Supporting Information

Synthesis of α-iodoketals from methyl ketones via sustainable and orthogonal tandem catalysis

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Appendix
Spectral copies of $^1$H NMR and $^{13}$C NMR of compounds obtained in this study
1 General methods:

All reagents were purchased from commercial suppliers and used without further purification. IR spectra were recorded on an infrared spectrometer as KBr pellets with absorption in cm\(^{-1}\). \(^1\)H spectra were recorded in CDCl\(_3\) on 400/600 MHz NMR spectrometers and resonances (\(\delta\)) are given in ppm relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet), coupling constants (Hz) and integration. \(^1^3\)C spectra were recorded in CDCl\(_3\) on 100/150 MHz spectrometers and resonances (\(\delta\)) are given in ppm relative to the center line of a triplet at 77.0 ppm of chloroform-\(d\). HRMS were obtained on an Apex-Ultra MS equipped with APCI or ESI source. Melting points were determined using XT-4 apparatus and not corrected. The X-ray crystal-structure determination of 3ba, 3ia and 4aa was obtained on a Bruker SMART APEX CCD system. Column chromatography was performed on silica gel (200–300 mesh).
2 General procedure for the preparation of (Z)-2-arylidene-1-arylbutane-1,3-dione (3aa as an example):

\[ \text{Ph} \cdots \text{H} + \text{Ph} \cdots \text{O} \cdots \text{O} \xrightarrow{\text{piperidine, AcOH, rt}} \text{Ph} \cdots \text{O} \cdots \text{O} \]

Piperidine (20 mL) was added dropwise to the stirred solution of acetic acid (25 mL) in ice bath. Benzaldehyde 1a (1.06 g, 10.0 mmol) and 1-phenylbutane-1,3-dione 2a (1.62 g, 10.0 mmol) were then added into the mixture solution and stirred at room temperature for overnight. After the reaction completed, the mixture was diluted with water and extracted with CH\(_2\)Cl\(_2\) (3 × 200 mL), the combined organic extracts were washed with NaOH (5% w/w, aq.) and brine successively, then dried with Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1) to afford a white solid 3aa (2.15 g, 86%).

Table 1. Scope of substrates.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>3</th>
<th>Yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a (C(_6)H(_5))</td>
<td>2a (C(_6)H(_5))</td>
<td>3aa</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>1b (4-MeC(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3ba</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>1c (4-MeOC(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3ca</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>1d (4-NO(_2)C(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3da</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>1e (1-naphthyl)</td>
<td>2a (C(_6)H(_5))</td>
<td>3ea</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>1f (2-naphthyl)</td>
<td>2a (C(_6)H(_5))</td>
<td>3fa</td>
<td>78</td>
</tr>
<tr>
<td>7</td>
<td>1g (4-ClC(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3ga</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>1h (4-BrC(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3ha</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>1i (4-FC(_6)H(_4))</td>
<td>2a (C(_6)H(_5))</td>
<td>3ia</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>1j (2-thienyl)</td>
<td>2a (C(_6)H(_5))</td>
<td>3ja</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>1a (C(_6)H(_5))</td>
<td>2b (4-MeC(_6)H(_4))</td>
<td>3ab</td>
<td>83</td>
</tr>
<tr>
<td>12</td>
<td>1a (C(_6)H(_5))</td>
<td>2c (2-naphthyl)</td>
<td>3ac</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>1a (C(_6)H(_5))</td>
<td>2d (4-ClC(_6)H(_4))</td>
<td>3ad</td>
<td>83</td>
</tr>
<tr>
<td>14</td>
<td>1a (C(_6)H(_5))</td>
<td>2e (4-BrC(_6)H(_4))</td>
<td>3ae</td>
<td>84</td>
</tr>
<tr>
<td>15</td>
<td>1a (C(_6)H(_5))</td>
<td>2f (2-furfuryl)</td>
<td>3af</td>
<td>60</td>
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<tr>
<td>16</td>
<td>1a (C(_6)H(_5))</td>
<td>2g (2-thienyl)</td>
<td>3ag</td>
<td>70</td>
</tr>
</tbody>
</table>

\(^a\) Reaction was performed with aldehyde 1 (10.0 mmol), 1-arylbute–1,3-dione 2 (10.0 mmol), and piperidine (20 mL) in acetic acid (25 mL) at rt overnight. \(^b\) Isolated yield.
General procedure for the preparation of α-iodoketals of (Z)-2-arylidene-1-arylbutane-1,3-dione (4aa as an example):

\[
\begin{align*}
\text{Ph} & \quad \text{CuO, I}_2 \\
3\text{aa} & \quad \text{ethylene glycol, 60 °C} \\
\text{Ph} & \quad \text{4aa}
\end{align*}
\]

(Z)-2-benzylidene-1-phenylbutane-1,3-dione 3aa (250 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous ethylene glycol (5 mL), the mixture was stirred at 60 °C for 5 h. After the reaction completed, the mixture was diluted with water and treated with Na₂S₂O₃ (5% w/w, aq.). The mixture was then extracted with CH₂Cl₂ (3 × 20 mL), the combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1) to afford a white solid 4aa (357 mg, 85%).

