: Calculated for C$_{23}$H$_{20}$F$_2$O: 350.1482; Found: 350.1483.

**Ethyl 2,2-difluoro-3-(4-methoxybenzoyl)-5-phenylpentanoate (7l).** The product (70 mg, 37% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 15/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 8.9$ Hz, 2H), 7.30 – 7.14 (m, 3H), 7.08 (d, $J = 7.2$ Hz, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 4.28 – 4.10 (m, 3H), 3.86 (s, 3H), 2.76 – 2.65 (m, 1H), 2.62 – 2.50 (m, 1H), 2.40 – 2.14 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -103.6 (dd, $J = 263.5$ Hz, 13.1 Hz, AB,1F), -107.7 (dd, $J = 263.5$ Hz, 13.1 Hz, AB,1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.1, 164.1, 163.3 (t, $J = 32.5$ Hz), 140.4, 131.0, 129.5, 128.6, 128.5, 126.3, 115.3 (t, $J = 253.5$ Hz), 113.9, 63.0, 55.6, 49.2 (t, $J = 21.3$ Hz), 33.2, 28.3, 13.8. MS (EI): m/z (%) 376.1 (M$^+$), 199.1 (100). HRMS: Calculated for C$_{21}$H$_{22}$F$_2$O$_4$: 376.1486; Found: 376.1483.

**1-(4-(tert-Butyl)phenyl)-2-phenylpropan-1-one (7m).** The product (77 mg, 58% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 50/1) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.31 – 7.30 (m, 2H), 7.24 – 7.15 (m, 1H), 4.68 (q, $J = 6.8$ Hz, 1H), 1.53 (d, $J = 6.8$ Hz, 3H), 1.29
(s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.8, 156.4, 141.7, 133.8, 128.9, 128.7, 127.7, 126.8, 125.4, 47.7, 35.0, 31.0, 19.6. MS (EI): m/z (%) 251.1 ([M-CH$_3$]+), 161.2 (100). HRMS: Calculated for C$_{19}$H$_{22}$O: 266.1671; Found: 266.1669.

1-(9,9-Dimethyl-9H-fluoren-2-yl)-2-(3-(trifluoromethyl)phenyl)propan-1-one (7n). The product (120 mg, 61% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 30/1) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 1.7$ Hz, 1H), 7.98 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.67 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.52 – 7.32 (m, 5H), 4.87 (q, $J = 6.9$ Hz, 1H), 1.62 (d, $J = 6.9$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.5. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 199.4, 154.8, 153.9, 144.2, 142.6, 137.7, 134.8, 131.1, 131.1 (q, $J = 31.9$ Hz), 129.3, 128.6, 128.4, 127.2, 124.7, 123.8, 123.0, 122.8, 120.9, 119.8, 47.4, 46.9, 26.8, 26.7, 19.5. MS (EI): m/z (%) 394.2 (M$^+$), 221.2 (100). HRMS: Calculated for C$_{25}$H$_{21}$OF$_3$: 394.1545; Found: 394.1546.

2-(4-Chlorophenyl)-1-(4-(ethylthio)phenyl)propan-1-one (7o). The product (79 mg, 55% yield) was purified by prep-HPLC (Prep Nova-Pak® HR C18 60 Å 6 μm 19*300mm; MeCN/H$_2$O = 10/1 V/V %) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (dd, $J = 8.6$ Hz, 1.3 Hz, 2H), 7.28 – 7.15 (m, 6H), 4.59 (q, $J = 7.2$ Hz, 1H), 2.96 (q, $J = 7.4$ Hz, 2H), 1.48 (d, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 199.7, 144.7, 140.0, 132.8, 132.7, 129.2, 129.1, 129.1, 126.2, 46.9, 25.9, 19.4, 13.9. MS (EI): m/z (%) 304.1 (M$^+$), 165.1 (100). HRMS: Calculated for C$_{17}$H$_{17}$OSCl: 304.0689; Found: 304.0680.

