Selective Difluoroalkylation of Alkenes
by Using Visible Light Photoredox Catalysis

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Supporting Information

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General considerations

General reagent information
Anhydrous DCM and DMF were purchased from Sigma-Aldrich chemical company in Sure-Seal bottles and degassed by repeated sonication reduced vacuum and replenishing the atmosphere with argon. All reagents including fac-[Ir(ppy)₃] and BrCF₂CO₂Et were purchased from Sigma-Aldrich, Alfa Aesar, or TCI chemical companies. Flash column chromatography was performed using Merck silica gel 60 (70-230 mesh).

General analytical information
The synthesized alkenes were characterized by ¹H, ¹³C NMR, and FT-IR spectroscopy, and difluoroalkylated products were characterized by ¹H, ¹³C, and ¹⁹F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Bruker 400 MHz instrument (400 MHz for ¹H NMR, 101 MHz for ¹³C NMR, and 377 MHz for ¹⁹F NMR). Copies of ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra can be found at the end of the Supporting Information. ¹H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ¹³C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ¹H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using KBr plates. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.
**Table S1. Additional Optimization Studies for Selective Difluoroalkylation**

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<th>entry</th>
<th>photocatalyst (1 mol%)</th>
<th>base (2 equiv.)</th>
<th>Stochiometry</th>
<th>solvent</th>
<th>Yield (%)</th>
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<td>[Ru(bpy)3]Cl2</td>
<td>TMEDA</td>
<td>MeCN (0.2 M)</td>
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<td>46</td>
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<tr>
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<td>DBU/TMEDA (2 eq: 2 eq)</td>
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<td>2.0 equiv.</td>
<td>DCM</td>
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<td>DCM</td>
<td>trace</td>
<td>-</td>
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<td>33</td>
<td>fac-[trilpy]3</td>
<td>-</td>
<td>DCM</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>fac-[trilpy]3 (no light)</td>
<td>DBU/TMEDA (2 eq: 2 eq)</td>
<td>DCM</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>fac-[trilpy]3</td>
<td>K2CO3/DBU (2 eq: 2 eq)</td>
<td>MeCN</td>
<td>49</td>
<td>-</td>
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<td>36</td>
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<td>K2CO3/DBU (2 eq: 2 eq)</td>
<td>1,4-dioxane</td>
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<td>(35%)</td>
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<td>37</td>
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<td>K2CO3/DBU (2 eq: 2 eq)</td>
<td>DMF</td>
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<td>38</td>
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<td>(24%)</td>
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<td>K2CO3/DBU (2 eq: 2 eq)</td>
<td>DMF (0.25 M)</td>
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<td>K2CO3/DBU (2 eq: 2 eq)</td>
<td>DMF (0.5 M)</td>
<td>trace</td>
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</table>

[a]Conditions: 1a (0.1 mmol), BrCF2CO2Et (0.15 mmol), 24 h. [b]Yields were determined by using gas chromatography and 19F NMR spectroscopy with internal standards dodecane and 4-fluorotoluene, respectively. [c]CF2CO2Me substituted alkane was formed. [d]DBU was added after complete conversion of 1a to 4a. [e]In parenthesis are yields after 1 h reaction times.
Experimental Details

Synthesis of hydridofluoroalkylation of alkenes

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (0.5 mmol), fac-[Ir(ppy)₃] (1 mol%, 0.005 mmol), TMEDA (1.0 mmol), DBU (1.0 mmol), and BrCF₂CO₂Et (0.75 mmol) in dichloromethane (5.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the solution was degassed by bubbling argon through the mixture. The test tube was placed under blue LEDs (7 W) at room temperature for 18-24 h, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with dichloromethane and washed with saturated NH₄Cl solution and brine. The organic
layers were dried over MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography to give the hydrodifluoroalkylated alkane.

**Alkenyl-difluoroalkylations**

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (1.0 mmol), $fac$-[Ir(ppy)$_3$] (1 mol%, 0.01 mmol), K$_2$CO$_3$ (2.0 mmol), and BrCF$_2$CO$_2$Et (1.5 mmol) in DMF (10.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the mixture was degassed by bubbling argon through the reaction. The test tube was placed under blue LEDs (7 W) at room temperature. After 1-2 h, DBU (2.0 mmol) was added to the mixture, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with ethyl acetate and washed with saturated NH$_4$Cl solution and brine. The organic layers were dried over MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography to give the difluoroalkylated alkene.

**Alkenyl-difluoroalkylations of electron-rich aromatic alkenes**

An oven-dried resealable tube equipped with a magnetic stir bar was charged with an alkene (1.0 mmol), $fac$-[Ir(ppy)$_3$] (1 mol%, 0.01 mmol), K$_2$CO$_3$ (3.0 mmol), and BrCF$_2$CO$_2$Et (1.5 mmol) in DMF (10.0 mL, 0.1 M). The tube was sealed with a silicone septum screw cap, and the mixture was degassed by bubbling argon through the reaction. The test tube was placed under blue LEDs (7 W) at room temperature for 5 h, and the reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with ethyl acetate and washed with saturated NH$_4$Cl solution and brine. The organic layers were dried over MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography to give the difluoroalkylated alkene.