General procedure for the preparation of 5:

\[
\begin{align*}
\text{Ph} & \quad \text{CuO, I}_2 \\
3\text{aa} & \quad 1,3\text{-propanediol, 60 °C} \\
\text{Ph} & \quad \text{5}
\end{align*}
\]

(Z)-2-benzylidene-1-phenylbutane-1,3-dione 3aa (250 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous 1,3-propanediol (5 mL), the mixture was stirred at 60 °C for 5 h. After the reaction completed, the mixture was diluted with water and treated with Na₂S₂O₃ (5% w/w, aq.). The mixture was then extracted with CH₂Cl₂ (3 × 20 mL), the combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 15:1) to afford a yellow solid 5 (339 mg, 90%).

General procedure for the preparation of α-iodoketals of (Z)-2-arylidene-1-arylbutane-1,3-dione (7a as an example):

\[
\begin{align*}
\text{Ph} & \quad \text{CuO, I}_2 \\
6\text{a} & \quad \text{ethylene glycol, 60 °C} \\
& \quad \text{7a}
\end{align*}
\]

Acetophenone 6a (120 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous 1,3-propanediol (5 mL), the mixture was stirred at 60 °C for 5 h. After the reaction completed, the mixture was diluted with water and treated with Na₂S₂O₃ (5% w/w, aq.). The mixture was then extracted with CH₂Cl₂ (3 × 20 mL), the combined organic extracts were
dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 80:1) to afford a yellow solid 7a (104 mg, 36%).

3 Control experiments to provide insight into the mechanism:

![Chemical structures and reactions](image)

(10) Results and discussion of the control experiments:
When 3aa was used as substrate, no ketalization product 8 was obtained without I₂ (Eq. 1, 2, 3); when 5 was used as substrate, no desired product 4aa was obtained without I₂ (Eq. 6, 7, 8); when 3aa was used as substrate, the desired product 4aa was obtained in 45% yield with I₂ (Eq. 4) and 85% yield with CuO and I₂ (Eq. 5); when 5 was used as substrate, the desired product 4aa was obtained in 92% yield in the presence of I₂ (Eq. 9).

Based on our previous studies and the control experiments, it’s clearly confirmed that copper oxide could promote the iodination reaction and iodine could promote the ketalization reaction with ethylene glycol.

4 Spectroscopic Data:
(Z)-2-Benzylidene-1-phenylbutane-1,3-dione (3aa). Yield 86%; White solid; m.p. 92.8–93.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.92 (d, $J = 7.6$ Hz, 2H), 7.79 (s, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.41–7.38 (m, 2H), 7.35–7.33 (m, 2H), 7.28–7.20 (m, 3H), 2.39 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 198.0, 195.8, 141.1, 139.6, 135.9, 134.0, 132.8, 130.4, 130.2, 129.1, 128.9, 128.8, 27.2; IR (KBr): 1678, 1651, 1619, 1233, 1207 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{17}$H$_{15}$O$_2$: 251.1067; found: 251.1068.

(Z)-2-(4-Methylbenzylidene)-1-phenylbutane-1,3-dione (3ba). Yield 82%; White solid; m.p. 72.5–74.2 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.94–7.91 (m, 2H), 7.76 (s, 1H), 7.55–7.51 (m, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 2.38 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 198.3, 195.9, 141.3, 141.1, 138.5, 136.0, 134.0, 130.4, 129.9, 129.5, 129.1, 128.9, 27.0, 21.3; IR (KBr): 1669, 1646, 1601, 1246, 1234, 1210 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{18}$H$_{17}$O$_2$: 265.1223; found: 265.1224.
(Z)-2-(4-Methoxybenzylidene)-1-phenylbutane-1,3-dione (3ca). Yield 80%; White solid; m.p. 70.6–72.1 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.93 (d, $J = 7.2$ Hz, 2H), 7.74 (s, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 2H), 7.31–7.27 (m, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 3.72 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 198.5, 195.8, 161.4, 141.0, 137.2, 136.0, 133.9, 132.4, 129.0, 128.8, 125.2, 114.3, 55.2, 26.9; IR (KBr): 1670, 1645, 1601, 1513, 1178 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{18}$H$_{17}$O$_3$: 281.1172; found: 281.1173.

(Z)-2-(4-Nitrobenzylidene)-1-phenylbutane-1,3-dione (3da). Yield 88%; Light yellow solid; m.p. 152.1–153.6 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.08–8.05 (m, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.82 (s, 1H), 7.60–7.56 (m, 1H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.45–7.41 (m, 2H), 2.41 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 196.9, 195.1, 148.2, 142.7, 139.2, 137.7, 135.4, 134.7, 130.6, 129.2, 129.1, 123.9, 27.5; IR (KBr): 1678, 1657, 1595, 1519, 1347, 1231 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{17}$H$_{14}$NO$_4$: 296.0917; found: 296.0917.
(Z)-2-(Naphthalen-1-ylmethylene)-1-phenylbutane-1,3-dione (3ea). Yield 77%;

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.60 (s, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.80–7.78 (m, 3H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.63–7.59 (m, 1H), 7.54–7.50 (m, 1H), 7.40–7.35 (m, 2H), 7.24–7.19 (m, 3H), 2.48 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 197.4, 195.5, 141.4, 139.2, 136.1, 133.7, 133.3, 131.4, 130.6, 130.4, 128.9, 128.8, 128.6, 127.9, 127.0, 126.4, 125.2, 123.7, 27.8; IR (KBr): 1679, 1658, 1595, 1231 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{21}$H$_{17}$O$_2$: 301.1223; found: 301.1224.