5,5,5-Trifluoro-4-(4-methylbenzoyl)pentyl 2-(2-(4-(4-(5-chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)acetate (7p). The product (165 mg, 52% yield) was purified with silica gel chromatography (ethyl acetate) as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.0$ Hz, 2H), 7.38 – 7.33 (m, 4H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.28 – 7.21 (m, 4H), 7.20 – 7.16 (m, 1H), 4.25 – 4.06 (m, 4H), 4.04 (s, 2H), 3.64 (t, $J = 5.6$ Hz, 2H), 2.63 (t, $J = 5.6$ Hz, 2H), 2.61 – 2.30 (br, 8H), 2.43 (s, 3H), 2.22 – 2.10 (m, 1H), 1.97 –
1.88 (m, 2H), 1.67 – 1.59 (m, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -66.2 (d, $J = 8.5$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 193.3, 170.4, 145.4, 142.1, 141.3, 134.1, 132.5, 129.7, 129.2, 128.8, 128.61, 128.56, 127.8, 127.1, 124.8 (q, $J = 280.9$ Hz), 75.4, 68.8, 68.2, 63.8, 57.7, 53.6, 51.5, 48.5 (q, $J = 25.6$ Hz), 25.9, 23.3, 21.7. MS (ESI): m/z (%) 631.2 ([M+H]$^+$, 100). HRMS (ESI): Calculated for C$_{34}$H$_{39}$F$_3$O$_4$N$_2$Cl ([M+H]$^+$): 631.2545; Found: 631.2537.

5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate (7q). The product (146 mg, 48% yield) was purified with silica gel chromatography (petroleum ether / ethyl acetate = 5/1) as a yellow solid (m.p. 74.3 – 75.1 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 8.9$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 6.99 – 6.91 (m, 3H), 6.66 (dd, $J = 9.0$, 2.5 Hz, 1H), 4.18 – 4.02 (m, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 3.64 (s, 2H), 2.37 (s, 3H), 2.18 – 2.06 (m, 1H), 1.92 – 1.80 (m, 1H), 1.67 – 1.53 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.3 (d, $J = 8.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.0, 170.8, 168.2, 164.4, 156.0, 139.2, 135.9, 133.8, 131.1, 131.0, 130.7, 130.5, 129.5, 129.0, 124.8 (q, $J = 280.9$ Hz), 114.9, 114.1, 112.3, 111.6, 101.1, 63.9, 55.58, 55.55, 48.1 (q, $J = 25.5$ Hz), 30.2, 25.9, 23.2, 13.2. MS (ESI): m/z (%) 638.1 ([M+Na]$^+$, 100). HRMS (ESI): Calculated for C$_{32}$H$_{30}$F$_3$O$_6$NCl ([M+H]$^+$): 616.1708; Found: 616.1702.

7. Transformations of compound 3b

Procedure: Sodium borohydride (1 mmol 3.3 equiv) was added to a solution of 3a (0.3 mmol, 1 equiv) in methanol (3 mL) under nitrogen at 0° C. The reaction was stirred at room temperature for 4 hours. The reaction was quenched with water and the methanol was evaporated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over Na$_2$SO$_4$ and concentrated. The residue was purified with silica gel chromatography (petroleum ether / ethyl acetate = 10:1) to give compound 8 (76 mg, 72% yield, dr > 20:1 determined by $^{19}$F NMR) as a
colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.25 (m, 2H), 7.20 – 7.00 (m, 5H), 6.88 – 6.78 (m, 2H), 4.81 – 4.73 (m, 1H), 2.58 – 2.39 (m, 2H), 2.40 – 2.25 (m, 1H), 2.10 (s, 1H), 1.75 – 1.51 (m, 2H), 1.26 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -66.4 (d, $J = 9.8$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.5, 140.9, 137.7, 129.2 (q, $J = 361.2$ Hz), 128.33, 128.32, 126.7, 126.0, 125.4, 72.7 (q, $J = 2.6$ Hz), 48.6 (q, $J = 23.1$ Hz), 34.6, 33.3, 31.3, 27.2. MS (EI): m/z (%) 350.2 ([M$^+$]), 163.2 (100). HRMS: Calculated for C$_{21}$H$_{25}$OF$_3$: 350.1858; Found: 350.1864.

