Halogen bond promoted aryl migration of allyl alcohols under visible light irradiation

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1. General information

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Advance and JEOL III–400 spectrometer at 25 °C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance refereed to the standard position (CDCl$_3$: $^1$H NMR: $\delta = 7.26$; $^{13}$C NMR: $\delta = 77.16$). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants $J$ are reported in Hertz (Hz). HRMS were obtained on a QTOF micro spectrometer. Melting points were measured using open glass capillaries in SGW® X–4A apparatus.

All reactions were conducted in oven–dried Round bottom flask under an atmosphere of nitrogen. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Conversion of the reactions was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh). All the allylic alcohols were prepared according to reported method.$^1$
2. Optimization of the reaction conditions

2.1 Optimization of reaction conditions for perfluorobutyl iodide 2a

Table S1: Screening of the additives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Yield of 3aa&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;N (2.0 equiv)</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>DIPEA (2.0 equiv)</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Bu&lt;sub&gt;3&lt;/sub&gt;N (2.0 equiv)</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>Bu&lt;sub&gt;3&lt;/sub&gt;N (2.0 equiv) + HCOOH (2.0 equiv.)</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>HCOOH (2.0 equiv.)</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>_</td>
<td>NR</td>
</tr>
</tbody>
</table>

<sup>a</sup> All reactions were carried out with 1,1-diphenylprop-2-en-1-ol 1a (0.1 mmol), perfluorobutyl iodide 2a (0.2 mmol), and the additive as indicated in DMSO (2.0 mL) under N<sub>2</sub> at rt for 24 h. <sup>b</sup> Isolated yield. NR means no reaction occurred.

Note: For the reactions running under conditions indicated in entries 1-3, the atom transfer radical addition (ATRA) product 3b was also formed as the main side-product. While only trace amount of 3b was observed when the combination of Bu<sub>3</sub>N and HCOOH were employed as the additive, and the yield was further improved to 82%. Control experiment revealed that additive was crucial to the transformation, since no reaction occurred when the reaction mixture was irradiated with blue LEDs without additives.
Table S2: Screening of light source

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light source</th>
<th>Yield of 3aa (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 W blue LEDs (465nm)</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>20 W blue LEDs (465 nm)</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>30 W blue LEDs (465nm)</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>30 W purple LEDs (390 nm)</td>
<td>58</td>
</tr>
</tbody>
</table>

All reactions were carried out with 1,1–diphenylprop–2–en–1–ol 1a (0.1 mmol), perfluorobutyl iodide 2a (0.2 mmol), Bu3N (0.2 mmol), HCOOH (0.2mmol) in DMSO (2.0 mL) under N2 at rt for 24 h. Isolated yield.

Table S3: Control experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variations of the reaction conditions</th>
<th>Yield of 3aa (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>_</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>Without HCOOH</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>Without Bu3N</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>HCOONa instead of Bu3N/HCOOH</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>No light</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>With 20% Bu3N/HCOOH</td>
<td>20</td>
</tr>
</tbody>
</table>

All reactions were carried out with 1,1–diphenylprop–2–en–1–ol 1a (0.1 mmol), perfluorobutyl iodide 2a (0.2 mmol the additive as indicated in DMSO (2.0 mL) under N2 at rt for 24 h. Isolated yield.
2.2 Optimization of reaction conditions for ethyl 2–bromo–2,2–difluoroacetate 2b

Table S4: Screening of concentration

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration (M)</th>
<th>Yield of 3ba a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>75</td>
</tr>
</tbody>
</table>

a All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol 1c (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate 2b (0.2 mmol), Bu3N (0.2 mmol), HCOOH (0.2 mmol) in MeCN/DMSO (1:1, v/v) (2.0 mL) under N2 at rt for 24 h. b Isolated yield.

Table S5: Screening of light source

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light source</th>
<th>Yield of 3ba a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 W blue LEDs</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>10 W blue LEDs</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>20 W blue LEDs</td>
<td>88</td>
</tr>
</tbody>
</table>

a All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol 1c (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate 2b (0.2 mmol), Bu3N (0.2 mmol), HCOOH (0.2 mmol) in DMSO (2.0 mL) under N2 at rt for 24 h. b Isolated yield.
Table S6: Screening of the solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of 3ba (^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)CN</td>
<td>55</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol 1c (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate 2b (0.2 mmol), Bu\(_3\)N (0.2 mmol), HCOOH (0.2 mmol) in Solvent (2.0 mL) under N\(_2\) at rt for 24 h. \(^b\) Isolated yield.

Table S7: Screening of the base

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (2.0 equiv)</th>
<th>Yield of 3ba (^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et(_3)N</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>DIPEA</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>Bu(_3)N</td>
<td>88</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out with 1,1–bis(4–chlorophenyl)prop–2–en–1–ol 1c (0.1 mmol), ethyl 2–bromo–2,2–difluoroacetate 2b (0.2 mmol), base (0.2 mmol), HCOOH (0.2 mmol) in DMSO (2.0 mL) under N\(_2\) at rt for 24 h. \(^b\) Isolated yield.

3. General procedure

General procedure for the preparation of allyl alcohols

Following the reported procedure,\(^1\) to a solution of aldehyde/ketone (5 mmol) in dry THF was added vinylmagnesium bromide (1 M in THF, 1.2 equiv.) under nitrogen atmosphere by a syringe over 5 min at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for additional 3 hours. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with a saturated NH\(_4\)Cl aqueous solution (20 mL) and extracted with ethyl acetate (3×70 mL). The combined organic layer was washed with brine (50 mL), dried over Na\(_2\)SO\(_4\) and concentrated under reduce pressure.
to give the crude allylic alcohols which was purified by a flash chromatograph (PE/EA) on silica gel with petroleum ether/ethyl acetate mixture as eluent to afford the corresponding pure products. The NMR data were consistent with the reported reference.

**General procedure for the synthesis of aryl migration products**

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with α,ω-diaryllallylic alcohols (1, 0.1 mol). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of perfluorobutyl iodide 2a (0.2 mmol, 34.4 µL), tributylamine (0.2 mmol, 47.5 µL) and formic acid (0.2 mmol, 6.6 µL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 20 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C. After 24 hours, the reaction was then quenched with satd. NH₄Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated, the crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate mixture as eluent to give the corresponding products.

4. Characterization of products

**4,4,5,6,6,7,7,7–Nonafluoro–1,2–diphenylheptan–1–one (3aa)**

\[
\text{CH}_2_N=O_{C_4F_9}
\]

82% yield, 35.1 mg; yellow oil;¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.97 (m, 2H), 7.55 – 7.51 (m, 1H), 7.43 (t, J₁ = 7.5 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 5.05 (dd, J₁ = 8.4 Hz, J₂ = 4.2 Hz, 1H), 3.54 – 3.39 (m, 1H), 2.53 – 2.38 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ = -81.0 to -81.1 (m, 3F), -111.8 to -113.9 (m, 2F), -124.3 to -124.4 (m, 2F), -125.9 to -126.1 (m, 2F); ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 137.8, 135.7, 133.5, 129.6, 129.0, 128.8, 128.2, 128.0, 45.7, 34.4 (t, J_C,F = 26.0 Hz); The spectra data are consistent with the reported reference.²

**4,4,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–fluorophenyl)heptan–1–one (3ab)**

\[
\text{CH}_2_N=O_{C_4F_9}
\]

35% yield, 16.3 mg; yellow oil;¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.97 (m, 2H), 7.30 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 7.04 – 7.00 (m, 2H), 4.97 (dd, J₁ = 8.2 Hz, J₂ = 4.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.35 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ = -81.0 to -81.1 (m, 3F), -103.9 to -104.0 (m, 2F), -113.6 to -113.7 (m, 2F), -124.4 to -124.5 (m, 2F), -125.9 to -126.0 (m, 2F); ¹³C NMR (100 MHz, CDCl₃) δ 195.2, 166.0 (d, J_C,F = 254.7 Hz), 162.5 (d, J_C,F = 246.5 Hz), 133.3 (d, J_C,F = 3.6 Hz), 131.9 (d, J_C,F = 3.5 Hz), 131.6 (d, J_C,F = 9.6 Hz), 129.8 (d, J_C,F = 8.4 Hz), 116.7 (d, J_C,F = 21.6 Hz),
116.1 (d, $J_{C,F} = 21.9$ Hz), 44.9, 34.5 (t, $J_{C,F} = 22.1$ Hz); The spectra data are consistent with the reported reference.²

1,2–Bis(4–chlorophenyl)–4,4,5,5,6,6,7,7,7–nonafluorohex–1–one (3ac)