(Z)-2-(Naphthalen-2-ylmethylene)-1-phenylbutane-1,3-dione (3fa). Yield 78%;

Light yellow solid; m.p. 98.7–99.4 $^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.97–7.95 (m, 3H), 7.89 (s, 1H), 7.73–7.68 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.51–7.35 (m, 6H), 2.43 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 198.2, 195.8, 141.2, 139.5, 136.1, 134.1, 133.8, 132.8, 131.9, 130.3, 129.1, 128.9, 128.6, 128.5, 127.7, 127.5, 126.7, 125.9,
27.2; IR (KBr): 1675, 1648, 1610, 1262, 1231, 1174 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{21}\)H\(_{17}\)O\(_2\): 301.1223; found: 301.1224.

(Z)-2-(4-Chlorobenzylidene)-1-phenylbutane-1,3-dione (3ga). Yield 83%; White solid; m.p. 90.2–91.7 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.90 (d, \(J = 7.6\) Hz, 2H), 7.74 (s, 1H), 7.58–7.54 (m, 1H), 7.42 (t, \(J = 7.2\) Hz, 2H), 7.29–7.27 (m, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 2.39 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.7, 195.5, 139.9, 139.5, 136.5, 135.7, 134.3, 131.4, 131.3, 129.1, 129.0, 27.2; IR (KBr): 1679, 1655, 1618, 1230, 1210, 1089 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{17}\)H\(_{14}\)ClO\(_2\): 285.0677; found: 285.0679.

(Z)-2-(4-Bromobenzylidene)-1-phenylbutane-1,3-dione (3ha). Yield 84%; White solid; m.p. 88.0–89.4 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.90 (d, \(J = 8.0\) Hz, 2H), 7.71 (s, 1H), 7.54 (t, \(J = 7.6\) Hz, 1H), 7.41 (t, \(J = 7.6\) Hz, 2H), 7.35–7.33 (m, 2H), 7.20 (d, \(J = 8.4\) Hz, 2H), 2.38 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.6, 195.5,
140.0, 139.5, 135.6, 134.2, 131.9, 131.6, 131.4, 129.0, 128.9, 124.9, 27.1; IR (KBr): 1673, 1653, 1616, 1583, 1238 cm\(^{-1}\); HRMS (APCI): m/z \([M + H]^+\) calcd for C\(_{17}\)H\(_{14}\)BrO\(_2\): 329.0172; found: 329.0173.

(Z)-2-(4-Fluorobenzylidene)-1-phenylbutane-1,3-dione (3ia). Yield 80%; Light yellow solid; m.p. 110.6--111.8 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.92--7.90 (m, 2H), 7.76 (s, 1H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.42 (t, \(J = 7.6\) Hz, 2H), 7.36--7.33 (m, 2H), 6.92 (t, \(J = 8.4\) Hz, 2H), 2.38 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 198.0, 195.6, 165.0, 162.5, 139.8, 139.27, 139.25, 135.8, 134.3, 132.4, 132.3, 129.1, 129.0, 116.2, 116.0, 27.3; IR (KBr): 1681, 1650, 1620, 1596, 1508, 1164 cm\(^{-1}\); HRMS (APCI): m/z \([M + H]^+\) calcd for C\(_{17}\)H\(_{14}\)FO\(_2\): 269.0972; found: 269.0974

(Z)-1-Phenyl-2-(thiophen-2-ylmethylene)butane-1,3-dione (3ja). Yield 84%; White solid; m.p. 123.6--124.9 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.99--7.97 (m, 2H), 7.90 (s, 1H), 7.59 (t, \(J = 7.6\) Hz, 1H), 7.45 (t, \(J = 7.6\) Hz, 2H), 7.38 (d, \(J = 4.8\) Hz, 1H),
7.27–7.26 (m, 1H), 6.98–6.96 (m, 1H), 2.36 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$
197.7, 195.2, 136.5, 136.2, 135.9, 134.2, 133.2, 132.0, 129.2, 128.9, 128.0, 27.0; IR
(KBr): 1670, 1647, 1601, 1267, 1238, 1219, 1202 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$
calcd for C$_{13}$H$_{13}$O$_2$S: 257.0631; found: 257.0632.

(Z)-2-Benzylidene-1-(p-tolyl)butane-1,3-dione (3ab). Yield 83%; White solid; m.p.
106.0–107.2 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.82 (d, $J = 8.0$ Hz, 2H), 7.77 (s, 1H),
7.35 (d, $J = 7.6$ Hz, 2H), 7.26–7.19 (m, 5H), 2.37 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR
(CDCl$_3$, 100 MHz): $\delta$ 197.5, 195.8, 145.1, 140.8, 139.7, 133.6, 132.8, 130.3, 130.2,
129.6, 129.2, 128.7, 27.2, 21.6; IR (KBr): 1675, 1649, 1620, 1605, 1237, 1208, 1182
cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{18}$H$_{17}$O$_2$: 265.1223; found: 265.1224.

(Z)-2-Benzylidene-1-(naphthalen-2-yl)butane-1,3-dione (3ac). Yield 75%; Yellow
solid; m.p. 86.5–87.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.37 (s, 1H), 8.07 (d, $J = 8.4$
Hz, 1H), 7.88–7.81 (m, 4H), 7.56 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 6.8 Hz, 1H),
7.40–7.38 (m, 2H), 7.20–7.16 (m, 3H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$
197.9, 195.8, 141.2, 139.6, 136.0, 133.4, 132.8, 132.5, 131.8, 130.5, 130.3, 129.7,
129.0, 128.9, 128.8, 127.7, 126.8, 123.8, 27.3; IR (KBr): 1668, 1653, 1620, 1243,
1182 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{21}$H$_{17}$O$_2$: 301.1223; found:
301.1224.

