Supplementary Information

Facile and highly atom-economic approach to biaryl-containing medium-ring bislactones

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Contents

<table>
<thead>
<tr>
<th>Description</th>
<th>Page number</th>
</tr>
</thead>
<tbody>
<tr>
<td>General experimental</td>
<td>S1</td>
</tr>
<tr>
<td>Detailed description on reaction condition optimization</td>
<td>S1-S2</td>
</tr>
<tr>
<td>Investigations on active oxygen species for the photo-oxidation step</td>
<td>S3-S4</td>
</tr>
<tr>
<td>Synthesis of DOP substrates</td>
<td>S4-S5</td>
</tr>
<tr>
<td>Compound data</td>
<td>S6-S9</td>
</tr>
<tr>
<td>X-Ray crystal structure of 5e, 3j and 7</td>
<td>S9-S10</td>
</tr>
<tr>
<td>Copies of NMR</td>
<td>S11-S39</td>
</tr>
</tbody>
</table>

General

Nuclear magnetic resonance spectra were recorded on a Bruker DPX 300 at 300MHz with CDCl₃ as solvent. Chemical shifts are reported in δ (ppm) with the solvent resonance as the internal standard (chloroform, H, 7.263 ppm; C, 77.66, 77.23, 76.81 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br s = broad), coupling constant in Hz, integration, and assignment. Mass spectra were recorded with a VG ZAB-HS spectrometer or a LCQ FLEET mass spectrometer (ESI). Elemental analyses were done on a Elementar Vario MICRO analyzer. Reagents: Benzene (AR grade) was dried with sodium and distilled. Acetonitrile (AR grade) was first refluxed with CaH₂ and distilled. Chloroform was also refluxed with CaH₂ and distilled. THF was dried with sodium and distilled.

Optimization for photoreaction

To make the DOP type [4+2] cycloadducts as the predominant product with high yields, solvent for the photo-induced reaction of PQ and bicyclopropylidene 1a was optimized. As shown in Table 1, photoinduced reaction of PQ with 1a in benzene gave the corresponding DOP type product 2a with higher yield than the reaction in acetonitrile.
Table 1  Optimization on photocycloaddition conditions of PQ with 1a leading to DOP 2a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Solvents</th>
<th>DOP product and yields a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>PhH</td>
<td>2a (95%)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>CH3CN</td>
<td>2a (81%)</td>
</tr>
</tbody>
</table>

a Isolated yield after flash column chromatography.

Photo-cycloaddition of 9, 10-phenanthrenedione (PQ) with strained alkenes 1a in anhydrous benzene. A solution of PQ (416 mg, 2 mmol) and 1a (4 mmol) in anhydrous benzene (100 mL) was photolyzed by \( \lambda > 400 \) nm light and monitored by TLC to reach a complete conversion of PQ. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded pure analytic final DOP product 1a.

2a, colorless oil; \(^1H\) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.71 (d, \( J = 8.1 \) Hz, 2H), 8.27 (dd, \( J = 8.1, 1.4 \) Hz, 2H), 7.75-7.63 (m, 4H), 1.36-1.31 (m, 4H), 0.95-0.90 (m, 4H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \( \delta \) 134.7 (2C), 132.3 (2C), 126.8 (2C), 126.5 (2C), 125.0 (2C), 122.6 (2C), 120.8 (2C), 62.0 (2C), 11.0 (4C) ppm; MS m/z (% base): 236 (14), 194 (24), 181 (73), 152 (100), 68 (55); EA Found: C, 83.27; H, 5.43. Calc. for C\(_{20}\)H\(_{16}\)O\(_2\): C, 83.31; H, 5.59%.

Photooxidation of 2a in anhydrous CH\(_3\)CN. A solution of DOP 2a (0.02M) in anhydrous acetonitrile was photolyzed by \( \lambda > 400 \) nm light and purged with dry O\(_2\). The reactions were monitored by TLC to reach a complete conversion of the DOP. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone products 3a.

3a, white powder; m.p. 192-194°C; \(^1H\) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.58-7.36 (m, 8H), 1.78-1.69 (m, 2H), 1.44-1.35 (m, 2H), 0.99-0.90 (m, 2H), 0.28-0.19 (m, 2H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \( \delta \) 170.0 (2C), 137.9 (2C), 133.7 (2C), 131.1 (2C), 131.0 (2C), 127.8 (2C), 126.2 (2C), 63.5 (2C), 14.2 (2C), 6.4 (2C) ppm; IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1754, 1443, 1274, 1224, 1069, 756, 748; MS m/z (% base): 236 (14), 194 (24), 181 (73), 152 (100), 68 (55); EA Found: C, 75.05; H, 5.05. Calc. for C\(_{20}\)H\(_{16}\)O\(_4\): C, 74.99; H, 5.03%.

