Palladium-catalysed Cyclisation of Vinylethylene Carbonates and Anhydrides: A New Approach to Diverse Medium-sized Bislactones

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1. General Information

General Procedures

- All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40–63 μm, 230–400 mesh).
- Analytical thin layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub> aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I<sub>2</sub>.
- Organic solutions were concentrated at 30–50 °C on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

- Commercial reagents and solvents were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF, Et<sub>2</sub>O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.<sup>1</sup> The isatoic anhydrides<sup>1</sup> and vinylethylene carbonates<sup>2,3</sup> were prepared according to literature procedure.

Instrumentation

- Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent (CDCl<sub>3</sub>: δ 7.26 (CHCl<sub>3</sub>)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded with JEOL 150 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.0 (CHCl<sub>3</sub>)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C<sub>q</sub> = fully substituted carbon)].
- High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 using an electrospray (ESI) ionisation source.
- Melting points were recorded on WRX-X-4A melting point apparatus.
2. Bioactive Molecules Bearing a (Bis-)Lactone Skeleton and its Synthetic Motivation

The medium-sized lactones including bislactones are prevalent in several bioactive molecules (for deatail, see Figure S1). However, medium-sized skeletons are rarely found in the current approved drug list. A main reason is probably the difficulty in developing efficient catalytic system to establish diverse medium-sized compound (especially for lactones or bislactones) libraries for drug-leads screening. Therefore, a general protocol for the rapid and diversity-oriented synthesis of medium-sized bislactones in a single-step reaction is significant and highly desirable.

Figure S1. Bioactive molecules bearing a (bis-)lactone skeleton.
3. **Optimisation Studies**

Table S1. Optimisation of the cyclisation reaction of isatoic anhydride 1a and VEC 2a with 10 mol% of the palladium catalyst.\(^a\)

\[
\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{P} & \quad \text{OMe} \\
\text{MeO} & \quad \text{P} \\
\text{OMe} & \quad \text{L1} \\
\text{Ph}_2\text{P} & \quad \text{L2} \\
\text{L5} & \quad n = 0 \\
\text{L6} & \quad n = 1 \\
\text{L7} & \quad n = 2 \\
\text{Ph}_2\text{P} & \quad \text{L3} \\
\text{L8} & \quad \text{L9} \\
\text{L10} & \quad \text{L4} \\
\end{align*}
\]

<table>
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<th>Entry</th>
<th>[Pd]</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Yield (%)(^b)</th>
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<td>33</td>
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<tr>
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<tr>
<td>11</td>
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<td>L10</td>
<td>DCM</td>
<td>59</td>
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</tbody>
</table>

\(^a\) Unless otherwise noted, reactions were performed with 0.10 mmol of 1a, 0.15 mmol of 2a, 10 mol% of the palladium catalyst in 1.0 mL of solvent at room temperature for 4 hours, the Pd/ligand complex was pre-prepared with Pd\(_2\)(dba)\(_3\)·CHCl\(_3\) and ligand in solvent at rt for 1 h. \(^b\) Isolated yield. \(^c\) The reaction was performed for 12 hours. Pd\(_2\)(dba)\(_3\): tris(dibenzylideneacetone)dipalladium.
<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
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<td>L₁</td>
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<td>L₂</td>
<td>DCM</td>
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<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>L₃-8</td>
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<td>Pd₂(dbac₃)·CHCl₃</td>
<td>L₁₀</td>
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<td>L₁₀</td>
<td>DCM</td>
<td>49</td>
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<td>61</td>
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<tr>
<td>9&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Pd₂(dbac₃)·CHCl₃</td>
<td>L₁₀</td>
<td>DCM</td>
<td>59</td>
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<td>L₁₀/Mg(tBuO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DCM</td>
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<td>L₁₀/Al(iPrO)&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
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<td>L₁₀/Ti(iPrO)&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>L₁₀</td>
<td>PhCl</td>
<td>68</td>
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<tr>
<td>15</td>
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<td>L₁₀</td>
<td>CHCl₃</td>
<td>56</td>
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<tr>
<td>16&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Pd₂(dbac₃)·CHCl₃</td>
<td>L₁₀</td>
<td>MeCN</td>
<td>&lt;5</td>
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<td>Pd₂(dbac₃)·CHCl₃</td>
<td>L₁₀</td>
<td>THF</td>
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<td>19</td>
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<td>L₁₀</td>
<td>toluene</td>
<td>49</td>
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<tr>
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<tr>
<td>21</td>
<td>Pd₂(dbac₃)·CHCl₃</td>
<td>-</td>
<td>toluene</td>
<td>-</td>
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</table>

<sup>a</sup> Unless otherwise noted, reactions were performed with 0.10 mmol of 1a, 0.15 mmol of 2a, 5 mol% of the palladium catalyst in 1.0 mL of solvent at room temperature for 4 hours, the Pd/ligand complex was pre-prepared with Pd₂(dbac₃)·CHCl₃ and ligand in solvent at rt for 1 h. <sup>b</sup> Isolated yield. <sup>c</sup> The reaction was performed for 12 hours. <sup>d</sup> The reaction was performed at 40 °C. <sup>e</sup> The reaction was performed at 60 °C. <sup>f</sup> 0.5 mL of solvent was used. <sup>g</sup> 0.25 mL of solvent was used.
Table S3. Optimisation of the cyclisation reaction of isatoic anhydride 1a and VEC 2a.\(^a\)

![Chemical structure of 1a, 2a, and 5a](image)

<table>
<thead>
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<th>Entry</th>
<th>[Pd]</th>
<th>x mol%</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Yield (%)(^b)</th>
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<tr>
<td>1</td>
<td>Pd(PPh(_3))(_4)</td>
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<td>-</td>
<td>THF</td>
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</tr>
<tr>
<td>2</td>
<td>Pd(PPh(_3))(_4)</td>
<td>5</td>
<td>-</td>
<td>MeCN</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh(_3))(_4)</td>
<td>5</td>
<td>-</td>
<td>PhCl</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh(_3))(_4)</td>
<td>5</td>
<td>-</td>
<td>DCM</td>
<td>&lt;5</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh(_3))(_4)</td>
<td>5</td>
<td>-</td>
<td>toluene</td>
<td>&lt;5</td>
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<tr>
<td>6</td>
<td>Pd(PPh(_3))(_4)</td>
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<td>-</td>
<td>CHCl(_3)</td>
<td>&lt;5</td>
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<td>7(^c)</td>
<td>Pd(_2)(dba)(_3)\cdot CHCl(_3)</td>
<td>2.5</td>
<td>L1-8</td>
<td>toluene</td>
<td>-</td>
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<tr>
<td>8</td>
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<td>2.5</td>
<td>L9</td>
<td>toluene</td>
<td>59</td>
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<td>9(^c)</td>
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<td>L10</td>
<td>THF</td>
<td>42</td>
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<td>2.5</td>
<td>L10</td>
<td>MeCN</td>
<td>-</td>
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<td>12</td>
<td>Pd(_2)(dba)(_3)\cdot CHCl(_3)</td>
<td>2.5</td>
<td>L10</td>
<td>PhCl</td>
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<tr>
<td>13</td>
<td>Pd(_2)(dba)(_3)\cdot CHCl(_3)</td>
<td>2.5</td>
<td>L10</td>
<td>DCM</td>
<td>-</td>
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<tr>
<td>14</td>
<td>Pd(_2)(dba)(_3)\cdot CHCl(_3)</td>
<td>2.5</td>
<td>L10</td>
<td>CHCl(_3)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise noted, reactions were performed with 0.10 mmol of 4a, 0.15 mmol of 2a, 2.5 mol% of the palladium catalyst and 10 mol% of the ligand in 1.0 mL of solvent at room temperature for 4 hours. \(^b\) Isolated yield. \(^c\) The reaction was performed for 12 hours.
4. General Procedure for the Cyclisation of Isatoic Anhydrides and VECs

*General procedure for the synthesis of 11-membered lactones 3*

![Chemical structures](image)

To an oven-dried Schlenk tube was added Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, isatoic anhydrides 1 (0.10 mmol) and vinylenethylene carbonates 2 (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1, then petroleum ether/ethyl acetate = 10/1 to 3/1) to afford the corresponding 3 in 68–95% yields, which were dried under vacuum and further analyzed by $^1$H NMR, $^{13}$C NMR, HRMS, etc. Influenced by the flexibility of medium-sized rings, the NMR analysis of the following compounds at room temperature met some spin splitting problems and couldn’t provide the clear NMR spectra.

*Gram-scale synthesis of the eleven-membered lactone 3a*

![Chemical structures](image)

To an oven-dried 100 mL Schlenk flask, was added Pd$_2$(dba)$_3$·CHCl$_3$ (0.225 mmol, 0.233 g) and XantPhos (0.90 mmol, 0.521 g), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (10 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, isatoic anhydride 1a (6.00 mmol, 1.06 g) and vinylenethylene carbonate 2a (9.00 mmol, 1.71 g) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/
dichloromethane = 3/1, then petroleum ether/ethyl acetate = 10/1) to afford 3a (0.81 g) as white solid in 76% yields.

(Z)-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3a

Prepared according to the general procedure to afford 3a (30.7 mg, m. p. = 115 – 117 °C) in 95% yield as white solid.

NMR and HRMS data for the product 3a:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 7.55 (d, J = 7.8 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.38 – 7.35 (m, 2H), 7.33 – 7.31 (m, 1H), 7.24 – 7.23 (m, 2H), 6.08 (t, J = 7.2 Hz, 1H), 5.23 (br s, 2H), 4.67 (s, 2H), 3.42 (s, 3H).

^13C NMR (150 MHz, CDCl₃) δ (ppm): 167.8, 154.1, 145.7, 141.0, 140.7, 131.2, 130.0, 128.1, 127.4, 126.7, 125.4, 124.5, 64.1, 61.5, 38.1.

HRMS (ESI) m/z calculated for C₁₉H₁₇NO₄Na+: 346.1050, found: 346.1047.

(Z)-6-(4-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3b

Prepared according to the general procedure to afford 3b (26.6 mg) in 78% yield as colorless semisolid.

NMR and HRMS data for the product 3b:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 7.55 (d, J = 7.2 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.25 – 7.22 (m, 2H), 7.07 – 7.03 (m, 2H), 6.04 (t, J = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

^13C NMR (150 MHz, CDCl₃) δ (ppm): 167.8, 162.7 (d, J = 245.6 Hz, 1C), 154.0, 144.7, 140.8,
137.1, 131.2, 130.0, 128.6 (d, \(J = 7.2\) Hz, 1C), 127.4, 125.4, 124.4 (d, \(J = 28.7\) Hz, 1C), 115.4 (d, \(J = 21.5\) Hz, 1C), 64.3, 61.3, 38.0.