**Procedure:** To a solution of 3b (0.3 mmol, 1 equiv) in THF (3 mL) was added dropwise allylmagnesium chloride (0.36 mmol, 1.2 equiv) over 10 mins at -78 ºC. After the addition was complete, the reaction was stirred at -78 ºC for 3 h. The reaction was quenched with saturated aqueous NH$_4$Cl solution (1 mL). The organic solvent was evaporated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$ and purified with silica gel chromatography (petroleum ether / ethyl acetate = 10:1) to give compound 9 as a colorless oil (73 mg, 62% yield, dr > 20:1 determined by $^{19}$F NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.31 (m, 4H), 7.28 – 7.20 (m, 2H), 7.20 – 7.13 (m, 1H), 7.01 (d, $J = 6.8$ Hz, 2H), 5.63 – 5.47 (m, 1H), 5.28 – 5.09 (m, 2H), 2.96 (dd, $J = 14.0$ Hz, 5.4 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.58 – 2.45 (m, 1H), 2.42 – 2.23 (m, 2H), 2.05 – 1.95 (m, 1H), 1.87 – 1.73 (m, 1H), 1.33 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.1 (d, $J = 10.0$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.2, 141.2, 139.6, 132.7, 128.5, 128.4, 127.7 (q, $J = 282.2$ Hz), 126.2, 126.0, 124.9, 120.9, 75.7, 52.6 (q, $J = 22.9$ Hz), 42.5, 35.3, 34.4, 31.3, 27.2. MS (EI): m/z (%) 375.2 ([M-CH$_3$]$^+$), 349.2 (100). HRMS: Calculated for C$_{23}$H$_{26}$OF$_3$ ([M-CH$_3$]).375.1936; Found: 375.1942.
**Procedure:**

To a solution of Pd(PPh₃)₄ (0.0015 mmol, 5 mol%) in THF (3 mL) was added 3b (0.3 mmol, 1 equiv) and allyl ethyl carbonate (0.48 mmol, 1.6 equiv) under Ar. The resulting mixture was stirred at room temperature for 8 h. The reaction was quenched with 10% HCl, and extracted with 

Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (AcOEt : hexane = 1 : 50) to give product 10 as a colorless oil (63 mg, 54%).

1H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.30 – 7.12 (m, 3H), 6.98 (d, J = 7.1 Hz, 2H), 5.79 (dq, J = 17.0, 7.9 Hz, 1H), 5.24 – 5.08 (m, 2H), 2.89 (qd, J = 15.0, 7.3 Hz, 2H), 2.62 – 2.51 (m, 2H), 2.37 – 2.27 (m, 2H), 1.35 (s, 9H).

19F NMR (376 MHz, CDCl₃) δ -65.9.

13C NMR (101 MHz, CDCl₃) δ 199.0, 155.5, 141.2, 136.0, 131.9, 128.5, 128.2, 127.8, 126.7 (q, J = 285.6 Hz), 126.2, 125.3, 119.6, 60.4 (q, J = 22.2 Hz), 37.1, 35.0, 34.6, 31.1, 30.5. MS (EI): m/z (%) 373.2 ([M-CH₃]⁺), 161.1 (100). HRMS: Calculated for C₂₄H₂₇OF₃: 388.2014; Found: 388.2024.

**Procedure:**

To a Schlenk tube were added 3a (0.3 mmol, 1 equiv), phenylboronic acid (0.3 mmol, 1.0 equiv), Pd(PPh₃)₂Cl₂ (5 mol%), and K₃PO₄ (0.9 mmol, 3equiv) under Ar. Toluene (3 mL) was then added. The reaction mixture was stirred at 110 °C for 8 h. After the reaction was cooled to room temperature, water was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate = 30:1) to give compound 11 as a light-yellow oil (93 mg, 80%).