83% yield, 41.3 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 – 7.86 (m, 2H), 7.41 – 7.38 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 4.95 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.6$ Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.36 (m, 1H); $^1$F NMR (376 MHz, CDCl$_3$) $\delta$ – 81.0 (t, $J = 9.5$, 3F), – 111.6 to – 114.0 (m, 2F), – 124.3(9) to – 124.4(3) (m, 2F), – 125.9 to – 126.0 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.3, 140.4, 135.8, 134.3, 133.7, 130.3, 129.9, 129.5, 129.3, 45.1, 34.3 (t, $J_{C,F} = 20.8$ Hz); The spectra data are consistent with the reported reference.²

1,2–Bis(4–bromophenyl)–4,4,5,5,6,6,7,7,7–nonafluorohex–1–one (3ad)

58% yield, 34.0 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 – 7.78 (m, 2H), 7.58 – 7.55 (m, 2H), 7.47 – 7.44 (m, 2H), 7.19 – 7.15 (m, 2H), 4.92 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.6$ Hz, 1H), 3.45 – 3.30 (m, 1H), 2.50 – 2.35 (m, 1H); $^1$F NMR (376 MHz, CDCl$_3$) $\delta$ – 80.9(7) to – 81.0(2) (m, 3F), – 111.5 to – 113.9 (m, 2F), – 124.3 to – 124.4 (m, 2F), – 125.9 to – 126.0 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.4, 136.3, 134.1, 132.9, 132.3, 130.4, 129.8, 129.2, 122.4, 45.2, 34.2 (t, $J_{C,F} = 20.6$ Hz); The spectra data are consistent with the reported reference.²

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–di–p–tolylhept–1–one (3ae)

69% yield, 31.7 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 – 7.87 (m, 2H), 7.22 – 7.19 (m, 4H), 7.13 – 7.10 (m, 2H), 4.99 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.2$ Hz, 1H), 3.51 – 3.35 (m, 1H), 2.44 – 2.36 (m, 4H), 2.28 (s, 3H); $^1$F NMR (376 MHz, CDCl$_3$) $\delta$ – 81.0 (t, $J = 10.0$, 3F), – 111.8 to – 114.1 (m, 2F), – 124.3 to – 124.5 (m, 2F), – 125.9 to – 126.0 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.5, 144.4, 137.7, 135.0, 133.2, 130.2, 129.5, 129.1, 128.0, 45.1, 34.4 (t, $J_{C,F} = 20.2$ Hz), 21.8, 21.1; The spectra data are consistent with the reported reference.²

4,4,5,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–methoxyphenyl)hept–1–one (3af)
31% yield, 15.1 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.94 (m, 2H), 7.25 – 7.21 (m, 2H), 6.90 – 6.80 (m, 4H), 4.94 (dd, J₁ = 8.2 Hz, J₂ = 4.4 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.47 – 3.31 (m, 1H), 2.47 – 2.33 (m, 1H); ¹³F NMR (376 MHz, CDCl₃) δ – 81.0 to – 81.1 (m, 3F), – 111.8 to – 114.1 (m, 2F), – 124.4 to – 124.5 (m, 2F), – 125.9 to – 126.0 (m, 2F); ¹²C NMR (100 MHz, CDCl₃) δ 195.4, 163.8, 159.2, 131.3, 130.2, 129.2, 128.6, 114.9, 114.0, 55.6, 55.4, 44.5, 34.4 (t, J_C-F = 20.6 Hz); The spectra data are consistent with the reported reference.²

4,4,5,6,6,7,7,7–Nonafluoro–1,2–bis(4–(trifluoromethyl)phenyl)heptan–1–one (3ag)

80% yield, 45.0 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.62 – 7.47 (m, 5H), 5.09 (dd, J₁ = 8.4 Hz, J₂ = 4.4 Hz, 1H), 3.54 – 3.38 (m, 1H), 2.56 – 2.42 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ – 62.8 (s, 3F), – 63.1 (s, 3F), – 81.1 (t, J₁ = 9.6 Hz, 3F), – 111.5 to – 113.7 (m, 2F), – 124.3 to – 124.4 (m, 2F), – 125.9 to – 126.0 (m, 2F); ¹²C NMR (100 MHz, CDCl₃) δ 195.1, 138.0. 135.8, 132.3 (q, J_C-F=32.5), 131.9, 131.8 (q,J_C-F=32.9), 131.5, 130.4 (q, J_C-F = 3.9), 130.3, 129.8, 126.5 (q, J_C-F = 245.2 Hz), 125.8 (q, J_C-F = 3.9 Hz), 125.4 (q, J_C-F = 3.7 Hz), 125.0 (q, J_C-F = 3.8 Hz), 123.8 (q, J_C-F = 270.8 Hz), 123.6 (d, J_C-F = 278.9 Hz), 45.7, 34.5 (t, J_C-F = 20.7 Hz); HRMS (ESI) m/z calefd for C₂₁H₁₂F₁₅O⁺ [M + H]⁺ m/z 565.0643, found m/z 565.0607.

1,2–Bis(4–chlorophenyl)–4,4,5,6,6,7,7,7–nonafluoro–2–methylheptan–1–one (3ah)

41% yield, 21.2 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 4H), 7.25 – 7.20 (m, 2H), 3.10 – 2.97 (m, 1H), 2.73 – 2.59 (m, 1H), 1.86 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ – 81.1 (t, J₁ = 9.8 Hz, 3F), – 107.4 to – 111.3 (m, 2F), – 124.6 (s, 2F), – 125.7 to – 125.8 (m, 2F); ¹²C NMR (100 MHz, CDCl₃) δ 199.9, 139.5 138.7, 134.3, 134.0, 130.9, 129.8, 128.7, 127.8, 52.1, 39.7 (t, J_C-F = 18.3 Hz), 22.5; The spectra data are consistent with the reported reference.²

1,2–Bis(4–chlorophenyl)–4,4,5,6,6,7,7,8,8,9,9,9–tridecafluorononan–1–one (3ai)

53% yield, 31.1 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.86 (m, 2H), 7.41 – 7.39 (m, 2H), 7.33 – 7.22 (m, 4H), 4.94 (dd, J₁ = 8.1 Hz, J₂ = 4.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.50 – 2.36 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ – 80.6 to – 80.7 (m, 3F), – 111.2 to – 113.6 (m, 2F), – 121.6(6) to – 121.7(5) (m, 2F), – 121.8 (s, 2F), – 123.3 to – 123.4 (m, 2F), – 126.0 to – 126.1 (m, 2F); ¹²C NMR (100 MHz, CDCl₃) δ 195.3, 140.4, 135.9, 134.3, 133.7, 130.3, 129.9, 129.5, 45.1, 34.4 (t, J_C-F = 19.3 Hz); HRMS (ESI) m/z calefd for C₂₁H₁₂F₁₃O⁺ [M + H]⁺ m/z 597.0052, found m/z 597.0066.

2–(4–Chlorophenyl)–4,4,5,6,6,7,7,7–nonafluoro–1–phenyleheptan–1–one (3aj)
1–(4-Chlorophenyl)–4,4,5,5,6,6,7,7–nonafluoro–2–phenylheptan–1–one (3aj')

![Chemical Structure](image)

69% yield, 30.5 mg; 3i/3i' = 3 : 1; yellow oil; 1H NMR (400 MHz, CDCl3) δ major isomer 7.96 – 7.94 (m, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.43 (overlapped, 1H), 7.41 – 7.37 (overlapped, 1H), 7.31 – 7.25 (overlapped, 4H), 5.02 (dd, J1 = 8.0 Hz, J2 = 4.7 Hz, 1H), 3.50 – 3.32 (overlapped, 1H), 2.51 – 2.37 (overlapped, 1H); minor isomer 7.92 – 7.89 (m, 2H), 7.45 – 7.43 (overlapped, 2H), 7.41 – 7.37 (overlapped, 1H), 7.31 – 7.25 (overlapped, 4H), 4.96 (dd, J1 = 8.3 Hz, J2 = 4.1 Hz, 1H), 3.50 – 3.32 (overlapped, 1H), 2.51 – 2.37 (overlapped, 1H); 19F NMR (376 MHz, CDCl3) δ major isomer –80.9 to –81.0 (overlapped, 3F), –111.5 to –113.8 (overlapped, 2F), –124.2 to –124.3 (overlapped, 2F), –125.8 to –125.9 (overlapped, 2F); minor isomer –80.9 to –81.0 (overlapped, 3F), –111.5 to –113.8 (overlapped, 2F), –124.2 to –124.3 (overlapped, 2F), –125.8 to –125.9 (overlapped, 2F); 13C NMR (100 MHz, CDCl3) δ major isomer 196.5, 136.2, 135.5, 134.1, 133.8, 129.8, 129.6, 129.0, 128.1, 45.0, 34.4 (overlapped, JCF = 20.9 Hz); minor isomer 195.6, 140.1, 137.5, 134.0, 130.4, 129.7, 129.2, 128.8, 128.2, 45.8, 34.4 (overlapped, JCF = 20.9 Hz); The spectra data are consistent with the reported reference.2