**HRMS (ESI)** m/z calculated for C\(_{19}\)H\(_{16}\)FNO\(_4\)+Na\(^+\): 364.0956, found: 364.0952.

(Z)-6-(4-chlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxacycloundecine-2,9(1H)-dione 3c

![Structure of 3c](image)

Prepared according to the general procedure to afford 3c (32.9 mg, m. p. = 120 – 123 °C) in 92% yield as white solid.

**NMR and HRMS data for the product 3c:**

\(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 (d, \(J = 7.8\) Hz, 1H), 7.46 (t, \(J = 7.2\) Hz, 1H), 7.41 (d, \(J = 8.4\) Hz, 2H), 7.33 (d, \(J = 7.8\) Hz, 2H), 7.24 (d, \(J = 7.2\) Hz, 2H), 6.06 (t, \(J = 6.6\) Hz, 1H), 5.18 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

\(^13C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.8, 154.0, 144.5, 140.8, 139.5, 134.1, 131.3, 129.9, 128.7, 128.2, 127.4, 125.4, 124.9, 124.6, 64.1, 61.3, 38.0.

**HRMS (ESI)** m/z calculated for C\(_{19}\)H\(_{16}\)ClNO\(_4\)+Na\(^+\): 380.0660 (\({}^{35}\)Cl), 382.0631 (\({}^{37}\)Cl), found: 380.0667, 382.0636.

(Z)-6-(4-bromophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxacycloundecine-2,9(1H)-dione 3d

![Structure of 3d](image)

Prepared according to the general procedure to afford 3d (35.0 mg, m. p. = 114 – 118 °C) in 87% yield as yellowish solid.

**NMR and HRMS data for the product 3d:**

\(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 (d, \(J = 7.2\) Hz, 1H), 7.50 – 7.43 (m, 3H), 7.34 (d, \(J = 7.2\) Hz, 2H), 7.25 – 7.21 (m, 2H), 6.06 (t, \(J = 6.6\) Hz, 1H), 5.17 (br s, 2H), 4.65 (s, 2H), 3.41
(s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.7, 154.0, 144.5, 140.8, 140.0, 131.6, 131.3, 129.9, 128.5, 127.4, 125.4, 124.9, 124.6, 122.3, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for C$_{19}$H$_{18}$BrNO$_4$+Na$^+$: 424.0155 ($^{79}$Br), 426.0134 ($^{81}$Br), found: 424.0159, 426.0141.


Prepared according to the general procedure to afford 3e (31.3 mg, m. p. = 97 – 100 °C) in 93% yield as white solid.

NMR and HRMS data for the product 3e:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.55 (d, $J = 7.8$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 6.06 (t, $J = 7.2$ Hz, 1H), 5.22 (br s, 2H), 4.65 (s, 2H), 3.42 (s, 3H), 2.36 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.9, 154.1, 145.7, 140.7, 138.0, 131.1, 130.0, 129.2, 128.0, 127.4, 126.6, 125.3, 124.5, 123.6, 64.0, 61.6, 38.1, 21.1.

HRMS (ESI) m/z calculated for C$_{20}$H$_{19}$NO$_4$+Na$^+$: 360.1206, found: 360.1215.

(Z)-6-(4-ethylphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxao[3]azacycloundecine-2,9(1H)-dione 3f

Prepared according to the general procedure to afford 3f (31.6 mg) in 90% yield as colorless semisolid.

NMR and HRMS data for the product 3f:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.54 (d, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.40
(Z)-6-(4-isopropylphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3g

Prepared according to the general procedure to afford 3g (32.5 mg) in 89% yield as colorless semisolid.

NMR and HRMS data for the product 3g:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 (d, $J = 6.6$ Hz, 1H), 7.47 – 7.40 (m, 3H), 7.24 – 7.21 (m, 4H), 6.07 (t, $J = 6.0$ Hz, 1H), 5.23 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H), 2.95 – 2.87 (m, 1H), 1.25 (d, $J = 7.2$ Hz, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.9, 154.1, 149.1, 145.7, 140.8, 138.4, 131.1, 130.1, 127.4, 126.7, 126.6, 125.3, 124.5, 123.7, 64.0, 61.6, 38.1, 33.8, 23.9.

HRMS (ESI) m/z calculated for C$_{22}$H$_{23}$NO$_4$Na$^+$: 388.1519, found: 388.1519.

(Z)-6-(4-methoxyphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3h

Prepared according to the general procedure to afford 3h (32.8 mg) in 93% yield as colorless semisolid.

NMR and HRMS data for the product 3h:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.53 (d, $J = 7.8$ Hz, 1H), 7.47 – 7.37 (m, 3H), 7.23 (d, $J$
= 7.8 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.03 (t, J = 7.2 Hz, 1H), 5.20 (br s, 2H), 4.64 (s, 2H), 3.81 (s, 3H), 3.41 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.9, 159.6, 154.2, 145.5, 140.7, 133.4, 131.1, 130.0, 127.9, 127.4, 125.3, 124.5, 122.8, 113.9, 64.0, 61.6, 55.3, 38.1.

HRMS (ESI) m/z calculated for C$_{20}$H$_{19}$NO$_5$ + Na$^+$: 376.1155, found: 376.1158.

(Z)-6-(3-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2, 9(1H)-dione 3i

Prepared according to the general procedure to afford 3i (28.0 mg) in 82% yield as colorless semisolid.

NMR and HRMS data for the product 3i:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.56 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.25 – 7.23 (m, 3H), 7.19 (d, J = 9.6 Hz, 1H), 7.01 (td, J = 8.4, 2.4 Hz, 1H), 6.10 (t, J = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.8, 165.5 (d, J = 224.2 Hz, 1C), 154.0, 144.5, 143.3 (d, J = 8.6 Hz, 1C), 140.8, 131.3, 130.0 (d, J = 8.6 Hz, 1C), 129.9, 127.5, 125.4 (d, J = 8.6 Hz, 1C), 124.6, 122.5, 115.1 (d, J = 20.1 Hz, 1C), 113.9 (d, J = 21.5 Hz, 1C), 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$FNO$_4$ + H$^+$: 342.1136, found: 342.1133


Prepared according to the general procedure to afford 3j (32.6 mg, m. p. = 121 – 127 ºC) in 91% yield as yellowish solid.

NMR and HRMS data for the product 3j:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.56 (d, \(J = 7.2\) Hz, 1H), 7.51 – 7.43 (m, 2H), 7.38 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H), 6.08 (t, \(J = 7.2\) Hz, 1H), 5.18 (br s, 2H), 4.66 (s, 2H), 3.42 (s, 3H).

\(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.8, 154.0, 144.3, 142.9, 140.8, 134.4, 131.3, 129.9, 129.8, 128.2, 127.5, 127.0, 125.5, 125.1, 124.6, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)ClNO\(_4\)+Na\(^+\): 380.0660 (\(^{35}\)Cl), 382.0631 (\(^{37}\)Cl), found: 380.0656, 382.0618.

\((Z)-6-(3\text{-bromophenyl})-1\text{-methyl}-4,7\text{-dihydro-2H-benzo[\text{d}][1,7]\text{dioxa[3]azacycloundecine-2,9(1H)-dione ~3k}

\[
\text{Prepared according to the general procedure to afford ~3k (35.0 mg, m. p. = 123} \text{ – 127 °C) in 87% yield as white solid.}
\]

NMR and HRMS data for the product 3:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.62 (s, 1H), 7.56 (d, \(J = 7.8\) Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 (d, \(J = 7.8\) Hz, 1H), 7.25 – 7.21 (m, 3H), 6.07 (t, \(J = 7.2\) Hz, 1H), 5.17 (br s, 2H), 4.65 (s, 2H), 3.41 (s, 3H).

\(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.7, 154.0, 144.1, 143.1, 140.8, 131.3, 131.1, 130.0, 129.9, 127.5, 125.5, 125.4, 124.5, 122.5, 64.0, 61.2, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)BrNO\(_4\)+Na\(^+\):424.0155 (\(^{79}\)Br), 426.0134 (\(^{81}\)Br), found: 424.0154, 426.0138.

\((Z)-6-(3\text{-methoxyphenyl})-1\text{-methyl}-4,7\text{-dihydro-2H-benzo[\text{d}][1,7]\text{dioxa[3]azacycloundecine-2,9(1H)-dione ~3l}

\[
\text{Prepared according to the general procedure to afford ~3l (31.8 mg) in 90% yield as colorless}
\]
semisolid.

NMR and HRMS data for the product 3i:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.56 (d, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 1H), 7.01 (s, 1H), 6.87 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.09 (t, $J = 6.0$ Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.83 (s, 3H), 3.42 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.8, 159.6, 154.1, 145.5, 142.5, 140.8, 131.2, 129.9, 129.5, 127.5, 125.4, 119.2, 113.5, 112.5, 64.1, 61.5, 55.3, 38.1.

HRMS (ESI) m/z calculated for C$_{20}$H$_{19}$NO$_5$+Na$: 376.1155$, found: 376.1150.

(Z)-6-(2-fluorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]diox[3]acycloundecine-2,9(1H)-dione 3m

Prepared according to the general procedure to afford 3m (29.3 mg) in 86% yield as colorless semisolid.

NMR and HRMS data for the product 3m:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 (d, $J = 7.2$ Hz, 1H), 7.48 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 9.0$ Hz, 1H), 6.08 (t, $J = 6.6$ Hz, 1H), 5.15 (br s, 2H), 4.67 (s, 2H), 3.43 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 159.5 (d, $J = 245.6$ Hz, 1C), 154.0, 140.8 (d, $J = 15.8$ Hz, 1C), 131.2, 130.5, 130.1, 129.7 (d, $J = 14.4$ Hz, 1C), 129.2 (d, $J = 14.4$ Hz, 1C), 127.4, 127.2, 125.4, 124.5, 115.5 (d, $J = 21.6$ Hz, 1C), 64.2 (d, $J = 4.2$ Hz, 1C), 61.2, 37.9.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$FNO$_4$+Na$: 364.0956$, found: 364.0958.

(Z)-6-(2-chlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]diox[3]acycloundecine-2,9(1H)-dione 3n
Prepared according to the general procedure to afford 3n (27.9 mg) in 78% yield as colorless semisolid.

NMR and HRMS data for the product 3n:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.55 (d, J = 7.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.28 – 7.20 (m, 4H), 5.94 (t, J = 6.6 Hz, 1H), 5.12 (br s, 2H), 4.68 (s, 2H), 3.43 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 154.0, 143.5, 141.0, 131.8, 131.3, 131.2, 130.1, 129.2, 129.1, 127.7, 127.3, 127.1, 125.4, 124.6, 64.4, 61.2, 37.9.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$ClNO$_4$+Na$: 380.0660 (35Cl), 382.0631 (37Cl), found: 380.0656, 382.0618.


Prepared according to the general procedure to afford 3o (30.2 mg) in 75% yield as colorless semisolid.