(Z)-2-Benzylidene-1-(4-chlorophenyl)butane-1,3-dione (3ad). Yield 83%; White
solid; m.p. 108.4–111.0 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.86–7.82 (m, 2H), 7.79
(s, 1H), 7.39–7.35 (m, 2H), 7.33–7.22 (m, 5H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100
MHz): $\delta$ 196.7, 195.9, 141.6, 140.6, 139.1, 134.3, 132.6, 130.7, 130.4, 130.2, 129.3,
128.9, 27.1; IR (KBr): 1681, 1648, 1621, 1586, 1230, 1208 cm$^{-1}$; HRMS (APCI): m/z
[M + H]$^+$ calcd for C$_{17}$H$_{14}$ClO$_2$: 285.0677; found: 285.0679.
(Z)-2-Benzylidene-1-(4-bromophenyl)butane-1,3-dione (3ae). Yield 84%; White solid; m.p. 125.4–126.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.79–7.75 (m, 3H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.33–7.23 (m, 5H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 196.9, 195.9, 141.6, 139.1, 134.7, 132.5, 132.2, 130.7, 130.5, 130.2, 129.4, 128.9, 27.0; IR (KBr): 1680, 1647, 1622, 1583, 1230, 1209 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{17}$H$_{14}$BrO$_2$: 329.0172; found: 329.0173.

\[ \text{\includegraphics{image1.png}} \]

(Z)-2-Benzylidene-1-(furan-2-yl)butane-1,3-dione (3af). Yield 60%; White solid; m.p. 118.5–119.6 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.79 (s, 1H), 7.56 (brs, 1H), 7.39–7.37 (m, 2H), 7.33–7.25 (m, 3H), 7.06 (d, $J = 3.6$ Hz, 1H), 6.45–6.43 (m, 1H), 2.42 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 195.3, 184.6, 152.2, 147.9, 142.1, 138.5, 132.8, 130.5, 130.1, 128.8, 120.4, 112.6, 27.2; IR (KBr): 1665, 1646, 1617, 1242 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{15}$H$_{13}$O$_3$: 241.0859; found: 241.0860.

\[ \text{\includegraphics{image2.png}} \]

(Z)-2-Benzylidene-1-(thiophen-2-yl)butane-1,3-dione (3ag). Yield 70%; White solid; m.p. 96.3–97.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.79 (s, 1H), 7.66 (d, $J = 4.0$ Hz, 1H), 7.51 (d, $J = 2.8$ Hz, 1H), 7.43–7.41 (m, 2H), 7.32–7.24 (m, 3H), 7.01 (t, $J =$
4.4 Hz, 1H), 2.41 (s, 3H); ^1^H NMR (CDCl$_3$, 100 MHz): \( \delta \) 195.1, 189.8, 143.6, 141.2, 139.2, 135.7, 134.7, 132.8, 130.6, 130.3, 128.8, 128.5, 27.3; IR (KBr): 1660, 1638, 1615, 1413, 1246 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{15}$H$_{13}$O$_2$: 257.0631; found: 257.0633.

\[
\begin{array}{c}
\text{(E)-2-(2-Iodomethyl)-1,3-dioxolan-2-yl)-1,3-diphenylprop-2-en-1-one (4aa).} \\
\text{Yield 85%; White solid; m.p. 135.5–136.4 °C; } ^1^H \text{ NMR (CDCl}_3, \text{ 400 MHz): } \delta \\
7.84–7.82 (m, 2H), 7.43 (t, } J = 7.6 \text{ Hz, 1H), 7.30 (t, } J = 7.6 \text{ Hz, 2H), 7.21 (s, 1H),} \\
7.19–7.12 (m, 5H), 4.19–4.16 (m, 2H), 4.04–4.01 (m, 2H), 3.88 (s, 2H); ^1^C \text{ NMR} \\
(CDCl}_3, \text{ 100 MHz): } \delta 197.7, 137.6, 135.9, 134.1, 133.4, 131.4, 129.2, 129.1, 128.6, \\
128.5, 128.4, 107.2, 66.1, 13.3; IR (KBr): 1650, 1283, 1036 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{19}$H$_{18}$O$_3$: 421.0295; found: 421.0295.
\end{array}
\]

\[
\begin{array}{c}
\text{(E)-2-(2-Iodomethyl)-1,3-dioxolan-2-yl)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (4ba).} \\
\text{Yield 83%; White solid; m.p. 145.1–146.9 °C; } ^1^H \text{ NMR (CDCl}_3, \text{ 400 MHz): } \delta \\
\end{array}
\]
7.86–7.83 (m, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.16 (s, 1H),
7.07 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 4.17–4.14 (m, 2H), 4.02–3.99 (m,
2H), 3.87 (s, 2H), 2.19 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.9, 138.7, 136.4,
136.0, 133.3, 131.3, 131.1, 129.1, 128.5, 107.2, 66.0, 21.1, 13.4; IR (KBr): 1648,
1237, 1038 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^{+}\) calcd for C\(_{20}\)H\(_{20}\)IO\(_3\): 435.0452; found:
435.0452.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(4-methoxyphenyl)-1-phenylprop-2-en
-1-one (4ca). Yield 82%; White solid; m.p. 127.2–128.7 °C; \(^{1}\)H NMR (CDCl\(_3\), 400
MHz): \(\delta\) 7.86–7.84 (m, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.2 Hz, 2H),
7.14–7.10 (m, 3H), 6.65 (d, J = 8.8 Hz, 2H), 4.17–4.14 (m, 2H), 4.02–3.99 (m, 2H),
3.87 (s, 2H), 3.69 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 198.1, 159.8, 136.0, 135.2,
133.4, 131.0, 130.7, 129.2, 128.5, 126.6, 113.8, 107.2, 66.0, 55.1, 13.5; IR (KBr):
1643, 1608, 1511, 1261, 1178, 1032 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^{+}\) calcd for
C\(_{20}\)H\(_{20}\)IO\(_4\): 451.0401; found: 451.0401.
(E)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (4da). Yield 84%; White solid; m.p. 163.7–164.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.99 (d, $J = 8.8$ Hz, 2H), 7.81–7.79 (m, 2H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.35–7.31 (m, 4H), 7.25 (s, 1H), 4.23–4.19 (m, 2H), 4.07–4.03 (m, 2H), 3.85 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 196.8, 147.3, 142.0, 140.6, 135.5, 134.0, 129.6, 129.1, 128.8, 128.76, 123.7, 107.2, 66.3, 12.4; IR (KBr): 1656, 1594, 1515, 1342, 1234, 1034 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{19}$H$_{17}$INO$_5$: 466.0146; found: 466.0146.

