Supporting Information
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Iron-Catalyzed 1,2-Addition of Perfluoroalkyl Iodides to Alkynes and Alkenes**
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anie_201402511_sm_m miscellaneous_information.pdf
1. General Considerations.

All commercially available compounds were used as received. $^1$H and $^{13}$C spectra were recorded on a Bruker Avance 400 spectrometer, and CDCl$_3$ was purchased from Aldrich. The chemical shifts ($\delta$) are given in parts per million relative to internal standard TMS (0 ppm for $^1$H), CDCl$_3$ (77.0 ppm for $^{13}$C). Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

2. Screening Results.

In a 4 mL sealed glass vial, 1-Octyne (1a), C$_4$F$_9$I (1.2-1.5 equiv.) and base were dissolved in dry solvent under N$_2$ following the condition listed in the table below. The mixture was stirred at 60°C in the dark for 18-24h. The reaction was quenched by aq.HCl solution and diluted with diethyl ether. Decane (60 ul) was added to the organic layer as an internal standard and the solution was analyzed by GC to give the yield.

2.1 Screening different metal catalysts.

Table S1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>co-Cat.</th>
<th>Base</th>
<th>Solvent</th>
<th>o-TMEDA</th>
<th>Conversion</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>---</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>---</td>
<td>74%</td>
<td>51%</td>
</tr>
<tr>
<td>2</td>
<td>CuI</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>---</td>
<td>89%</td>
<td>49%</td>
</tr>
<tr>
<td>3</td>
<td>CoBr$_2$</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>2 equiv.</td>
<td>67%</td>
<td>30%</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OTf)$_2$</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>2 equiv.</td>
<td>77%</td>
<td>23%</td>
</tr>
<tr>
<td>5</td>
<td>NiCl$_2$.dme</td>
<td>Cul</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>---</td>
<td>98%</td>
<td>61%</td>
</tr>
<tr>
<td>6</td>
<td>NiCl$_2$.dme</td>
<td>Cul</td>
<td>Cs$_2$CO$_3$</td>
<td>THF</td>
<td>---</td>
<td>77%</td>
<td>27%</td>
</tr>
<tr>
<td>7</td>
<td>NiCl$_2$.dme</td>
<td>Cul</td>
<td>tBuOK</td>
<td>Dioxane</td>
<td>---</td>
<td>97%</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>NiCl$_2$.dme</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>2 equiv.</td>
<td>68%</td>
<td>30%</td>
</tr>
<tr>
<td>9</td>
<td>FeBr$_2$</td>
<td>Cul</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>---</td>
<td>94%</td>
<td>63%</td>
</tr>
<tr>
<td>10</td>
<td>FeBr$_2$</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>---</td>
<td>96%</td>
<td>68%</td>
</tr>
<tr>
<td>11</td>
<td>FeBr$_2$</td>
<td>---</td>
<td>Cs$_2$CO$_3$</td>
<td>Dioxane</td>
<td>2 equiv.</td>
<td>65%</td>
<td>31%</td>
</tr>
</tbody>
</table>

Condition: 1a (0.5 mmol), 2a (1.2 equiv.), Catalyst (10 mol%), co-Catalyst (10 mol%), Base (1.5 equiv.), o-TMEDA (2 equiv.), Solvent (2 mL), 60°C, 18-24h.

o-TMEDA = bis[2-(N,N-dimethylaminoethyl)]ether
2.2 Screening concentration.

Table S2

\[
\begin{align*}
\text{C}_6\text{H}_{13} & \quad + \quad \text{C}_4\text{F}_9\text{I} \\
\text{cat. FeBr}_2 \text{ (Loading)} & \\
\text{Dioxane, 60°C} & \\
\rightarrow & \\
\text{C}_6\text{H}_{13} & \quad \text{C}_4\text{F}_9
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Loading</th>
<th>Alkyne (Con.)</th>
<th>Base (equiv.)</th>
<th>Conversion</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5%</td>
<td>0.25M</td>
<td>Cs$_2$CO$_3$ (0.8)</td>
<td>99%</td>
<td>95%(87%)</td>
</tr>
<tr>
<td>2</td>
<td>5%</td>
<td>0.25M</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>---</td>
<td>0.25M</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>---</td>
<td>0.25M</td>
<td>Cs$_2$CO$_3$ (2.0)</td>
<td>97%</td>
<td>63%</td>
</tr>
<tr>
<td>5</td>
<td>---</td>
<td>0.25M</td>
<td>Cs$_2$CO$_3$ (0.2)</td>
<td>58%</td>
<td>47%</td>
</tr>
<tr>
<td>6</td>
<td>---</td>
<td>0.25M</td>
<td>CsCl (0.2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>---</td>
<td>0.25M</td>
<td>K$_2$CO$_3$ (0.2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>---</td>
<td>0.25M</td>
<td>DABCO (0.2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>---</td>
<td>0.25M</td>
<td>Cs$_2$CO$_3$ (0.2)</td>
<td>43%</td>
<td>17%</td>
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<tr>
<td>10</td>
<td>---</td>
<td>0.50M</td>
<td>Cs$_2$CO$_3$ (0.2)</td>
<td>81%</td>
<td>79%</td>
</tr>
<tr>
<td>11</td>
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<td>1.00M</td>
<td>Cs$_2$CO$_3$ (0.2)</td>
<td>91%</td>
<td>90%</td>
</tr>
<tr>
<td>12</td>
<td>---</td>
<td>1.00M</td>
<td>Cs$_2$CO$_3$ (0.25)</td>
<td>96%</td>
<td>95%(87%)</td>
</tr>
</tbody>
</table>

Condition: 1a (1.0 mmol), 2a (1.5 equiv.), Catalyst (5 mol%), Base (1.5 equiv.), Dioxane, 60°C, 18-24h.


3.1 General procedure for addition to alkyne.

Cs$_2$CO$_3$-catalyed reaction:

In a 4 mL sealed glass vial, Cs$_2$CO$_3$ (81.5 mg, 0.25 mmol, 0.25equiv.), alkyne (1.0 mmol) or alkene (1.0 mmol), Perfluoroalkyl iodide (1.5 mmol, 1.5equiv.) were dissolved in dry dioxane (1 mL) under N$_2$. The mixture was stirred at 60°C in the dark for 18-24h, and the reaction was quenched by aq.HCl solution and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of Hexane and ethyl acetate affording the product.

FeBr$_2$-catalyed reaction:

In a 4 mL sealed glass vial, FeBr$_2$ (10.8 mg, 0.05mmol, 0.1equiv.), Cs$_2$CO$_3$ (130.4 mg, 0.4 mmol, 0.8equiv.), alkyne or alkene (0.5 mmol), Perfluoroalkyl iodide (0.75 mmol, 1.5equiv.) were dissolved in dry dioxane (2 mL) under N$_2$. The mixture was stirred at 60°C in the dark for 18-24h, and the reaction was quenched by aq.HCl solution and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography.
on silica gel with a gradient eluant of Hexane and ethyl acetate affording the product.

For CF₃I, firstly, CF₃I (1.5 mmol, 3 equiv.) was dissolved in the dioxane (2 mL) at room temperature, then this solvent was added to the mixture of FeBr₂ (10.8 mg, 0.05 mmol, 0.1 equiv.), Cs₂CO₃ (130.4 mg, 0.4 mmol, 0.8 equiv.), alkyne or alkene (0.5 mmol) in a 4 mL sealed glass vial under N₂. The mixture was stirred at 60°C in the dark for 18-24 h, and the reaction was quenched by aq. HCl solution and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of Hexane and ethyl acetate affording the product.

3.2 Procedures for coupling reactions.

In a 4 mL sealed glass vial, Fe(acac)₃ (13.1 mg, 0.0373 mmol, 0.5 equiv.) and compound 4a (27.0 mg, 0.0746 mmol) were dissolved in dry THF (1 mL) and NMP (200 uL) under N₂. Then n-C₅H₉MgBr (75 uL, 2.0 M, 0.15 mmol, 2.0 equiv.) was added. The mixture was stirred at -30°C for 1 h, and the reaction was quenched by aq. NH₄Cl solution and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of hexane affording the product 6a (15.8 mg, 69%).