1H NMR (500 MHz, CDCl₃) δ 7.67 (d, J = 8.6 Hz, 2H), 7.31 – 7.21 (m, 9H), 7.21 – 7.11 (m, 4H), 2.95 – 2.89 (m, 2H), 2.88 – 2.83 (m, 2H), 1.24 (s, 9H).

19F NMR (376 MHz, CDCl₃) δ -99.8. 13C NMR (126 MHz, CDCl₃) δ 196.8 (d, J = 10.8 Hz), 159.0 (d, J = 259.1 Hz), 156.8, 141.2, 134.1 (d, J = 3.8 Hz), 131.6 (d, J = 29.7 Hz), 129.6, 129.5,
128.5, 128.3, 128.1, 127.9 (d, \( J = 5.3 \) Hz), 126.0, 125.3, 120.2 (d, \( J = 17.5 \) Hz), 35.0, 34.4, 30.9, 30.6 (d, \( J = 5.3 \) Hz). MS (EI): \( m/z \) (%) 371.2 ([M-CH\(_3\)]\(^+\), 329.2 (100). HRMS: Calculated for C\(_{27}\)H\(_{27}\)OF: 386.2046; Found: 386.2049.

8. References


9. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

Nickel Complex (B1)
Nickel complex (B2)
Methyl 4-fluorobenzoate (12)
4-(4-Phenyl-2-(trifluoromethyl)butyl)-1,2-dihydronaphthalene (16)
Chemical Formula: C_{25}H_{21}F_3
Exact Mass: 330.1595
(4,4,4-Trifluoro-3-iodobutyl)benzene (1a)
1,1,1-Trifluoro-2-iodooctane (1b)
(Z)-1,1,1-Trifluorooct-5-en-2-ol (17d)
(Z)-8,8,8-Trifluoro-7-iodooct-3-ene (1d)
Chemical Formula: C₆H₄F₃I
Exact Mass: 291.9936

Chemical Formula: C₆H₅F₂I
Exact Mass: 291.9936
1,1,1-Trifluoro-4-(5-methylfuran-2-yl)butan-2-ol (17e)

Chemical Formula: C$_9$H$_8$F$_5$O$_2$

Exact Mass: 206.0711
2-Methyl-5-(4,4,4-trifluoro-3-iodobutyl)furan (1e)
5,5,5-Trifluoro-4-iodopentyl benzoate (1f)
(4,4-Difluoro-3-iodobutyl)benzene (1k)
Chemical Formula: C₅H₆F₄I
Exact Mass: 265.9873

Chemical Formula: C₅H₆F₄I
Exact Mass: 265.9873
5,5,5-Trifluoro-4-iodopentan-1-ol (1f')
5,5,5-Trifluoro-4-iodopentyl cyclopropanecarboxylate (1h)
1-(tert-Butyl) 2-(5,5,5-trifluoro-4-iodopentyl) (2S)-pyrrolidine-1,2-dicarb-oxylate (1j)
5,5,5-Trifluoro-4-iodopentyl 2-(2-((4-chlorophenyl) (phenyl)methyl)piperazin-1-yl)ethoxy)acetate (1p)
5,5,5-Trifluoro-4-iodopentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (1q)
1-(4-Fluorophenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3a)
1-(4-(tert-Butyl)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3b)
1-([1,1'-Biphenyl]-4-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3c)
1-(4-(Benzyloxy)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3d)
1-(3,5-Dimethoxyphenyl)-4-phenyl-2-(trifluoromethyl)but-1-one (3e)
1-(Benzo[d][1,3]dioxol-5-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3f)
1-(4-(Diphenylamino)phenyl)-4-phenyl-2-(trifluoromethyl) butan-1-one (3g)
1-(4-Morpholinophenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3h)
1-(4-(Ethylthio)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3i)
Ethyl-(4-phenyl-2-(trifluoromethyl)butanoyl)benzoate (3j)
Ethyl 3-(4-phenyl-2-(trifluoromethyl)butanoyl)benzoate (3k)
Chemical Formula: C_{32}H_{41}F_{2}O_{3}
Exact Mass: 364.1286