(E)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one (4ea). Yield 60%; White solid; m.p. 131.3–132.4 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.05 (d, $J = 8.4$ Hz, 1H), 7.95 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.67–7.65 (m, 2H), 7.60–7.56 (m, 2H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.25–7.16 (m, 2H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 2H), 4.29–4.23 (m, 2H), 4.22–4.16 (m, 2H), 4.01 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 197.2, 139.5, 136.3, 133.2, 132.9, 131.6, 131.2, 130.6, 129.0, 128.63, 128.58, 128.0, 127.6, 126.5, 126.0, 125.1, 123.8, 107.5, 66.2, 13.1; IR
(KBr): 1658, 1230, 1176, 1036 cm⁻¹; HRMS (APCI): m/z [M + H]⁺ calcd for C₂₃H₂₀IO₃: 471.0452; found: 471.0452.

\[
\begin{align*}
\text{(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (4fa). Yield 72%; White solid; m.p. 120.1–122.0 °C; } & \text{H NMR (CDCl₃, 400 MHz): } \\
\delta & 7.88–7.86 (m, 2H), 7.69–7.65 (m, 3H), 7.55 (d, } J = 8.4 \text{ Hz, 1H), 7.41–7.35 (m, 4H), 7.27–7.23 (m, 3H), 4.21–4.18 (m, 2H), 4.07–4.03 (m, 2H), 3.93 (s, 2H); } \text{C NMR (CDCl₃, 100 MHz): } \\
\delta & 197.8, 137.7, 136.0, 133.4, 132.91, 132.87, 131.6, 131.4, 129.4, 129.0, 128.5, 128.1, 128.0, 127.4, 126.6, 126.3, 126.0, 107.3, 66.1, 13.3; IR (KBr): 1645, 1233, 1038 cm⁻¹; HRMS (APCI): m/z [M + H]⁺ calcd for C₂₃H₂₀IO₃: 471.0452; found: 471.0453.
\end{align*}
\]

\[
\begin{align*}
\text{(E)-3-(4-Chlorophenyl)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ga). Yield 85%; White solid; m.p. 123.7–124.6 °C; } & \text{H NMR (CDCl₃, 400 MHz): } \\
\delta & 7.83–7.81 (m, 2H), 7.47 (t, } J = 7.2 \text{ Hz, 1H), 7.32 (t, } J = 7.2 \text{ Hz, 2H), 7.15 (s,}
\end{align*}
\]
(E)-3-(4-Bromophenyl)-2-(2-iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ha). Yield 78%; White solid; m.p. 126.0–127.0 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.83–7.81 (m, 2H), 7.47 (t, \(J = 7.6\) Hz, 1H), 7.32 (t, \(J = 7.6\) Hz, 2H), 7.25 (d, \(J = 8.4\) Hz, 2H), 7.12 (s, 1H), 7.04 (d, \(J = 8.4\) Hz, 2H), 4.19–4.15 (m, 2H), 4.03–4.00 (m, 2H), 3.85 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.4, 138.4, 135.7, 133.7, 133.0, 131.6, 130.5, 129.9, 129.1, 128.6, 122.8, 107.1, 66.1, 13.0; IR (KBr): 1648, 1236, 1038 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{19}\)H\(_{17}\)BrI\(_3\): 498.9400; found: 498.9402.
(E)-3-(4-Fluorophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ia). Yield 73%; White solid; m.p. 113.7–115.1 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.83–7.81 (m, 2H), 7.46 (t, $J$ = 7.6 Hz, 1H), 7.31 (t, $J$ = 7.6 Hz, 2H), 7.17–7.14 (m, 3H), 6.81 (t, $J$ = 8.8 Hz, 2H), 4.20–4.16 (m, 2H), 4.04–4.00 (m, 2H), 3.87 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 197.6, 163.8, 161.3, 137.5, 135.8, 133.6, 130.9, 130.8, 130.3, 130.25, 130.2, 129.1, 128.5, 115.6, 115.4, 107.2, 66.1, 13.1; IR (KBr): 1657, 1597, 1505, 1234, 1035 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{19}$H$_{17}$FIO$_3$: 439.0201; found: 439.0201.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (4ja). Yield 89%; White solid; m.p. 144.4–146.0 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.95–7.93 (m, 2H), 7.52 (d, $J$ = 7.6 Hz, 1H), 7.39 (t, $J$ = 7.6 Hz, 2H), 7.23 (s, 1H), 7.15 (d, $J$ = 5.2 Hz, 1H), 6.94 (d, $J$ = 3.6 Hz, 1H), 6.84–6.82 (m, 1H), 4.18–4.14 (m, 2H), 4.04–4.01 (m, 2H), 3.81 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 197.2, 137.0, 136.0, 135.7, 133.7, 129.9, 129.2, 128.7, 128.1, 127.3, 123.3, 106.9, 66.1, 13.1; IR (KBr): 1653, 1232, 1209, 1170, 1035 cm$^{-1}$; HRMS (APCI): m/z [M + H]$^+$ calcd for C$_{17}$H$_{16}$IO$_3$S: 426.9859; found: 426.9860.
(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-phenyl-1-(p-tolyl)prop-2-en-1-one