2–(3,4–Dichlorophenyl)–4,4,5,5,6,6,7,7–nonafluoro–1–phenylheptan–1–one (3ak)
1–(3,4–Dichlorophenyl)–4,4,5,5,6,6,7,7–nonafluoro–2–phenylheptan–1–one (3ak')

![Chemical Structure](image)

77% yield, 38.1 mg; 3j/3j' = 6 : 1; yellow oil; 1H NMR (400 MHz, CDCl3) δ major isomer 7.97 – 7.90 (m, 2H), 7.59 – 7.50 (m, 1H), 7.47 – 7.39 (overlapped, 4H), 7.20 – 7.17 (m, 1H), 5.00 (dd, J1 = 8.0 Hz, J2 = 4.7 Hz, 1H), 3.45 – 3.30 (overlapped, 1H), 2.52 – 2.38 (overlapped, 1H); minor isomer 8.04 (d, J = 2.0 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.52 – 7.50 (m, 1H), 7.47 – 7.39 (overlapped, 4H), 7.30 – 7.29 (m, 1H), 4.91 (dd, J1 = 8.5 Hz, J2 = 4.1 Hz, 1H), 3.45 – 3.30 (overlapped, 1H), 2.52 – 2.38 (overlapped, 1H); 19F NMR (376 MHz, CDCl3) δ major isomer –80.9 to –81.0 (overlapped, 3F), –111.5 to –113.8 (overlapped, 2F), –124.2 to –124.3 (overlapped, 2F), –125.8 to –126.0 (overlapped, 2F); minor isomer –80.9 to –81.0 (overlapped, 3F), –111.5 to –113.8 (overlapped, 2F), –124.2 to –124.3 (overlapped, 2F); 13C NMR (100 MHz, CDCl3) δ major isomer 196.1, 137.7, 135.2, 134.0, 133.7, 132.6, 131.5, 130.1, 129.1, 128.9, 127.5, 44.6, 34.4 (t, JCF = 20.6 Hz); HRMS (ESI) m/z caleed for C13H12F13ClO' [M + H] + m/z 497.0116, found m/z 497.0123.

2–(4-Chlorophenyl)–4,4,5,5,6,6,7,7–nonafluoro–1–(4-methoxyphenyl)heptan–1–one (3al)
1–(4-Chlorophenyl)–4,4,5,5,6,6,7,7–nonafluoro–2–(4-methoxyphenyl)heptan–1–one (3al')
43% yield, 21.4 mg, 3j/3j' = 14 : 1; yellow oil; 1H NMR (400 MHz, CDCl3) δ major isomer 7.96 – 7.91 (m, 2H), 7.30 – 7.25 (m, 4H), 6.91 – 6.88 (overlapped, 2H), 4.96 (dd, J1 = 7.9 Hz, J2 = 4.7 Hz, 1H), 3.84 (s, 1H), 3.45 – 3.30 (overlapped, 1H), 2.50 – 2.35 (overlapped, 1H); minor isomer 7.91 – 7.89 (m, 2H), 7.39 – 7.37 (m, 2H), 7.21 – 7.18 (m, 2H), 6.85 – 6.83 (m, 2H), 7.30 – 7.29 (m, 1H), 4.91 (dd, J1 = 8.2 Hz, J2 = 4.7 Hz, 1H), 3.76 (s, 1H), 3.45 – 3.30 (overlapped, 1H), 2.50 – 2.35 (overlapped, 1H); 19F NMR (376 MHz, CDCl3) δ major isomer – 80.9(9) to – 81.0(4) (overlapped, 3F), – 111.6 to – 114.1 (overlapped, 2F), – 124.3(5) to – 124.4(3) (overlapped, 2F); – 125.9 to – 126.0 (overlapped, 2F); minor isomer – 80.9(9) to – 81.0(4) (overlapped, 3F), – 111.6 to – 114.1 (overlapped, 2F), – 124.3(5) to – 124.4(3) (overlapped, 2F), – 125.9 to – 126.0 (overlapped, 2F); 13C NMR (100 MHz, CDCl3) δ 194.9, 164.0, 136.7, 133.9, 129.7, 129.5, 128.3, 114.1, 55.6, 44.6, 34.3 (t, J,C,F = 20.5 Hz); HRMS (ESI) m/z calcd for C20H17ClF5O4 + [M + H] + m/z 493.0611, found m/z 493.0610.

4,4,5,5,6,6,7,7,7-Nonafluoro-1-phenyl-2-(pyridin-2-yl)heptan-1-one (3am)

4,4,5,5,6,6,7,7,7-Nonafluoro-2-phenyl-1-(pyridin-3-yl)heptan-1-one (3am')

71% yield, 30.5 mg; 3i/3i' = 3 : 1; yellow oil; 1H NMR (400 MHz, CDCl3) δ major isomer 8.66 (d, J = 2.4 Hz, 1H), 8.52 – 8.50 (m, 1H), 7.78 – 7.75 (overlapped, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.25 (overlapped, 2H), 5.09 (dd, J1 = 8.2 Hz, J2 = 5.0 Hz, 1H), 3.54 – 3.33 (overlapped, 1H), 2.56 – 2.39 (overlapped, 1H); minor isomer 9.18 (d, J = 1.7 Hz, 1H), 8.72 – 8.70 (m, 1H), 8.24 – 8.21 (overlapped, 1H), 7.98 – 7.95 (overlapped, 2H), 7.38 – 7.25 (overlapped, 4H), 4.97 (dd, J1 = 8.4 Hz, J2 = 4.0 Hz, 1H), 3.54 – 3.33 (overlapped, 1H), 2.56 – 2.39 (overlapped, 1H); 19F NMR (376 MHz, CDCl3) δ major isomer – 81.0 (overlapped, J = 10.5 Hz, 3F), – 111.5 to – 113.8 (overlapped, 2F), – 124.3 to – 124.4 (overlapped, 2F), – 125.9 to – 126.0 (overlapped, 2F); minor isomer – 81.0 (overlapped, J = 10.5 Hz, 3F), – 111.5 to – 113.8 (overlapped, 2F), – 124.3 to – 124.4 (overlapped, 2F), – 125.9 to – 126.0 (overlapped, 2F); 13C NMR (100 MHz, CDCl3) δ major isomer 196.2, 149.8, 149.4, 136.3, 135.3, 134.0, 129.8, 129.1 128.2, 124.3, 42.9, 34.3 (t, J,C,F = 20.4 Hz); minor isomer 195.7, 153.8, 150.2, 136.8, 135.1, 133.6, 131.1, 128.9, 128.4, 123.8, 46.3, 34.2 (t, J,C,F = 21.1 Hz); The spectra data are consistent with the reported reference.²

4,4,5,5,6,6,7,7,7-nonfluoro-2-(furan-2-yl)-1-(p-tolyl)heptan-1-one (3an)

4,4,5,5,6,6,7,7,7-nonfluoro-1-(furan-2-yl)-2-(p-tolyl)heptan-1-one (3an')

40% yield, 17.3 mg; 3an/3an' = 10 : 1; yellow oil; spectrum date of the major one; 1H NMR (400 MHz, CDCl3) δ 7.91 – 7.89 (m, 2H), 7.33 – 7.32 (m, 1H), 7.26 – 7.23 (m, 2H), 6.27 – 6.26 (m, 1H), 6.15 – 6.14 (m, 1H), 5.14 (dd, J1 = 7.8 Hz, J2 = 5.0 Hz, 1H), 3.36 – 3.21 (m, 1H), 2.69 – 2.54 (m, 1H), 2.39 (s, 3H); 19F NMR (376 MHz, CDCl3) δ – 80.9 to – 81.0 (m, 3F), – 113.1 to – 113.4 (m, 2F), – 124.2(5) to – 124.3(3) (m, 2F), – 125.8 to – 125.9 (m, 2F); 13C NMR (100 MHz, CDCl3) δ 193.8, 150.3, 144.9, 142.8, 132.8, 129.6, 129.1, 111.1, 108.2, 39.2, 31.9 (t, J,C,F = 20.4 Hz), 21.8; HRMS (ESI) m/z calcd for C18H14F5O2 + [M + H] + m/z 433.0839, found m/z 433.0835.
4,4,5,6,6,7,7,7–Nonfluoro–1–phenyl–2–(thiophen–3–yl)heptan–1–one (3ao)

\[
\begin{align*}
\text{O} & \quad \text{C}_\text{F}_9 \\
\text{O} & \quad \text{C}_\text{F}_9
\end{align*}
\]

40% yield, 17.3 mg; yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 – 8.00 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.23 – 7.21 (m, 1H), 6.96 – 6.91 (m, 2H), 5.34 (dd, \(J_1 = 8.9\) Hz, \(J_2 = 3.8\) Hz, 1H), 3.55 – 3.40 (m, 1H), 2.62 – 2.48 (m, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) – 80.9 to – 81.0 (m, 3F), – 112.7 to – 113.1 (m, 2F), – 124.3 to – 124.4 (m, 2F), – 125.9 to – 126.0 (m, 2F); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 195.6, 139.5, 135.3, 133.8, 129.2, 129.0, 127.6, 126.6, 126.1, 40.2, 35.1 (t, \(J_{C-F} = 21.4\) Hz); HRMS (ESI) m/z calcld for C\(_7\)H\(_7\)Cl\(_3\)OS\(^+\) [M + H\(^+\)] m/z 435.0460, found m/z 435.0431.