NMR and HRMS data for the product 3o:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.55 (d, J = 7.8 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 5.90 (t, J = 6.6 Hz, 1H), 5.11 (br s, 2H), 4.68 (s, 2H), 3.43 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 154.0, 144.6, 142.9, 141.0, 132.3, 131.3, 131.3, 130.0, 129.2, 127.7, 127.6, 127.1, 125.4, 124.5, 121.6, 64.4, 61.1, 37.9.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$BrNO$_4$+H$: 402.0335 (79Br), 404.0315 (81Br), found: 402.0342, 404.0306.
(Z)-1-methyl-6-(2-nitrophenyl)-4,7-dihydro-2H-benzo[d][1,7]diox[a][3]azacycloundecine-2,9(1H)-dione 3p

Prepared according to the general procedure to afford 3p (34.2 mg) in 93% yield as colorless semisolid.

**NMR and HRMS data for the product 3p:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 8.00 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.27 – 7.21 (m, 2H), 5.88 (t, J = 7.2 Hz, 1H), 5.12 (br s, 2H), 4.61 (s, 2H), 3.42 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 167.9, 153.9, 147.5, 143.2, 140.9, 137.3, 133.7, 132.5, 131.2, 130.6, 128.8, 127.2, 125.5, 125.3, 124.5, 124.1, 65.1, 60.8, 37.7

**HRMS (ESI) m/z calculated for C₁₉H₁₆N₂O₆⁺Na⁺: 391.0901, found: 391.0902.**

(Z)-1-methyl-6-(o-tolyl)-4,7-dihydro-2H-benzo[d][1,7]diox[a][3]azacycloundecine-2,9(1H)-dione 3q

Prepared according to the general procedure to afford 3q (25.6 mg) in 76% yield as colorless semisolid.

**NMR and HRMS data for the product 3q:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.63 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.22 – 7.16 (m, 3H), 5.70 (t, J = 6.0 Hz, 1H), 5.01 (br s, 2H), 4.68 (s, 2H), 3.45 (s, 3H), 2.35 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 167.6, 154.1, 143.5, 141.3, 135.3, 131.6, 130.3, 129.4, 128.9, 128.3, 127.7, 125.8, 125.5, 125.4, 124.5, 64.7, 61.6, 38.0, 19.8.

**HRMS (ESI) m/z calculated for C₂₀H₁₉NO₄⁺Na⁺: 360.1206, found: 360.1207.**
(Z)-6-(3,4-dichlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3r

Prepared according to the general procedure to afford 3r (34.5 mg) in 88% yield as colorless semisolid.

NMR and HRMS data for the product 3r:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.60 – 7.52 (m, 2H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.08 (t, $J = 6.6$ Hz, 1H), 5.14 (br s, 2H), 4.65 (s, 2H), 3.41 (br s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.7, 153.9, 143.3, 141.1, 140.8, 132.6, 132.2, 131.4, 130.4, 129.8, 128.8, 127.4, 126.3, 125.8, 125.5, 124.6, 64.0, 61.0, 38.0.

HRMS (ESI) m/z calculated for C$_{19}$H$_{15}$Cl$_2$NO$_4$Na$^+$: 414.0270 ($^{35}$Cl), 416.0241 ($^{37}$Cl), found: 414.0273, 416.0249.

(Z)-6-(3,4-dimethoxyphenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3s

Prepared according to the general procedure to afford 3s (27.6 mg) in 72% yield as colorless semisolid.

NMR and HRMS data for the product 3s:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.54 (d, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 2H), 7.08 – 6.96 (m, 2H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.04 (t, $J = 6.6$ Hz, 1H), 5.21 (br s, 2H), 4.65 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.41 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.9, 154.1, 149.2, 148.8, 145.5, 140.7, 133.8, 131.2, 130.0, 127.4, 125.4, 124.5, 123.0, 119.4, 110.9, 110.0, 64.2, 61.6, 55.9, 38.0, 29.7.
HRMS (ESI) m/z calculated for C_{21}H_{21}NO_{6}+Na^+: 406.1261, found: 406.1257.

(Z)-6-(2,4-dichlorophenyl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]dioxao[3]azacycloundecene-2,9(1H)-dione 3t

![Chemical Structure](image)

Prepared according to the general procedure to afford 3t (28.2 mg, m. p. = 112 – 117 °C) in 72% yield as white solid.

NMR and HRMS data for the product 3t:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 7.54 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.29 – 7.23 (m, 3H), 5.93 (t, J = 6.6 Hz, 1H), 5.06 (br s, 2H), 4.66 (s, 2H), 3.43 (s, 3H).

^13C NMR (150 MHz, CDCl₃) δ (ppm): 167.6, 154.0, 142.3, 141.0, 139.5, 134.3, 132.6, 132.1, 131.4, 130.1, 129.0, 127.8, 127.6, 127.4, 125.5, 124.6, 64.4, 61.0, 37.8.

HRMS (ESI) m/z calculated for C_{19}H_{15}Cl_{2}NO_{4}+Na^+: 414.0270 (^{35}Cl), 416.0241 (^{37}Cl), found: 414.0274, 416.0248.


![Chemical Structure](image)

Prepared according to the general procedure to afford 3u (26.7 mg) in 68% yield as colorless semisolid.

NMR and HRMS data for the product 3u:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 7.56 (d, J = 6.6 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 5.93 (t, J = 6.0 Hz, 1H), 5.07 (br s, 2H), 4.67 (s, 2H), 3.44 (s, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.5, 154.0, 142.3, 142.1, 141.0, 132.9, 131.4, 130.9, 130.4, 129.8, 129.2, 128.0, 127.8, 125.5, 124.6, 64.1, 60.9, 37.9.

HRMS (ESI) m/z calculated for C$_{19}$H$_{15}$Cl$_2$NO$_4$+Na$^+$: 414.0270 ($^{35}$Cl), 416.0241 ($^{37}$Cl), found: 414.0274, 416.0253.

(Z)-1-methyl-6-(naphthalen-2-yl)-4,7-dihydro-2H-benzo[d][1,7]diox[3]azacycloundecine-2,9(1H)-dione 3v

Prepared according to the general procedure to afford 3v (29.8 mg, m. p. = 118 – 122 °C) in 80% yield as white solid.

NMR and HRMS data for the product 3v:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.92 (s, 1H), 7.89 – 7.80 (m, 4H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.51 – 7.43 (m, 3H), 7.24 – 7.21 (m, 1H), 6.22 (t, $J = 6.6$ Hz, 1H), 5.34 (br s, 2H), 4.73 (s, 2H), 3.44 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.9, 154.2, 145.6, 140.8, 138.3, 133.2, 133.0, 131.2, 130.0, 128.2, 127.6, 126.4, 126.3, 125.8, 125.4, 124.9, 124.8, 124.6, 64.1, 61.6, 38.1.

HRMS (ESI) m/z calculated for C$_{23}$H$_{19}$NO$_4$+Na$^+$: 396.1206, found: 396.1216.

(Z)-6-([1,1'-biphenyl]-4-yl)-1-methyl-4,7-dihydro-2H-benzo[d][1,7]diox[3]azacycloundecine-2,9(1H)-dione 3w

Prepared according to the general procedure to afford 3w (33.9 mg, m. p. = 177 – 179 °C) in 85% yield as white solid.

NMR and HRMS data for the product 3w:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.64 – 7.59 (m, 4H), 7.56 – 7.55 (m, 3H), 7.46 – 7.44 (m, 3H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.25 – 7.21 (m, 2H), 6.15 (t, $J = 6.6$ Hz, 1H), 5.28 (br s, 2H),
4.69 (s, 2H), 3.43 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.9, 154.1, 145.3, 141.0, 140.8, 139.9, 131.2, 130.0, 128.8, 127.5, 127.2, 127.0, 125.4, 124.6, 124.4, 64.0, 64.3, 38.1.

HRMS (ESI) m/z calculated for C$_{25}$H$_{21}$NO$_4$+$\text{Na}^+$: 422.1363, found: 422.1359.

(Z)-12-fluoro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxa[3]azacycloundecine-2,9(1H)-dione 3x

Prepared according to the general procedure to afford 3x (30.7 mg) in 90% yield as colorless semisolid.

NMR and HRMS data for the product 3x:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.58 (br s, 1H), 7.46 (d, $J$ = 7.8 Hz, 2H), 7.37 (t, $J$ = 7.8 Hz, 2H), 7.34 – 7.31 (m, 1H), 6.97 – 6.92 (m, 2H), 6.05 (br s, 1H), 5.23 (br s, 2H), 4.68 (s, 2H), 3.41 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.1, 163.9 (d, $J$ = 249.9 Hz, 1C), 153.9, 145.6, 143.0, 140.9, 129.6, 128.5, 128.2, 126.7, 125.9, 124.3, 112.3 (d, $J$ = 21.5 Hz, 1C), 112.00 (d, $J$ = 23.1 Hz, 1C), 64.1, 61.7, 38.0.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$FNO$_4$+$\text{Na}^+$: 364.0956, found: 364.0952.


Prepared according to the general procedure to afford 3y (31.1 mg) in 87% yield as colorless semisolid.

NMR and HRMS data for the product 3y:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.51 (d, $J$ = 7.8 Hz, 1H), 7.46 (d, $J$ = 7.8 Hz, 2H), 7.39
 – 7.31 (m, 3H), 7.24 – 7.18 (m, 2H), 6.07 (br s, 1H), 5.23 (br s, 2H), 4.67 (s, 2H), 3.41 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.1, 153.8, 145.6, 142.2, 140.9, 136.9, 128.8, 128.6, 128.2, 126.7, 125.5, 124.9, 124.3, 64.2, 61.7, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)ClNO\(_4\)+Na\(^+\): 380.0660 (\(^{35}\)Cl), 382.0631 (\(^{37}\)Cl), found: 380.0659, 382.0635.

(Z)-12-bromo-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3z

Prepared according to the general procedure to afford 3z (34.6 mg) in 86% yield as colorless semisolid.

NMR and HRMS data for the product 3z:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.50 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 6.07 (t, \(J = 6.0\) Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.41 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.2, 153.8, 145.7, 142.1, 140.8, 128.8, 128.7, 128.5, 128.4, 128.2, 127.7, 126.7, 124.9, 124.2, 64.2, 61.7, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)BrNO\(_4\)+Na\(^+\): 424.0155 (\(^{79}\)Br), 426.0134 (\(^{81}\)Br), found: 424.0155, 426.0138.


Prepared according to the general procedure to afford 3aa (28.9 mg) in 82% yield as colorless semisolid.

NMR and HRMS data for the product 3aa:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.63 (d, \(J = 8.4\) Hz, 1H), 7.46 (d, \(J = 7.8\) Hz, 2H), 7.36
(t, \( J = 7.2 \) Hz, 2H), 7.33 – 7.29 (m, 1H), 6.82 – 6.72 (m, 2H), 5.98 (t, \( J = 7.2 \) Hz, 1H), 5.21 (br s, 2H), 4.71 (s, 2H), 3.84 (s, 3H), 3.41 (s, 3H).