In a 4 mL sealed glass vial, PdCl₂(PPh₃)₂ (7.0 mg, 0.01 mmol, 0.1 equiv.), K₂CO₃ (3.1 mg, 0.022 mmol, 0.22 equiv.), PhB(OH)₂ (36.6 mg, 0.3 mmol, 3 equiv.) and compound 3n (57.0 mg, 0.1 mmol) were dissolved in Toluene (1 mL) and H₂O (200 uL) under N₂. The mixture was stirred at 80°C for 16 h. After that, another K₂CO₃ (3.0 mg, 0.022 mmol, 0.22 equiv.) and PhB(OH)₂ (36.6 mg, 0.3 mmol, 3 equiv.) were added and the reaction was stirred at 80°C for additional 16 h followed by quenched with water and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of hexane and ethyl acetate affording the product 6b (45.3 mg, 86%).

In a 4 mL sealed glass vial, 4l (58.0 mg, 0.126 mmol), Pd(PPh₃)₄ (9.3 mg, 0.008 mmol, 0.063 equiv.), K₂CO₃ (43.5 mg, 0.315 mmol, 2.5 equiv.), E-C₆H₁₃-CH=CH-B(OH)₂ (49.1 mg, 0.315 mmol, 2.5 equiv.) were dissolved in THF (1 mL) under N₂. The mixture was stirred at 65°C for 18 h. The reaction was filtered by fast column and washed with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of Hexane and ethyl acetate affording the product 6c (42.2 mg, 75%).

In a 4 mL sealed glass vial, 4h (56.0 mg, 0.142 mmol), Pd(PPh₃)₄ (16.4 mg, 0.014 mmol, 0.1 equiv.), CuI (5.4 mg, 0.028 mmol, 0.2 equiv.), 1-Octyne (35.8 mg, 0.325 mmol, 2.3 equiv.) were dissolved in TEA (1 mL) under N₂. The mixture was stirred at
50°C for 16h. The reaction was filtered by fast column and washed with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of hexane and ethyl acetate affording the product 6d (49.2 mg, 92%).

In a 4 mL sealed glass vial, CuI (4.7 mg, 0.024 mmol, 0.2equiv.), 1,10-Phenanthroline (4.4 mg, 0.024 mmol, 0.2equiv.), PPh₃ (13.1 mg, 0.050 mmol, 0.4equiv.), K₃PO₄ (44.0 mg, 0.207 mmol, 1.7equiv.) and compound 3j (59.0 mg, 0.124 mmol) were dissolved in Toluene (1 mL) under N₂, then PhSH (26.0 mg, 0.236 mmol, 1.9 equiv.) was added. The mixture was stirred at 110°C for 16h. The reaction was quenched with aq. HCl and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of hexane and ethyl acetate affording the product 6e (45.9 mg, 81%).

In a 4 mL sealed glass vial, FeBr₂ (7.1 mg, 0.01 mmol, 0.1equiv.) and compound 5e (60.0 mg, 0.174 mmol) were dissolved in NMP (0.73 mL) under N₂, then the relevant alkyne Gridge reagent (0.55 mL, 0.5M, 0.275 mmol, 1.6 equiv.) was added. The mixture was stirred at room temperature for 16h. The reaction was quenched with aq. HCl and extracted with diethyl ether. The organic layer was combined and concentrated under vacuum and the residue was purified by column chromatography on silica gel with a gradient eluant of hexane and ethyl acetate affording the product 6f (36.1 mg, 50%).

3.3 General procedure for the synthesis of the substrates

These substrates were synthesized according to the literature by Mitsunobu reaction.¹

³H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 4.16 (t, J = 6.4 Hz, 2H), 2.43 (td, J = 6.8, 2.8 Hz, 2H), 2.04 (tt, J = 6.8, 6.4 Hz, 2H), 1.99 (t, J = 2.8 Hz, 1H); ³¹C NMR (100 MHz, CDCl₃) δ 195.5, 162.5, 138.3, 132.5, 131.8, 130.2, 129.7, 128.2, 114.0, 83.1, 69.1, 66.3, 28.0, 15.1; HRMS: m/z (ESI) calculated [M+H]⁺: 265.1229, measured: 265.1238.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 4.05 (t, $J = 6.4$ Hz, 2H), 2.96 (q, $J = 7.2$ Hz, 2H), 2.37-2.25 (m, 2H), 2.07-1.88 (m, 3H), 1.81-1.68 (m, 2H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.5, 162.7, 130.2, 129.8, 114.0, 83.9, 68.7, 67.4, 31.3, 28.0, 24.9, 18.1, 8.4; HRMS: m/z (ESI) calculated [M+Ag]$^+$: 337.0358, measured: 337.0357.

These substrates were synthesized from the acyl chloride and alcohol with pyridine or TEA as base in DCM at room temperature according to the literature.$^{S2}$

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.09 (t, $J = 6.4$ Hz, 2H), 2.37-2.18 (m,4H), 2.01-1.93 (m,1H), 1.82-1.71 (m,2H), 1.67-1.55(m,4H),1.39-1.15 (m,16H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.0, 83.8, 68.6, 63.6, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 27.6, 24.9, 24.8, 22.6, 18.0, 14.1; HRMS: m/z (ESI) calculated [M+Ag]$^+$: 387.1453, measured: 387.1434.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 4.23 (t, $J = 6.0$ Hz, 2H), 2.41-2.32 (m, 2H), 2.04-1.93 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.4, 139.2, 130.8, 128.5, 128.6, 82.8, 69.1, 63.6, 27.5, 15.2; HRMS: m/z (ESI) calculated [M+Ag]$^+$: 328.9499, measured: 328.9495.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, $J = 8.8$ Hz, 2H), 7.76 (d, $J = 8.8$ Hz, 2H), 4.47

(t, J = 6.4 Hz, 2H), 2.69 (td, J = 6.4, 2.8 Hz, 2H), 2.05 (t, J = 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6, 133.7, 132.2, 130.1, 117.9, 116.5, 79.6, 70.2, 63.2, 19.0; HRMS: m/z (ESI) calculated [M+Ag]$^+$: 305.9684, measured: 305.9682.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.32 (t, J = 6.4 Hz, 2H), 2.23 (td, J = 6.8, 2.4 Hz, 2H), 1.97 (t, J = 2.4 Hz, 1H), 1.78 (tt, J = 7.2, 6.8 Hz, 2H), 1.65-1.50 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.6, 139.1, 130.8, 128.7, 128.5, 84.0, 68.4, 64.9, 28.0, 27.9, 25.0, 18.2; HRMS: m/z (ESI) calculated [M+Ag]$^+$: 356.9811, measured: 356.9796.