(4ab). Yield 82%; White solid; m.p. 92.6–94.2 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.74 (d, \(J = 8.0\) Hz, 2H), 7.20–7.17 (m, 3H), 7.13–7.08 (m, 5H), 4.18–4.14 (m, 2H), 4.03–3.99 (m, 2H), 3.87 (s, 2H), 2.31 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.3, 144.3, 137.7, 134.1, 133.5, 131.0, 129.3, 129.2, 129.1, 128.5, 128.4, 107.2, 66.0, 21.6, 13.4; IR (KBr): 1651, 1604, 1240, 1211, 1179, 1039 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{20}\)H\(_{20}\)I\(_2\)O\(_3\): 435.0452; found: 435.0452.

S20
124.3, 107.3, 66.2, 13.3; IR (KBr): 1653, 1626, 1218, 1184, 1033 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{23}\)H\(_{20}\)IO\(_3\): 471.0452; found: 471.0452.

\((E)-1-(4-\text{Chlorophenyl})-2-(2-\text{iodomethyl})-1,3-\text{dioxolan-2-yl})-3-\text{phenylprop-2-en-1-one} \ (4\text{ad}).\) Yield 78%; White solid; m.p. 98.7–100.1 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.77–7.75 (m, 2H), 7.27–7.25 (m, 2H), 7.23 (s, 1H), 7.15 (brs, 5H), 4.20–4.17 (m, 2H), 4.02–3.99 (m, 2H), 3.86 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 196.5, 139.8, 137.1, 134.3, 133.9, 131.7, 130.5, 129.1, 128.84, 128.80, 128.5, 107.3, 66.1, 13.0; IR (KBr): 1658, 1228, 1040 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{19}\)H\(_{17}\)ClIO\(_3\): 454.9905; found: 454.9906.

\((E)-1-(4-\text{Bromophenyl})-2-(2-\text{iodomethyl})-1,3-\text{dioxolan-2-yl})-3-\text{phenylprop-2-en-1-one} \ (4\text{ae}).\) Yield 73%; White solid; m.p. 111.5–112.6 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.68 (d, \(J = 8.4\) Hz, 2H), 7.43 (d, \(J = 8.4\) Hz, 2H), 7.22 (s, 1H), 7.15 (brs,
5H), 4.20–4.17 (m, 2H), 4.02–3.99 (m, 2H), 3.86 (s, 2H); 13C NMR (CDCl3, 100 MHz): δ 196.7, 137.1, 134.7, 133.8, 131.8, 131.7, 130.5, 129.0, 128.8, 128.7, 128.5, 107.2, 66.1, 13.0; IR (KBr): 1658, 1221, 1040 cm⁻¹; HRMS (APCI): m/z [M + H]^+ calcd for C19H17BrO3: 498.9400; found: 498.9402.

(E)-1-(Furan-2-yl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-phenylprop-2-en-1-one (4af). Yield 85%; White solid; m.p. 137.6–139.2 °C; 1H NMR (CDCl3, 400 MHz): δ 7.434–7.428 (m, 1H), 7.21–7.17 (m, 6H), 6.93 (d, J = 3.6 Hz, 1H), 6.34–6.33 (m, 1H), 4.21–4.17 (m, 2H), 4.07–4.04 (m, 2H), 3.88 (s, 2H); 13C NMR (CDCl3, 100 MHz): δ 184.6, 152.4, 147.1, 137.0, 134.2, 132.7, 128.6, 128.0, 119.7, 112.3, 106.8, 66.0, 12.8; IR (KBr): 1641, 1624, 1040 cm⁻¹; HRMS (APCI): m/z [M + H]^+ calcd for C17H16IO4: 411.0088; found: 411.0087

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (4ag). Yield 88%; White solid; m.p. 136.4–137.3 °C; 1H NMR (CDCl3, 400 MHz): δ 7.53–7.51 (m, 1H), 7.45–7.44 (m, 1H), 7.26–7.23 (m, 2H), 7.19–7.16 (m,
4H), 6.91–6.89 (m, 1H), 4.20–4.19 (m, 2H), 4.07–4.04 (m, 2H), 3.89 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 189.5, 143.8, 138.0, 134.7, 134.2, 133.9, 131.8, 129.1, 128.7 128.4, 128.1, 107.0, 66.1, 13.0; IR (KBr): 1642, 1625, 1411, 1245, 1054 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{17}\)H\(_{16}\)IO\(_3\)S: 426.9859; found: 426.9860.