3–(4–Chlorophenyl)–5,5,6,6,7,7,8,8,8–nonfluorooctan–2–one (3ap)

\[
\begin{align*}
\text{O} & \quad \text{C}_\text{F}_9 \\
\text{Cl}
\end{align*}
\]

31% yield, 12.4 mg; yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.33 (m, 2H), 7.19 – 7.15 (m, 2H), 4.06 (dd, \(J_1 = 7.0\) Hz, \(J_2 = 5.5\) Hz, 1H), 3.27 – 3.11 (m, 1H), 2.35 – 2.12 (m, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) – 80.9 (t, \(J = 10.2\) Hz, 3F), – 111.5 to – 114.3 (m, 2F), – 124.3 to – 124.4 (m, 2F), 125.8 to – 125.9 (m, 2F); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 204.4, 135.7, 134.4, 129.8, 129.5, 50.7, 32.9 (t, \(J_{C-F} = 20.4\) Hz), 28.9; HRMS (ESI) m/z calcld for C\(_9\)H\(_9\)\(^{35}\)Cl\(_3\)ONa\(^+\) [M + Na\(^+\)] m/z 423.0169, found m/z 423.0109.

Ethyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3ba)

\[
\begin{align*}
\text{O} & \quad \text{Cl} \\
\text{Cl} & \quad \text{C}_\text{F}_9 \\
\text{O} & \quad \text{Cl}
\end{align*}
\]

88% yield, 35.2 mg; yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 – 7.85 (m, 2H), 7.40 – 7.37 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 4.88 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 5.1\) Hz, 1H), 4.24 – 4.07 (m, 2H), 3.30 – 3.15 (m, 1H), 2.55 – 2.42 (m, 1H), 2.16 (t, \(J = 7.2\) Hz, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) – 104.9 to – 105.0 (m, 2F); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.0, 163.8 (t, \(J_{C-F} = 32.0\) Hz), 140.1, 136.1, 134.1 134.0, 130.3, 129.7 (two peaks overlapped), 129.2, 115.2 (t, \(J_{C-F} = 249.5\) Hz), 63.2, 46.3 (t, \(J_{C-F} = 3.3\) Hz), 38.1 (t, \(J_{C-F} = 23.0\) Hz), 13.9; The spectra data are consistent with the reported reference.\(^3\)

Hexyl 4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoate (3bb)

\[
\begin{align*}
\text{O} & \quad \text{Cl} \\
\text{Cl} & \quad \text{C}_\text{F}_9 \\
\text{O} & \quad \text{Cl}
\end{align*}
\]

77% yield, 35.1 mg; yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 – 7.84 (m, 2H), 7.39 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 4.87 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 5.2\) Hz, 1H), 4.16 – 3.99 (m, 2H), 3.29 – 3.15 (m, 1H), 2.55 – 2.42 (m, 1H), 1.65 – 1.54 (m, 2H), 1.34 – 1.22 (m, 7H), 0.90 – 0.86 (m, 2H);
19F NMR (376 MHz, CDCl3) δ = -104.3 to -104.4 (m, 2F); 13C NMR (100 MHz, CDCl3) δ 195.9, 163.8 (t, J c-F = 31.8 Hz), 140.1, 136.1, 134.0, 133.9, 130.3, 129.7 (two peaks overlapped), 129.2, 115.2 (t, J c-F = 249.6 Hz), 67.3, 46.3 (t, J c-F = 3.6 Hz), 38.1 (t, J c-F = 23.1 Hz), 31.4, 28.2, 25.4, 22.6, 14.1; HRMS (ESI) m/z calcd for C23H25Cl2F2O+ [M + H]+ m/z 457.1143, found m/z 457.1161.

Cyclopentyl 4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanamide (3bc)

75% yield, 33.0 mg; yellow oil; 1H NMR (400 MHz, CDCl3) δ 7.87 – 7.84 (m, 2H), 7.38 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 5.14 – 5.10 (m, 1H), 4.87 (dd, J1 = 7.8 Hz, J2 = 5.2 Hz, 1H), 3.27 – 3.13 (m, 1H), 2.53 – 2.40 (m, 1H), 1.88 – 1.54 (m, 8H); 19F NMR (376 MHz, CDCl3) δ = -104.3 to -104.5 (m, 2F); 13C NMR (100 MHz, CDCl3) δ 196.0, 163.6 (t, J c-F = 32.1 Hz), 140.1, 136.2, 134.0(1), 133.9(7), 130.3, 129.6 (two peaks overlapped), 129.2, 115.2 (t, J c-F = 249.7 Hz), 80.7, 46.3 (t, J c-F = 3.7 Hz), 38.0 (t, J c-F = 23.1 Hz), 32.6, 32.5, 23.8, 23.7; HRMS (ESI) m/z calcd for C23H19Cl2F2O+ [M + Na]+ m/z 463.0650, found m/z 463.0655.

Benzy1 4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanamide (3bd)

56% yield, 26.0 mg; yellow oil; 1H NMR (400 MHz, CDCl3) δ 7.81 – 7.78 (m, 2H), 7.38 – 7.30 (m, 7H), 7.24 – 7.22 (m, 2H), 7.16 – 7.12 (m, 2H), 5.19 – 5.04 (m, 2H), 4.81 (dd, J1 = 7.9 Hz, J2 = 5.1 Hz, 1H), 3.30 – 3.16 (m, 1H), 2.55 – 2.42 (m, 1H); 19F NMR (376 MHz, CDCl3) δ = -104.1 (t, J = 16.3 Hz, 2F); 13C NMR (100 MHz, CDCl3) δ 195.9, 163.6 (t, J c-F = 32.9 Hz), 140.1, 136.0, 134.1, 134.0, 133.9, 130.3, 129.6(4), 129.6(0), 129.2, 129.0, 128.9, 128.7, 115.2 (t, J c-F = 249.8 Hz), 68.6, 46.3 (t, J c-F = 3.8 Hz), 38.1 (t, J c-F = 23.1 Hz); HRMS (ESI) m/z calcd for C23H19Cl2F2O+ [M + H]+ m/z 463.0674, found m/z 463.0690.

4,5–Bis(4-chlorophenyl)–N–cyclopropyl-2,2-difluoro–5–oxopentanamide (3be)

66% yield, 27.1 mg; white solid; mp. 133–135 °C; 1H NMR (400 MHz, CDCl3) δ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.18 (m, 2H), 6.34 (s, 1H), 4.99 (dd, J1 = 8.4 Hz, J2 = 4.4 Hz, 1H), 3.24 – 3.18 (m, 1H), 2.70 – 2.66 (m, 1H), 2.53 – 2.47 (m, 1H), 0.83 – 0.80 (m, 2H), 0.55 – 0.54 (m, 2H); 19F NMR (376 MHz, CDCl3) δ = -104.2 to -104.3 (m, 2F); 13C NMR (100 MHz, CDCl3) δ 196.2, 165.1 (t, J c-F = 28.1 Hz), 139.9, 136.4, 134.1, 133.8, 130.3, 129.6, 129.5, 129.1, 116.8 (t, J c-F = 252.0 Hz), 46.2 (t, J c-F = 3.6 Hz), 37.6 (t, J c-F = 23.0 Hz), 22.6, 6.5(3), 6.5(1); HRMS (ESI) m/z calcd for C24H17Cl2F2NO+ [M + H]+ m/z 412.0677, found m/z 412.0671.

4,5–Bis(4-chlorophenyl)–2,2–difluoro–5–oxo–N–phenylpentanamide (3bf)
88% yield, 39.6 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 – 7.87 (m, 3H), 7.59 – 7.47 (m, 3H), 7.38 – 7.33 (m, 4H), 7.27 – 7.17 (m, 4H), 5.02 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.8$ Hz, 1H), 3.39 – 3.24 (m, 1H), 2.71 – 2.58 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-$ 103.5 (t, $J = 16.8$ Hz, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.2, 161.6 (t, $J = 28.0$ Hz), 140.1, 136.2, 135.8, 134.1, 134.0, 130.3, 129.6(2), 129.6(0), 129.4, 129.2, 125.9, 120.4, 117.0 (t, $J_{C.F} = 253.3$ Hz), 46.3 (t, $J_{C.F} = 3.7$ Hz), 37.6 (t, $J_{C.F} = 22.7$ Hz); HRMS (ESI) m/z calcd for C$_{129}$H$_{185}$Cl$_2$F$_2$NO$_2$ $^+$ [M + H]$^+$ m/z 448.0677, found m/z 448.0673.