### 3.4 The characterization of the new products

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.32 (d, J = 14.4 Hz, 1H), 2.69-2.56 (m, 2H), 1.65-1.49 (m, 2H), 1.41-1.21 (m, 6H), 0.95-0.83 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 126.6 (t, J = 243.0 Hz), 126.1 (t, J = 5.7 Hz), 120-100 (m), 41.2, 31.5, 30.1, 28.2, 22.5, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.2 (t, J = 9.8 Hz, 3F), -105.6 (t, J = 12.0 Hz, 2F), -121.9 (m, 2F), -123.1 (m, 2F), -123.5 (m, 2F), -126.4 (m, 2F); HRMS: m/z (APCI) calculated [M]$^+$: 555.9933, measured: 555.9920.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.40 (t, J = 12.8 Hz, 1H), 4.40-4.27 (m, 2H), 2.63-2.54 (m, 2H), 1.62-1.47 (m, 2H), 1.46-1.21 (m, 9H), 0.95-0.84 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.2 (t, J = 34.2 Hz), 131.2 (t, J = 26.8 Hz), 119.6 (t, J = 7.4 Hz), 111.5 (t, J = 251.0 Hz), 63.3, 40.7, 31.5, 29.8, 28.0, 22.5, 14.0, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -97.7(s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 383.0296, measured: 383.0286.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.37 (t, \(J = 11.6\) Hz, 1H), 4.41-4.31 (m, 2H), 2.59 (t, \(J = 7.2\) Hz, 2H), 1.61-1.50 (m, 2H), 1.37 (t, \(J = 7.2\) Hz, 3H), 1.33-1.24 (m, 6H), 0.89 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.6 (t, \(J = 34.2\) Hz), 128.1 (t, \(J = 29.5\) Hz), 115.0 (t, \(J = 10.0\) Hz), 112.1 (t, \(J = 240.9\) Hz), 63.2, 46.7, 31.4, 28.9, 27.6, 22.5, 14.0, 13.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -97.9 (s); HRMS: m/z (ESI) calculated [M+Na]\(^+\): 383.0296, measured: 383.0291.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.4\) Hz, 2H), 7.75 (d, \(J = 8.0\) Hz, 2H), 7.57 (t, \(J = 6.8\) Hz, 1H), 7.48 (t, \(J = 6.8\) Hz, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 6.40 (t, \(J = 14.6\) Hz, 1H), 4.08 (t, \(J = 6.4\) Hz, 2H), 2.94-2.83 (m, 2H), 2.18-2.05 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 195.4, 162.2, 138.2, 132.5, 131.8, 130.2, 129.7, 128.1, 127.3 (t, \(J = 23.8\) Hz), 120.9 (t, \(J = 6.0\) Hz), 113.9, 120-100 (m), 66.1, 37.8, 29.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -81.0 (t, \(J = 9.4\) Hz, 3F), -105.8 (t, \(J = 12.0\) Hz, 2F), -124.1 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+H]\(^+\): 611.0129, measured: 611.0131. Z product: \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -81.0 (m, 3F), -108.9 (t, \(J = 12.4\) Hz, 2F), -123.8 (m, 2F), -125.7 (m, 2F); HRMS: m/z (ESI) calculated [M+H]\(^+\): 611.0129, measured: 611.0126.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.34 (t, \(J = 14.4\) Hz, 1H), 4.63-4.57 (m, 1H), 3.93-3.84 (m, 1H), 3.77 (tt, \(J = 10.0, 6.4\) Hz, 1H), 3.56-3.49 (m, 1H), 3.44 (tt, \(J = 10.0, 6.4\) Hz, 1H), 2.67 (t, \(J = 7.2\) Hz, 2H), 1.90-1.80 (m, 1H), 1.78-1.70 (m, 1H), 1.69-1.51 (m, 8H), 1.49-1.38 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 126.4 (t, \(J = 23.8\) Hz), 122.8 (t, \(J = 6.4\) Hz), 120-100 (m), 98.8, 67.2, 62.2, 41.1, 30.7, 29.8, 29.4, 25.4, 25.2, 19.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -81.0 (t, \(J = 9.4\) Hz, 3F), -105.6 (t, \(J = 12.0\) Hz, 2F), -124.2 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]\(^+\): 565.0262, measured: 565.0263.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.24 (t, \(J = 12.8\) Hz, 1H), 4.63-4.50 (m, 1H), 3.91-3.81
(m, 1H), 3.80-3.70 (m, 1H), 3.55-3.46 (m, 1H), 3.43-3.35 (m, 1H), 2.76-2.63 (m, 2H), 1.80-1.33 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 121.6 (t, $J = 23.5$ Hz), 116.5 (t, $J = 6.1$ Hz), 120-100 (m), 98.9, 67.2, 62.4, 48.3, 30.7, 29.3, 28.9, 25.4, 24.8, 19.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (t, $J = 10.1$ Hz, 3F), -108.7 (t, $J = 12.4$ Hz, 2F), -123.9 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 565.0262, measured: 565.0247.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.28-7.19 (m, 2H), 6.87-6.77 (m, 2H), 6.36 (t, $J = 14.0$ Hz, 1H), 4.00-3.89 (m, 2H), 2.78-2.64 (m, 2H), 1.87-1.70 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.5, 129.3, 126.9 (t, $J = 23.5$ Hz), 125.5, 122.2 (t, $J = 6.4$ Hz), 115.7, 120-100 (m), 67.6, 40.6, 27.8, 26.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (t, $J = 9.4$ Hz, 3F), -105.5 (t, $J = 12.4$ Hz, 2F), -124.2 (m, 2F), -125.8 (m, 2F); HRMS: m/z (APCI) calculated [M]$^+$: 553.9556, measured: 553.9550.

Z product: $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (t, $J = 9.4$ Hz, 3F), -108.8 (t, $J = 12.4$ Hz, 2F), -123.8 (m, 2F), -125.8 (m, 2F); LRMS: m/z (EI) 427 (M-I), 299, 128 (100), 127, 111.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.89-7.78 (m, 2H), 7.74-7.65 (m, 2H), 6.38 (t, $J = 12.8$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 3.67 (t, $J = 6.4$ Hz, 2H), 2.69-2.56 (m, 2H), 1.72-1.51 (m, 4H), 1.31 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.3, 163.1 (t, $J = 34.2$ Hz), 133.9, 132.1, 131.8 (t, $J = 26.8$ Hz), 123.2, 118.4 (t, $J = 7.4$ Hz), 111.5 (t, $J = 251.0$ Hz), 63.4, 39.9, 37.6, 27.2, 27.1, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -97.7(s); HRMS: m/z (ESI) calculated [M+H]$^+$: 478.0327, measured: 478.0329.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.02-7.80 (m, 2H), 7.78-7.58 (m, 2H), 6.41 (t, $J = 11.2$ Hz, 1H), 4.35 (q, $J = 7.2$ Hz, 2H), 3.82-3.63 (m, 2H), 2.76-2.55 (m, 2H), 1.76-1.56(m, 4H), 1.36 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.3, 162.6, 134.0, 132.0, 128.8 (t, $J = 29.5$ Hz), 123.2, 113.8 (t, $J = 9.7$ Hz), 111.9 (t, $J = 247.0$ Hz), 63.3, 45.9, 37.3, 26.9, 26.1, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -98.0(s); HRMS: m/z (ESI)

\[ \text{S10} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 6.38 (t, $J = 14.0$ Hz, 1H), 3.97 (t, $J = 6.0$ Hz, 2H), 2.86 (t, $J = 7.2$ Hz, 2H), 2.45 (s, 3H), 2.12-1.99 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.2, 130.0, 129.0, 127.2 (t, $J = 24.0$ Hz), 121.2, 115.1, 120-100 (m), 66.1, 38.0, 29.7, 18.0; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (t, $J = 9.8$ Hz, 3F), -105.8 (t, $J = 13.2$ Hz, 2F), -124.1 (m, 2F), -125.8 (m, 2F); LRMS: m/z (EI) 425 (M-I), 413, 285, 140 (100), 125, 117, 97, 77. Z product: $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (t, $J = 9.4$ Hz, 3F), -108.9 (t, $J = 12.4$ Hz, 2F), -123.8 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+K]$^+$: 590.9303, measured: 590.9391.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.36 (t, $J = 14.4$ Hz, 1H), 4.17-4.02 (m, 2H), 2.77-2.59 (m, 2H), 2.37-2.25 (m, 2H), 1.73-1.58 (m, 6H), 1.34-1.20 (m, 16H), 0.92-0.83 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.8, 126.9 (t, $J = 23.5$ Hz), 121.9, 120-100 (m), 63.5, 40.5, 34.3, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.3, 26.5, 25.0, 22.6, 14.0; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (m, 3F), -105.6 (m, 2F), -124.2 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+H]$^+$: 627.1382, measured: 627.1381.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.27 (t, $J = 13.2$ Hz, 1H), 4.09 (t, $J = 6.0$ Hz, 2H), 2.77-2.66 (m, 2H), 2.30 (t, $J = 7.6$ Hz, 2H), 1.70-1.57 (m, 6H), 1.32-1.21 (m, 16H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.9, 122.1 (t, $J = 23.5$ Hz), 115.9, 120-100 (m), 63.5, 47.8, 34.3, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 27.0, 25.6, 25.0, 22.7, 14.1; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.0 (m, 3F), -108.8 (m, 2F), -123.8 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 649.1201, measured: 649.1210.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 8.8$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 6.44 (t, $J = 12.8$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 3.97-3.89 (m, 2H), 2.69 (t, $J = 6.4$ Hz, 2H), 1.83-1.67 (m, 4H), 1.35 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.5, 131.7 (t, $J = 26.8$ Hz), 129.2, 125.4, 118.7, 115.7, 115.6, 111.5 (t, $J = 255.0$ Hz), 67.6, 63.4, 40.2, 27.7, 26.4, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -97.7 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 480.9855, measured: 480.9862.