**Analytic Data for synthesized alkenes**

**1b**: white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 8.4 Hz, 2H), 7.33 (d, $J$ = 8.4 Hz, 2H), 7.24 (bs, 1H), 5.87 (ddt, $J$ = 17.0, 10.2, 5.6 Hz, 1H), 5.20 (ddt, $J$ = 17.0, 1.6, 1.2 Hz, 1H), 5.12 (ddt, $J$ = 10.2, 1.6, 1.2 Hz, 1H), 4.03-3.98 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.75, 137.65, 134.02, 132.84, 128.70, 128.65, 116.52, 42.57; IR (neat): $\nu_{max}$ = 3329, 3076, 1631, 1540, 1300, 1093 cm$^{-1}$; HRMS m/z (EI) calc. for C$_{10}$H$_{10}$ClNO [M$^+$] 195.0451, found 195.0450; $R_f$ 0.33 (hex/EtOAc, 2/1).
1c: white solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.67 (d, J = 8.6 \text{ Hz}, 2H), 7.48 (d, J = 8.6 \text{ Hz}, 2H), 7.39 (bs, 1H), 5.87 (ddt, J = 17.0, 10.2, 5.6 \text{ Hz}, 1H), 5.19 (ddt, J = 17.0, 1.6, 1.2 \text{ Hz}, 1H), 5.13 (ddt, J = 10.2, 1.6, 1.2 \text{ Hz}, 1H), 4.02-3.96 (m, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 166.85, 133.97, 133.24, 131.64, 128.82, 126.11, 116.49, 42.54; \) IR (neat): \(\nu_{\text{max}} = 3295, 3074, 2248, 1633, 1538 \text{ cm}^{-1}; \) HRMS \(m/z\) (EI) calc. for C\textsubscript{10}H\textsubscript{10}BrNO [M\textsuperscript{+}] 238.9946, found 238.9946; \(R_f 0.28 \text{ (hex/EtOAc, 2/1)}.\)

1d: colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 6.18 (bs, 1H), 5.77 (ddt, J = 17.2, 10.0, 5.6 \text{ Hz}, 1H), 5.11 (ddt, J = 17.2, 1.6, 1.6 \text{ Hz}, 1H), 5.05 (ddt, J = 10.0, 1.6, 1.2 \text{ Hz}, 1H), 3.83-3.78 (m, 2H), 2.15 (t, J = 7.6 \text{ Hz}, 2H), 1.58 (tt, J = 7.6, 7.6 \text{ Hz}, 2H), 1.30-1.16 (m, 8H), 0.82 (t, J = 7.0 \text{ Hz}, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 173.37, 134.54, 166.10, 41.92, 36.76, 31.78, 29.38, 29.12, 25.93, 22.68, 14.13; \) IR (neat): \(\nu_{\text{max}} = 3289, 2927, 1644, 1547 \text{ cm}^{-1}; \) HRMS \(m/z\) (EI) calc. for C\textsubscript{11}H\textsubscript{21}NO [M\textsuperscript{+}] 183.1623, found 183.1624; \(R_f 0.30 \text{ (hexanes:EtOAc, 2/1)}.\)

1e: colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 5.81 (ddt, J = 16.9, 10.0, 7.0 \text{ Hz}, 1H), 5.00 (ddt, J = 16.9, 2.0, 1.6 \text{ Hz}, 1H), 4.94 (ddt, J = 10.0, 2.0, 1.2 \text{ Hz}, 1H), 3.61 (t, J = 6.4 \text{ Hz}, 2H), 2.06 (dtdd, J = 7.0, 6.9, 1.6, 1.2 \text{ Hz}, 2H), 1.57-1.49 (m, 2H), 1.47-1.38 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 139.16, 114.57, 63.29, 33.76, 32.52, 26.20, 25.38, 18.59, -5.06; \) IR (neat): \(\nu_{\text{max}} = 2930, 2859, 1472, 1255, 1103 \text{ cm}^{-1}; \) \(R_f 0.83 \text{ (only hexanes)}.\)