![Chemical Structure](image)

\((E)-2\)-Benzyldene-4-iodo-1-phenylbutane-1,3-dione (5). Yield 90%; Yellow solid; m.p. 112.5–113.6 °C; \(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 7.98 (s, 1H), 7.95 (d, \(J = 7.2\) Hz, 2H), 7.52 (t, \(J = 7.8\) Hz, 1H), 7.39 (t, \(J = 7.8\) Hz, 2H), 7.33 (d, \(J = 7.2\) Hz, 2H), 7.29–7.26 (m, 1H), 7.22 (t, \(J = 7.2\) Hz, 2H), 4.20 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 196.8, 190.6, 143.6, 135.9, 135.8, 134.1, 132.6, 130.8, 130.5, 129.4, 128.8, 128.7, 2.3; IR (KBr): 1668, 1639, 1616, 1258, 1233, 1211 cm\(^{-1}\); HRMS (APCI): m/z [M + H]\(^+\) calcd for C\(_{17}\)H\(_{14}\)IO\(_2\): 377.0033; found: 377.0034.

![Chemical Structure](image)

\(2\)-(Iodomethyl)-2-phenyl-1,3-dioxolane (7a). Yield 36%; Yellow solid; m.p. 65.5–67.0 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.51–7.49 (m, 2H), 7.38–7.33 (m, 3H), 4.20–4.17 (m, 2H), 3.88–3.84 (m, 2H), 3.58 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\)
139.1, 128.6, 128.3, 125.8, 106.7, 65.6, 14.0; IR (KBr): 1208, 1159, 1035, 960, 703 cm\(^{-1}\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{10}\)H\(_{12}\)IO\(_2\): 290.9876; found: 290.9877.

![Chemical Structure](image)

**2-(4-Chlorophenyl)-2-(iodomethyl)-1,3-dioxolane (7b).** Yield 43%; Yellow oil; \(^1\)H NMR (CDCl\(_3\), 600 MHz): \(\delta\) 7.44 (d, \(J = 8.4\) Hz, 2H), 7.33 (d, \(J = 8.4\) Hz, 2H), 4.20–4.18 (m, 2H), 3.87–3.84 (m, 2H), 3.54 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz): \(\delta\) 137.7, 134.6, 128.5, 127.4, 106.4, 65.7, 13.5; IR (KBr): 1487, 1208, 1091, 1040, 978, 832 cm\(^{-1}\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{10}\)H\(_{11}\)ClIO\(_2\): 324.9487; found: 424.9488.

![Chemical Structure](image)

**2-(3,4-Dichlorophenyl)-2-(iodomethyl)-1,3-dioxolane (7c).** Yield 46%; Yellow oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.60 (d, \(J = 2.4\) Hz, 1H), 7.33 (d, \(J = 8.4\) Hz, 1H), 7.35–7.32 (m, 1H), 4.21–4.18 (m, 2H), 3.89–3.85 (m, 2H), 3.51 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 139.7, 132.6, 130.4, 128.1, 125.4, 106.0, 65.9, 12.8; IR (KBr): 1467, 1378, 1208, 1167, 1033, 977 cm\(^{-1}\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{10}\)H\(_{10}\)Cl\(_2\)IO\(_2\): 358.9097; found: 358.9099.
2-(4-Bromophenyl)-2-(iodomethyl)-1,3-dioxolane (7d). Yield 52%; Yellow solid; m.p. 56.2–58.3 °C; ^1H NMR (CDCl₃, 400 MHz): δ 7.49 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.20–4.17 (m, 2H), 3.87–3.84 (m, 2H), 3.53 (s, 2H); ^13C NMR (CDCl₃, 100 MHz): δ 138.3, 131.5, 127.7, 122.9, 106.5, 65.7, 13.3; IR (KBr): 1584, 1479, 1208, 1039, 976, 956, 830 cm⁻¹; HRMS (ESI): m/z [M + H]^+ calcd for C₁₀H₁₁BrIO₂: 368.8982; found: 368.8982.

2-(4-Fluorophenyl)-2-(iodomethyl)-1,3-dioxolane (7e). Yield 44%; Yellow oil; ^1H NMR (CDCl₃, 600 MHz): δ 7.49–7.47 (m, 2H), 7.05–7.02 (m, 2H), 4.20–4.19 (m, 2H), 3.87–3.85 (m, 2H), 3.55 (s, 2H); ^13C NMR (CDCl₃, 150 MHz): δ 163.6, 162.0, 135.0, 127.8, 127.7, 115.2, 115.1, 106.4, 65.7, 13.8; IR (KBr): 1602, 1504, 1225, 1158, 1040, 978, 840, 566 cm⁻¹; HRMS (ESI): m/z [M + H]^+ calcd for C₁₀H₁₁FIO₂: 308.9782; found: 308.9784.

2-(Iodomethyl)-2-(4-nitrophenyl)-1,3-dioxolane (7f). Yield 98%; White solid; m.p. 108.1–111.4 °C; ^1H NMR (CDCl₃, 400 MHz): δ 8.22 (d, J = 8.8 Hz, 2H), 7.70 (d, J =
8.8 Hz, 2H), 4.26–4.23 (m, 2H), 3.91–3.88 (m, 2H), 3.55 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.1, 146.4, 127.1, 123.5, 106.3, 66.0, 12.3; IR (KBr): 1518, 1345, 1214, 1037, 855, 700 cm$^{-1}$; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{10}$H$_{11}$NO$_4$: 335.9727; found: 335.9723.