![Chemical structure](image1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.14 (m, 2H), 6.87-6.70 (m, 2H), 6.42 (t, $J = 11.6$ Hz, 1H), 4.42-4.24 (m, 2H), 3.99-3.83 (m, 2H), 2.72-2.56 (m, 2H), 1.83-1.67 (m, 4H), 1.42-1.30 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.4, 129.3, 128.7 (t, $J = 28.7$ Hz), 125.5, 115.7, 114.4, 114.1 (t, $J = 9.4$ Hz), 112.0 (t, $J = 246.4$ Hz), 67.6, 63.3, 46.3, 27.5, 25.6, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -98.0 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 480.9855, measured: 480.9850.

![Chemical structure](image2)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.37 (t, $J = 14.4$ Hz, 1H), 4.05 (t, $J = 6.0$ Hz, 2H), 2.96 (q, $J = 7.2$ Hz, 2H), 2.79-2.69 (m, 2H), 1.93-1.74 (m, 4H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.3, 162.6, 130.1, 129.9, 126.8 (t, $J = 23.5$ Hz), 122.0, 114.0, 120-100 (m), 67.4, 40.5, 31.3, 27.7, 26.5, 8.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.2 (m, 3F), -105.5 (t, $J = 11.7$ Hz, 2F), -124.2 (m, 2F), -125.9 (m, 2F); HRMS: m/z (ESI) calculated [M+H]$^+$: 577.0286, measured: 577.0280.

![Chemical structure](image3)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.30 (t, $J = 12.8$ Hz, 1H), 4.15-4.00 (m, 2H), 2.96 (q, $J = 7.2$ Hz, 2H), 2.84-2.71 (m, 2H), 1.90-1.77 (m, 4H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.5, 162.6, 130.2, 130.0, 122.1 (t, $J = 23.5$ Hz), 115.9 (t, $J = 6.0$ Hz), 114.1, 120-100 (m), 67.5, 47.9, 31.4, 27.5, 25.8, 8.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.0 (t, $J = 9.4$ Hz,
3F), -108.8 (t, J = 11.7 Hz, 2F), -123.8 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+H]^+: 577.0286, measured: 577.0223.

\[
\text{CF}_2\text{COOEt}
\]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.96 (d, \( J = 8.8 \text{ Hz, 2H} \)), 7.42 (d, \( J = 8.8 \text{ Hz, 2H} \)), 6.39 (t, \( J = 14.4 \text{ Hz, 1H} \)), 4.36 (t, \( J = 6.0 \text{ Hz, 2H} \)), 2.85 (t, \( J = 7.6 \text{ Hz, 2H} \)), 2.14-2.02 (m, 2H); \( ^{13}\text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 165.5, 139.5, 130.9, 128.7, 128.4, 127.3 (t, \( J = 23.8 \text{ Hz} \)), 120.7 (t, \( J = 6.7 \text{ Hz} \)), 120-100 (m), 63.4, 38.0, 29.2; \( ^{19}\text{F NMR (376 MHz, CDCl}_3 \) \( \delta \) -81.1 (t, \( J = 9.4 \text{ Hz, 3F} \)), -105.8 (t, \( J = 14.3 \text{ Hz, 2F} \)), -124.1 (m, 2F), -125.9 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]^+: 590.9246, measured: 590.9293.

\( \text{Z product: } ^{19}\text{F NMR (376 MHz, CDCl}_3 \) \( \delta \) -81.0 (t, \( J = 9.4 \text{ Hz, 3F} \)), -108.9 (t, \( J = 12.4 \text{ Hz, 2F} \)), -123.8 (m, 2F), -125.8 (m, 2F); LRMS: m/z (EI) 441 (M-I), 285, 157, 139 (100), 127, 111.

\[ \text{CF}_2\text{COOEt} \]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.26 (d, \( J = 8.0 \text{ Hz, 2H} \)), 6.84 (d, \( J = 8.0 \text{ Hz, 2H} \)), 6.46 (t, \( J = 13.2 \text{ Hz, 1H} \)), 4.30 (q, \( J = 7.2 \text{ Hz, 2H} \)), 3.96 (t, \( J = 6.4 \text{ Hz, 2H} \)), 2.83 (t, \( J = 7.2 \text{ Hz, 2H} \)), 2.44 (s, 3H), 2.10-1.98 (m, 2H), 1.34 (t, \( J = 7.2 \text{ Hz, 3H} \)); \( ^{13}\text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 157.2, 131.9 (t, \( J = 26.8 \text{ Hz} \)), 129.9, 128.7, 117.7 (t, \( J = 7.4 \text{ Hz} \)), 115.1, 114.0, 111.4 (t, \( J = 252.3 \text{ Hz} \)), 66.2, 63.4, 37.5, 29.4, 17.9, 13.8; \( ^{19}\text{F NMR (376 MHz, CDCl}_3 \) \( \delta \) -97.7 (s); HRMS: m/z (ESI) calculated [M+Na]^+: 478.9966, measured: 478.9955.

\[ \text{CF}_2\text{COOEt} \]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.26 (d, \( J = 8.8 \text{ Hz, 2H} \)), 6.84 (d, \( J = 8.8 \text{ Hz, 2H} \)), 6.44 (t, \( J = 11.6 \text{ Hz, 1H} \)), 4.34 (q, \( J = 7.2 \text{ Hz, 2H} \)), 3.94 (t, \( J = 6.0 \text{ Hz, 2H} \)), 2.81 (t, \( J = 6.4 \text{ Hz, 2H} \)), 2.44 (s, 3H), 2.11-1.97 (m, 2H), 1.35 (t, \( J = 7.2 \text{ Hz, 3H} \)); \( ^{13}\text{C NMR (100 MHz, CDCl}_3 \) \( \delta \) 157.2, 130.0, 129.1 (t, \( J = 29.5 \text{ Hz} \)), 129.0, 116.4, 115.1, 113.1, 111.9 (t, \( J = 245.4 \text{ Hz} \)), 65.6, 63.3, 43.2, 28.5, 17.9, 13.9; \( ^{19}\text{F NMR (376 MHz, CDCl}_3 \) \( \delta \) -98.1(s); HRMS: m/z (ESI) calculated [M+Na]^+: 478.9966, measured: 478.9972.
$^1$H NMR (400 MHz, CDCl₃) δ 8.13 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 6.54 (t, $J = 14.0$ Hz, 1H), 4.58 (t, $J = 6.0$ Hz, 2H), 3.17 (d, $J = 6.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl₃) δ 164.5, 133.4, 132.2, 130.1, 129.3 (t, $J = 23.5$ Hz), 117.8, 116.6, 115.7 (t, $J = 5.6$ Hz), 120-100 (m), 63.8, 39.7. $^{19}$F NMR (376 MHz, CDCl₃) δ -81.1 (t, $J = 9.4$ Hz, 3F), -105.5 (t, $J = 12.4$ Hz, 2F), -124.1 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 567.9432, measured: 567.9432.

Z product: $^{19}$F NMR (376 MHz, CDCl₃) δ -81.0 (t, $J = 9.4$ Hz, 3F), -109.4 (t, $J = 12.4$ Hz, 2F), -123.8 (m, 2F), -125.8 (m, 2F); LRMS: m/z (EI) 418 (M-I), 130 (100), 127, 102, 69.

$^1$H NMR (400 MHz, CDCl₃) δ 7.94 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.45 (t, $J = 13.2$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 4.04 (t, $J = 6.0$ Hz, 2H), 2.95 (q, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 6.4$ Hz, 2H), 1.89-1.70 (m, 4H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 199.2, 163.0 (t, $J = 34.2$ Hz), 162.6, 131.7 (t, $J = 26.8$Hz), 130.0, 129.8, 118.5 (t, $J = 7.8$Hz), 114.0, 111.4 (t, $J = 251.0$ Hz), 67.4, 63.3, 40.0, 31.2, 27.6, 26.2, 13.8, 8.3. $^{19}$F NMR (376 MHz, CDCl₃) δ -97.6 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 481.0688, measured: 481.0696.