1f: colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 8.05 (dd, J = 8.4, 1.2 \text{ Hz}, 2H), 7.55 (tt, J = 7.6, 1.2 \text{ Hz}, 1H), 7.43 (dd, J = 8.4, 7.6 \text{ Hz}, 2H), 5.82 (ddt, J = 17.0, 10.0, 6.8 \text{ Hz}, 1H), 5.04 (ddt, J = 17.0, 2.0, 1.6 \text{ Hz}, 1H), 4.98 (ddt, J = 10.0, 2.0, 1.2 \text{ Hz}, 1H), 4.33 (t, J = 6.4 \text{ Hz}, 2H), 2.13 (tddd, J = 6.9, 6.8, 1.6, 1.2 \text{ Hz}, 2H), 1.83-1.75 (m, 2H), 1.60-1.51 (m, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 166.79, 138.50, 132.98, 130.64, 129.70, 128.49, 115.05, 65.04, 33.50, 28.34, 25.48; \) IR (neat): \(\nu_{\text{max}} = 2938, 2861, 1720, 1641, 1452, 1274 \text{ cm}^{-1}; \) HRMS \(m/z\) (EI) calc. for C\textsubscript{13}H\textsubscript{16}O\textsubscript{2} [M\textsuperscript{+}] 204.1150, found 204.1153; \(R_f 0.63 \text{ (hex/EtOAc, 8/1)}.\)
1g: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.79 (ddt, $J = 17.2$, 10.0, 6.8 Hz, 1H), 5.01 (ddt, $J = 17.2$, 2.0, 1.6 Hz, 1H), 4.96 (ddt, $J = 10.0$, 2.0, 1.2 Hz, 1H), 4.07 (t, $J = 6.8$ Hz, 2H), 2.29 (t, $J = 7.6$ Hz, 2H), 2.08 (tddd, $J = 6.9$, 6.8, 1.6, 1.2 Hz, 2H), 1.68-1.58 (m, 2H), 1.50-1.41 (m, 2H), 1.35-1.25 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.93, 138.37, 114.87, 64.17, 34.44, 33.39, 31.78, 29.22, 29.04, 28.21, 25.32, 25.11, 22.70, 14.12; IR (neat): $\nu_{max}$ = 2929, 2858, 1740, 1641, 1459, 1168 cm$^{-1}$; HRMS m/z (EI) calc. for C$_{14}$H$_{26}$O$_2$ [M$^+$] 226.1933, found 226.1936; $R_f$ 0.70 (hex/EtOAc, 8/1).

1h: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.71-5.63 (m, 1H), 5.17-5.11 (m, 2H), 3.57 (ddd, $J = 7.2$, 7.0, 6.8 Hz, 1H), 3.47 (dt, $J = 9.2$, 6.8 Hz, 1H), 3.23 (dt, $J = 9.2$, 6.8 Hz, 1H), 1.60-1.49 (m, 4H), 1.45-1.20 (m, 12H), 0.88 (t, $J = 6.2$ Hz, 3H), 0.87 (t, $J = 6.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.96, 116.23, 81.54, 68.75, 35.68, 31.99, 31.90, 30.07, 26.11, 25.28, 22.82, 22.80, 14.22; IR (neat): $\nu_{max}$ = 2931, 2859, 1740, 1466, 1097, 922 cm$^{-1}$; $R_f$ 0.61 (only hexanes).

1i: solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.86 (s, 2H), 5.99 (ddt, $J = 16.8$, 10.4, 6.4 Hz, 1H), 5.27 (ddt, $J = 16.8$, 1.6, 1.6 Hz, 1H), 5.18 (ddt, $J = 10.4$, 1.6, 1.2 Hz, 1H), 3.77 (s, 2H), 3.38 (bs, 1H), 3.34 (ddd, $J = 6.4$, 1.6, 1.6 Hz, 2H), 2.39 (s, 6H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.32, 137.04, 135.04, 132.38, 129.23, 117.39, 52.35, 46.47, 21.06, 19.80; IR (neat): $\nu_{max}$ = 2916, 2858, 1713, 1448 cm$^{-1}$; $R_f$ 0.69 (only hexanes).

1j: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.64 (ddt, $J = 17.2$, 10.4, 5.6 Hz, 1H), 4.93 (ddt, $J = 17.2$, 1.6, 1.2 Hz, 1H), 4.83 (ddt, $J = 10.4$, 1.6, 1.2 Hz, 1H), 3.91 (bs, 1H), 3.63 (ddd, $J = 5.6$, 1.2, 1.2 Hz, 2H), 3.25 (t, $J = 6.2$ Hz, 2H), 3.13 (t, $J = 6.0$ Hz, 2H), 1.37-1.23 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.51, 116.51, 71.54, 70.01, 61.86, 29.41, 26.17; IR (neat): $\nu_{max}$ = 3384, 2940, 2886, 1647, 1347, 1061 cm$^{-1}$; HRMS m/z (FAB) calc. for C$_7$H$_{15}$O$_2$ [M+H$^+$] 131.1072, found 131.1070; $R_f$ 0.18 (hex/EtOAc, 4/1).
Analytic Data for Synthesized Difluoroalkylated Products