Photooxidation of 2a in anhydrous CH\(_3\)OH. A solution of DOP 2a (0.02M) in anhydrous CH\(_3\)OH was photolyzed by \( \lambda > 400 \) nm light and purged with dry O\(_2\). The reactions were monitored by TLC to reach a complete conversion of the DOP. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the major product A and the minor bislactone product 3a.

\[
\begin{align*}
\text{A, white powder; m.p. 142-144°C; } &\text{ } ^1H\text{ NMR (300 MHz, CDCl}_3\text{): } \delta \text{ 7.69 (d, } J = 7.9 \text{ Hz, 2H), 7.64 (d, } J = 8.1 \text{ Hz, 2H), 7.52 (d, } J = 7.6 \text{ Hz, 2H), 7.39-7.32 (m, 6H), 7.29-7.23 (m, 4H), 2.79 (s, 6H), 1.46-1.38 (m, 2H), 1.09-0.76 (m, 10H), 0.16-0.07 (m, 4H) ppm; } ^{13}C\text{ NMR (75 MHz, CDCl}_3\text{): } \delta \text{ 132.9, 132.6, 132.5, 132.0, 129.2, 129.1, 127.4, 127.3, 126.6, 125.4, 124.1, 123.6, 102.0, 96.5, 77.4, 57.1, 56.9, 50.7, 13.4, 13.2, 6.3, 6.0 ppm; MS m/z (% base): 239 (100), 211 (23), 195 (91), 180 (77), 152 (47).}
\end{align*}
\]
Investigations on active oxygen species for photooxidation step

**TPP sensitized \(^{1}\mathrm{O}_2\) generation.** A solution of \(2\text{a} (0.02\text{M})\) and tetraphenylporphin (TPP, 0.002M) in anhydrous benzene was photolyzed and purged with dry \(\mathrm{O}_2\). The reaction was monitored by TLC and no obvious conversion of \(2\text{a}\) was observed extended the reaction time to 24h.

**Thermal decomposition to provide \(^{1}\mathrm{O}_2\).** A solution of 1,4-dimethylnaphthalene (0.02M) in anhydrous benzene was purged with dry \(\mathrm{O}_2\) and photolyzed by \(\lambda > 400\) nm light at 0-5°C. The reaction was monitored by TLC to reach a complete conversion of 1,4-dimethylnaphthalene. There was only one major product and the reaction mixture was evaporated at 0-5°C to get the product which was the endoperoxide of 1,4-dimethylnaphthalene and could release the pure \(^{1}\mathrm{O}_2\) at room temperature. Then dissolved the endoperoxide (0.04M) and \(1\text{a} (0.02\text{M})\) in anhydrous \(\mathrm{CH}_3\text{CN}\) and the solution was stirred at 25°C. The reaction was monitored by TLC and no obvious conversion of \(2\text{a}\) was observed extended the reaction time to 12h while the endoperoxide was converted to 1,4-dimethylnaphthalene.

![Scheme 1](image)

**Scheme 1** Thermal decomposition to provide \(^{1}\mathrm{O}_2\)

**Detection of the active oxygen species by ESR.** The generation of the active oxygen species under photolysis was evaluated by electron spin resonance spectroscopy (ESR) analysis using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as spin-trapping agent. The results were shown in Figure 1.

![Figure S1](image)

Figure S1. ESR spectrum using DMPO (200 mM) as the spin trapper were measured after photolysis of 2a in \(\mathrm{O}_2\)-saturated acetonitrile for A, 2min; B, 4min; C, 7min and D, 10min. The sample was oxygen-saturated.
Quenching superoxide anion radical by BQ. A solution of 2a (0.02M) and benzoquinone (BQ, 0.002M) in anhydrous acetonitrile was photolyzed and purged with dry O₂. The reaction was monitored by TLC and no obvious conversion of 2a was observed extended the reaction time to 24h.

Detection of CTC complex of 2a by UV spectrum. The absorption changement from the substrate to the ground-state CT complex with molecular oxygen can be measured by direct recording the UV spectrum of oxygen-saturated and oxygen-free solutions of 2a. The results were shown in Figure 2.