$^1$H NMR (400 MHz, CDCl₃) δ 7.95 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.43 (t, $J = 11.6$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 4.10-4.00 (m, 2H), 2.96 (q, $J = 7.2$ Hz, 2H), 2.74-2.64 (m, 2H), 1.87-1.72 (m, 4H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.22 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 199.4, 162.6, 162.5 (t, $J = 34.2$ Hz), 130.2, 130.0, 128.7 (t, $J = 28.9$ Hz), 114.1, 114.0, 112.0 (t, $J = 246.3$Hz), 67.5, 63.3, 46.2, 31.4, 27.4, 25.5, 13.9, 8.4; $^{19}$F NMR (376 MHz, CDCl₃) δ -98.0 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 481.0688, measured: 481.0699.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.8$ Hz, 2H), 6.78 (d, $J = 8.8$ Hz, 2H), 6.44 (t, $J = 13.2$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 3.93 (t, $J = 6.4$ Hz, 2H), 2.69 (q, $J = 6.4$ Hz, 2H), 1.85-1.66 (m, 4H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.0 (t, $J = 33.8$ Hz), 157.9, 132.1, 131.7 (t, $J = 26.8$ Hz), 118.7 (t, $J = 7.4$ Hz), 116.2, 112.6, 111.4 (t, $J = 250.5$ Hz), 67.5, 63.4, 40.1, 27.7, 26.3, 13.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -97.6 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 524.9350, measured: 524.9343.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 8.4$ Hz, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 6.43 (t, $J = 11.2$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 3.99-3.86 (m, 2H), 2.75-2.59 (m, 2H), 1.83-1.69 (m, 4H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 157.9, 132.2, 128.7 (t, $J = 29.1$ Hz), 116.2, 114.1 (t, $J = 9.8$ Hz), 112.8, 112.0 (t, $J = 243.9$ Hz), 67.5, 63.3, 46.3, 27.5, 25.6, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -98.0 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 524.9350, measured: 524.9324.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90-7.83 (m, 2H), 7.77-7.70 (m, 2H), 6.34 (t, $J = 14.4$ Hz, 1H), 3.72 (t, $J = 7.2$ Hz, 2H), 2.77-2.63 (m, 2H), 1.80-1.60 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.2, 133.8, 132.0, 126.9 (t, $J = 23.4$ Hz), 123.1, 121.8, 120-100 (m), 40.2, 37.4, 27.1, 27.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.2 (t, $J = 9.0$ Hz, 3F), -105.6 (t, $J = 12.0$ Hz, 2F), -124.2 (m, 2F), -125.9 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 595.9745, measured: 595.9846. 

Z product: $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.0 (m, 3F), -108.8 (m, 2F), -123.8 (m, 2F), -125.8 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 595.9745, measured: 595.9846.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.43 (t, $J = 13.2$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.16-4.04 (m, 2H), 2.75-2.60 (m, 2H), 2.31 (t, $J = 7.2$ Hz, 2H), 1.70-1.56 (m, 6H), 1.42-1.19 (m, 1H), 0.88 (t, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.7, 163.0, 131.7 (t, $J = 26.9$Hz), 118.5 (t, $J = 7.3$Hz), 111.4 (t, $J = 251.0$Hz), 63.6, 63.3, 40.1, 34.2, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.2, 26.2, 24.9, 22.6, 14.0, 13.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -97.7 (s); HRMS: m/z (ESI) calculated [M+H$^+$]: 531.1783, measured: 531.1777.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.41 (t, $J = 11.6$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 4.14-4.04 (m, 2H), 2.68-2.59 (m, 2H), 2.30 (t, $J = 7.2$ Hz, 2H), 1.70-1.57 (m, 6H), 1.41-1.19 (m, 19H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.9, 161.8, 128.7 (t, $J = 28.8$Hz), 114.0 (t, $J = 6.2$Hz), 112.0 (t, $J = 246.3$Hz), 63.5, 63.3, 46.1, 34.3, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.0, 25.4, 25.0, 22.7, 14.1, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -98.0 (s); HRMS: m/z (ESI) calculated [M+H$^+$]: 531.1783, measured: 531.1776.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 6.35 (t, $J = 14.4$ Hz, 1H), 4.33 (t, $J = 6.4$ Hz, 2H), 2.67 (q, $J = 7.2$ Hz, 2H), 1.85-1.76 (m, 2H), 1.72-1.62 (m, 2H), 1.54-1.44 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 139.3, 130.9, 128.8, 128.7, 126.9 (t, $J = 24.2$Hz), 122.2, 120-100 (m), 64.9, 40.8, 29.6, 28.4, 24.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.0 (t, $J = 13.9$ Hz, 2F), -105.3 (t, $J = 13.5$ Hz, 2F), -120.1 (m, 2F), -121.3 (m, 2F), -121.5 (m, 2F), -123.2 (m, 2F); LRMS: m/z (EI) 429, 409, 157, 139 (100), 127, 111.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 6.26 (t, $J = 13.2$ Hz, 1H), 4.33 (t, $J = 6.4$ Hz, 2H), 2.70 (q, $J = 7.2$ Hz, 2H), 1.85-1.76 (m, 2H), 1.73-1.63 (m, 2H), 1.51-1.41 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 139.4, 130.9, 128.7, 128.6, 122.0 (t, $J = 23.5$ Hz), 116.0 (t, $J = 6.0$ Hz), 120-100 (m), 64.8, 48.1, 28.7, 28.3, 24.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.0 (t, $J = 13.9$ Hz, 2F), -108.5 (t, $J = 13.5$ Hz, 2F), -120.1 (m, 2F), -121.2 (m, 2F), -121.4 (m, 2F), -122.8 (m,
2F); LRMS: m/z (EI) 429, 409, 207, 157, 139 (100), 127, 111.

\[
\begin{align*}
\text{CF}_2\text{COOEt} \\
\text{C}_4\text{H}_3
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.44-4.26 (m, 2H), 2.76-2.61 (m, 2H), 2.52-2.37 (m, 2H), 1.59-1.43 (m, 4H), 1.40-1.25 (m, 7H), 1.01-0.84 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.6 (t, \(J = 34.9\)Hz), 136.5 (t, \(J = 22.5\)Hz), 119.5 (t, \(J = 6.1\)Hz), 111.9 (t, \(J = 254.3\)Hz), 63.1, 42.5, 39.0, 32.6, 30.1, 22.6, 21.7, 13.9, 13.8, 13.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -96.6 (s); HRMS: m/z (ESI) calculated [M+Na]\(^+\): 411.0608, measured: 411.0595.

Z product: \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -98.0 (s); LRMS: m/z (EI) 261 (M-I), 233, 157, 127 (100), 111, 91, 55.

\[
\begin{align*}
\text{Br} \\
\text{CF}_3
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 8.8\) Hz, 2H), 6.78 (d, \(J = 8.8\) Hz, 2H), 6.44 (q, \(J = 7.6\) Hz, 1H), 3.94 (t, \(J = 7.2\) Hz, 2H), 2.69 (t, \(J = 7.6\) Hz, 2H), 1.86-1.70 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.0, 132.2, 129.5 (q, \(J = 34.2\) Hz), 121.8 (q, \(J = 272.5\) Hz), 120.1 (t, \(J = 6.0\) Hz), 116.2, 112.8, 67.5, 40.2, 27.7, 26.2; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.7 (s); HRMS: m/z (APCI) calculated [M]\(^+\): 447.9147, measured: 447.9141.

\[
\begin{align*}
\text{Cl} \\
\text{CF}_3
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 8.4\) Hz, 2H), 7.43 (d, \(J = 8.4\) Hz, 2H), 6.46 (q, \(J = 7.6\) Hz, 1H), 4.35 (t, \(J = 6.0\) Hz, 2H), 2.83 (t, \(J = 7.2\) Hz, 2H), 2.07 (tt, \(J = 7.2, 6.0\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.5, 139.4, 130.9, 129.9 (q, \(J = 34.2\) Hz), 128.7, 128.4, 121.6 (q, \(J = 272.5\) Hz), 118.5 (q, \(J = 6.1\) Hz), 63.3, 37.5, 28.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.9 (s); HRMS: m/z (APPI) calculated [M+H]\(^+\): 418.9523, measured: 418.9520.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 8.0\) Hz, 2H), 7.43 (d, \(J = 8.0\) Hz, 2H), 6.38 (q, \(J = 6.4\) Hz, 1H), 4.35 (t, \(J = 7.2\) Hz, 2H), 2.79 (t, \(J = 8.4\) Hz, 2H), 2.08 (tt, \(J = 8.4, 7.2\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.5, 139.6, 131.0, 128.8, 128.4, 125.9 (q, \(J = 35.5\) Hz), 125.7, 121.4 (q, \(J = 254.8\) Hz), 63.2, 43.6, 29.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -60.2 (s); LRMS: m/z (EI) 291 (M-I), 157, 139 (100), 127, 111, 75.