$N$–(4–Bromophenyl)–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bg)

99% yield, 52.0 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (s, 1H), 7.88 – 7.85 (m, 2H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 4H), 7.26 – 7.20 (m, 4H), 4.99 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.9$ Hz, 1H), 3.37 – 3.23 (m, 5H), 2.70 – 2.56 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-$ 104.9 to $-$ 105.0 (m, 1F), $-$ 105.2 – $-$ 105.3 (m, 1F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.1, 161.7 (t, $J_{C.F} = 28.8$ Hz), 140.1, 136.1, 134.9, 134.1, 134.0, 132.4, 130.3, 129.7, 129.6, 129.2, 121.9, 118.7, 116.9 (t, $J_{C.F} = 253.7$ Hz), 46.3, 37.6 (t, $J_{C.F} = 23.3$ Hz); HRMS (ESI) m/z calcd for C$_{129}$H$_{185}$Br$^{35}$Cl$_2$F$_2$NO$_2$ $^+$ [M + H]$^+$ m/z 525.9782, found m/z 525.9785.

$N$–((3s,5s,7s)–Adamantan–1–yl)–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bh)

83% yield, 42.0 mg; white oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.20 (m, 2H), 5.90 (s, 1H), 4.97 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.4$ Hz, 1H), 3.23 – 3.13 (m, 1H), 2.55 – 2.42 (m, 1H), 2.08 (s, 3H), 1.95 (d, $J = 3.0$, 6H), 1.67 (t, $J = 3.1$, 6H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-$ 103.6 to $-$ 103.8 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.3, 162.6 (t, $J_{C.F} = 27.7$ Hz), 139.9, 136.5, 134.3, 133.8, 130.3, 129.6, 129.5, 129.1, 116.7 (t, $J_{C.F} = 253.3$ Hz), 52.7, 46.3 (t, $J_{C.F} = 3.8$ Hz), 41.2, 37.6 (t, $J_{C.F} = 23.9$ Hz), 36.2, 29.4; HRMS (ESI) m/z calcd for C$_{129}$H$_{185}$Br$^{35}$Cl$_2$F$_2$NO$_2$ $^+$ [M + H]$^+$ m/z 506.1460, found m/z 506.1456.

$N$,$N$–Dibuty–4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanamide (3bi)
78% yield, 37.6 mg; white oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.22 (m, 4H), 4.98 (dd, $J_F$ = 8.6 Hz, $J_C$ = 3.8 Hz, 1H), 3.44 – 3.26 (m, 5H), 2.58 – 2.45 (m, 1H), 1.55 – 1.46 (m, 4H), 1.32 – 1.24 (m, 4H), 0.91 (q, $J_F$ = 7.3 Hz, 6H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 97.6 to – 97.7 (m, 1F), – 97.9 to – 98.0 (m, 1F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.6, 162.6 (t, $J_{C_F}$ = 41.6 Hz), 139.8, 137.0, 134.4, 133.6, 130.3, 129.6, 129.5, 129.1, 118.7 (t, $J_{C_F}$ = 239.0 Hz), 47.5 (t, $J_{C_F}$ = 6.5 Hz), 47.0, 46.4 (t, $J_{C_F}$ = 4.2 Hz), 38.7 (t, $J_{C_F}$ = 22.7 Hz), 31.1, 29.2, 20.3, 20.0, 13.9, 13.8; HRMS (ESI) m/z calcd for C$_2$I$_3$NO$_2$ [M + H]$^+$ m/z 484.1616, found m/z 484.1615.

4,5-Bis(4-chlorophenyl)-2,2-difluoro-1-(pyrrolidin-1-yl)pentane-1,5-dione (3bj)

55% yield, 23.4 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.85 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 – 7.21 (m, 4H), 4.99 (dd, $J_F$ = 8.8 Hz, $J_C$ = 4.0 Hz, 1H), 3.64 – 3.60 (m, 2H), 3.48 – 3.42 (m, 2H), 3.39 – 3.27 (m, 1H), 2.57 – 2.43 (m, 1H), 1.96 – 1.71 (m, 2H), 1.85 – 1.81 (m, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 101.1 (t, $J_F$ = 18.2 Hz, 1F), – 101.5 (t, $J_F$ = 18.2 Hz, 1F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.6, 161.8 (t, $J_{C_F}$ = 29.4 Hz), 139.9, 136.8, 134.4, 133.7, 130.3, 129.6, 129.5, 129.1, 118.0 (t, $J_{C_F}$ = 251.8 Hz), 47.5, 46.7 (t, $J_{C_F}$ = 5.8 Hz), 46.4 (t, $J_{C_F}$ = 3.3 Hz), 38.0 (t, $J_{C_F}$ = 22.9 Hz), 26.6, 23.4; HRMS (ESI) m/z calcd for C$_2$I$_3$Cl$_5$NO$_2$ $^+$ [M + H]$^+$ m/z 426.0834, found m/z 426.0832.

4,5-Bis(4-chlorophenyl)-2,2-difluoro-1-(piperidin-1-yl)pentane-1,5-dione (3bk)

65% yield, 28.8 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 7.28 – 7.22 (m, 4H), 4.97 (dd, $J_F$ = 8.6 Hz, $J_C$ = 3.8 Hz, 1H), 3.59 – 3.46 (m, 4H), 3.44 – 3.35 (m, 1H), 2.57 – 2.43 (m, 1H), 1.68 – 1.54 (m, 7H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 98.1 (t, $J_F$ = 17.7, 1F), – 98.2 (t, $J_F$ = 17.7, 1F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.7, 161.4 (t, $J_{C_F}$ = 28.3 Hz), 139.9, 137.0, 134.4, 133.7, 130.3, 129.6, 129.5, 129.1, 118.8 (t, $J_{C_F}$ = 253.5 Hz), 47.0 (t, $J_{C_F}$ = 6.5 Hz), 46.4 (t, $J_{C_F}$ = 3.3 Hz), 44.6, 38.6 (t, $J_{C_F}$ = 22.7 Hz), 26.5 25.7, 24.5; HRMS (ESI) m/z calcd for C$_2$I$_3$Cl$_5$NO$_2$ $^+$ [M + H]$^+$ m/z 440.0990, found m/z 440.0982.

terr-Butyl 4-(4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanoyl)piperazine-1-carboxylate (3bl)

65% yield, 35.2 mg; white solid; mp. 124 – 126 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.85 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 – 7.21 (m, 4H), 4.94 (dd, $J_F$ = 8.7 Hz, $J_C$ = 3.7 Hz, 1H), 3.75 – 3.72 (m, 2H), 3.63 (t, $J_C$ = 5.3 Hz, 2H), 3.55 (t, $J_C$ = 5.5 Hz, 2H), 3.50 – 3.38 (m, 3H), 2.56 – 2.43 (m, 1H), 1.46 (s, 9H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 97.5 to – 97.8 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.4, 161.8 (t,
$J_{C,F} = 28.8$ Hz), 154.5, 140.0, 136.8, 134.2, 133.8, 130.3, 129.6, 129.5, 129.1, 118.5 (t, $J_{C,F} = 253.4$ Hz), 80.6, 46.3 (t, $J_{C,F} = 3.4$ Hz), 45.8 (t, $J_{C,F} = 4.9$ Hz), 43.1, 38.4 (t, $J_{C,F} = 22.6$ Hz), 28.5; HRMS (ESI) m/z calcd for C$_{26}$H$_{35}$Cl$_{3}$F$_{2}$O$_{2}$Na$^+$ [M + Na]$^+$ m/z 563.1286, found m/z 563.1296.

4,5–Bis(4-chlorophenyl)–2,2–difluoro–1–(4–(pyrimidin–2–yl)piprazin–1–yl)pentane–1,5–dione (3bm)

78% yield, 40.0 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J = 4.7$ Hz, 2H), 7.89 – 7.86 (m, 2H), 7.39 – 7.35 (m, 2H), 7.28 – 7.22 (m, 4H), 6.55 (t, $J = 4.7$ Hz, 1H), 4.97 (dd, $J_1 = 8.6$ Hz, $J_2 = 3.7$ Hz, 1H), 3.93 – 3.81 (m, 4H), 3.74 (t, $J = 5.1$ Hz, 2H), 3.67 (t, $J = 5.2$ Hz, 2H), 3.50 – 3.35 (m, 1H), 2.56 – 2.50 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 98.0 to – 98.3 (m, 2F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.4, 161.8 (t, $J_{C,F} = 28.6$ Hz), 161.3, 157.9, 139.9, 136.8, 134.2, 133.8, 130.3, 129.6, 129.5, 129.1, 118.6 (t, $J_{C,F} = 253.4$ Hz), 110.8, 46.3 (t, $J_{C,F} = 3.5$ Hz), 45.7 (t, $J_{C,F} = 6.0$ Hz), 44.0, 43.4, 43.1, 38.4 (t, $J_{C,F} = 22.3$ Hz); HRMS (ESI) m/z calcd for C$_{26}$H$_{35}$Cl$_{3}$F$_{2}$O$_{2}$Na$^+$ [M + H]$^+$ m/z 519.1161, found m/z 519.1160.