Figure 2. UV spectrum of CTC complex of 2a.

Synthesis of DOP substrates

Photo-cycloaddition of 9, 10-phenanthrenedione (PQ) with alkenes in anhydrous benzene. A solution of PQ (416 mg, 2 mmol) and alkenes (4 mmol) in anhydrous benzene (100 mL) was photolyzed by λ > 400 nm light and monitored by TLC to reach a complete conversion of PQ. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded pure analytic final DOP products.

Photo-cycloaddition of 1,10-phenanthroline-5,6-dione (PN) with alkenes in anhydrous CH₃CN. A solution of PN (204mg, 1 mmol) and alkenes (2mmol) in anhydrous acetonitrile (50 mL) was photolyzed by λ > 400 nm light and monitored by TLC to reach a complete conversion of PN. Flash column chromatograph on 300-400 mesh silica gel with chloroform/methanol as eluents afforded pure analytic final DOP products.

2b, colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 8.75 (dd, J = 7.9, 2.1 Hz, 2H), 8.51 (dd, J = 8.1, 0.9 Hz, 1H), 8.30 (dd, J = 8.1, 1.1 Hz, 1H), 7.84-7.65 (m, 4H), 2.65-2.54(m, 2H), 2.38-2.29(m, 2H), 2.20-2.09(m, 1H), 1.89-1.78(m, 1H), 1.36-1.31(m, 2H), 1.16-1.11(m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 134.1, 132.5, 126.9, 126.7 (2C), 126.5, 126.4, 125.0, 124.8, 122.6 (2C), 121.1, 120.7, 78.7, 61.8, 31.6 (2C), 13.0, 9.0 (2C) ppm; MS m/z (% base): 302 (4), 234 (100); EA Found: C, 83.40; H, 5.88. Calc. for C₂₁H₁₈O₂: C, 83.42; H, 6.00%.
2c, colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.64-8.59 (m, 2H), 8.29 (dd, $J_1$ = 8.1, 0.9 Hz, 1H), 8.05-8.02 (m, 1H), 7.66-7.49 (m, 4H), 2.08-2.04 (m, 2H), 1.94-1.79 (m, 3H), 1.68-1.63 (m, 2H), 1.39-1.24 (m, 3H), 1.09-0.96 (m, 4H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ 127.2, 127.1, 126.8, 126.7, 125.0, 124.6, 122.7, 122.6, 121.1, 120.6, 76.1, 64.5, 30.9 (2C), 25.9, 21.5 (2C), 9.6 (2C) ppm; MS m/z (% base): 180 (92), 152 (100), 76 (42); EA Found: C, 83.70; H, 6.75. Calc. for C$_{23}$H$_{22}$O$_2$: C, 83.60; H, 6.71%.

2d, white powder; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.62 (d, $J_1$ = 7.8 Hz, 2H), 8.26 (dd, $J_1$ = 8.0, 1.3 Hz, 1H), 7.64-7.51 (m, 4H), 2.00-1.21 (m, 20H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ 134.1, 132.5, 126.9, 126.7 (2C), 126.5, 126.4, 125.0, 124.8, 122.6 (2C), 121.1, 120.7, 78.7, 61.8, 31.6 (2C), 13.0, 9.0 (2C) ppm; MS m/z (% base): 208 (82), 180 (100), 152 (97), 104 (24), 76 (31); EA Found: C, 83.78; H, 7.63. Calc. for C$_{26}$H$_{28}$O$_2$: C, 83.83; H, 7.58%.

4a, white powder; m.p. 164-166°C; $^1$H NMR (300 MHz, CDCl$_3$): δ 9.03 (d, $J_1$ = 3.2 Hz, 2H), 8.35 (d, $J_1$ = 8.1 Hz, 2H), 7.54 (dd, $J_1$ = 8.0, 4.4 Hz, 2H), 1.21-1.15 (m, 4H), 0.83-0.78 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 148.4, 142.5, 133.8, 128.8, 123.2, 122.8, 62.5, 11.0 ppm; MS m/z (% base): 290 (100), 262 (24), 233 (16), 182 (16), 79 (17); EA Found: C, 74.55; H, 4.89; N, 9.50. Calc. for C$_{18}$H$_{14}$N$_2$O$_2$: C, 74.47; H, 4.86; N, 9.65%.