![Chemical structure]

**2-(Iodomethyl)-2-(3-nitrophenyl)-1,3-dioxolane (7g).** Yield 84%; White solid; m.p. 83.0–84.1 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.39–8.38 (m, 1H), 8.22–8.20 (m, 1H), 7.87–7.85 (m, 1H), 7.57 (t, $J$ = 8.0 Hz, 1H), 4.27–4.23 (m, 2H), 3.92–3.89 (m, 2H), 3.56 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.2, 141.8, 132.1, 129.4, 123.7, 121.2, 106.2, 66.0, 12.5; IR (KBr): 1524, 1347, 1213, 1045, 979, 690 cm$^{-1}$; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{10}$H$_{11}$NO$_4$: 335.9727; found: 335.9726.

![Chemical structure]

**2-(Iodomethyl)-2-(2-nitrophenyl)-1,3-dioxolane (7h).** Yield 72%; White solid; m.p. 108.3–110.5 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.72 (d, $J$ = 7.6 Hz, 1H), 7.57–7.47 (m, 3H), 4.18–4.15 (m, 2H), 3.92 (s, 2H), 3.79–3.76 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 149.6, 132.0, 131.2, 129.9, 129.0, 123.5, 105.7, 65.9, 12.5; IR (KBr): 1539, 1361, 1205, 1030, 976, 786 cm$^{-1}$; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{10}$H$_{11}$NO$_4$: 335.9727; found: 335.9727.
5. X-ray structure of compound 3ba, 3ia, 4aa

Figure S1. X-ray structure of compound 3ba (all Hydrogen atoms are omitted for clarity, CCDC 884836).

Figure S2. X-ray structure of compound 3ia (all Hydrogen atoms are omitted for clarity, CCDC 884837).

Figure S3. X-ray structure of compound 4aa (all Hydrogen atoms are omitted for clarity, CCDC 885165).
Appendix

Spectral Copies of $^1$H NMR and $^{13}$C NMR of Compounds Obtained in This Study
$^{13}$C NMR 100 MHz
CDCl$_3$

3aa
$^{13}$C NMR 100 MHz
CDCl$_3$

3ba
$^1{H}$NMR (400 MHz, CDCl$_3$)

3ca

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$^1$C NMR 100 MHz
CDCl$_3$

3ca
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$^{13}$C NMR 100 MHz
CDCl$_3$

3da

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

3ea
$^1$H NMR 400 MHz
CDCl₃

3fa
$^{13}$C NMR 100 MHz
CDCl$_3$

3fa
$\text{Cl}$

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

3ga
$^1$H NMR 400 MHz
CDCl$_3$

3ha
$^{13}$C NMR 100 MHz
CDCl$_3$

3ha
$^1$H NMR 400 MHz
CDCl$_3$

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

3ia
$^1$H NMR 400 MHz
CDCl$_3$

3ja
$^{13}\text{C NMR} 100 \text{ MHz}$

$\text{CDCl}_3$

3ja
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$^1$H NMR 400 MHz

CH$_3$

O

CH$_3$

O

3ab

ppm (t1)
$^1$H NMR 100 MHz
CDCl$_3$

3ab
$^1$H NMR 400 MHz
CDCl$_3$

3ac
$^{13}$C NMR 100 MHz
CDCl$_3$

3ac
$^1$H NMR 400 MHz
CDCl$_3$

3ad
$^{13}$C NMR 100 MHz
CDCl$_3$

3ad
$^{13}$C NMR 100 MHz
CDCl$_3$

3af
$^1$H NMR 400 MHz
CDCl$_3$

4aa
$^{13}$C NMR 100 MHz
CDCl$_3$

4aa
$^{13}$C NMR 100 MHz
CDCl$_3$

4ba
$^1$H NMR 400 MHz
CDCl$_3$

4ca
$^{13}$C NMR 100 MHz
CDCl$_3$

4ca
$^1$H NMR 400 MHz
CDCl$_3$

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$^{13}$C NMR 100 MHz

CDCl$_3$

4da
\(^1\text{H} \text{ NMR} \ 400 \text{ MHz}

\text{CDCl}_3

4ea
$^{13}$C NMR 100 MHz
CDCl$_3$

4ea
4fa
$^{13}$C NMR 100 MHz
CDCl$_3$

4fa
$^{1}$H NMR 400 MHz
CDCl$_3$

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

4ga
$^1$H NMR 400 MHz
CDCl$_3$

4ha

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

![Chemical structure of 4ha](image)

**4ha**
$^{13}$C NMR 100 MHz
CDCl$_3$

4ia
$^{13}$C NMR 100 MHz
CDCl$_3$

4ja
$^1$H NMR 400 MHz
CDCl$_3$
$^{13}$C NMR 100 MHz

CDCl$_3$

**4ab**
$^1$H NMR 400 MHz
CDCl$_3$

4ac
$^{13}$C NMR 100 MHz
CDCl$_3$

4ac
$^1$H NMR 400 MHz
CDCl$_3$

4ad
$^1$H NMR 400 MHz
CDCl$_3$

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4ae
$^{13}$C NMR 100 MHz
CDCl$_3$

**Chart: 4ae**
$^1$H NMR 400 MHz
CDCl$_3$

**4af**
$^1$H NMR 100 MHz
CDCl$_3$

4af
^1H NMR 400 MHz
CDCl₃

4ag
$^{13}$C NMR 100 MHz
CDCl$_3$

4ag
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$^1$H NMR 600 MHz
CDCl$_3$

5

ppm (t1)
$^1$C NMR 100 MHz
CDCl$_3$

5
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$^1$H NMR 100 MHz
CDCl$_3$

7d

138.271  131.489  127.862  106.463  77.317  77.000  76.682  65.745  13.337
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H NMR 600 MHz
CDCl₃

7e
7f
7g
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