\(^{13}\text{C NMR (150 MHz, CDCl}_3\) \( \delta \) (ppm): 167.5, 162.1, 154.5, 144.8, 143.0, 141.4, 130.1, 128.5, 128.0, 126.8, 124.8, 121.7, 111.2, 110.3, 63.9, 61.7, 55.6, 38.3.

\( \text{HRMS (ESI)} \) m/z calculated for C\(_{20}\)H\(_{19}\)NO\(_5\)+Na\(^+\): 376.1155, found: 376.1156.

\((Z)-11\text{-fluoro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo}[d][1,7]\text{dioxo[3]azacycloundecine-2,9(1H)-dione 3ab}\)

\[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{Me} \\
\text{O} \\
\text{Me}
\end{array}
\]

Prepared according to the general procedure to afford 3ab (30.7 mg, m. p. = 124 – 126 °C) in 90% yield as white solid.

\( \text{NMR and HRMS data for the product 3ab:} \)

\(^1\text{H NMR (600 MHz, CDCl}_3\) \( \delta \) (ppm): 7.47 (d, \( J = 7.2 \) Hz, 2H), 7.37 (t, \( J = 7.2 \) Hz, 2H), 7.35 – 7.31 (m, 1H), 7.28 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 1H), 6.10 (t, \( J = 6.6 \) Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.39 (s, 3H).

\(^{13}\text{C NMR (150 MHz, CDCl}_3\) \( \delta \) (ppm): 166.6, 159.0 (d, \( J = 245.7 \) Hz, 1C), 154.0, 145.6, 140.9, 136.9, 131.6 (d, \( J = 4.2 \) Hz, 1C), 128.6, 128.3, 126.7, 126.5 (d, \( J = 7.2 \) Hz, 1C), 124.5, 118.1 (d, \( J = 24.5 \) Hz, 1C), 114.6 (d, \( J = 24.5 \) Hz, 1C), 64.4, 61.5, 38.3.

\( \text{HRMS (ESI)} \) m/z calculated for C\(_{19}\)H\(_{16}\)FNO\(_4\)+Na\(^+\): 364.0956, found: 364.0954.

\((Z)-11\text{-chloro-1-methyl-6-phenyl-4,7-dihydro-2H-benzo}[d][1,7]\text{dioxo[3]azacycloundecine-2,9(1H)-dione 3ac}\)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{Me} \\
\text{O}
\end{array}
\]

Prepared according to the general procedure to afford 3ac (29.7 mg, m. p. = 121 – 124 °C) in 83% yield as yellowish solid.
NMR and HRMS data for the product 3ac:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.52 (s, 1H), 7.46 (d, \(J = 6.6\) Hz, 2H), 7.42 (d, \(J = 8.4\) Hz, 1H), 7.39 – 7.35 (m, 2H), 7.35 – 7.31 (m, 1H), 7.17 (d, \(J = 9.0\) Hz, 1H), 6.10 (t, \(J = 6.6\) Hz, 1H), 5.23 (br s, 2H), 4.65 (s, 2H), 3.39 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 166.6, 153.9, 145.8, 140.8, 139.4, 131.3, 131.1, 130.9, 128.6, 128.3, 127.5, 126.7, 125.8, 124.3, 64.3, 61.6, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)ClNO\(_4\)H\(^{+}\): 358.0841 (\(^{35}\)Cl), 360.0811 (\(^{37}\)Cl), found: 358.0836, 360.0801.

(Z)-11-bromo-1-methyl-6-phenyl-4,7-dihydro-2H-benzo[1,7]dioxacycloundecine-2,9(1H)-dione 3ad

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{Me} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Prepared according to the general procedure to afford 3ad (36.6 mg, m. p. = 117 – 123 \(^\circ\)C) in 91% yield as white solid.

NMR and HRMS data for the product 3ad:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.66 (s, 1H), 7.56 (d, \(J = 8.4\) Hz, 1H), 7.47 (d, \(J = 7.8\) Hz, 2H), 7.37 (t, \(J = 7.8\) Hz, 2H), 7.35 – 7.30 (m, 1H), 7.11 (d, \(J = 9.0\) Hz, 1H), 6.10 (t, \(J = 6.6\) Hz, 1H), 5.24 (br s, 2H), 4.65 (s, 2H), 3.39 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 166.5, 153.8, 145.9, 140.8, 139.8, 134.1, 131.6, 130.3, 128.6, 128.4, 128.3, 126.7, 126.1, 124.3, 118.5, 64.3, 61.6, 38.0.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)BrNO\(_4\)H\(^{+}\): 402.0335 (\(^{79}\)Br), 404.0315 (\(^{81}\)Br), found: 402.0331, 404.0307.

(Z)-1,11-dimethyl-6-phenyl-4,7-dihydro-2H-benzo[1,7]dioxacycloundecine-2,9(1H)-dione 3ae

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Prepared according to the general procedure to afford 3ae (24.9 mg, m. p. = 83 – 90 °C) in 74% yield as yellowish solid.

**NMR and HRMS data for the product 3ae:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.48 (d, J = 7.8 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.08 (t, J = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.66 (s, 2H), 3.39 (s, 3H), 2.36 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 167.9, 154.3, 145.6, 141.0, 138.2, 135.4, 131.8, 129.7, 128.5, 128.1, 126.8, 124.5, 64.0, 61.4, 38.1, 30.7.

**HRMS (ESI) m/z calculated for C₂₀H₁₉NO₄⁺Na⁺: 360.1206, found: 360.1194.**


Prepared according to the general procedure to afford 3af (25.4 mg) in 72% yield as colorless semisolid.

**NMR and HRMS data for the product 3af:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.48 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 6.6 Hz, 1H), 7.16 (d, J = 9.0 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.98 (dd, J = 9.0, 3.0 Hz, 1H), 6.08 (t, J = 7.2 Hz, 1H), 5.21 (br s, 2H), 4.66 (s, 2H), 3.82 (s, 3H), 3.37 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 167.5, 156.8, 154.4, 145.3, 141.1, 133.8, 130.9, 128.5, 128.1, 126.8, 124.7, 116.8, 112.5, 64.2, 61.4, 55.6, 38.3.

**HRMS (ESI) m/z calculated for C₂₀H₁₉NO₅⁺Na⁺: 376.1155, found: 376.1149.**

Prepared according to the general procedure to afford 3ag (32.2 mg, m. p. = 74 – 82 °C) in 90% yield as yellowish solid.

**NMR and HRMS data for the product 3ag:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.52 (d, J = 7.8 Hz, 2H), 7.43 – 7.31 (m, 4H), 7.28 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 6.17 (t, J = 7.2 Hz, 1H), 5.22 (br s, 2H), 4.65 (s, 2H), 3.33 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 165.7, 153.3, 145.4, 142.1, 140.6, 131.6, 131.0, 130.8, 128.5, 128.2, 127.1, 127.0, 124.1, 123.4, 65.4, 61.4, 38.1.

**HRMS (ESI)** m/z calculated for C₁₉H₁₆ClNO₄⁺Na⁺: 380.0660 (³⁵Cl), 382.0631 (³⁷Cl), found: 380.0662, 382.0636.


Prepared according to the general procedure to afford 3ah (31.1 mg) in 88% yield as colorless semisolid.

**NMR and HRMS data for the product 3ah:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.52 (d, J = 7.8 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.32 – 7.28 (m, 1H), 6.83 (dd, J = 12.0, 8.4 Hz, 2H), 6.14 (t, J = 7.2 Hz, 1H), 5.19 (br s, 2H), 4.66 (s, 2H), 3.87 (s, 3H), 3.32 (s, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 166.9, 156.4, 153.6, 145.0, 141.7, 141.0, 130.9, 128.4, 128.1, 127.1, 124.2, 121.6, 117.2, 108.9, 65.5, 61.4, 56.2, 37.9.

**HRMS (ESI)** m/z calculated for C₂₀H₁₉NO₅⁺Na⁺: 376.1155, found: 376.1151.
(Z)-1-ethyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3ai

Prepared according to the general procedure to afford 3ai (28.6 mg, m. p. = 109 – 113 °C) in 85% yield as yellowish solid.

NMR and HRMS data for the product 3ai:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.57 (d, $J = 7.8$ Hz, 1H), 7.51 – 7.42 (m, 3H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.29 – 7.21 (m, 2H), 6.08 (t, $J = 7.2$ Hz, 1H), 5.21 (br s, 2H), 4.66 (s, 2H), 3.89 (br s, 2H), 1.25 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 153.7, 145.6, 141.1, 139.5, 131.2, 128.5, 127.6, 126.1, 125.9, 124.6, 64.0, 61.4, 46.0, 13.2.

HRMS (ESI) m/z calculated for C$_{20}$H$_{19}$NO$_4$+Na$: 360.1206$, found: 360.1204.

(Z)-1-benzyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3aj

Prepared according to the general procedure to afford 3aj (27.1 mg, m. p. = 170 – 173 °C) in 68% yield as white solid.

NMR and HRMS data for the product 3aj:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.55 (d, $J = 7.2$ Hz, 1H), 7.48 (d, $J = 7.2$ Hz, 2H), 7.43 – 7.28 (m, 7H), 7.25 – 7.23 (m, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 8.4$ Hz, 1H), 6.09 (t, $J = 7.2$ Hz, 1H), 5.40 – 4.91 (m, 4H), 4.73 (s, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.7, 154.5, 145.8, 141.0, 140.0, 137.5, 131.2, 129.8, 128.5, 128.4, 128.2, 127.8, 127.6, 127.3, 126.7, 125.5, 124.4, 124.2, 63.8, 61.8, 54.4.

HRMS (ESI) m/z calculated for C$_{25}$H$_{21}$NO$_4$+Na$: 422.1363$, found: 422.1362.

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(Z)-1-allyl-6-phenyl-4,7-dihydro-2H-benzo[d][1,7]dioxo[3]azacycloundecine-2,9(1H)-dione 3ak

Prepared according to the general procedure to afford 3ak (25.8 mg, m. p. = 108 – 110 °C) in 74% yield as white solid.

*NMR and HRMS data for the product 3ak:*

**1H NMR (600 MHz, CDCl₃) δ (ppm):** 7.56 (d, J = 6.6 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.23 (t, J = 7.8 Hz, 1H), 6.10 – 6.00 (m, 2H), 5.37 – 5.05 (m, 4H), 4.68 (br s, 2H), 4.43 (br s, 2H).

**13C NMR (150 MHz, CDCl₃) δ (ppm):** 167.7, 153.8, 145.8, 141.0, 139.9, 133.9, 131.1, 130.0, 128.5, 128.1, 127.5, 126.7, 125.4, 124.4, 116.9, 63.9, 61.6, 53.7.