4d, white powder; $^1$H NMR (300 MHz, CDCl$_3$): δ 9.04 (dd, $J_1$ = 4.3, 1.7 Hz, 2H), 8.54 (dd, $J_1$ = 8.2, 1.2 Hz, 1H), 7.60 (dd, $J_1$ = 8.3, 4.4 Hz, 1H), 1.96-1.22 (m, 20H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ 148.0, 142.5, 130.7, 128.7, 123.8, 122.9, 79.4, 25.9, 21.6 ppm; MS m/z (% base): 374 (57.1), 212 (100), 81 (37.8); EA Found: C, 77.03; H, 7.11; N, 7.29. Calc. for C$_{24}$H$_{26}$N$_2$O$_2$: C, 76.98; H, 7.00; N, 7.48%.

6, white powder; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.66-8.60 (m, 2H), 8.29-8.25 (m, 1H), 8.22-8.18 (m, 1H), 8.03 (d, $J_1$ = 7.5 Hz, 2H), 7.69-7.50 (m, 5H), 7.37 (t, $J_1$ = 7.7 Hz, 2H), 7.05 (s, 1H), 4.74 (dd $J_1$ = 11.5, 1.5 Hz, 1H), 4.49 (d, $J_1$ = 11.6 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ 133.4, 130.8, 127.1, 125.7, 125.5, 122.7, 122.6, 121.2, 121.0, 88.2, 85.6, 32.2, 29.9, 29.6, 22.9, 14.3 ppm; EA Found: C, 74.47; H, 4.86; N, 9.65%.
Photooxidation of DOPs in anhydrous CH₃CN

A solution of DOP (0.02M) in anhydrous acetonitrile was photolyzed by λ > 400 nm light (used λ > 300 nm light for the photooxidation of substrate 4a and 4d) and purged with dry O₂. The reactions were monitored by TLC to reach a complete conversion of the DOPs. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone products.

3b, white powder; m.p. 145-147°C; ¹H NMR (300 MHz, CDCl₃): δ 7.74 (d, J = 7.5 Hz, 1H), 7.58-7.35 (m, 7H), 3.10-2.99 (m, 1H), 2.63-2.51 (m, 1H), 2.05-1.57 (m, 4H), 1.54-1.45 (m, 1H), 1.18-1.09 (m, 1H). IR (KBr) νmax/cm⁻¹: 1742, 1727, 1478, 1279, 1233, 1125, 1063, 746; MS m/z (% base): 224 (1), 180 (100), 152 (60), 76 (5), 54 (11); EA Found: C, 75.44; H, 5.32. Calc. for C₂₁H₁₈O₄: C, 75.43; H, 5.43%.

3c, white powder; m.p. 171-172°C; ¹H NMR (300 MHz, CDCl₃): δ 7.60-7.39 (m, 8H), 3.43-3.38 (d, J = 13.8 Hz, 1H), 1.99-1.94 (d, J = 12.9 Hz, 1H), 1.74-0.54 (m, 12H). IR (KBr) νmax/cm⁻¹: 1743, 1726, 1445, 1288, 1234, 1125, 1070, 747; MS m/z (% base): 225 (1), 180 (100), 152 (26), 81 (20), 67 (19). EA Found: C, 76.13; H, 6.15. Calc. for C₂₃H₂₂O₄: C, 76.22; H, 6.12%.

3d, white powder; m.p. 176-180°C; ¹H NMR (300 MHz, CDCl₃): δ 7.72-7.68 (dd, J = 7.5, 0.8 Hz, 2H), 7.56-7.50 (td, J = 7.5, 1.3 Hz, 2H), 7.45-7.36 (m, 16H). ¹³C NMR (75 MHz, CDCl₃): δ 170.9, 168.7, 138.8, 138.7, 134.0, 132.5, 131.4, 131.3, 130.9, 130.8, 127.7, 127.6, 127.3, 125.9, 87.1, 66.0, 33.0, 30.4, 15.6, 11.2, 6.1 ppm; IR (KBr) νmax/cm⁻¹: 1742, 1727, 1478, 1279, 1233, 1125, 1063, 746; MS m/z (% base): 224 (1), 180 (100), 152 (60), 76 (5), 54 (11); EA Found: C, 75.44; H, 5.32. Calc. for C₂₁H₁₈O₄: C, 75.43; H, 5.43%.