Analytic Data for hydrodifluoroalkylated products

3a: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.31 (q, $J = 7.2$, 2H), 2.16-1.96 (m, 2H), 1.34 (t, $J = 7.2$, 3H), 1.38-1.21 (m, 20H), 0.87 (t, $J = 6.8$, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.29 (t, $J = 33.2$ Hz), 116.55 (t, $J = 248.3$ Hz), 62.75, 34.68 (t, $J = 23.3$ Hz), 32.1, 29.81, 29.76, 29.57, 29.53, 29.42, 29.24, 28.31, 22.85, 21.62 (t, $J = 4.4$ Hz), 14.2, 14.05; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.97; IR (neat): $\nu_{\text{max}}$ = 2927, 2856, 1771, 1467, 1192, 1093 cm$^{-1}$; $R_f$ 0.54 (only hexanes).

3b: yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J =$ 8.8 Hz, 2H), 7.38 (d, $J =$ 8.8 Hz, 2H), 6.49 (bs, 1H), 4.30 (q, $J =$ 7.2 Hz, 2H), 3.48 (td, $J =$ 6.8, 6.4 Hz, 2H), 2.14 (tt, $J =$ 16.8, 7.6 Hz, 2H), 1.86-1.76 (m, 2H), 1.33 (t, $J =$ 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.87, 164.29 (t, $J =$ 32.7 Hz), 137.95, 132.89, 129.00, 128.51, 116.17 (t, $J =$ 251.3 Hz), 63.20, 39.37, 32.03 (t, $J =$ 23.7 Hz), 22.07 (t, $J =$ 4.0 Hz), 14.10; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.77; IR (neat): $\nu_{\text{max}}$ = 3307, 1762, 1639, 1095 cm$^{-1}$; $R_f$ 0.49 (hex/EtOAc, 2/1).

3c: yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J =$ 8.6 Hz, 2H), 7.54 (d, $J =$ 8.6 Hz, 2H), 6.46 (bs, 1H), 4.31 (q, $J =$ 7.2 Hz, 2H), 3.48 (td, $J =$ 6.8, 6.4 Hz, 2H), 2.15 (tt, $J =$ 16.8, 7.6 Hz, 2H), 1.86-1.76 (m, 2H), 1.33 (t, $J =$ 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.95, 164.27 (t, $J =$ 32.9 Hz), 133.31, 131.97, 128.67, 126.39, 116.14 (t, $J =$ 251.2 Hz), 63.20, 39.35, 32.00 (t, $J =$ 23.7 Hz), 22.04 (t, $J =$ 4.0 Hz), 14.09; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.77; $R_f$ 0.43 (hex/EtOAc, 2/1).

3d: yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.60 (bs, 1H), 4.28 (q, $J =$ 7.2 Hz, 2H), 3.27 (td, $J =$ 6.8, 6.0 Hz, 2H), 2.12 (t, $J =$ 7.3 Hz, 2H), 2.03 (tt, $J =$ 16.4, 8.4 Hz, 2H), 1.72-1.67 (m, 2H), 1.67-1.58 (m, 2H), 1.31 (t, $J =$ 7.2 Hz, 3H), 1.28-1.20 (m, 8H), 0.84 (t, $J =$ 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.57, 164.31 (t, $J =$ 33.3 Hz), 116.19 (t, $J =$ 251.5 Hz), 63.15, 38.65, 36.98, 32.02 (t, $J =$ 24.2 Hz), 31.85, 29.43, 29.19, 25.94, 22.78, 22.18 (t, $J =$ 4.0 Hz), 14.24,
14.13; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.95; IR (neat): $\nu_{\text{max}}$ = 3370, 1637, 1142 cm$^{-1}$; $R_f$ 0.41 (hex/EtOAc, 2/1).

3e: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.35 (q, $J = 7.0$ Hz, 2H), 3.58 (t, $J = 6.4$ Hz, 2H), 2.03 (tt, $J = 16.8$, 7.6 Hz, 2H), 1.60-1.40 (m, 4H), 1.39-1.27 (m, 4H), 1.34 (t, $J = 7.0$ Hz, 3H), 0.88 (s, 9H), 0.03 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.61 (t, $J = 35.5$ Hz), 137.93, 116.56 (t, $J = 250.7$ Hz), 63.22, 62.86, 34.64 (t, $J = 23.2$ Hz), 32.75, 29.06, 26.15, 25.67, 21.64 (t, $J = 4.3$ Hz), 18.54, 14.15, -5.12; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.97; IR (neat): $\nu_{\text{max}}$ = 2933, 2859, 1771, 1256, 1100 cm$^{-1}$; $R_f$ 0.62 (only hexanes).