5,5,5–Trifluoro–1,2–diphenylpentan–1–one (3bn)

37% yield, 13.4 mg; white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.82 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.21 – 7.17 (m, 2H), 4.52 (t, $J = 7.0$ Hz, 1H), 2.40 – 2.34 (m, 1H), 2.14 – 2.00 (m, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 66.7 (m, $J = 7.9$, 3F); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 140.0, 136.6, 134.4, 133.9, 130.2, 129.8, 129.5, 129.2, 51.6, 31.5 (d, $J_{C,F} = 28.9$ Hz), 26.1 (q, $J_{C,F} = 3.4$ Hz); HRMS (ESI) m/z calcd for C$_{17}$H$_{14}$Cl$_{2}$F$_{2}$O$^+$ [M + H]$^+$ m/z 361.0368, found m/z 361.0376.

1,2–Bis(4-chlorophenyl)–4–(methylsulfonyl)butan–1–one (3bo)

66% yield, 24.5 mg; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.82 (m, 2H), 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.19 (m, 2H), 4.84 (t, $J = 7.4$ Hz, 1H), 3.06 – 2.94 (m, 2H), 2.91 (s, 3H), 2.66 – 2.57 (m, 1H), 2.39 – 2.31 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.2, 140.1, 136.2, 134.2, 134.1, 130.3, 129.8, 129.6, 129.2, 52.1, 50.9, 41.0, 26.6; HRMS (ESI) m/z calcd for C$_{17}$H$_{14}$Cl$_{2}$O$_{2}$S$^+$ [M + H]$^+$ m/z 371.0270, found m/z 371.0260.

Dimethyl 2–(2,3–bis(4–chlorophenyl)–3–oxopropyl)malonate (3bp)
20% yield, 8.0 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.82 (m, 2H), 7.38 – 7.34 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.17 (m, 2H), 4.65 (t, J = 7.4 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.30 (dd, J₁ = 8.1 Hz, J₂ = 6.7 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.42 – 2.34 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 169.6(2) 169.5(5), 139.9, 136.4, 134.4, 133.9, 130.3, 129.8, 129.6, 129.1, 52.9, 52.8, 50.2, 49.2, 32.3; HRMS (ESI) m/z calc for C₂₀H₁₈Cl₂O₃Na⁺ [M + Na]⁺ m/z 431.0424, found m/z 431.0409.

**Methyl (4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoyl)glycinate (3bq)**

90% yield, 40.0 mg; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.21 (m, 4H), 6.79 (s, 1H), 4.98 (dd, J₁ = 8.0 Hz, J₂ = 5.2 Hz, 1H), 4.08 – 3.97 (m, 2H), 3.80 (s, 3H), 3.31 – 3.17 (m, 1H), 2.63 – 2.50 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ −104.5 to −104.7 (m, 2F); ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 169.3, 164.1 (t, J c–F = 28.9 Hz), 140.0, 136.3, 134.1, 133.9, 130.4, 129.7, 129.6, 129.2, 117.0 (t, J c–F = 250.2 Hz), 52.9, 46.1 (t, J c–F = 3.9 Hz), 41.1, 37.5 (t, J c–F = 23.2 Hz); HRMS (ESI) m/z calc for C₂₀H₁₈ Cl₂F₂NO₄⁺ [M + H]⁺ m/z 444.0575, found m/z 444.0566.

**Methyl (4,5–bis(4–chlorophenyl)–2,2–difluoro–5–oxopentanoyl)–L–phenylalaninate (3br)**

82% yield, 43.8 mg; yellow oil; dr = 1:1; ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.16 (m, 7H), 7.12 – 7.05 (m, 2H), 6.72 (d, J = 7.8 Hz, 1H), 4.95 – 4.90 (m, 1H), 4.84 – 4.74 (m, 1H), 3.77 (d, J = 6.5 Hz, 3H), 3.21 – 3.07 (m, 3H), 2.56 – 2.42 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃, two diastereoisomers) δ one isomer −102.9 to −103.5 (m, 1F), −105.5 to −106.1 (m, 1F); another isomer −102.2 to −102.8 (m, 1F), −106.2 to −106.8 (m, 1F); ¹³C NMR (100 MHz, CDCl₃; two diastereoisomers) δ one isomer 196.1, 170.9(overlapped), 163.5 (t, J c–F = 29.3 Hz ), 140.0(overlapped), 136.4, 135.1,134.1, 133.8, 130.3, 129.6, 129.5, 129.3,129.1, 128.9, 127.6, 116.9 (t, J c–F = 252.0 Hz), 53.2, 52.8, 46.1, 37.9, 37.6, 37.4 (t, J c–F =23.4 Hz); another isomer 196.1, 170.9(overlapped), 163.4 (t, J c–F = 28.5 Hz ), 140.0(overlapped), 136.2, 135.0, 134.1, 133.8, 130.3, 129.6, 129.5, 129.3, 129.1, 128.9, 127.6, 116.8 (t, J c–F = 252.6 Hz), 53.1, 52.8, 46.0, 37.9, 37.6, 37.4 (t, J c–F =23.4 Hz); HRMS (ESI) m/z calc for C₂₁H₂₃Cl₂F₂NO₄⁺ [M + H]⁺ m/z 534.1045, found m/z 534.1045.

**4,5–Bis(4–chlorophenyl)–2,2–difluoro–N–((1S,4aS,10aS)–7–isopropyl–1,4a,10a–trimethyl–1,2,3,4,4a,9,10,10a–octahydrophenanthren–1–yl)methyl)–5–oxopentanamide (3bs)**

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56% yield, 35.8 mg; yellow oil, dr = 1 : 1; 1H NMR (400 MHz, CDCl3) δ 7.88 – 7.82 (m, 2H), 7.39 – 7.34 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 3H), 7.03 – 6.99 (m, 1H), 6.89 – 6.87 (m, 1H), 6.25 (s, 1H), 5.00 – 4.93 (m, 1H), 3.31 – 3.13 (m, 3H), 2.95 – 2.75 (m, 3H), 2.56 – 2.43 (m, 1H), 2.32 – 2.28 (m, 1H), 1.87 – 1.63 (m, 5H), 1.46 – 1.32 (m, 3H), 1.23 – 1.20 (m, 9H), 0.95 (s, 3H); 13F NMR (376 MHz, CDCl3, two diastereoisomers) δ one isomer –103.5 to –103.6 (m, 2F); another isomer –103.6(5) to –103.7(4) (m, 2F); 13C NMR (100 MHz, CDCl3) δ one isomer 196.3, 164.1 (overlapped, t, J C-F =28.23 Hz), 146.9(overlapped), 145.9(overlapped), 140.0(overlapped), 136.4(overlapped), 134.6(overlapped), 134.2(overlapped), 133.9(overlapped), 130.3, 129.6, 129.2(overlapped), 127.1, 124.4(overlapped), 124.1(overlapped), 117.2 (t, J C-F =251.8 Hz), 90.1, 86.2, 58.5, 38.3(overlapped), 37.7, 37.5, 36.3, 33.6(overlapped), 30.4, 25.5, 24.(overlapped), 19.2(overlapped), 18.6; another isomer 196.3, 164.1 (overlapped, t, J C-F =28.23 Hz), 146.9(overlapped), 145.9(overlapped), 140.0(overlapped), 136.4(overlapped), 134.6(overlapped), 134.2(overlapped), 133.9(overlapped), 130.3, 129.6, 129.2(overlapped), 127.0, 124.4(overlapped), 124.1(overlapped), 117.1 (t, J C-F =251.8 Hz), 50.1, 46.2, 46.0, 38.3(overlapped), 37.6, 37.5, 36.2, 33.6(overlapped), 30.3, 25.5, 24.(overlapped), 19.2(overlapped), 18.6; HRMS (ESI) m/z calcd for C35H52F2NO6 [M + H] + m/z 640.2555, found m/z 640.2556.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate (3bt)