**HRMS (ESI) m/z calculated for C₂₁H₁₉NO₄⁺Na⁺:** 372.1206, found: 372.1211.
5. General Procedure for the Cyclisation of Cyclic Anhydride and VECs

General procedure for the synthesis of 10-, 11- or 12-membered products 5, 6 or 7

![Chemical Structure](image)

To an oven-dried Schlenk tube was added Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, cyclic anhydrides 4 or 8 (0.10 mmol) and vinylethylene carbonates 2 or 12 (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1, then petroleum ether/ethyl acetate = 30/1 to 10/1) to afford the corresponding products in 52–88% yields, which were dried under vacuum and further analyzed by $^1$H NMR, $^{13}$C NMR, HRMS, etc.

Gram-scale synthesis of the 10-membered lactone 5q

![Chemical Structure](image)

To an oven-dried 100 mL Schlenk flask, was added Pd$_2$(dba)$_3$·CHCl$_3$ (0.225 mmol, 0.233 g) and XantPhos (0.90 mmol, 0.521 g), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (10 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, phthalic anhydride 1a (6.00 mmol, 0.89 g) and vinylethylene carbonate 2v (9.00 mmol, 2.16 g) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/
dichloromethane = 3/1, then petroleum ether/ethyl acetate = 30:1 to afford 5q (0.51 g) as white solid in 57% yields.

(Z)-4-phenyl-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5a

Prepared according to the general procedure to afford 5a (23.5 mg, m. p. = 82 – 90 °C) in 80% yield as white solid.

_NMR and HRMS data for the product 5a:_

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.51 – 7.48 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 6.27 (t, $J = 6.6$ Hz, 1H), 5.19 (s, 2H), 4.95 (d, $J = 6.0$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.4, 168.0, 143.8, 140.8, 132.7, 132.6, 131.6, 129.1, 129.1, 128.2, 126.7, 126.5, 124.8, 66.2, 62.1.

HRMS (ESI) m/z calculated for C$_{18}$H$_{14}$O$_4$Na$^+$: 317.0784, found: 317.0783.

(Z)-4-(4-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5b

Prepared according to the general procedure to afford 5b (25.6 mg, m. p. = 150 – 152 °C) in 82% yield as white solid.

_NMR and HRMS data for the product 5b:_

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 – 7.46 (m, 2H), 7.05 (t, $J = 9.0$ Hz, 2H), 6.22 (t, $J = 6.6$ Hz, 1H), 5.14 (s, 2H), 4.93 (d, $J = 6.0$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.3, 168.1, 162.7 (d, $J = 247.1$ Hz, 1C), 143.1, 136.9 (d, $J = 4.4$ Hz, 1C), 132.8, 132.5, 131.7 (d, $J = 11.6$ Hz, 1C), 129.1, 129.1, 128.6, 128.5, 126.3, 115.5 (d, $J = 21.6$ Hz, 1C), 66.2, 62.1.
**HRMS (ESI) m/z calculated for C_{18}H_{13}FO_{4}^{+}Na^{+}:** 335.0690, found: 335.0682.

**(Z)-4-(4-chlorophenyl)-3,6-dihydropbenzo[c][1,6]dioxocene-1,8-dione 5c**

Prepared according to the general procedure to afford 5c (26.3 mg, m. p. = 132 – 138 °C) in 80% yield as white solid.

**NMR and HRMS data for the product 5c:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.59 (m, 2H), 7.44 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 6.26 (t, J = 6.0 Hz, 1H), 5.14 (s, 2H), 4.94 (d, J = 6.0 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.3, 168.0, 143.0, 139.3, 132.7, 132.5, 131.8, 131.7, 129.1, 128.8, 128.1, 127.0, 125.7, 66.0, 62.0.

**HRMS (ESI) m/z calculated for C_{18}H_{13}ClO_{4}^{+}Na^{+}:** 351.0395 ($^{35}$Cl), 353.0365 ($^{37}$Cl), found: 351.0401, 353.0367.

**(Z)-4-(4-bromophenyl)-3,6-dihydropbenzo[c][1,6]dioxocene-1,8-dione 5d**

Prepared according to the general procedure to afford 5d (26.9 mg, m. p. = 139 – 141 °C) in 72% yield as white solid.

**NMR and HRMS data for the product 5d:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 – 7.78 (m, 2H), 7.64 – 7.58 (m, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 6.26 (t, J = 6.6 Hz, 1H), 5.13 (s, 2H), 4.93 (d, J = 6.0 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.3, 168.0, 143.0, 139.7, 132.7, 132.4, 131.7, 131.7, 131.7, 129.1, 128.4, 127.0, 122.4, 65.9, 62.0.

**HRMS (ESI) m/z calculated for C_{18}H_{13}BrO_{4}^{+}Na^{+}:** 394.9889 ($^{79}$Br), 396.9869 ($^{81}$Br), found:
(Z)-4-((p-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5e

Prepared according to the general procedure to afford 5e (25.6 mg, m. p. = 101 – 105 °C) in 83% yield as white solid.

NMR and HRMS data for the product 5e:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.83 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.39 (d, \(J = 7.8\) Hz, 2H), 7.17 (d, \(J = 7.8\) Hz, 2H), 6.24 (t, \(J = 6.0\) Hz, 1H), 5.17 (s, 2H), 4.94 (d, \(J = 6.6\) Hz, 2H), 2.35 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 168.4, 168.1, 143.8, 138.2, 137.9, 132.8, 132.7, 131.6, 129.3, 129.1, 126.6, 125.8, 125.6, 124.9, 66.3, 62.2, 21.1.

HRMS (ESI) m/z calculated for C\(_{19}\)H\(_{16}\)O\(_4\)+Na\(^+\): 331.0941, found: 331.0935.

(Z)-4-(4-ethylphenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5f

Prepared according to the general procedure to afford 5f (26.1 mg, m. p. = 63 – 66 °C) in 81% yield as white solid.

NMR and HRMS data for the product 5f:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.83 – 7.76 (m, 2H), 7.62 – 7.57 (m, 2H), 7.43 (d, \(J = 7.8\) Hz, 2H), 7.20 (d, \(J = 8.4\) Hz, 2H), 6.23 (t, \(J = 6.6\) Hz, 1H), 5.18 (s, 2H), 4.94 (d, \(J = 6.0\) Hz, 2H), 2.65 (q, \(J = 7.8\) Hz, 2H), 1.24 (t, \(J = 7.8\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 168.4, 168.0, 144.5, 143.8, 138.1, 132.8, 132.6, 131.6, 129.1, 128.1, 126.7, 125.6, 66.3, 62.2, 28.5, 15.5.

HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{18}\)O\(_4\)+Na\(^+\): 345.1097, found: 345.1095.
**\((Z)\)-4-(4-iso-propylphenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione \(5g\)**

![Structure of \(5g\)](image)

Prepared according to the general procedure to afford \(5g\) (25.5 mg, m. p. = 54 – 58 °C) in 76% yield as white solid.

\[NMR \text{ and HRMS data for the product } 5g:\]

\[\text{\(^1H\ NMR (}\text{600 MHz, CDCl}_3\text{)} \quad \delta (\text{ppm}): 7.83 – 7.78 (\text{m, 2H}), 7.63 – 7.58 (\text{m, 2H}), 7.43 (\text{d, } J = 8.4 \text{ Hz, 2H}), 7.20 (\text{d, } J = 7.8 \text{ Hz, 2H}), 6.25 (\text{t, } J = 6.6 \text{ Hz, 1H}), 5.18 (\text{s, 2H}), 4.94 (\text{d, } J = 6.0 \text{ Hz, 2H}), 2.95 – 2.87 (\text{m, 1H}), 1.25 (\text{d, } J = 6.6 \text{ Hz, 6H}).\]

\[\text{\(^{13}C\ NMR (}\text{150 MHz, CDCl}_3\text{)} \quad \delta (\text{ppm}): 168.4, 168.0, 149.1, 143.8, 138.2, 136.0, 132.8, 132.7, 131.6, 129.1, 126.7, 125.7, 66.3, 62.2, 33.8, 23.9.\]

\[\text{HRMS (ESI) } m/z \text{ calculated for } \text{C}_{21}\text{H}_{20}\text{O}_4\text{Na}^+: 359.1254, \text{ found: 359.1259.}\]

**\((Z)\)-4-(3-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione \(5h\)**

![Structure of \(5h\)](image)

Prepared according to the general procedure to afford \(5h\) (23.1 mg, m. p. = 81 – 85 °C) in 74% yield as white solid.

\[NMR \text{ and HRMS data for the product } 5h:\]

\[\text{\(^1H\ NMR (}\text{600 MHz, CDCl}_3\text{)} \quad \delta (\text{ppm}): 7.83 – 7.78 (\text{m, 2H}), 7.63 – 7.59 (\text{m, 2H}), 7.36 – 7.30 (\text{m, 2H}), 7.22 (\text{dt, } J = 10.2, 2.4 \text{ Hz, 1H}), 7.02 (\text{td, } J = 8.4, 3.0 \text{ Hz, 1H}), 6.30 (\text{t, } J = 6.0 \text{ Hz, 1H}), 5.15 (\text{s, 2H}), 4.94 (\text{d, } J = 7.2 \text{ Hz, 2H}).\]

\[\text{\(^{13}C\ NMR (}\text{150 MHz, CDCl}_3\text{)} \quad \delta (\text{ppm}): 168.4, 167.9, 162.8 (\text{d, } J = 244.1 \text{ Hz, 1C}), 143.0 (\text{d, } J = 7.2 \text{ Hz, 1C}), 142.7, 132.7, 132.5, 131.7 (\text{d, } J = 2.9 \text{ Hz, 1C}), 130.1 (\text{d, } J = 7.2 \text{ Hz, 1C}), 129.2, 129.1, 127.6, 125.7, 122.4 (\text{d, } J = 5.7 \text{ Hz, 1C}), 115.1 (\text{d, } J = 21.6 \text{ Hz, 1C}), 113.8 (\text{d, } J = 21.5 \text{ Hz, 1C}), 66.0, 61.9.\]

\[\text{HRMS (ESI) } m/z \text{ calculated for } \text{C}_{18}\text{H}_{13}\text{FO}_4\text{Na}^+: 335.0690, \text{ found: 335.0699.}\]
**(Z)-4-(3-chlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5i**

![Image of compound 5i](image)

Prepared according to the general procedure to afford 5i (25.0 mg, m. p. = 91 – 93 °C) in 76% yield as white solid.

*NMR and HRMS data for the product 5i:*

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.48 (s, 1H), 7.40 – 7.36 (m, 1H), 7.31 – 7.28 (m, 2H), 6.29 (t, J = 6.0 Hz, 1H), 5.14 (s, 2H), 4.94 (d, J = 6.6 Hz, 2H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 168.4, 167.9, 142.6, 134.5, 132.6, 132.4, 131.7, 131.7, 129.8, 129.2, 129.1, 128.3, 127.7, 126.9, 124.9, 65.9, 61.9.

*HRMS (ESI) m/z calculated for C₁₈H₁₃ClO₄⁺Na⁺: 351.0395 (³⁵Cl), 353.0365 (³⁷Cl), found: 351.0392, 353.0356.*

**(Z)-4-(3-bromophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5j**

![Image of compound 5j](image)

Prepared according to the general procedure to afford 5j (26.5 mg, m. p. = 91 – 94 °C) in 71% yield as white solid.