Chemical Formula: C_{32}H_{41}F_{2}O_{3}
Exact Mass: 364.1286
1-(4-Acetylphenyl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3l)
4-Phenyl-2-((trifluoromethyl)-1-(4-(trifluoromethyl)phenyl) butan-1-one (3m)
4-Phenyl-1-(o-tolyl)-2-(trifluoromethyl)butan-1-one (3n)
4-Phenyl-2-(trifluoromethyl)-1-(4-(trimethylsilyl)phenyl)butan-1-one (3o)
1-(Furan-3-yl)-4-phenyl-2-(trifluoromethyl)butan-1-one (3p)
4-Phenyl-1-(thiophen-3-yl)-2-(trifluoromethyl)butan-1-one (3q)
1-(Dibenzo[b,d]furan-2-yl)-4-phenyl-2-(trifluoromethyl) butan-1-one (3r)
Ethyl 4-(8-(4-phenyl-2-(trifluoromethyl)butanoyl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (3s)
1-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)octan-1-one (7a)
1-Phenyl-2-(trifluoromethyl)octan-1-one (7b)
1-(4-Acetylphenyl)-2-(trifluoromethyl)octan-1-one (7c)
(Z)-1-(4-(tert-Butyl)phenyl)-2-(trifluoromethyl)oct-5-en-1-one (7d)
Ethyl 3-(4-(5-methylfuran-2-yl)-2-(trifluoromethyl)butanoyl)benzoate (7e)
4-\(\{(1,1^\prime\text{-Biphenyl})-4\text{-carbonyl}\}\)-5,5,5-trifluoropentyl benzoate (7f).
5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl benzoate (7g).
4-(4-(Benzyloxy)benzoyl)-5,5,5-trifluoropentyl cyclopropanecarboxylate (7h)
5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl cyclopropanecarboxylate (7i)
2-(4-([1,1'-Biphenyl]-4-carbonyl)-5,5,5-trifluoropentyl) 1-(tert-butyl) (2R)-pyrroldine-1,2-dicarboxylate (7j)
1-((1,1’-Biphenyl)-4-yl)-2-(difluoromethyl)-4-phenylbutan-1-one (7k)
Ethyl 2,2-difluoro-3-(4-methoxybenzoyl)-5-phenylpentanoate (7l)
1-(4-(tert-Butyl)phenyl)-2-phenylpropan-1-one (7m)
1-(9,9-Dimethyl-9H-fluoren-2-yl)-2-(3-(trifluoromethyl)phenyl)propan-1-one (7n)
2-(4-Chlorophenyl)-1-(4-(ethylthio)phenyl)propan-1-one (7o)
5,5,5-Trifluoro-4-(4-methylbenzoyl)penty1 2-(2-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)ethoxy)acetate (7p)
5,5,5-Trifluoro-4-(4-methoxybenzoyl)pentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate (7q).
1-(4-(tert-Butyl)phenyl)-4-phenyl-2-(trifluoromethyl)butan-1-ol (8)
Chemical Formula: C₈H₁₂O₂
Exact Mass: 350.1858

Chemical Formula: C₈H₁₂O₂
Exact Mass: 350.1858
4-(4-(tert-Butyl)phenyl)-7-phenyl-5-(trifluoromethyl)hept-1-en-4-ol (9)
1-(4-(tert-Butyl)phenyl)-2-phenethyl-2-(trifluoromethyl)pent-4-en-1-one (10)
(Z)-1-(4-(tert-Butyl)phenyl)-2-(fluoro(phenyl)methylene)-4-phenylbutan-1-one (11)