95% yield, 48.5 mg; yellow oil, dr = 1 : 1; 1H NMR (400 MHz, CDCl3, two diastereoisomers) δ one isomer 7.88 – 7.84 (overlapped, 2H), 7.40 – 7.36 (overlapped, 2H), 7.28 – 7.25 (overlapped, 2H), 7.23 – 7.19 (overlapped, 2H), 4.92 – 4.87 (overlapped, 1H), 4.80 – 4.70 (overlapped, 1H), 3.34 – 3.17 (overlapped, 1H), 2.53 – 2.38 (overlapped, 1H), 1.98 – 1.79 (overlapped, 2H), 1.72 – 1.65 (overlapped, 2H), 1.51 – 1.39 (overlapped, 2H), 0.93 – 0.86 (overlapped, 9H), 0.75 – 0.73 (overlapped, 3H); 19F NMR (376 MHz, CDCl3, two diastereoisomers) δ one isomer –104.0 (overlapped, J = 16.8 Hz, 1F), –104.1 to –104.2 (m, 1F); another isomer –104.0 (overlapped, J = 16.8 Hz, 1F), –104.3 to –104.4 (m, 1F); 13C NMR (100 MHz, CDCl3, two diastereoisomers) δ one isomer 195.9, 163.3 (t, J C-F = 32.2 Hz ), 139.9(overlapped), 136.2, 133.9(2), 133.8(5)(overlapped), 130.2, 129.5(2), 129.4(8), 129.0(overlapped), 115.2 (t, J C-F = 250.3 Hz), 46.7(overlapped), 46.0 (t, J C-F=7.5 Hz), 40.1, 37.8 (t, J C-F=23.3 Hz), 33.9, 31.4, 26.1, 23.3, 21.9, 20.6 (overlapped), 16.1 (overlapped); another isomer 195.8, 163.3 (t, J C-F = 31.3 Hz), 139.9(overlapped), 136.1, 133.8(5)(overlapped), 133.8(2), 130.1, 129.51, 129.41, 129.0(overlapped), 115.2 (t, J C-F = 249.9 Hz), 46.7(overlapped), 46.0 (t, J C-F=7.5 Hz), 40.2, 37.8 (t, J C-F=22.9 Hz), 33.9, 31.3, 26.1, 23.2, 21.9, 20.6 (overlapped), 16.1 (overlapped); HRMS (ESI) m/z calcd
5. TEMPO inhibition experiment

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with TEMPO (0.2 mmol, 31.2 mg) and 1,1–bis(4–chlorophenyl) prop–2–en–1–ol 1c (0.1 mmol, 27.9 mg). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate 2a (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C. After 24 hours, the reaction was then quenched satd. NH₄Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of product formed was determined by ¹⁹F NMR with trifluorotoluene as internal standard. The ¹⁹F NMR signal of compound 5 was consistent with the reported data.²

6. Sunlight irradiation experiment
A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol 1c (0.1 mol, 27.9mg). The vessel was then evacuated and filled with nitrogen three times. Next, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate 2a (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. The tube was then sealed and irradiated with sunlight for 8 hours. The reaction was quenched with satd. NH₄Cl solution (15 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was concentrated to give the crude product, which was purified by column chromatography on silica gel with petroleum ether/ethyl acetate mixtures to give the product in 54% yield.

7. Scaleup experiment

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol 1c (3.6 mmol, 1.04g, 1 equiv.). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate 2a (7.2 mmol, 0.92 mL, 2 equiv.), tributylamine (7.2 mmol, 1.7mL, 2 equiv.) and formic acid (7.2 mmol, 0.24mL, 2 equiv.) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C. After 24 hours, the reaction was then quenched with satd. NH₄Cl solution (100 mL) and extracted with ethyl acetate (3 x 50 mL). The organic layer was concentrated, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give compound 3ba (1.02 g, 71% yield).
8. Quantum yield measurement

Quantum yield experiments were performed according to the procedure of Yoon.\textsuperscript{5,6}

8.1 Determination of the photo flux of the light source:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H\textsubscript{2}SO\textsubscript{4}. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H\textsubscript{2}SO\textsubscript{4}. Both solutions were covered in foil and stored in dark. To determine the photon flux of our lamp source, 2.0 mL of the ferrioxalate solution was placed in a 5 mL screw-top test tube and irradiated for 10.0 s with the photoreactor 2 cm away from a 30 W blue LEDs light irradiation. After irradiation, 0.35 mL of the phenanthroline solution was added to the test tube. The solution was then allowed to rest for 1 h in dark to make sure the ferrous ions completely coordinating to phenanthroline. The absorbance of the solution was then measured at 510 nm. Conversion was calculated using eq. 1

\[
\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \quad (1)
\]

Where \( V \) is the total volume (0.00235 L) of the solution after addition of phenanthroline, \( \Delta A \) is the difference in the absorbance at 510 nm between the irradiated and non-irradiated solutions, \( l \) is the path length (1.000 cm), and \( \varepsilon \) is the molar absorptivity at 510 nm (11,100 L mol\textsuperscript{-1} cm\textsuperscript{-1}). The photon flux can be calculated using eq. 2

\[
\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (2)
\]

Where \( \Phi \) is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at \( \lambda = 460 \text{ nm} \)), \( t \) is the irradiation time (10.0 s), and \( f \) is the fraction of light absorbed at \( \lambda = 460 \text{ nm} \). The fraction of light absorbed \( (f) \) by this solution was calculated using eq. 3, where \( A \) is the measured absorbance at 460 nm.

\[
f = 1 - 10^{-A} \quad (3)
\]
The absorbance of the above ferrioxalate solution at 460 nm was measured to be 0.840, which means 

\[ f = 0.840, \text{ vide infra.} \]

Then, the photo flux of the light source could be calculated:

**Sample calculation:**

\[
\text{Mol Fe}^{2+} = \frac{0.00235 \text{ L} \cdot 1.233}{1 \text{ cm} \cdot 11100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}} = 2.61 \times 10^{-7} \text{ mol}
\]

\[
\text{Photon flux} = \frac{2.61 \times 10^{-7} \text{ mol}}{0.845 \cdot 10^{-7} \text{ s} \cdot 0.85546} = 3.61 \times 10^{-8} \text{ einsteins s}^{-1}
\]

The photon flux was calculated (average of three experiments) to be \( 3.61 \times 10^{-8} \text{ einsteins s}^{-1} \).

### 8.2 Determination of quantum yield

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol 1c (0.1 mol, 27.9mg). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate 2a (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation with a water chiller to maintain the temperature at 25 °C.
°C. After 20 min, the reaction was then quenched with satd. NH₄Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of product formed was determined by ¹H NMR with a 1,3,5–Trimethoxybenzene as internal standard. Average yield of three experiments was 24% yield. The fraction of light absorbed (ϕ) by this solution was calculated to be 0.89 using eq. 3. The quantum yield was calculated using eq. 4 the average yield of three experiments to be 0.62.

\[
\phi = \frac{\text{moles of product formed}}{\text{einstein s of light absorbed}}
\]  

(4)

Sample quantum yield calculation:

\[
\phi = \frac{2.4 \times 10^{-5} \text{ mol}}{3.61 \times 10^{-8} \text{ einsteins s}^{-1} \cdot 1200 \text{ s} \cdot 1.00 \cdot 0.89183} = 0.62
\]

9. Light on/off Experiment

A 5 mL Schlenk tube containing a PTFE–coated stirring bar was charged with 1,1–bis(4–chlorophenyl) prop–2–en–1–ol 1c (0.1 mol, 27.9 mg). The vessel was then evacuated and filled with nitrogen three times. Then, DMSO (2 mL) was added, followed by the addition of ethyl difluorobromoacetate 2a (0.2 mmol, 25.4 μL), tributylamine (0.2 mmol, 47.5 μL) and formic acid (0.2 mmol, 6.6 μL) under nitrogen flow. Finally, the tube was sealed and placed in the photoreactor about 2 cm away from a 30 W blue LEDs light irradiation and kept in the dark in 1 hour intervals with a water chiller to maintain the temperature at 25 °C. The reaction was then quenched satd. NH₄Cl solution (15 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was concentrated. The yield of 3ba was determined by ¹H NMR with 1,3,5–trimethoxybenzene as internal standard.
Figure S1. Reaction profile of light on/off experiment

10. UV–vis absorption spectra
**Conclusion:** UV-Vis spectrum of the mixture of Et₃N/C₄F₉I shows a strong bathochromic shift and a charge transfer band, which support the formation of halogen bonded complex in the reaction mixture between Et₃N and C₄F₉I.
Figure S4. UV–visible absorption spectra of Bu$_3$N, C$_4$F$_9$I, HCOOH, mixture solution of Bu$_3$N/C$_4$F$_9$I and mixture solution of Bu$_3$N/C$_4$F$_9$I/HCOOH in DMSO (c = 0.01 M).