*NMR and HRMS data for the product 5j:*

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.83 – 7.78 (m, 2H), 7.65 – 7.58 (m, 3H), 7.45 (t, J = 9.6 Hz, 2H), 7.24 (t, J = 8.4 Hz, 1H), 6.29 (t, J = 6.0 Hz, 1H), 5.13 (s, 2H), 4.94 (d, J = 6.6 Hz, 2H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 168.4, 167.9, 142.9, 142.5, 132.6, 132.4, 131.7, 131.2, 130.1, 129.8, 129.2, 129.1, 127.8, 125.4, 122.7, 65.9, 61.9.

*HRMS (ESI) m/z calculated for C₁₈H₁₃BrO₄⁺H⁺:373.0070 (⁷⁹Br), 375.0050 (⁸¹Br), found: 373.0083, 375.0042.*
(Z)-4-(m-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5k

![Chemical structure of 5k](image)

Prepared according to the general procedure to afford 5k (22.2 mg, m. p. = 75 – 78 °C) in 72% yield as white solid.

**NMR and HRMS data for the product 5k:**

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.83 – 7.78 (m, 2H), 7.63 – 7.57 (m, 2H), 7.32 – 7.23 (m, 3H), 7.14 (d, $J = 7.8$ Hz, 1H), 6.26 (t, $J = 6.0$ Hz, 1H), 5.18 (s, 2H), 4.94 (d, $J = 5.4$ Hz, 2H), 2.37 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 168.5, 168.0, 143.8, 140.8, 138.2, 132.8, 132.7, 131.6, 129.2, 129.1, 129.0, 128.5, 127.4, 126.3, 123.8, 66.3, 62.1, 21.4.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$O$_4$+Na$: 331.0941, found: 331.0941.

(Z)-4-(2-fluorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5l

![Chemical structure of 5l](image)

Prepared according to the general procedure to afford 5l (22.2 mg) in 71% yield as colorless semisolid.

**NMR and HRMS data for the product 5l:**

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.82 – 7.76 (m, 2H), 7.62 – 7.58 (m, 2H), 7.39 (td, $J = 7.8$, 1.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.14 (t, $J = 7.8$ Hz, 1H), 7.09 – 7.04 (m, 1H), 6.25 (t, $J = 6.0$ Hz, 1H), 5.12 (s, 2H), 4.96 (d, $J = 6.0$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 168.3, 167.9, 159.6 (d, $J = 244.2$ Hz, 1C), 138.7, 132.6 (d, $J = 4.4$ Hz, 1C), 131.7 (d, $J = 5.7$ Hz, 1C), 130.1(d, $J = 4.4$ Hz, 1C), 129.8, 129.8, 129.1, 129.1, 129.0, 124.4 (d, $J = 2.9$ Hz, 1C), 115.7 (d, $J = 21.5$ Hz, 1C), 65.8 (d, $J = 5.9$ Hz, 1C), 61.9.

HRMS (ESI) m/z calculated for C$_{18}$H$_{13}$FO$_4$+Na$: 335.0690, found: 335.0700.
(Z)-4-(o-tolyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5m

![Structure of 5m]

Prepared according to the general procedure to afford 5m (16.0 mg) in 52% yield as colorless semisolid.

NMR and HRMS data for the product 5m:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.84 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 7.24 – 7.16 (m, 4H), 5.96 (t, $J$ = 6.0 Hz, 1H), 5.02 (s, 2H), 4.98 (d, $J$ = 6.0 Hz, 2H), 2.31 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.4, 167.9, 143.1, 141.5, 135.0, 132.7, 132.7, 131.7, 130.3, 129.2, 129.1, 128.8, 128.1, 127.8, 125.9, 66.2, 61.9, 20.0.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$O$_4$+Na$: 331.0941, found: 331.0945.

(Z)-4-(2,4-dichlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5n

Prepared according to the general procedure to afford 5n (27.2 mg, m. p. = 58 – 65 °C) in 75% yield as white solid.

NMR and HRMS data for the product 5n:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.82 – 7.75 (m, 2H), 7.63 – 7.58 (m, 2H), 7.40 (d, $J$ = 1.8 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.09 (t, $J$ = 6.6 Hz, 1H), 5.06 (s, 2H), 4.95 (d, $J$ = 6.6 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.0, 168.0, 141.4, 139.3, 134.5, 132.7, 132.7, 132.5, 131.7, 131.7, 131.6, 130.2, 129.2, 129.1, 129.0, 127.4, 65.4, 61.8.

HRMS (ESI) m/z calculated for C$_{18}$H$_{12}$Cl$_2$O$_4$+Na$: 385.0005 (35Cl), 386.9975 (37Cl), found: 385.0000, 386.9964.

(Z)-4-(2,5-dichlorophenyl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5o

535
Prepared according to the general procedure to afford \textbf{5o} (30.5 mg, m. p. = 106 – 108 °C) in 84\% yield as yellowish solid.

\textit{NMR and HRMS data for the product 5o:}

$^1\text{H NMR (600 MHz, CDCl}_3$) \(\delta\) (ppm): 7.82 – 7.76 (m, 2H), 7.63 – 7.57 (m, 2H), 7.37 (d, \(J = 8.4\) Hz, 1H), 7.31 (d, \(J = 9.0\) Hz, 1H), 7.25 – 7.22 (m, 1H), 6.12 (t, \(J = 6.0\) Hz, 1H), 5.07 (s, 2H), 4.95 (d, \(J = 6.0\) Hz, 2H).

$^{13}\text{C NMR (150 MHz, CDCl}_3$) \(\delta\) (ppm): 168.0, 167.9, 143.3, 142.1, 141.1, 132.9, 132.6, 132.4, 131.7, 130.6, 130.5, 130.3, 129.3, 129.1, 128.4, 125.4, 65.3, 61.7.

HRMS (ESI) m/z calculated for C$_{18}$H$_{12}$Cl$_2$O$_4$+Na+: 385.0005 (35Cl), 386.9975 (37Cl), found: 385.0011, 386.9982.

\textbf{(Z)-4-([1,1'-biphenyl]-4-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5p}

Prepared according to the general procedure to afford \textbf{5p} (28.5 mg, m. p. = 143 – 147 °C) in 77\% yield as white solid.

\textit{NMR and HRMS data for the product 5p:}

$^1\text{H NMR (600 MHz, CDCl}_3$) \(\delta\) (ppm): 7.84 – 7.79 (m, 2H), 7.64 – 7.57 (m, 8H), 7.45 (t, \(J = 7.8\) Hz, 2H), 7.36 (t, \(J = 7.8\) Hz, 1H), 6.35 (t, \(J = 6.0\) Hz, 1H), 5.22 (s, 2H), 4.98 (d, \(J = 6.0\) Hz, 2H).

$^{13}\text{C NMR (150 MHz, CDCl}_3$) \(\delta\) (ppm): 168.5, 168.0, 143.4, 141.1, 140.4, 139.6, 132.8, 132.6, 131.7, 131.7, 129.1, 129.1, 128.8, 127.5, 127.3, 127.1, 127.0, 126.4, 66.1, 62.2.

HRMS (ESI) m/z calculated for C$_{24}$H$_{18}$O$_4$+Na+: 393.1097, found:393.1103 .

\textbf{(Z)-4-(naphthalen-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5q}
Prepared according to the general procedure to afford 5q (25.1 mg, m. p. = 80 – 85 °C) in 73% yield as yellowish solid.

NMR and HRMS data for the product 5q:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.04 – 8.01 (m, 1H), 7.94 (s, 1H), 7.92 – 7.88 (m, 1H), 7.86 – 7.80 (m, 4H), 7.64 – 7.59 (m, 2H), 7.50 – 7.46 (m, 2H), 6.42 (t, $J$ = 6.6 Hz, 1H), 5.29 (s, 2H), 5.01 (d, $J$ = 6.6 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.6, 168.0, 143.7, 138.1, 136.0, 133.0, 132.8, 132.6, 131.7, 129.2, 129.1, 128.3, 128.2, 127.6, 127.0, 126.4, 126.3, 125.8, 125.7, 124.6, 66.3, 62.2.

HRMS (ESI) m/z calculated for C$_{22}$H$_{16}$O$_4$+H$: 345.1121, found: 345.1120.

(E)-4-(furan-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5r

Prepared according to the general procedure to afford 5r (19.9 mg, m. p. = 145 – 150 °C) in 70% yield as white solid.

NMR and HRMS data for the product 5r:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.81 – 7.76 (m, 2H), 7.61 – 7.57 (m, 2H), 7.40 (s, 1H), 6.63 (t, $J$ = 6.0 Hz, 1H), 6.52 (d, $J$ = 3.6 Hz, 1H), 6.42 (dd, $J$ = 3.6, 1.2 Hz, 1H), 5.13 (s, 2H), 4.99 (d, $J$ = 6.6 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.6, 167.6, 152.5, 143.1, 132.7, 132.4, 131.7, 131.6, 131.3, 129.3, 128.9, 122.6, 111.7, 107.7, 63.2, 61.9.

HRMS (ESI) m/z calculated for C$_{16}$H$_{12}$O$_5$+H$: 285.0757, found: 285.0757.

(E)-4-(thiophen-2-yl)-3,6-dihydrobenzo[c][1,6]dioxecine-1,8-dione 5s
Prepared according to the general procedure to afford 5s (18.9 mg, m. p. = 136 – 138 °C) in 63% yield as white solid.

_NMR and HRMS data for the product 5s:_

**1H NMR (600 MHz, CDCl3) δ (ppm):** 7.82 – 7.78 (m, 2H), 7.62 – 7.58 (m, 2H), 7.24 (d, J = 4.8 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.45 (t, J = 6.6 Hz, 1H), 5.22 (s, 2H), 4.93 (d, J = 6.6 Hz, 2H).

**13C NMR (150 MHz, CDCl3) δ (ppm):** 168.4, 167.9, 143.5, 136.7, 132.7, 132.4, 131.7, 129.2, 129.1, 127.8, 125.7, 124.9, 124.3, 65.4, 62.1.

**HRMS (ESI) m/z calculated for C_{16}H_{12}O_{4}S+Na⁺: 323.0349 (34S), 324.0382 (32S), found: 323.0354, 324.0377.**

(\textit{Z})-4-phenyl-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-dione 6a

Prepared according to the general procedure to afford 6a (29.6 mg, m. p. = 174 – 177 °C) in 86% yield as white solid.

_NMR and HRMS data for the product 6a:_

**1H NMR (600 MHz, CDCl3) δ (ppm):** 8.02 – 7.99 (m, 2H), 7.93 – 7.89 (m, 2H), 7.58 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 6.46 (t, J = 7.2 Hz, 1H), 5.39 (s, 2H), 5.11 (d, J = 7.2 Hz, 2H).