3f: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 7.2$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.41 (dd, $J = 7.4$, 7.2 Hz, 2H), 4.29 (q, $J = 7.0$ Hz), 4.28 (t, $J = 6.8$ Hz), 2.01 (tt, $J = 16.4$, 7.2 Hz, 2H), 1.86-1.68 (m, 2H), 1.63-1.52 (m, 2H), 1.52-1.35 (m, 4H), 1.31 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.71, 164.46 (t, $J = 33.1$ Hz), 132.97, 130.55, 129.63, 128.46, 116.43 (t, $J = 250.9$ Hz), 64.93, 62.83, 34.49 (t, $J = 23.2$ Hz), 28.82, 28.61, 25.85, 21.49 (t, $J = 4.1$ Hz), 14.05; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.93; IR (neat): $\nu_{\text{max}}$ = 2942, 1768, 1720, 1276, 1114 cm$^{-1}$; $R_f$ 0.58 (hex/EtOAc, 4/1).

3g: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.29 (q, $J = 7.2$ Hz, 2H), 4.02 (t, $J = 6.0$ Hz, 2H), 2.52 (t, $J = 7.4$ Hz, 2H), 2.03 (tt, $J = 16.4$, 7.6 Hz, 2H), 1.65-1.53 (m, 4H), 1.53-1.46 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H), 1.29-1.18 (m, 12H), 0.84 (t, $J = 6.4$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.13, 164.55 (t, $J = 32.8$ Hz), 116.46 (t, $J = 250.9$ Hz), 64.25, 62.91, 34.54, 34.50 (t, $J = 19.1$ Hz), 31.84, 29.29, 29.10, 28.86, 28.60, 25.81, 25.18, 22.77, 21.53 (t, $J = 4.2$ Hz), 14.22, 14.14 (t, $J = 2.8$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -105.99; IR (neat): $\nu_{\text{max}}$ = 2932, 2859, 1770, 1736, 1183 cm$^{-1}$; $R_f$ 0.61 (hex/EtOAc, 4/1).

3h: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.30 (q, $J = 7.2$ Hz, 2H), 3.45-3.31 (m, 2H), 3.30-3.25 (m, 1H), 2.24-2.00 (m, 2H), 1.73-1.64 (m, 2H), 1.61-1.45 (m, 4H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.37-1.22 (m, 12H), 0.88 (t, $J = 6.8$ Hz, 3H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.54 (t, $J = 33.3$ Hz), 140.51 (t, $J = 8.2$ Hz), 116.73 (t, $J = 250.7$ Hz).
Analytic Data for alkenyl-CF₂CO₂Et compounds

**3i**: colorless oil; $^1$H NMR (400 MHz, CDCl₃) δ 6.87 (s, 2H), 4.14 (s, 2H), 3.00 (t, $J = 6.2$ Hz, 1H), 2.27 (s, 3H), 2.25 (s, 6H), 1.88 (tt, $J = 9.2$, 4.0 Hz, 2H), 1.25 (m, 2H); $^{13}$C NMR (101 MHz, CDCl₃) δ 161.69 (t, $J = 29.3$), 138.32, 137.99, 129.65, 128.33, 112.92 (t, $J = 242.5$, Hz), 44.55, 43.53, 32.12 (t, $J = 22.9$, Hz), 21.11, 20.16, 19.28 (t, $J = 5.2$, Hz); $^{19}$F NMR (377 MHz, CDCl₃) δ -99.95; HRMS m/z (EI) calc. for C₁₅H₁₉F₂NO [M⁺] 267.1435, found 267.1430; $R_f$ 0.51 (hex/EtOAc, 4/1).

**6a**: colorless oil; $^1$H NMR (400 MHz, CDCl₃) δ 6.27 (dtt, $J = 15.8$, 6.8, 2.6 Hz, 1H), 5.66 (dtt, $J = 15.8$, 11.1, 1.4 Hz, 1H), 4.32 (q, $J = 7.2$ Hz, 2H), 2.18-2.08 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.46-1.21 (m, 16H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl₃) δ 164.43 (t, $J = 34.9$ Hz), 140.26 (t, $J = 8.9$ Hz), 121.12 (t, $J = 25.1$ Hz), 112.62 (t, $J = 248.4$ Hz), 63.06, 32.11, 29.79, 29.75, 29.59, 29.53, 29.25, 28.33, 22.89, 14.32, 14.15; $^{19}$F NMR (377 MHz, CDCl₃) δ -103.01; IR (neat): νₘₐₓ = 2926, 2855, 1769, 1674, 1083 cm⁻¹; $R_f$ 0.75 (hex/EtOAc, 8/1).