![Image](image1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98-7.80 (m, 2H), 7.78-7.62 (m, 2H), 6.41 (q, \(J = 7.2\) Hz, 1H), 3.82-3.56 (m, 2H), 2.75-2.52 (m, 2H), 1.82-1.47 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.3, 133.9, 132.0, 129.5 (q, \(J = 34.2\) Hz), 123.2, 121.6 (q, \(J = 247.7\) Hz), 119.8 (q, \(J = 6.0\) Hz), 39.8, 37.4, 27.1, 26.8; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.7 (s); HRMS: m/z (ESI) calculated [M+H]\(^+\): 424.0021, measured: 424.0022.

![Image](image2)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92-7.81 (m, 2H), 7.78-7.68 (m, 2H), 6.34 (q, \(J = 7.2\) Hz, 1H), 3.72 (t, \(J = 6.4\) Hz, 2H), 2.66 (t, \(J = 6.4\) Hz, 2H), 1.75-1.57 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.4, 134.0, 132.0, 125.4 (q, \(J = 35.6\)Hz), 123.3, 121.2 (q, \(J = 269.1\)Hz), 115.0 (q, \(J = 6.0\) Hz), 46.0, 37.3, 27.0, 26.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -60.1 (s); HRMS: m/z (ESI) calculated [M+H]\(^+\): 424.0021, measured: 424.0027.

![Image](image3)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.39 (q, \(J = 7.6\) Hz, 1H), 4.59 (dd, \(J = 4.4, 2.4\) Hz, 1H), 3.93-3.82 (m, 1H), 3.75 (dt, \(J = 9.6, 6.4\) Hz, 1H), 3.56-3.46 (m, 1H), 3.39 (dt, \(J = 9.6, 6.4\) Hz, 1H), 2.62 (t, \(J = 7.2\) Hz, 2H), 1.88-1.78 (m, 1H), 1.77-1.68 (m, 1H), 1.66-1.50 (m, 8H), 1.46-1.37 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 129.0 (q, \(J = 34.3\) Hz), 121.8 (q, \(J = 272.5\) Hz), 120.6 (q, \(J = 6.0\) Hz), 98.8, 67.2, 62.2, 40.7, 30.7, 29.4, 29.3, 25.4, 25.1, 19.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.8 (s); HRMS: m/z (ESI) calculated [M+Na]\(^+\): 415.0358, measured: 415.0353.
\[ 1^H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 6.30 (q, J = 7.2 \text{ Hz}, 1H), 4.58 \text{ dd, } J = 4.4, 2.0 \text{ Hz, } 1H), 3.91-3.82 \text{ (m, } 1H), 3.75 \text{ (dt, } J = 9.6, 6.8 \text{ Hz, } 1H), 3.56-3.46 \text{ (m, } 1H), 3.39 \text{ (dt, } J = 9.6, 6.4 \text{ Hz, } 1H), 2.62 \text{ (t, } J = 7.2 \text{ Hz, } 2H), 1.88-1.77 \text{ (m, } 1H), 1.76-1.68 \text{ (m, } 1H), 1.66-1.49 \text{ (m, } 8H), 1.43-1.36 \text{ (m, } 2H); 13^C \text{ NMR (100 MHz, CDCl}_3) \delta 124.9 \text{ (q, } J = 35.6 \text{ Hz), } 121.4 \text{ (q, } J = 269.1 \text{ Hz), } 115.9, 98.9, 67.2, 62.4, 46.8, 30.7, 29.3, 28.8, 25.4, 24.8, 19.7; 19^F \text{ NMR (376 MHz, CDCl}_3) \delta -60.0 \text{ (s); HRMS: m/z (ESI) calculated [M+Na]'}^+: 415.0358, measured: 415.0349.

\[ 1^H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.13 \text{ (d, } J = 8.0 \text{ Hz, } 2H), 7.76 \text{ (d, } J = 8.0 \text{ Hz, } 2H), 6.59 \text{ (q, } J = 7.6 \text{ Hz, } 1H), 4.56 \text{ (t, } J = 7.2 \text{ Hz, } 2H), 3.14 \text{ (t, } J = 7.2 \text{ Hz, } 2H); 13^C \text{ NMR (100 MHz, CDCl}_3) \delta 164.5, 133.4, 132.2, 131.8 \text{ (q, } J = 34.2 \text{ Hz), } 130.1, 121.6 \text{ (q, } J = 272.4 \text{ Hz), } 117.8, 116.5, 113.7 \text{ (q, } J = 6.0 \text{ Hz), } 63.4, 39.5; 19^F \text{ NMR (376 MHz, CDCl}_3) \delta -57.7 \text{ (s); LRMS: m/z (EI) 268 (M-I), 130 (100), 127, 121, 102, 75.} \]

\[ Z \text{ product: } 19^F \text{ NMR (376 MHz, CDCl}_3) \delta -60.6 \text{ (s); LRMS: m/z (EI) 268 (M-I), 130 (100), 127, 121, 102, 75.} \]

\[ 1^H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.26 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 6.83 \text{ (d, } J = 8.4 \text{ Hz, } 2H), 6.45 \text{ (q, } J = 7.2 \text{ Hz, } 1H), 3.96 \text{ (t, } J = 6.0 \text{ Hz, } 2H), 2.84 \text{ (t, } J = 6.4 \text{ Hz, } 2H), 2.44 \text{ (s, } 3H), 2.14-2.01 \text{ (m, } 2H); 13^C \text{ NMR (100 MHz, CDCl}_3) \delta 157.2, 130.0, 129.8 \text{ (q, } J = 34.3 \text{ Hz), } 129.0, 121.8 \text{ (q, } J = 272.5 \text{ Hz), } 119.1 \text{ (q, } J = 6.1 \text{ Hz), } 115.1, 66.0, 37.5, 29.3, 17.9; 19^F \text{ NMR (376 MHz, CDCl}_3) \delta -57.9 \text{ (s); HRMS: m/z (ESI) calculated [M+K]'}^+: 440.9399, measured: 440.9635. \]

\[ 1^H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 6.43 \text{ (q, } J = 7.2 \text{ Hz, } 1H), 4.17-4.00 \text{ (m, } 2H), 2.71-2.58 \text{ (m, } 2H), 2.36-2.27 \text{ (m, } 2H), 1.71-1.57 \text{ (m, } 6H), 1.37-1.18 \text{ (m, } 16H), 0.92-0.83 \text{ (m,} \]