**13C NMR (150 MHz, CDCl3) δ (ppm):** 169.6, 169.4, 145.8, 140.6, 134.1, 132.3, 132.3, 129.5, 129.4, 129.1, 128.6, 128.3, 127.7, 126.7, 126.1, 125.3, 125.3, 62.5, 59.5.

**HRMS (ESI) m/z calculated for C_{22}H_{16}O_{4}+Na⁺: 367.0941, found: 367.0940.**

(\textit{Z})-4-(4-chlorophenyl)-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-dione
Prepared according to the general procedure to afford 6b (32.2 mg, m. p. = 142 – 147 °C) in 85% yield as white solid.

_NMR and HRMS data for the product 6b:_

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.02 – 7.99 (m, 2H), 7.93 – 7.89 (m, 2H), 7.58 – 7.54 (m, 2H), 7.37 (d, $J = 9.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.44 (t, $J = 7.8$ Hz, 1H), 5.33 (s, 2H), 5.09 (d, $J = 7.8$ Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 169.5, 169.3, 144.6, 139.0, 134.3, 139.0, 134.0, 132.4, 129.4, 129.3, 128.8, 128.2, 127.5, 126.7, 125.3, 125.3, 62.3, 59.3.

HRMS (ESI) m/z calculated for C$_{22}$H$_{15}$ClO$_4$Na$: 401.0551$ (35Cl), 403.0522$ (37Cl), found: 401.0549, 403.0523.

**(Z)-4-(p-tolyl)-3,6-dihydro-1H,8H-naphtho[1,8-hi][1,6]dioxacycloundecine-1,8-dione 6c**

Prepared according to the general procedure to afford 6c (31.5 mg, m. p. = 123 – 130 °C) in 88% yield as white solid.

_NMR and HRMS data for the product 6c:_

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.99 – 7.97 (m, 2H), 7.94 – 7.88 (m, 2H), 7.58 – 7.50 (m, 2H), 7.35 (d, $J = 7.8$ Hz, 2H), 7.18 – 7.15 (m, 2H), 6.43 (t, $J = 7.2$ Hz, 1H), 5.38 (s, 2H), 5.10 (d, $J = 8.4$ Hz, 2H), 2.34 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 169.6, 169.3, 145.6, 138.2, 137.6, 134.0, 132.2, 132.2, 129.4, 129.2, 129.2, 129.0, 126.6, 126.0, 125.2, 62.4, 59.6, 21.1.

HRMS (ESI) m/z calculated for C$_{23}$H$_{18}$O$_4$Na$: 381.1097$, found: 381.1103.
(Z)-8-phenyl-7,10-dihydridibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7a

Prepared according to the general procedure to afford 7a (31.1 mg, m. p. = 146 – 153 °C) in 84% yield as white solid.

NMR and HRMS data for the product 7a:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 (d, $J = 7.2$ Hz, 1H), 7.70 (d, $J = 9.0$ Hz, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.41 (m, 2H), 7.40 (d, $J = 9.0$ Hz, 1H), 7.38 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 5.98 (t, $J = 4.8$ Hz, 1H), 5.62 (d, $J = 13.2$ Hz, 1H), 5.23 – 5.17 (m, 1H), 4.86 (d, $J = 15.0$ Hz, 1H), 4.71 (q, $J = 6.0$ Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.9, 167.3, 140.9, 140.6, 140.5, 140.3, 132.7, 131.5, 131.2, 131.0, 130.8, 128.8, 128.5, 127.9, 127.5, 127.4, 126.7, 124.2, 64.9, 61.1.

HRMS (ESI) m/z calculated for C$_{24}$H$_{18}$O$_4$+Na⁺: 393.1097, found: 393.1097.

(Z)-8-(4-bromophenyl)-7,10-dihydridibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7b

Prepared according to the general procedure to afford 7b (23.3 mg, m. p. = 143 – 144 °C) in 52% yield as white solid.

NMR and HRMS data for the product 7b:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.41 (m, 4H), 7.40 – 7.34 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 5.97 (t, $J = 4.8$ Hz, 1H), 5.54 (d, $J = 15.0$ Hz, 1H), 5.23 – 5.17 (m, 1H), 4.81 (d, $J = 15.0$ Hz, 1H), 4.69 (dd, $J = 14.4$, 6.0 Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.8, 167.2, 140.6, 140.5, 139.9, 139.1, 132.4, 131.6, 131.3, 131.0, 130.8, 128.9, 128.4, 127.6, 127.5, 127.5, 125.1, 122.0, 64.5, 61.0.

HRMS (ESI) m/z calculated for C$_{24}$H$_{17}$BrO$_4$+Na⁺: 471.0202 (79Br), 473.0182 (81Br), found:
(Z)-8-(p-tolyl)-7,10-dihydrodibenzo[h,j][1,6]dioxacyclododecine-5,12-dione 7c

Prepared according to the general procedure to afford 7c (24.2 mg, m. p. = 136 – 137 °C) in 63% yield as white solid.

NMR and HRMS data for the product 7c:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.83 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.2$ Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 7.2$ Hz, 2H), 5.97 (t, $J = 6.6$ Hz, 1H), 5.63 (d, $J = 15.0$ Hz, 1H), 5.23 – 5.17 (m, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.69 (dd, $J = 14.4$, 6.0 Hz, 1H), 2.36 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.9, 167.3, 140.5, 140.4, 140.3, 137.9, 137.8, 132.8, 131.5, 131.1, 131.0, 130.8, 129.1, 128.8, 127.5, 127.4, 126.6, 123.3, 65.0, 61.1, 21.1.

HRMS (ESI) m/z calculated for C$_{25}$H$_{20}$O$_4$+H$^+$: 385.1434, found: 385.1438.

(Z)-3-phenyl-1,6-dioxacycloundec-3-ene-7,11-dione 8a

Prepared according to the general procedure to afford 8a (19.0 mg) in 73% yield as colorless liquid.

NMR and HRMS data for the product 8a:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.45 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 6.37 (t, $J = 7.8$ Hz, 1H), 4.98 (s, 2H), 4.72 (d, $J = 7.8$ Hz, 2H), 2.46 – 2.41 (m, 4H), 2.15 – 2.10 (m, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 172.9, 172.5, 144.4, 140.6, 128.6, 128.2, 127.5, 126.1, 62.3, 59.1, 34.7, 34.5, 21.9.
HRMS (ESI) m/z calculated for C_{15}H_{16}O_4+Na^+: 283.0941, found: 283.0940.

(Z)-3-(naphthalen-2-yl)-1,6-dioxacycloundec-3-ene-7,11-dione 8b

Prepared according to the general procedure to afford 8b (26.7 mg, m. p. = 105 – 108 °C) in 86% yield as white solid.

NMR and HRMS data for the product 8b:

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.88 (s, 1H), 7.86 – 7.81 (m, 3H), 7.59 – 7.56 (m, 1H), 7.52 – 7.47 (m, 2H), 6.52 (t, \(J = 7.2\) Hz, 1H), 5.09 (s, 2H), 4.78 (d, \(J = 6.6\) Hz, 2H), 2.50 – 2.44 (m, 4H), 2.18 – 2.13 (m, 2H).

\(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 173.0, 172.5, 144.2, 137.8, 133.2, 133.0, 128.3, 128.2, 127.9, 127.6, 126.5, 126.4, 125.2, 124.1, 62.2, 59.2, 34.7, 34.5, 21.9.

HRMS (ESI) m/z calculated for C_{19}H_{18}O_4+Na^+: 333.1097, found: 333.1103.

(Z)-3-([1,1'-biphenyl]-4-yl)-1,6-dioxacycloundec-3-ene-7,11-dione 8c

Prepared according to the general procedure to afford 8c (26.2 mg, m. p. = 135 – 137 °C) in 78% yield as white solid.

NMR and HRMS data for the product 8c:

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.63 – 7.58 (m, 4H), 7.54 – 7.51 (m, 2H), 7.45 (t, \(J = 7.8\) Hz, 2H), 7.36 (t, \(J = 7.2\) Hz, 1H), 6.44 (t, \(J = 7.2\) Hz, 1H), 5.02 (s, 2H), 4.75 (d, \(J = 7.2\) Hz, 2H), 2.49 – 2.42 (m, 4H), 2.17 – 2.11 (m, 2H).

\(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 172.9, 172.5, 143.9, 141.1, 140.4, 139.4, 128.8, 127.5, 127.4, 127.3, 127.0, 126.6, 62.1, 59.2, 34.7, 34.5, 21.9.

HRMS (ESI) m/z calculated for C_{21}H_{20}O_4+Na^+: 359.1254, found: 359.1260.
(Z)-11-phenyl-9,14-dioxaspiro[5.10]hexadec-11-ene-8,15-dione 8d

Prepared according to the general procedure to afford 8d (23.0 mg) in 70% yield as colorless liquid.

NMR and HRMS data for the product 8d:

**1H NMR** (600 MHz, CDCl₃) δ (ppm): 7.43 – 7.38 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 6.22 (t, J = 6.6 Hz, 1H), 4.99 (s, 2H), 4.74 (d, J = 7.2 Hz, 2H), 2.41 (s, 2H), 2.39 (s, 2H), 1.66 – 1.63 (m, 4H), 1.53 – 1.49 (m, 4H), 1.45 – 1.42 (m, 2H).

**13C NMR** (150 MHz, CDCl₃) δ (ppm): 171.6, 171.3, 143.1, 140.9, 128.5, 128.0, 127.0, 126.2, 62.5, 59.2, 43.5, 43.1, 37.7, 37.5, 25.8, 21.6.

**HRMS (ESI)** m/z calculated for C₂₀H₂₄O₄⁺Na⁺: 351.1567, found: 351.1567.

(Z)-4-phenyl-3,6,9,10,11,12-hexahydrobenzo[c][1,6]dioxecine-1,8-dione 8e

Prepared according to the general procedure to afford 8e (21.2 mg, m. p. = 82 – 87 °C) in 71% yield as pink solid.

NMR and HRMS data for the product 8e:

**1H NMR** (600 MHz, CDCl₃) δ (ppm): 7.45 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.32 – 7.29 (m, 1H), 6.16 (t, J = 6.0 Hz, 1H), 5.02 (s, 2H), 4.79 (d, J = 6.0 Hz, 2H), 2.45 – 2.41 (m, 4H), 1.82 – 1.79 (m, 1H), 1.71 – 1.67 (m, 3H).

**13C NMR** (150 MHz, CDCl₃) δ (ppm): 168.9, 168.5, 143.3, 140.9, 137.7, 137.4, 128.5, 128.1, 126.7, 126.1, 65.7, 61.5, 25.7, 21.2, 20.8, 20.7.

**HRMS (ESI)** m/z calculated for C₁₈H₁₈O₄⁺Na⁺: 321.1097, found: 321.1093.

(Z)-6-phenyl-4,7-dihydro-3H-benzo[c][1,6]dioxacycloundecine-1,9-dione 12
Prepared according to the general procedure to afford 12 (19.7 mg) in 64% yield as colorless liquid.