5a, white powder; m.p. 254-256°C; ¹H NMR (300 MHz, CDCl₃): δ 8.93 (d, J = 3.6 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.41 (dd, J = 7.5, 4.8 Hz, 2H), 1.78-1.65 (m, 2H), 1.03-0.94 (m, 2H), 0.33-0.24 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 168.6, 153.6, 152.0, 134.4, 130.3, 123.0, 64.5, 14.1, 6.7 ppm; IR (KBr) νmax/cm⁻¹: 1759, 1741, 1417, 1305, 1274, 1265, 1260, 89.9, 67.3, 33.2, 33.0, 25.1, 22.5, 22.1, 11.5, 8.2 ppm; IR (KBr) νmax/cm⁻¹: 1742, 1727, 1478, 1279, 1233, 1125, 1063, 746; MS m/z (% base): 224 (1), 180 (100), 152 (60), 76 (5), 54 (11); EA Found: C, 75.44; H, 5.32. Calc. for C₂₁H₁₈O₄: C, 75.43; H, 5.43%.

5d, white powder; m.p. 180-183°C; ¹H NMR (300 MHz, CDCl₃): δ 8.90 (dd, J = 4.8, 1.4 Hz, 2H), 8.13 (dd, J = 7.8, 1.5 Hz, 2H), 7.40 (dd, J = 7.8, 4.8 Hz, 2H), 2.44-2.34 (m, 4H), 1.72-1.14 (m, 16H). ¹³C NMR (75 MHz, CDCl₃): δ 167.9, 155.0, 151.7, 136.2, 130.0, 123.0, 96.3, 32.8, 31.1, 25.0, 22.7, 22.3 ppm; IR (KBr) νmax/cm⁻¹: 1730, 1557, 1416, 1305, 1274, 1080, 763; MS m/z (% base): 210 (13), 182 (100), 162 (42), 154 (32), 91 (74), 79 (73); EA Found: C, 71.11; H, 6.58; N, 6.69. Calc. for C₂₄H₂₆N₂O₄: C, 70.92; H, 6.45; N, 6.89%.

7, white powder; ¹H NMR (300 MHz, CDCl₃) of the predominant diastereoisomer: δ 8.14 (d, J = 7.5 Hz, 2H), 7.68-7.38 (m, 12H), 5.46 (t, J = 10.1 Hz, 1H), 4.30 (dd, J = 11.1, 2.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 169.2, 166.8, 163.9, 137.4, 137.2, 134.4, 134.3, 133.3, 133.2, 132.1, 132.9, 132.3, 131.7, 131.5, 131.2, 131.1, 130.4, 128.8, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 126.6, 126.3, 126.2,
90.8, 89.8, 64.7, 64.4 ppm; IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup>: 1754, 1733, 1438, 1235, 750, 707; MS m/z (% base): 180 (70), 152 (8), 105 (100), 77 (15); EA Found: C, 71.05; H, 4.40. Calc. for C<sub>23</sub>H<sub>16</sub>O<sub>6</sub>: C, 71.13; H, 4.15%.

9, white powder; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of the predominant diastereoisomer: δ 7.59-7.39 (m, 8H), 6.29 (dd, <i>J</i> = 8.8, 2.7 Hz, 1H), 5.16 (t, <i>J</i> = 10.0 Hz, 1H), 4.12 (dd, <i>J</i> = 11.2, 2.5 Hz, 1H), 3.75-3.67 (m, 1H), 1.72-1.62 (m, 2H), 1.50-1.42 (m, 2H), 0.98 (t, <i>J</i> = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 169.3, 169.0, 137.5, 137.0, 133.9, 133.4, 133.3, 133.0, 132.6, 131.5, 131.3, 131.2, 130.9, 130.8, 128.0, 127.8, 127.7, 127.4, 126.2, 126.0, 99.6, 98.9, 70.4, 70.3, 67.6, 65.7, 31.5, 31.4, 19.2, 19.1, 13.9 ppm; IR (KBr) ν<sub>max</sub>/cm<sup>-1</sup>: 1755, 1733, 1438, 1257, 1235, 1014, 751, 707; MS m/z (% base): 196 (100), 180 (58), 168 (43), 152 (18), 139 (43); EA Found: C, 70.66; H, 6.05. Calc. for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>: C, 70.57; H, 5.92%.