**6d**: yellow oil; $^1$H NMR (400 MHz, CDCl₃) δ 6.26 (dtt, $J = 15.8$, 5.2, 1.8 Hz, 1H), 5.79 (dtt, $J = 15.8$, 11.2, 3.6 Hz, 1H), 5.66 (bs, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 4.02-3.95 (m, 2H), 2.20 (t, $J = 7.6$ Hz, 2H), 1.67-1.57 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.31-1.22 (m, 8H), 0.86 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl₃) δ 173.35, 163.87 (t, $J = 35.8$ Hz), 135.80 (t, $J = 8.8$ Hz), 122.21 (t, $J = 25.6$ Hz), 112.21 (t, $J = 249.2$ Hz), 63.34, 39.96, 36.80, 31.84, 29.42, 29.17, 25.86, 22.77, 14.23, 14.09; $^{19}$F NMR (377 MHz, CDCl₃) δ -103.42; IR (neat): νₘₐₓ = 3288, 2870, 1768, 1650, 1142 cm⁻¹; HRMS m/z (FAB) calc. for C₁₀H₁₆F₂NO [M⁺] 236.1020, found 236.1100; $R_f$ 0.59 (hex/EtOAc, 1/1).

**6e**: colorless oil; $^1$H NMR (400 MHz, CDCl₃) δ 6.27 (dtt, $J = 15.6$, 6.8, 2.8 Hz, 1H), 5.67 (dtt, $J = 15.6$, 11.2, 1.6 Hz, 1H), 4.32 (q, $J =$
7.2 Hz, 2H), 3.60 (t, J = 6.0 Hz, 2H), 2.20-2.12 (m, 2H), 1.57-1.43 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.37 (t, J = 35.0 Hz), 139.98 (t, J = 8.9 Hz), 121.32 (t, J = 25.1 Hz), 112.56 (t, J = 248.3 Hz), 63.06, 62.96, 32.32, 31.85, 26.15, 24.69, 18.55, 14.14, -5.11; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.01; IR (neat): ν$_{max}$ = 2932, 2860, 1770, 1134, 1099 cm$^{-1}$; $R_f$ 0.71 (hex/EtOAc, 4/1).

6f: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (dd, J = 8.4, 1.2 Hz, 2H), 7.55 (tt, J = 7.4, 1.5 Hz, 1H), 7.43 (dd, J = 8.4, 7.4 Hz, 2H), 6.28 (dtt, J = 15.8, 6.8, 2.6 Hz, 1H), 5.76 (dtt, J = 15.8 11.0, 1.6 Hz, 1H), 4.32 (t, J = 6.4 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 2.27-2.18 (m, 2H), 1.78 (tt, J = 7.0, 6.8 Hz, 2H), 1.60 (tt, J = 7.6, 7.0 Hz, 2H), 1.32 (t, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.74, 164.22 (t, J = 34.9 Hz), 139.31 (t, J = 9.1 Hz), 133.08, 130.44, 129.67, 128.52, 121.70 (t, J = 25.1 Hz), 112.41 (t, J = 253.6 Hz), 64.68, 63.07, 31.59, 28.28, 24.83, 14.07; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.06; IR (neat): ν$_{max}$ = 2942, 2864, 1767, 1719, 1275 cm$^{-1}$; $R_f$ 0.50 (hex/EtOAc, 4/1).

6k: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (dd, J = 7.2, 7.2 Hz, 2H), 7.24-7.16 (m, 3H), 6.33 (dtt, J = 15.6, 6.8, 2.6 Hz, 1H), 5.72 (dtt, J = 15.6, 11.0, 1.6 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 2.76 (t, J = 7.8 Hz, 2H), 2.52-2.44 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.23 (t, J = 34.8 Hz), 140.87, 138.98 (t, J = 9.0 Hz), 128.63, 128.58, 126.35, 121.87 (t, J = 25.1 Hz), 112.44 (t, J = 248.6 Hz), 63.09, 34.68, 33.80, 14.11; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.17; IR (neat): ν$_{max}$ = 2988, 2870, 1767, 1142, 1077 cm$^{-1}$; HRMS m/z (EI) calc. for C$_{14}$H$_{16}$F$_2$O$_2$ [M$^+$] 254.1118, found 254.1120; $R_f$ 0.63 (hex/EtOAc, 4/1).