\[ \text{S18} \]
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.33 (q, $J = 7.2$ Hz, 1H), 4.17-3.99 (m, 2H), 2.75-2.54 (m, 2H), 2.38-2.23 (m, 2H), 1.72-1.52 (m, 6H), 1.38-1.13 (m, 16H), 0.95-0.80 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.9, 125.3 (q, $J = 35.6$ Hz), 121.2 (q, $J = 269.7$ Hz), 115.2 (q, $J = 5.6$ Hz), 63.5, 46.3, 34.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 27.1, 25.5, 25.0, 22.7, 14.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -60.1 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 499.1297, measured: 499.1287.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 2H), 6.41 (q, $J = 7.6$ Hz, 1H), 4.32 (t, $J = 6.4$ Hz, 2H), 2.64 (t, $J = 4.4$ Hz, 2H), 1.86-1.76 (m, 2H), 1.70-1.61 (m, 2H), 1.53-1.44 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 139.4, 130.9, 129.3 (q, $J = 34.2$ Hz), 128.9, 128.7, 121.8 (q, $J = 272.5$ Hz), 120.2 (q, $J = 6.1$ Hz), 64.9, 40.4, 29.2, 28.3, 24.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.7 (s); HRMS: m/z (APPI) calculated [M+H]$^+$: 446.9836, measured: 446.9830.
$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.0$ Hz, 2H), 6.44 (q, $J = 7.2$ Hz, 1H), 4.15-3.96 (m, 2H), 3.06-2.87 (m, 2H), 2.80-2.63 (m, 2H), 1.94-1.70 (m, 4H), 1.34-1.13 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.5, 162.6, 130.2, 130.1, 129.6 (q, $J = 34.2$ Hz), 124.5 (q, $J = 73.2$Hz), 119.9 (q, $J = 6.1$ Hz), 111.1, 67.4, 40.1, 31.4, 27.6, 26.1, 8.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.7 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 427.0382, measured: 427.0385.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.8$ Hz, 2H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.48 (dd, $J = 7.6$, 7.6 Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 6.47 (q, $J = 7.6$ Hz, 1H), 4.07 (t, $J = 6.0$ Hz, 2H), 2.87 (t, $J = 7.2$ Hz, 2H), 2.12 (tt, $J = 7.2$, 6.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.5, 162.3, 138.2, 132.5, 131.9, 130.2, 130.0 (q, $J = 34.2$ Hz), 129.7, 128.2, 121.8 (q, $J = 72.5$ Hz), 118.8 (q, $J = 5.3$Hz), 113.9, 66.0, 37.4, 29.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.9 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 461.0226, measured: 461.0229.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 4.54-4.44 (m, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 4.18-4.02 (m, 2H), 3.13-2.96 (m, 1H), 2.95-2.78 (m, 1H), 2.37-2.13 (m, 2H), 1.40 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2 (t, $J = 32.2$ Hz), 157.5, 132.2, 116.3, 115.0 (q, $J = 251.6$ Hz), 113.1, 67.6, 63.2, 45.3 (q, $J = 23.1$ Hz), 39.3, 18.4, 13.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -101.8 (d, $J = 264.0$ Hz, 1F), -106.3 (d, $J = 264.0$ Hz, 1F); HRMS: m/z (ESI) calculated [M+Na]$^+$: 498.9193, measured: 498.9215.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 4.40-4.27 (m, 3H), 3.05-2.70 (m, 2H), 1.97-1.68 (m, 5H), 1.65-1.53 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 139.4, 130.9, 128.7, 128.6, 120-100 (m), 64.6, 41.6 (t, $J = 20.8$Hz), 39.6, 27.6, 26.2, 20.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.0 (t, $J = 13.5$Hz, 2F), -111.5 (dt, $J = 269.6$, 14.7Hz, 1F), -114.6 (dt, $J = 269.6$, 12.8 Hz, 1F), -120.1 (m, 2F), -121.3 (m, 2F), -121.6 (m, 2F), -123.6 (m, 2F); LRMS: m/z (EI) 417, 157, 139 (100), 127, 111, 81.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 4.39-4.24 (m, 1H), 3.81 (s,3H), 3.25- 3.12 (m, 2H), 2.93-2,74 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 130.6, 130.0, 125.6 (q, $J = 276.5$Hz), 113.9, 55.2, 45.8, 43.5 (q, $J = 28.2$ Hz), 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.6 (s); LRMS: m/z (EI) 344 (M), 217 (M-I, 100), 134, 127, 121, 91, 77.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.29-4.18 (m, 1H), 4.05 (t, $J = 6.0$ Hz, 2H), 3.02-2.73 (m, 4H), 1.96-1.56 (m, 6H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.4, 162.6, 130.2, 129.9, 125.5 (q, $J = 277.2$Hz), 114.0, 67.6, 44.8 (q, $J = 28.2$ Hz), 39.2, 31.3, 28.0, 26.2, 21.2, 8.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.9 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 429.0538, measured: 429.0548.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H), 4.42-4.30 (m, 2H), 4.28-4.17 (m, 1H), 3.05-2.72 (m, 2H), 1.95-1.52 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 139.3, 130.9, 128.7, 125.5 (q, $J = 277.1$Hz), 114.9, 64.6, 44.9 (q, $J = 28.2$ Hz), 39.0, 27.6, 26.1, 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$
-63.9 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 456.9655, measured: 456.9665.

$^1$H NMR (400 MHz, CDCl$_3$) δ [4.36 (d, $J = 11.2$ Hz), 4.31-4.24] (1H), [2.54-2.42 (m)] (0.5H), [2.08-1.90 (m)] (1H), [1.87-1.62 (m)] (2.5H), [1.61-1.43 (m)] (3H), [1.42-1.21 (m)] (14H), [0.96-0.84 (m)] (6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ [126.7 (q, $J = 280.1$ Hz), 126.4 (q, $J = 281.5$ Hz)], [51.0 (q, $J = 23.2$ Hz), 48.6 (q, $J = 24.5$ Hz)], [38.9, 38.9], [35.7, 35.7], [32.8 (q, $J = 2.4$ Hz), 31.1 (q, $J = 3.1$ Hz)], [31.6, 31.5], [30.5, 30.5], [29.8, 29.8], [29.3, 29.3], [28.2, 28.2], [27.8, 27.7], [26.7, 26.7], [22.6, 22.5], [14.0, 14.0]; $^{19}$F NMR (376 MHz, CDCl$_3$) δ [-65.4 (s), -67.1 (s)]; LRMS: m/z (EI) 265 (M-I), 127, 85, 71, 57 (100).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, $J = 8.8$ Hz, 1H), 6.70 (dd, $J = 8.8$, 2.8 Hz, 1H), 6.63 (d, $J = 2.8$ Hz, 1H), 4.45-4.34 (m, 1H), 4.04-3.94 (m, 2H), 3.06-2.73 (m, 4H), 2.50 (dd, $J = 18.4$, 8.8 Hz, 1H), 2.43-2.36 (m, 1H), 2.30-2.21 (m, 1H), 2.20-1.83 (m, 8H), 1.69-1.36 (m, 1H), 0.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 137.6, 132.1, 126.2, 114.4, 111.9, 66.3, 50.3, 47.8, 43.9, 41.5 (t, $J = 20.8$ Hz), 38.2, 37.0, 35.7, 31.5, 29.5, 26.4, 25.8, 21.4, 19.9, 13.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.8 (t, $J = 9.4$ Hz, 3F), -111.7 (dm, $J = 269.4$ Hz, 1F), -114.4 (dt, $J = 269.4$, 13.9 Hz, 1F), -121.7 (m, 2F), -122.8 (m, 2F), -123.6 (m, 2F), -126.1 (m, 2F); HRMS: m/z (ESI) calculated [M+H]$^+$: 785.1161, measured: 785.1270.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.37 (q, $J = 8.8$ Hz, 1H), 2.22 (td, $J = 8.0$, 1.2 Hz, 2H), 2.11-2.04 (m, 2H), 1.48-1.36 (m, 4H), 1.35-1.20 (m, 18H), 0.94-0.83 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.2, 123.8 (q, $J = 269.1$ Hz), 113.6 (q, $J = 32.9$ Hz), 36.3, 31.9, 31.5, 31.4, 29.7, 29.6, 29.5, 29.4, 29.8, 28.2, 7.1, 22.7, 22.5, 14.1, 14.0; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -56.4 (s); LRMS: m/z (EI) 306 (M), 180, 165, 126, 97, 83, 69, 56 (100).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.0$ Hz, 2H), 7.45-7.30 (m, 5H), 6.84 (d, $J = 8.0$ Hz, 2H), 5.67 (t, $J = 15.6$ Hz, 1H), 3.94 (t, $J = 5.2$ Hz, 2H), 3.00-2.90 (m, 2H), 2.87-2.77 (m, 2H), 1.86-1.75 (m, 2H), 1.59-1.47 (m, 2H), 1.21 (t, $J = 6.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.5, 162.6, 156.2, 140.4, 130.1, 129.8, 129.0, 128.7, 126.6, 114.2 (t, $J = 22.1$ Hz), 114.0, 120-100 (m), 67.5, 31.3, 30.8, 28.7, 24.9, 8.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -81.0 (m, 3F), -105.0 (m, 2F), -124.2 (m, 2F), -125.6 (m, 2F); HRMS: m/z (ESI) calculated [M+H]$^+$: 527.1633, measured: 527.1630.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.8$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 6.09 (dt, $J = 16.0$, 6.8 Hz, 1H), 5.96 (d, $J = 16.0$ Hz, 1H), 5.52 (q, $J = 8.8$ Hz, 1H), 4.06 (t, $J = 6.0$ Hz, 2H), 6.63 (td, $J = 8.0$, 1.2 Hz, 2H), 2.13 (td, $J = 7.2$, 6.8 Hz, 2H), 2.05-1.95 (m, 2H), 1.44-1.34 (m, 2H), 1.32-1.21 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.5, 162.5, 149.4 (q, $J = 5.4$ Hz), 138.3, 136.6, 132.6, 131.9, 130.1, 129.7, 128.2, 123.9 (q, $J = 268.4$ Hz), 116.0 (q, $J = 32.9$ Hz), 113.9, 67.4, 32.9, 31.6, 28.9, 28.8, 24.3, 22.5, 14.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -56.3 (s); HRMS: m/z (ESI) calculated [M+H]$^+$: 445.2354, measured: 445.2346.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 5.95 (q, $J = 8.4$ Hz, 1H), 4.58 (t, $J = 6.4$ Hz, 2H), 2.82 (t, $J = 6.4$ Hz, 2H), 2.30 (t, $J = 7.2$ Hz, 2H), 1.15 (tt, $J = 7.6$, 6.8 Hz, 2H), 1.40-1.32 (m, 2H), 1.31-1.22 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.7, 133.8, 132.8 (q, $J = 5.4$ Hz), 132.1, 130.1, 123.9 (q, $J = 33.6$ Hz), 122.7 (q, $J = 268.4$ Hz), 117.9, 116.4, 96.8, 78.5, 63.0, 31.6, 31.2, 28.5, 28.2, 22.4, 19.3, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -56.8 (s); LRMS: m/z (EI) 377 (M), 308 (M-CF$_3$), 201, 130 (100), 102, 91, 69.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J = 5.2$, 2.8 Hz, 2H), 7.71 (dd, $J = 5.2$, 2.8 Hz, 2H), 7.47-7.42 (m, 2H), 7.41-7.36 (m, 3H), 5.06 (t, $J = 14.0$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 3.70 (t, $J = 6.4$ Hz, 2H), 2.52 (t, $J = 6.4$ Hz, 2H), 1.78-1.64 (m, 4H), 1.28 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 153.8, 135.1, 133.8, 132.3, 132.1, 130.1, 129.7, 129.5, 123.2, 113.5 (t, $J = 26.9$ Hz), 112.5 (t, $J = 248.3$ Hz), 62.9, 37.6, 31.9, 28.1, 26.6, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -96.3 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 482.1214, measured: 482.1211.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 4.57 (dd, $J = 4.4$, 2.4 Hz, 1H), 3.86 (ddd, $J = 10.8$, 7.2, 3.2 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.54-3.46 (m, 1H), 3.38 (dt, $J = 9.6$, 6.4 Hz, 1H), 2.94-2.84 (m, 1H), 2.76 (dd, $J = 6.8$, 4.8 Hz, 2H), 2.24-2.09 (m, 4H), 1.88-1.77 (m, 1H), 1.75-1.67 (m, 1H), 1.64-1.37 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 130.3, 130.2, 126.3 (q, $J = 275.8$ Hz), 113.6, 98.8, 83.2, 80.2, 67.4, 62.3, 55.2, 40.3, 38.2 (q, $J = 27.5$ Hz), 30.7, 29.2, 28.6, 27.8, 25.5, 25.4, 19.6, 18.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.9 (s); HRMS: m/z (ESI) calculated [M+Na]$^+$: 435.2123, measured: 435.2132.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.13 (ddd, $J = 2.8$, 2.8, 2.0 Hz, 1H), 4.37-4.19 (m, 3H), 3.75 (dd, $J = 8.8$, 7.2 Hz, 1H), 3.16-3.06 (m, 1H), 2.50-2.31 (m, 1H), 2.30-2.12 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.8, 120-100 (m), 75.6, 74.8 (d, $J = 4.0$ Hz), 68.8, 39.4, 32.9 (t, $J = 21.5$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.8 (t, $J = 10.1$ Hz, 3F), -112.1 (dm, $J = 270.0$ Hz, 1F), -113.9 (dm, $J = 270.0$ Hz, 1F), -121.7 (m, 2F), -122.8 (m, 2F), -123.4 (m, 2F), -126.1 (m, 2F); HRMS: m/z (ESI) calculated [M+Na]$^+$:
415.0368, measured: 415.0363.