11, white powder; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of the predominant diastereoisomer: δ 7.57-7.40 (m, 8H), 7.27 (dd, <i>J</i> = 9.2, 2.9 Hz), 5.26 (dd, <i>J</i> = 11.1, 9.4 Hz), 4.15 (dd, <i>H</i>, <i>J</i> = 11.0, 2.8 Hz), 2.20 (s, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 169.2, 168.3, 166.8, 137.4, 137.3, 133.3, 133.2, 132.9, 132.3, 131.7, 131.5, 131.3, 130.9, 130.6, 128.2, 127.9, 127.8, 127.7, 126.7, 126.3, 126.1, 90.3, 89.3, 64.5, 64.3, 20.8, 20.7 ppm; IR (KBr) cm<sup>-1</sup>: 1758, 1277, 1204, 1024, 755; MS m/z (% base); EA Found: C, 66.29; H, 4.19. Calc. for C<sub>18</sub>H<sub>14</sub>O<sub>6</sub> C, 66.26; H, 4.32%.

13, white powder; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of the predominant diastereoisomer: δ 7.87 (dd, <i>J</i> = 7.8, 1.4 Hz, 1H), 7.73 (dd, <i>J</i> = 7.8, 1.3 Hz, 1H), 7.60 (tt, <i>J</i> = 7.6, 1.6 Hz, 2H), 7.47 (tt, <i>J</i> = 7.6, 1.2 Hz, 2H), 7.38-7.32 (m, 2H), 5.89 (q, <i>J</i> = 5.7 Hz, 1H), 1.72 (d, <i>J</i> = 5.9 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 169.0, 167.9, 140.6, 140.5, 132.7, 132.4, 132.3, 131.7, 129.9, 129.2, 129.1, 127.9, 127.8, 127.7, 98.2, 29.8, 20.7 ppm; MS m/z (% base): 224 (3), 180 (100), 152 (37), 76 (2); EA Found: C, 71.56; H, 4.61. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>4</sub>: C, 71.64; H, 4.51%.

Substrate 14 was also prepared according to reported method, but only PQ obtained for 14 under photooxidation.

Sequential photocycloadditions and photooxidations of PQ or PN with aryl substituted alkenes

**One-pot photoreaction of PQ with styrene.** A solution of PQ (416 mg, 2 mmol) and styrene (4 mmol) in anhydrous acetonitrile (100 mL) was photolyzed by λ &gt; 400 nm light and purged with dry O<sub>2</sub>. The reactions were monitored by TLC to reach a complete conversion of PQ and DOP product. Flash column chromatograph on 300-400 mesh silica gel with petroleum ether/ethyl acetate as eluents afforded the bislactone with a yield of 67%.

Sequential photocycloadditions and photooxidations of PQ or PN with aryl substituted alkenes.

A solution of PQ (416 mg, 2 mmol) and aryl substituted alkenes (4 mmol) in 100 mL anhydrous benzene (PN (420 mg, 2 mmol) and le (4 mmol) in 100 mL anhydrous acetonitrile) was photolyzed by λ &gt; 400 nm light and monitored by TLC to reach a complete conversion of PQ (or PN). Then evaporation to remove benzene and the residue were dissolved by 100 mL anhydrous CH<sub>3</sub>CN. The solution was photolyzed and purged with dry O<sub>2</sub>. The reactions were monitored by TLC to reach a complete conversion of DOP products. Flash column chromatograph on 300-400 mesh silica gel with
petroleum ether/ethyl acetate as eluents afforded the bislactone products as a mixture of diastereoisomers.

3e, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 7.66-7.33 (m, 13H), 6.48 (dd, $J = 10.7$, 2.9 Hz, 1H), 5.33 (t, $J = 11.1$ Hz, 1H), 4.14 (dd, $J = 12.5$, 3.0 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.5, 169.0, 135.4, 137.3, 133.8, 133.7, 131.3, 131.2, 130.9, 129.3, 129.1, 127.8, 127.3, 126.8, 126.4, 126.2, 77.2, 69.1 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1742, 1599, 1280, 1238, 1128, 754; MS m/z (% base): 238 (35), 180 (100), 152 (49), 91 (4), 76 (4); EA Found: C, 76.70; H, 4.66.

5e, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 8.97 (s, 2H), 7.86-7.83 (m, 2H), 7.58-7.40 (m, 7H), 6.50 (d, $J = 9.5$ Hz, 1H), 5.37 (t, $J = 11.1$ Hz, 1H), 4.19 (d, $J = 10.6$ Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.9, 167.5, 155.6, 152.9, 152.8, 151.9, 134.3, 134.2, 133.2, 133.1, 130.2, 130.1, 129.7, 129.2 (2C), 128.4, 127.3, 123.1, 77.9, 69.3 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1754, 1741, 1562, 1413, 1271, 1235, 1082, 769, 704; MS m/z (% base): 240 (16), 210 (56), 182 (100), 154 (55), 127 (26); EA Found: C, 69.32; H, 4.18; N, 7.94. Calc. for C$_{20}$H$_{14}$N$_2$O$_4$: C, 69.36; H, 4.07; N, 8.09%.