6l: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (dd, J = 7.6, 2.0 Hz, 2H), 7.42-7.33 (m, 3H), 7.09 (dt, J = 16.4, 2.4 Hz, 1H), 6.32 (dt, J = 16.4, 11.4 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.13 (t, J = 35.0 Hz), 137.03 (t, J = 9.4 Hz), 129.85, 129.04, 128.40, 127.65, 119.01 (t, J = 25.1 Hz), 112.94 (t, J = 249.5 Hz), 63.33, 14.15; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.24; IR (neat): ν$_{max}$ = 2987, 2871, 1767, 1075 cm$^{-1}$; $R_f$ 0.63 (hex/EtOAc, 4/1).
**6m**: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (dd, $J$ = 8.6, 5.4 Hz, 2H), 7.06 (dd, $J$ = 8.6, 8.6 Hz, 2H), 7.04 (dt, $J$ = 16.2, 2.6 Hz, 1H), 6.23 (dt, $J$ = 16.2, 11.2 Hz, 1H), 4.35 (q, $J$ = 7.2 Hz, 2H), 1.37 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.07 (t, $J$ = 35.0 Hz), 163.68 (d, $J$ = 251.5 Hz), 135.82 (t, $J$ = 9.5 Hz), 130.52 (d, $J$ = 3.0 Hz), 129.46 (d, $J$ = 8.0 Hz), 118.79 (td, $J$ = 25.3, 2.0 Hz), 116.13 (d, $J$ = 22.2 Hz), 112.83 (t, $J$ = 249.6 Hz), 63.38, 14.15; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.21, -110.87; IR (neat): $\nu_{\text{max}}$ = 2987, 1767, 1511, 1225, 1077 cm$^{-1}$; $R_f$ 0.60 (hex/EtOAc, 4/1).

**6n**: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J$ = 8.8 Hz, 2H), 7.34 (d, $J$ = 8.8 Hz, 2H), 7.03 (dt, $J$ = 16.2, 2.4 Hz, 1H), 6.28 (dt, $J$ = 16.2, 11.4 Hz, 1H), 3.85 (q, $J$ = 7.2 Hz, 2H) 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.96 (t, $J$ = 34.9 Hz), 135.75 (t, $J$ = 9.5 Hz), 135.71, 132.77, 129.28, 128.85, 119.62 (t, $J$ = 25.1 Hz), 112.73 (t, $J$ = 249.7 Hz), 63.41, 14.14; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.34; IR (neat): $\nu_{\text{max}}$ = 2985, 1767, 1658, 1493, 1075 cm$^{-1}$; $R_f$ 0.65 (hex/EtOAc, 4/1).

**6o**: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J$ = 8.4 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 2H), 7.02 (dt, $J$ = 16.0, 2.4 Hz, 1H), 6.30 (dt, $J$ = 16.0, 11.4 Hz, 1H), 4.35 (q, $J$ = 7.2 Hz, 2H), 1.36(t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.94 (t, $J$ = 34.8 Hz), 135.84 (t, $J$ = 9.5 Hz), 133.21, 132.25, 129.11, 124.00, 119.75 (t, $J$ = 25.1 Hz), 112.71 (t, $J$ = 249.8 Hz), 63.43, 14.16; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.39; $R_f$ 0.62 (hex/EtOAc, 4/1).

**6p**: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (s, 4H), 7.06 (dt, $J$ = 16.2, 2.6 Hz, 1H), 6.27 (dt, $J$ = 16.2, 11.6 Hz, 1H), 4.35 (q, $J$ = 7.2 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 3H), 1.33 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.25 (t, $J$ = 35.4 Hz), 153.29, 136.83 (t, $J$ = 9.1 Hz), 131.57, 127.45, 126.01, 118.19 (t, $J$ = 25.3 Hz), 113.08 (t, $J$ = 249.5 Hz), 63.27, 35.00, 31.40, 14.18; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -103.14; IR (neat): $\nu_{\text{max}}$ = 2969, 2870, 1768, 1142, 1074 cm$^{-1}$; HRMS m/z (EI) calc. for C$_{16}$H$_{20}$F$_2$O$_2$ [M$^+$] 282.1431, found 282.1428; $R_f$ 0.68 (hex/EtOAc, 4/1).
6q: colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (d, \(J = 8.8\) Hz, 2H), 7.02 (dt, \(J = 16.2, 2.4\) Hz, 1H), 6.89 (d, \(J = 8.8\) Hz, 2H), 6.17 (dt, \(J = 16.2, 11.2\) Hz, 1H), 4.34 (q, \(J = 7.2\) Hz, 2H), 3.82 (s, 3H), 1.36 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 164.26 (t, \(J = 35.3\) Hz), 160.95, 136.47 (t, \(J = 9.5\) Hz), 129.08, 126.93, 116.48 (t, \(J = 25.1\) Hz), 114.39, 113.16 (t, \(J = 249.2\) Hz), 63.20, 55.47, 14.10; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -102.64; IR (neat): \(\nu_{\text{max}}\) = 1766, 1607, 1514, 1076 cm\(^{-1}\); \(R_f\) 0.51 (hex/EtOAc, 4/1).