\[ \begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \delta 6.19 (\text{ddd}, J = 2.0, 2.0, 2.0 \text{ Hz}, 1\text{H}), 4.36 (\text{dt}, J = 13.2, \\
& 1.6 \text{ Hz}, 1\text{H}), 4.23 (\text{dd}, J = 13.2, 2.0 \text{ Hz}, 1\text{H}), 4.06 (\text{dd}, J = 9.2, 2.0 \text{ Hz}, 1\text{H}), 3.96 (\text{dd}, \\
& J = 9.2, 5.6 \text{ Hz}, 1\text{H}), 3.23-3.14 (\text{m}, 1\text{H}), 2.68-2.50 (\text{m}, 1\text{H}), 2.34-2.15 (\text{m}, 1\text{H}); \\
\text{13C NMR (100 MHz, CDCl}_3) & \delta 152.8, 120-100 \text{ (m), 72.7} (\text{d}, J = 4.7 \text{ Hz}), 71.4, 69.7, 41.1, \\
& 31.7 (J = 20.5 \text{ Hz}); \quad \text{19F NMR (376 MHz, CDCl}_3) \delta -80.8 \text{ (bs, 3F), -112.7} (\text{dt}, J = \\
& 270.7, 23.3 \text{ Hz}, 1\text{F}), -114.0 \text{ (dt, } J = 270.7, 24.1 \text{ Hz}, 1\text{F}), -121.7 \text{ (bs, 2F), -122.8} \text{ (bs,} \\
& 2\text{F), -123.6} \text{ (bs, 2F), -126.1} \text{ (bs, 2F); HRMS: m/z (APPI) calculated [M-I]^+: 415.0368,} \\
& \text{measured: 415.0361.} \\
\end{align*} \]

\[ \begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \delta 6.39 (\text{t}, J = 14.8 \text{ Hz}, 1\text{H}), 1.57-1.46 (\text{m}, 1\text{H}), 0.89-0.79 \\
& (\text{m}, 4\text{H}); \quad \text{13C NMR (100 MHz, CDCl}_3) \delta 129.9, 125.6 (\text{t}, J = 3.5 \text{ Hz}), 120-100 \text{ (m),} \\
& 17.9, 11.1; \quad \text{19F NMR (376 MHz, CDCl}_3) \delta -80.8 \text{ (t, } J = 9.4 \text{ Hz, 3F), -104.5} \text{ (t, } J = 12.4 \\
& \text{Hz, 2F), -121.7} \text{ (m, 2F), -122.8} \text{ (m, 2F), -123.2} \text{ (m, 2F), -126.1} \text{ (m, 2F); LRMS: m/z} \\
& (\text{EI}) 385 \text{ (M-I, 100), 365, 196, 166, 146, 127, 115, 97, 69.} \\
\text{Z product: } \text{19F NMR (376 MHz, CDCl}_3) & \delta -80.8 \text{ (t, } J = 8.3 \text{ Hz, 3F), -107.2} \text{ (t, } J = 12.4 \\
& \text{Hz, 2F), -121.6} \text{ (m, 2F), -122.8} \text{ (m, 4F), -126.1} \text{ (m, 2F); LRMS: m/z (EI) 385 \text{ (M-I,} \\
& 100), 365, 196, 166, 146, 127, 115, 97, 69.} \\
\end{align*} \]

\[ \begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \delta 5.81-5.70 \text{ (m, 1H), 5.54-5.42} \text{ (m, 1H), 3.21} \text{ (td, } J = 7.2, \\
& 1.6 \text{ Hz, 2H), 2.70 (tdd, } J = 7.2, 6.8, 2.8 \text{ Hz, 2H); \quad \text{13C NMR (100 MHz, CDCl}_3) \delta 206.7} \\
& (\text{t, } J = 7.8 \text{ Hz}), 120-100 \text{ (m), 97.7, 85.7} \text{ (t, } J = 28.2 \text{ Hz), 31.5, 2.0; \quad \text{19F NMR (376} \\
& \text{MHz, CDCl}_3) \delta -80.8 \text{ (m, 3F), -108.2} \text{ (m, 2F), -121.6} \text{ (m, 2F), -122.9} \text{ (m, 2F), -123.2} \\
& \text{ (m, 2F), -126.1} \text{ (m, 2F); LRMS: m/z (EI) 385 \text{ (M-I, 100), 365, 345, 295, 196, 166,} \\
& 155, 146, 127, 115, 97, 69.} \\
\end{align*} \]