3f, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 7.66-7.39 (m, 10H), 7.00-6.94 (m, 2H), 6.42 (dd, $J = 10.7$, 2.9 Hz, 1H), 5.32 (t, $J = 11.6$ Hz, 1H), 4.09 (dd, $J = 11.5$, 3.1 Hz, 1H), 3.85 (s, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.5, 169.0, 160.4, 137.4, 137.2, 133.8, 133.7, 131.3, 131.1, 130.9, 130.8, 128.8, 128.4, 127.8, 126.4, 126.2, 125.7, 114.4, 77.0, 69.0, 55.5 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1742, 1516, 1276, 1237, 1133, 752; MS m/z (% base): 180 (100), 152 (55), 135 (23), 121 (15); EA Found: C, 73.77; H, 4.63. Calc. for C$_{23}$H$_{18}$O$_5$: C, 73.79; H, 4.85%.

3g, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 7.80-7.20 (m, 12H), 6.82 (d, $J = 9.4$ Hz, 1H), 5.14 (t, $J = 10.7$ Hz, 1H), 4.33 (d, $J = 10.6$ Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.7, 168.4, 137.5, 137.4, 133.6, 133.3, 131.4, 131.3, 131.1, 131.0, 130.6, 128.8, 128.3, 128.0, 127.9, 126.3, 126.2, 122.5, 76.3, 67.6 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1746, 1476, 1274, 1232, 1068, 748; MS m/z (% base): 224 (4), 180 (100), 152 (76), 76 (3); EA Found: C, 62.39; H, 3.62; Br, 18.77. Calc. for C$_{22}$H$_{15}$BrO$_4$: C, 62.43; H, 3.57; Br, 18.88%.

3h, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 8.67 (br s, 2H), 7.62-7.34 (m, 10H), 6.47 (dd, $J = 10.5$, 2.3 Hz, 1H), 5.22 (t, $J = 12.2$ Hz, 1H), 4.15 (dd, $J = 11.5$, 2.7 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.2, 168.5, 150.4, 142.6, 137.2, 133.6, 133.3, 131.4, 131.3, 131.0, 130.6, 128.8, 128.3, 128.0, 127.9, 126.3, 126.2, 122.5, 76.3, 67.6 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1745, 1440, 1285, 1240, 1133, 753, 700; MS m/z (% base): 315 (2), 238 (5), 208 (72), 180 (68), 152 (100), 76 (14); EA Found: C, 72.97; H, 4.44; N, 4.09. Calc. for C$_{21}$H$_{15}$NO$_4$: C, 73.03; H, 4.38; N, 4.06%.

3i, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 8.78 (br s, 2H), 7.62-7.34 (m, 10H), 6.47 (dd, $J = 10.5$, 2.3 Hz, 1H), 5.22 (t, $J = 12.2$ Hz, 1H), 4.15 (dd, $J = 11.5$, 2.7 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.0, 167.1, 142.0, 141.1, 138.3, 138.2, 133.9, 133.4, 131.3, 131.0, 130.9, 130.8, 128.5, 128.3, 127.9, 127.8, 127.6, 126.9, 126.5, 125.9, 89.5, 69.7 ppm; IR (KBr) $\nu_{max}$/cm$^{-1}$: 1732, 1721, 1451, 1278, 1269, 1135, 758, 700; MS m/z (% base): 196 (5), 180 (100), 167 (96), 152 (64), 76 (4); EA Found: C, 80.06; H, 4.75. Calc. for C$_{22}$H$_{16}$O$_4$: C, 79.98; H, 4.79%.
3j, white powder; $^1$H NMR (300 MHz, CDCl$_3$) of the predominant diastereoisomer: $\delta$ 7.65-7.33 (m, 13H), 6.06 (d, $J = 9.3$ Hz, 1H), 5.64-5.53 (m, 1H), 1.27 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 169.7, 169.0, 137.3, 137.2, 134.7, 134.2, 133.9, 131.3, 131.2, 130.8, 130.7, 129.5, 129.1, 128.3, 127.9, 127.8, 126.4, 126.3, 82.1, 76.0, 15.8 ppm; IR (KBr) $\nu_{\text{max}}$/cm$^{-1}$: 1754, 1734, 1445, 1275, 1234, 1121, 1062, 746; MS m/z (% base): 208 (100), 180 (15), 152 (75), 76 (10); EA Found: C, 76.91; H, 4.96. Calc. for: C$_{23}$H$_{18}$O$_4$: C, 77.08; H, 5.06%.