6r: colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.31 (m, 3H), 7.31-7.21 (m, 5H), 7.21-7.16 (m, 2H), 6.25 (t, \(J = 11.6\) Hz, 1H), 3.87 (q, \(J = 7.2\) Hz, 2H), 1.13 (t, \(J = 7.2\) Hz 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.57 (t, \(J = 34.1\) Hz), 151.14 (t, \(J = 9.5\) Hz), 140.58, 137.21, 129.99, 129.25, 128.73, 128.54, 128.15, 128.03, 119.63 (t, \(J = 28.5\) Hz), 112.71 (t, \(J = 245.8\) Hz), 62.89, 13.80; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -90.76; IR (neat): \(\nu_{\text{max}}\) = 1771, 1637, 1102, 1066 cm\(^{-1}\); \(R_f\) 0.56 (hex/EtOAc, 4/1).
1b: $^1$H NMR

[Chemical structure image]

[Graph of NMR spectrum with ppm axis]
1b: $^{13}$C NMR
1c: $^1$H NMR
1c: $^{13}$C NMR
$1d: ^1H$ NMR
1d: $^{13}$C NMR
TBSO\textsuperscript{+}H\textsubscript{4}

\textbf{1e: }\textsuperscript{1}H NMR
1e: $^{13}$C NMR
1f: $^1$H NMR
$^{13}$C NMR
$1g: \text{ }^{1}\text{H NMR}$
1g: $^{13}$C NMR
1h: $^1$H NMR
$1h: ^{13}\text{C NMR}$
1j: $^1^H$ NMR
$\text{HO-CH$_2$-CH$_2$-O-CH$_2$CH$_2$CH$_2$=}$

$1j: \text{${}^{13}\text{C}$ NMR}$
3a: $^1$H NMR (3a/6a = 4:1)
3a: $^{13}$C NMR (3a/6a = 4:1)
3b: $^1$H NMR (3b/6b = 11:1)
$^{13}$C NMR (3b/6b = 11:1)
$3b : ^{19}\text{F NMR (3b/6b = 11:1)}$
$3c: ^1H$ NMR (3c/6c = 8:1)
$3c: ^{13}$C NMR ($3c/6c = 8:1$)
3c: $^{19}$F NMR (3c/6c = 8:1)
3d: $^1\text{H}$ NMR ($3d/6d = 8:1$)
$3d: ^{13}C$ NMR ($3d/6d = 8:1$)
3d: $^{19}$F NMR ($3d/6d = 8:1$)
$\text{TBSO}_4\text{CF}_2\text{CO}_2\text{Et}$

$3e: ^1H\text{ NMR} \ (3e/6e = 4:1)$
$^{13}$C NMR (3e/6e = 4:1)
3e: $^{19}$F NMR (3e/6e = 4:1)
3g: $^1$H NMR (3g/6g = 6:1)
$3g: ^{13}\text{C NMR (3g/6g = 6:1)}$
$3g: ^{19}F$ NMR ($3g/6g = 6:1$)
$3h: ^1H$ NMR ($3h/6h = 11:1$)
$3h: ^{13}C$ NMR ($3h/6h = 11:1$)
3h: $^{19}$F NMR (3h/6h = 11:1)
3i: $^1$H NMR (3i/6i = 7:1)
$\text{3i: }^{13}\text{C NMR (3i/6i = 7:1)}$
3i: $^{19}$F NMR
6a: $^1$H NMR
6a: $^{13}$C NMR
6a: $^{19}$F NMR
6d: $^{13}$C NMR
6d: $^{19}$F NMR (6d/3d = 15:1)
6e: $^1$H NMR
$6e: ^{13}\text{C NMR}$
$^1$H NMR
$6f: ^1H$ NMR
6f: $^{13}$C NMR
6f: $^{19}$F NMR
6k: $^1$H NMR ($E/Z = 15:1$)
$^{13}$C NMR ($E/Z = 15:1$)
$6k: \text{^{19}F NMR}$
6l: $^1$H NMR ($E/Z = 11:1$)
6i: $^{13}$C NMR ($E/Z = 11:1$)
6i: $^{19}$F NMR ($E/Z = 11:1$)
$\text{F} \quad \text{CF}_2\text{CO}_2\text{Et}$

6m: $^1\text{H}$ NMR ($E/Z = 25:1$)
$6m: ^{13}\text{C NMR (E/Z = 25:1)}$
6m: $^{19}$F NMR ($E/Z = 25:1$)
6n: $^1$H NMR ($E/Z = 19:1$)
$^{13}$C NMR (E/Z = 19:1)
$^{19}$F NMR ($E/Z = 29:1$)
6o: $^1$H NMR ($E/Z = 11:1$)
60: $^{13}$C NMR ($E/Z = 11:1$)
6o: $^{19}$F NMR ($E/Z = 11:1$)
6p: $^1$H NMR ($E/Z = 9:1$)
$6p: ^{13}$C NMR ($E/Z = 9:1$)
$6p: ^{19}\text{F NMR} \ (E/Z = 9:1)$
6q: $^1$H NMR ($E/Z = 9:1$)
6q: $^{13}$C NMR ($E/Z = 9:1$)
6q: $^{19}$F NMR ($E/Z = 9:1$)
6r: $^1$H NMR
$6r: ^{13}C$ NMR
$6r: ^{19}\text{F NMR}$