NMR and HRMS data for the product 12:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.87 – 7.83 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.53 (m, 2H), 7.40 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 6.40 (t, $J$ = 6.6 Hz, 1H), 4.83 (d, $J$ = 6.6 Hz, 2H), 4.37 (br s, 2H), 3.02 (br s, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 168.6, 166.9, 145.8, 140.4, 133.5, 131.7, 130.9, 130.8, 129.6, 128.6, 128.4, 128.1, 126.9, 124.8, 61.2, 60.3, 30.8.

HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$O$_4$+H$: 309.1121$, found: 309.1123.
6. General Procedure for the Reactions of Linear Anhydrides and VECs

To an oven-dried Schlenk tube was added Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, linear anhydrides 9 (0.10 mmol) and vinylethylene carbonates 2 (0.15 mmol) were added and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1) to afford the corresponding 10 in 55–57% yields, which were dried under vacuum and further analyzed by $^1$H NMR, $^{13}$C NMR, HRMS, etc.

(Z)-2-phenylbut-2-ene-1,4-diyl dipropionate 10a

Prepared according to the general procedure to afford 10a (15.7 mg) in 57% yield as colorless semisolid.

NMR and HRMS data for the product 10a:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 6.07 (t, J = 6.6 Hz, 1H), 5.07 (s, 2H), 4.88 (d, J = 7.2 Hz, 2H), 2.36 (q, J = 7.8 Hz, 2H), 2.27 (q, J = 7.8 Hz, 2H), 1.16 (t, J = 7.8 Hz, 3H), 1.07 (t, J = 7.8 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 174.2, 174.1, 139.4, 138.7, 128.4, 127.9, 127.3, 126.4, 60.9, 60.7, 27.5, 27.4, 9.0, 9.0.

HRMS (ESI) m/z calculated for C$_{16}$H$_{20}$O$_4$+Na$: 299.1254, found: 299.1255.

(Z)-2-(4-chlorophenyl)but-2-ene-1,4-diyl diacetate 10b
Prepared according to the general procedure to afford 10b (15.6 mg, m. p. = 51 – 55 °C) in 55% yield as white solid.

NMR and HRMS data for the product 10b:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.32 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.02 (t, \(J = 6.6\) Hz, 1H), 4.99 (s, 2H), 4.83 (d, \(J = 7.2\) Hz, 2H), 2.05 (s, 3H), 1.97 (s, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 170.5, 170.4, 137.6, 137.4, 133.7, 128.4, 127.6, 127.5, 60.5, 60.5, 20.7, 20.6.

HRMS (ESI) m/z calculated for C\(_{14}\)H\(_{15}\)ClO\(_4\)+Na\(^+\): 305.0551 (\(^{35}\)Cl), 307.0522 (\(^{37}\)Cl), found: 305.0564, 307.0504.
7. Synthetic Transformation of 5a and 10b

7.1 Procedure for the hydrogenation of lactone 3a

The ten-membered lactone 3a (0.1 mmol, 29.4 mg) was dissolved in dry ethanol (1.0 mL). This mixture was degassed of dissolved air and purged with an argon atmosphere. To it 5% Pd/C (8.0 mg) was carefully added. The above reaction mixture was degassed and purged with hydrogen. Then the reaction was stirred for 12 hours at room temperature with hydrogen balloon. After the completion of the reaction, the mixture was filtered through a plug of silica (eluting with DCM) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 to 40/1) to afford 13 (12.4 mg) as white solid in 42% yields, which was dried under vacuum and further analyzed by \(^1\)H NMR, \(^13\)C NMR, HRMS, etc.

4-phenyl-3,4,5,6-tetrahydrobenzo[c][1,6]dioxecine-1,8-dione 13

Purification of the crude product via column chromatography delivered 13 (12.4 mg, m. p. = 135 – 136 °C) in 42% yield as white solid.

\textit{NMR and HRMS data for the product 13}:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.78 – 7.75 (m, 2H), 7.60 – 7.56 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 4.92 – 4.87 (m, 1H), 4.76 (dd, \(J = 11.4, 4.8\) Hz, 1H), 4.11 – 4.06 (m, 1H), 3.94 (t, \(J = 10.8\) Hz, 1H), 3.32 – 3.27 (m, 1H), 2.61 – 2.54 (m, 1H), 2.06 (d, \(J = 13.8\) Hz, 1H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 168.0, 167.7, 142.2, 133.0, 132.8, 131.5, 131.5, 128.9, 128.9, 128.7, 127.5, 127.2, 69.9, 65.2, 43.8, 34.3.

HRMS (ESI) m/z calculated for C\(_{18}\)H\(_{16}\)O\(_4\)+H\(^+\): 297.1121, found: 297.1126.
7.2 Procedure for the hydrolysis of the linear ester 10b

The linear ester 10b (0.1 mmol, 28.2 mg) was dissolved in the mixture of MeOH/Et₂O (2 mL, v/v = 1/1) and stirred at room temperature. To this solution was slowly added MeONa (0.02 mmol, 1 mg). The mixture was stirred for 5 h at the same temperature and quenched with 5 mL of saturated aqueous NH₄Cl. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1 to 1/1) to afford 14 (19.1 mg) as colorless semisolid in 96% yields, which was dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

**(Z)-2-(4-chlorophenyl)but-2-ene-1,4-diol 14**

Purification of the crude product via column chromatography delivered 14 (19.1 mg) in 96% yield as colorless semisolid.

*NMR and HRMS data for the product 14:*

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 6.07 (t, J = 6.6 Hz, 1H), 4.50 (s, 2H), 4.34 (d, J = 7.2 Hz, 2H), 2.82 (br s, 2H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 141.5, 138.9, 133.6, 130.1, 128.6, 127.6, 60.0, 58.7.

**HRMS (ESI) m/z calculated for C₁₀H₁₁ClO₂⁺Na⁺:** 221.0340 ([⁵⁵Cl]), 223.0310 ([⁵⁷Cl]), found: 221.0339, 223.0304.
8. Experiments for Mechanism Studies

8.1 The competition experiments

To explore the reaction mechanism, we performed several competition experiments based on the reaction of vinylethylene carbonate 2a with cyclic anhydride 4d or linear anhydride 9a.

To three oven-dried Schlenk tubes were added Pd$_2$(dba)$_3$:CHCl$_3$ (2.5 mol%) and XantPhos (10 mol%), after which the tubes were evacuated and back-filled with argon three times. Then under the protection of argon, dry toluene (1.0 mL) was added and stirred at room temperature for 30 min. Subsequently, under the protection of argon, anhydride 4d or 9a (0.10 mmol), sodium acetate and vinylethylene carbonate 2a (0.15 mmol) were added. The amounts of sodium acetate in the three reactions respectively refer to 0.10 mmol, 0.20 mmol and 0.30 mmol.

Then, the three reactions were stirred at room temperature for 4 hours, respectively. After then, the mixtures were filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum further analyzed by $^1$H NMR.

Even when three equivalents of the sodium acetate was added into the reaction mixture, the competitive product 8a’ or 10a’ was not observed, probably because the in-situ generated carboxylate is more likely to coordinate with palladium catalyst and then triggered an intramolecular attack of the $\pi$-allyl palladium moiety to deliver 8a or 10a.
8.2 Proposed reaction mechanism

Based on the results of competition experiments, a plausible mechanism for the catalytic cyclisation was proposed. As shown in Figure S1, the reaction was initiated by the palladium-catalysed decarboxylation of VEC \(2a\) to generate the zwitterionic \(\pi\)-allyl palladium intermediate \(I\). Subsequently, the anhydride substrate was attacked by the alkoxide to form the intermediate \(II\), in which the carboxylate moiety might be coordinated with palladium catalyst. Finally, a regioselective intramolecular allylation of the carboxylate and \(\pi\)-allyl palladium moieties occurred, which delivered diverse medium-sized lactone products.

![Proposed mechanism](image_url)

**Figure S1.** Proposed mechanism.
9. Crystal Data and Structure Refinement

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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.312</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.732</td>
</tr>
<tr>
<td>F(000)</td>
<td>712.0</td>
</tr>
<tr>
<td>Crystal size/Å³</td>
<td>0.5 × 0.3 × 0.1</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>9.56 to 143.526</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 12, -22 ≤ k ≤ 21, -10 ≤ l ≤ 8</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5135</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2438 [R_{int} = 0.0394, R_{sigma} = 0.0340]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2438/1/226</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.043</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R_1 = 0.0879, wR_2 = 0.2521</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.1008, wR_2 = 0.2838</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.60/-0.29</td>
</tr>
</tbody>
</table>
10. References and Notes


11. NMR Spectra

![NMR Spectra Image]

N: parts per Million; Proton
$5g$
S105
6b
PS: The purity of the compound 3d and 3u determined by HPLC.

### Table 1: Purity of Compound 3d

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time[min]</th>
<th>Area[mAU]*s</th>
<th>Height[mAU]</th>
<th>Rel. Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.04</td>
<td>3.958</td>
<td>1.0301</td>
<td>0.0414</td>
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<tr>
<td>2</td>
<td>2.98</td>
<td>15.655</td>
<td>2.4083</td>
<td>0.1638</td>
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<tr>
<td>3</td>
<td>4.08</td>
<td>21.322</td>
<td>1.6707</td>
<td>0.2231</td>
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<tr>
<td>4</td>
<td>4.75</td>
<td>17.843</td>
<td>0.9887</td>
<td>0.1867</td>
</tr>
<tr>
<td>5</td>
<td>6.32</td>
<td>9491.991</td>
<td>720.8486</td>
<td>99.3013</td>
</tr>
<tr>
<td>6</td>
<td>7.43</td>
<td>8.004</td>
<td>0.393</td>
<td>0.0837</td>
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</tbody>
</table>

### Table 2: Purity of Compound 3u

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time[min]</th>
<th>Area[mAU]*s</th>
<th>Height[mAU]</th>
<th>Rel. Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.01</td>
<td>3.862</td>
<td>1.579</td>
<td>0.0296</td>
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<tr>
<td>2</td>
<td>2.11</td>
<td>2.309</td>
<td>0.7374</td>
<td>0.0177</td>
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<tr>
<td>3</td>
<td>2.2</td>
<td>5.065</td>
<td>1.5223</td>
<td>0.0389</td>
</tr>
<tr>
<td>4</td>
<td>4.09</td>
<td>16.071</td>
<td>1.2893</td>
<td>0.1234</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
<td>75.925</td>
<td>5.1397</td>
<td>0.5828</td>
</tr>
<tr>
<td>6</td>
<td>6.31</td>
<td>38.917</td>
<td>2.9185</td>
<td>0.2987</td>
</tr>
<tr>
<td>7</td>
<td>7.65</td>
<td>12849.223</td>
<td>814.7239</td>
<td>98.6323</td>
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<tr>
<td>8</td>
<td>8.38</td>
<td>36.021</td>
<td>1.8596</td>
<td>0.2765</td>
</tr>
</tbody>
</table>