Figure S5. Photograph of solution of Bu$_3$N, C$_4$F$_9$I and mixture solution of Bu$_3$N/C$_4$F$_9$I in DMSO (c = 0.01 M).

Conclusion: UV-Vis spectrum of the mixture of Bu$_3$N/C$_4$F$_9$I/HCOOH shows a strong bathochromic shift and a charge transfer band, which support the formation of halogen bonded complex in the reaction mixture.
11. $^{19}$FNMR Titration of C₄F₉I (2a) with Et₃N.

**Figure S6.** $^{19}$F NMR shift of C₄F₉I with the addition of Et₃N in DMSO/CH₃OH (90:10, v/v)

**Figure S7.** $^{19}$F NMR shift of C₄F₉I with the addition of Et₃N in DMSO/CH₃OH (90:10, v/v)

**Conclusion:** A clear upfield-shift of the $^{19}$F NMR signal was observed with the addition of Et₃N into C₄F₉I, which indicated the interaction, namely, halogen bond between Et₃N and C₄F₉I.
12. Determination of binding stoichiometry of halogen bond between C₄F₉I (2a) and Et₃N.

Determination of binding stoichiometry experiments were performed by Job’s method according to the reported procedure. The binding stoichiometry between C₄F₉I (2a) and Et₃N was evaluated using a Job’s plot in 1.0 mL of DMSO/CH₃OH (90:10, v/v) solution. In an NMR tube, total constant concentration [2a + Et₃N] = 0.1 M. Samples were prepared for molar fractions χ(2a) = 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80, 0.90, 1.00. ¹⁹F NMR for each sample was recorded to measure the change in chemical shift for the F of C₄F₉I. Fluorobenzene was used as internal standard and δF-Ph = -113.066 ppm.

The data show formation of a 1:1 adduct (maximum in the plot at χ(2a) = 0.5).

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<th>χ(2a)</th>
<th>0</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.40</th>
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<tr>
<td>[2a]*Δδ</td>
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<tr>
<td>χ(2a)</td>
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<tr>
<td>Δδ</td>
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<td>0.0231</td>
<td>0</td>
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<tr>
<td>[2a]*Δδ</td>
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<td>0.07548</td>
<td>0.05784</td>
<td>0.02079</td>
<td>0</td>
</tr>
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</table>

Figure S8. Job’s plot

Conclusion: A clear upfield-shift of the ¹⁹F NMR signal of C₄F₉I was observed with the addition of Et₃N, which indicated the formation of halogen bonded complex between C₄F₉I and Et₃N. This is in consistent with the redshift of the UV-Vis spectrum. And the halogen bond donor:acceptor ratio in the solution was calculated to be 1:1 via Job’s method.
13. Reference


14. NMR Spectra

3aa

CDCl$_3$, $^1$H NMR, 400 MHz

H$_2$O

3aa

CDCl$_3$, $^{19}$F NMR, 376 MHz
3ab

CDCl₃, ¹H NMR, 376 MHz

3ab

CDCl₃, ¹³C NMR, 100 MHz
CDCl₃, $^{19}$F NMR, 376 MHz

CDCl₃, $^{13}$C NMR, 100 MHz
3af
CDCl₃, ¹⁹F NMR, 376 MHz

3af
CDCl₃, ¹³C NMR, 100 MHz
**$3_{ag}$**

C$_2$H$_5$, $^1$H NMR, 400 MHz

![NMR Spectrum](image1)

**$3_{ag}$**

C$_2$H$_5$, $^{19}$F NMR, 376 MHz

![NMR Spectrum](image2)
$^{19}$F NMR, 376 MHz

$^{13}$C NMR, 100 MHz
3ai
CDCl₃, ¹³C NMR, 100 MHz

3aj / 3aj' = 3 : 1
CDCl₃, ¹H NMR, 400MHz
$\text{CDCl}_3, ^{19}\text{F} \text{ NMR, 376 MHz}$

$3\text{aj} / 3\text{aj}' = 3 : 1$

$\text{CDCl}_3, ^{13}\text{C} \text{ NMR, 100 MHz}$

$3\text{aj} / 3\text{aj}' = 3 : 1$
3ak / 3ak' = 6 : 1
CDCl₃, ¹H NMR, 400MHz

3ak / 3ak' = 6 : 1
CDCl₃, ¹⁹F NMR, 376 MHz
$3a_k / 3a_k' = 6 : 1$

CDCl$_3$, $^{13}$C NMR, 100 MHz

$3a_l / 3a_l' = 14 : 1$

CDCl$_3$, $^1$H NMR, 400 MHz
$3a_l / 3a_l' = 14 : 1$

CDCl$_3$, $^{19}$F NMR, 376 MHz

$3a_l / 3a_l' = 14 : 1$

CDCl$_3$, $^{13}$C NMR, 100 MHz
$3\text{am} / 3\text{am'} = 3 : 1$

CDCl$_3$, $^1$H NMR, 400 MHz

$3\text{am} / 3\text{am'} = 3 : 1$

CDCl$_3$, $^{19}$F NMR, 376 MHz
3am / 3am' = 3 : 1
CDCl₃, ¹³C NMR, 100 MHz

3an
CDCl₃, ¹H NMR, 400 MHz
3an
CDCl₃, ¹⁹F NMR, 376 MHz

3ao
CDCl₃, ¹H NMR, 400MHz
3bb
CDCl₃, ¹H NMR, 400MHz

3bb
CDCl₃, ¹⁹F NMR, 376 MHz
$3bc$

CDCl$_3$, $^{19}$F NMR, 376 MHz

$3bc$

CDCl$_3$, $^{13}$C NMR, 100 MHz

558
3bd

CDCl₃, ¹H NMR, 400 MHz

3bd

CDCl₃, ¹⁹F NMR, 376 MHz
$\text{CDCl}_3$, $^{13}$C NMR, 100 MHz

$\text{CDCl}_3$, $^1$H NMR, 400MHz

S60
\[ \text{CDCl}_3, {^1}^\text{H NMR, 400MHz} \]

3bg

\[ \text{CDCl}_3, {^{13}}\text{C NMR, 100MHz} \]

3bf
$\text{CDCl}_3, ^{19}\text{F NMR, 376 MHz}$

$\text{CDCl}_3, ^{13}\text{C NMR, 100 MHz}$
3bh

CDCl₃, ¹H NMR, 400 MHz

3bh

CDCl₃, ¹⁹F NMR, 376 MHz
$\text{CDCI}_3, \ ^{13}\text{C NMR, 100 MHz}$

$\text{3bh}$

$\text{CDCI}_3, \ ^{1}\text{H NMR, 400MHz}$

$\text{3bi}$
\[ \text{CDCl}_3, ^{19}\text{F NMR, 376 MHz} \]

\[ \text{CDCl}_3, ^{12}\text{C NMR, 100 MHz} \]
3bj

CDCl₃, ¹H NMR, 400 MHz

3bj

CDCl₃, ¹F NMR, 376 MHz
$\text{CDCl}_3$, $^{13}$C NMR, 100 MHz

$\text{CDCl}_3$, $^1$H NMR, 400 MHz
$^{19}$F NMR, 376 MHz

$^{13}$C NMR, 100 MHz
$3b_l$

CDCl$_3$, $^1$H NMR, 400 MHz

$3b_l$

CDCl$_3$, $^{19}$F NMR, 376 MHz
3bm

CDCl₃, ¹⁹F NMR, 376 MHz

3bm

CDCl₃, ¹³C NMR, 100 MHz
$\text{CDCl}_3$, $^1H$ NMR, 400 MHz

$\text{CDCl}_3$, $^{19}F$ NMR, 376 MHz
3bn
CDCl₃, $^{13}$C NMR, 100 MHz

3bo
CDCl₃, $^1$H NMR, 400MHz
CDCl₃, $^{13}$C NMR, 100 MHz

CDCl₃, $^1$H NMR, 400 MHz
$^{19}$F NMR, 376 MHz

$^{13}$C NMR, 100 MHz
3br, dr = 1 : 1
CDCl₃, ¹H NMR, 400MHz

3br, dr = 1 : 1
CDCl₃, ¹⁹F NMR, 376 MHz

S79
$\text{3br, } \text{dr} = 1 : 1$

CDCl$_3$, $^{13}$C NMR, 100 MHz

$\text{3bs, } \text{dr} = 1 : 1$

CDCl$_3$, $^1$H NMR, 400MHz
3bs, dr = 1 : 1
CDCl₃, ¹⁹F NMR, 376 MHz

3bs, dr = 1 : 1
CDCl₃, ¹³C NMR, 100 MHz
3bt, dr = 1 : 1
CDCl₃, $^1$H NMR, 400MHz

3bt, dr = 1 : 1
CDCl₃, $^{19}$F NMR, 376 MHz
3bt, dr = 1 : 1
CDCl₃, $^{13}$C NMR, 100 MHz