3l, white powder; all the characterization data below are of the mixture of diastereoisomers; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J = 7.2$ Hz, 1H), 7.70-7.32 (m, 15H), 6.43 (d, $J = 1.9$ Hz, 1H), 6.03 (d, $J = 3.7$ Hz, 1H), 5.63 (t, $J = 9.6$ Hz, 1H), 5.26-5.07 (m, 5H), 4.46-4.09 (m, 6H), 2.12 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.86 (s, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 170.8, 170.7, 169.8 (2C), 169.5 (2C), 168.3, 168.2, 166.3, 166.0, 140.8, 140.4, 139.7, 137.4, 134.0, 133.8, 133.1, 132.7, 132.5, 132.4, 132.2, 131.7, 131.6, 131.0, 130.7, 130.4, 128.4, 128.3, 128.0 (2C), 126.8, 126.5, 125.9, 125.1 97.2, 95.0, 73.8, 72.3, 71.2, 70.9, 70.1, 69.2, 67.6, 67.4, 61.6, 61.3, 20.9, 20.8 (2C), 20.7, 20.6 (2C) ppm; IR (KBr) $\nu_{\text{max}}$/cm$^{-1}$: 1752, 1370, 1285, 1226, 1017; MS m/z (% base): 224 (0.5), 180 (100), 152 (31), 43 (85); EA Found: C, 60.74; H, 4.80. Calc. for C$_{26}$H$_{24}$O$_{11}$: C, 60.94; H, 4.72%.

Crystal structure of compound 5e:

Crystal structure of compound 3j:

Crystal structure of compound 7:
Copies of $^1$H NMR and $^{13}$C NMR spectra of all the new compounds

2a-$^1$H NMR(CDCl$_3$)

2a-$^{13}$C NMR(CDCl$_3$)
3a-¹H NMR(CDCl₃)

3a-¹³C NMR(CDCl₃)
2b-\textsuperscript{1}H NMR (CDCl\textsubscript{3})

2b-\textsuperscript{13}C NMR (CDCl\textsubscript{3})
2c-1H NMR(CDCl₃)

2c-13C NMR(CDCl₃)


2d-¹H NMR(CDCl₃)

![2d-¹H NMR(CDCl₃) spectrum](image)

2d-¹³C NMR(CDCl₃)

![2d-¹³C NMR(CDCl₃) spectrum](image)
4a-¹H NMR(CDCl₃)

4a-¹³C NMR(CDCl₃)
$^6$-$^1$H NMR (CDCl$_3$)

$^6$-$^{13}$C NMR (CDCl$_3$)
3b-$^1$H NMR (CDCl$_3$)

3b-$^{13}$C NMR (CDCl$_3$)
$3\text{c-}^1\text{H NMR(CDCl}_3\text{)}$

$3\text{c-}^{13}\text{C NMR(CDCl}_3\text{)}$
3d-^1^H NMR(CDCl₃)

3d-^1^3^C NMR(CDCl₃)
$\text{S26}$

$\text{5d-}^1\text{H NMR(CDCl}_3\text{)}$

$\text{5d-}^{13}\text{C NMR(CDCl}_3\text{)}$
7-¹H NMR(CDCl₃)

7-¹³C NMR(CDCl₃)
13-$^1$H NMR(CDCl$_3$)

13-$^{13}$C NMR(CDCl$_3$)
$^3$e-$^1$H NMR (CDCl$_3$)

$^3$e-$^{13}$C NMR (CDCl$_3$)
$^{5\text{e}}$H NMR(CDCl$_3$)

$^{5\text{e}}$C NMR(CDCl$_3$)
3i-¹H NMR(CDCl₃)

3i-¹³C NMR(CDCl₃)
3j from photoreaction of PQ with $^{1}j$ -$^{1}$H NMR(CDCl$_3$)

3j from photoreaction of PQ with $^{1}j$ -$^{13}$C NMR(CDCl$_3$)
3j from photoreaction of PQ with 1k $^1$H NMR(CDCl$_3$)

3j from photoreaction of PQ with 1k $^{13}$C NMR(CDCl$_3$)