Supplementary Figure 1. $^1$H and $^{13}$C NMR spectra for compound 3a
Supplementary Figure 2. $^1$H and $^{13}$C NMR spectra for compound 3b
Supplementary Figure 3. $^1$H and $^{13}$C NMR spectra for compound 3c
Supplementary Figure 4. $^1$H and $^{13}$C NMR spectra for compound 3d
Supplementary Figure 5. $^1$H and $^{13}$C NMR spectra for compound 3e
Supplementary Figure 6. $^1$H and $^{13}$C NMR spectra for compound 3f
Supplementary Figure 7. $^1$H and $^{13}$C NMR spectra for compound 3g
Supplementary Figure 8. $^1$H and $^{13}$C NMR spectra for compound 3h
Supplementary Figure 9. $^1$H and $^{13}$C NMR spectra for compound 3i
Supplementary Figure 10. $^1$H and $^{13}$C NMR spectra for compound 3j
Supplementary Figure 11. $^1$H and $^{13}$C NMR spectra for compound 3k
Supplementary Figure 12. $^1$H and $^{13}$C NMR spectra for compound 3l
Supplementary Figure 13. $^1$H and $^{13}$C NMR spectra for compound 3m
Supplementary Figure 14. $^1$H and $^{13}$C NMR spectra for compound 3n
Supplementary Figure 15. $^1$H and $^{13}$C NMR spectra for compound 3o
Supplementary Figure 16. $^1$H and $^{13}$C NMR spectra for compound 3p
Supplementary Figure 17. $^1$H and $^{13}$C NMR spectra for compound 3q
Supplementary Figure 18. {\textsuperscript{1}H} and {\textsuperscript{13}C} NMR spectra for compound 3r
Supplementary Figure 19. $^1$H and $^{13}$C NMR spectra for compound 3s
Supplementary Figure 20. $^1$H and $^{13}$C NMR spectra for compound 3t
Supplementary Figure 21. $^1$H and $^{13}$C NMR spectra for compound 4a
Supplementary Figure 22. $^1$H and $^{13}$C NMR spectra for compound 4b
Supplementary Figure 23. $^1$H and $^{13}$C NMR spectra for compound 4c
Supplementary Figure 24. $^1$H and $^{13}$C NMR spectra for compound 4d
Supplementary Figure 25. $^1$H and $^{13}$C NMR spectra for compound 4e
Supplementary Figure 26. $^1$H and $^{13}$C NMR spectra for compound 4f
Supplementary Figure 27. $^1$H and $^{13}$C NMR spectra for compound 4g
Supplementary Figure 28. $^1$H and $^{13}$C NMR spectra for compound 4h
Supplementary Figure 29. $^1$H and $^{13}$C NMR spectra for compound 4i
Supplementary Figure 30. $^1$H and $^{13}$C NMR spectra for compound 4j
Supplementary Figure 31. $^1$H and $^{13}$C NMR spectra for compound 8
Supplementary Figure 32. $^1$H and $^{13}$C NMR spectra for compound 9
Supplementary Figure 33. $^1$H and $^{13}$C NMR spectra for compound 10a
Supplementary Figure 34. $^1$H and $^{13}$C NMR spectra for compound 10b
Supplementary Figure 35. $^1$H and $^{13}$C NMR spectra for compound 10c
Supplementary Figure 36. $^1$H and $^{13}$C NMR spectra for compound 11a
Supplementary Figure 37. $^1$H and $^{13}$C NMR spectra for compound 11b
Supplementary Figure 38. $^1$H and $^{13}$C NMR spectra for compound 11c
Supplementary Figure 39. $^1$H-$^1$H NOESY spectrum for compound 4g
Supplementary Figure 40. $^1$H-$^1$H NOESY spectrum for compound 3t
Supplementary Figure 41. $^1$H-$^1$H NOESY spectrum for compound 10b
Supplementary Figure 42. Crystal structure of 3a. ORTEP drawing with 50% probability thermal ellipsoids. Coordinates have been deposited with the Cambridge crystallographic database (CCDC 979092).

Supplementary Figure 43. Crystal structure of 3n. ORTEP drawing with 50% probability thermal ellipsoids. Coordinates have been deposited with the Cambridge crystallographic database (CCDC 979091).
Supplementary Figure 44. HRMS spectrum of $^{18}$O-1n.

Supplementary Figure 45. HRMS spectrum of $^{18}$O-3n obtained from $^{18}$O-1n.
Supplementary Figure 46. HRMS spectrum of $^{18}\text{O}-3n$.

Supplementary Figure 47. HRMS spectrum of $1\text{n}$ after the oxygen scrambling experiment.
Supplementary Figure 48. HRMS spectrum of 3n after the oxygen scrambling experiment.

Supplementary Figure 49. HRMS spectra of the reaction mixture of 1b and 2a.
Supplementary Table 1. Optimization of the Rh-catalyzed reaction of indolyl aldehydes 1 with diphenyl acetylene 2a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Solvent</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>39%</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>none</td>
<td>dioxane</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>none</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>n. r.</td>
</tr>
<tr>
<td>4</td>
<td>Bn</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>48%</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>57%</td>
</tr>
<tr>
<td>6*</td>
<td>Ph</td>
<td>[Cp*Rh(CH₃CN)₃][SbF₆]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>35%</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>[Rh(cod)Cl]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>dioxane</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>60%</td>
</tr>
<tr>
<td>9</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>DCE</td>
<td>42%</td>
</tr>
<tr>
<td>11</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>CH₃CN</td>
<td>trace</td>
</tr>
<tr>
<td>12</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Cu(OAc)₂</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>35%</td>
</tr>
<tr>
<td>13</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>14</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>O₂</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>n. r.</td>
</tr>
<tr>
<td>15</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>-</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>n. r.</td>
</tr>
<tr>
<td>16†</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆/PivOH</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>17‡</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆/CsOPiv</td>
<td>THF</td>
<td>n. r.</td>
</tr>
<tr>
<td>18§</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>54%</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
</tr>
<tr>
<td>20†</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>63%</td>
</tr>
<tr>
<td>21**</td>
<td>Ph</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>THF</td>
<td>67%</td>
</tr>
</tbody>
</table>

Reactions conditions: indolyl aldehyde 1 (0.5 mmol, 2.0 equiv), alkyne 2a (0.25 mmol), catalyst (2.5 mol%), oxidant (2.0 equiv), AgSbF₆ (10 mol%) and solvent (2.0 mL) at 120 °C for 24 h under N₂. *5.0 mol% of catalyst was used. †PivOH (2.0 equiv). ‡CsOPiv (2.0 equiv). §At 100 °C. ¶12 h. ¶¶3.5 mol% of [Cp*RhCl₂]₂ and 14 mol% of AgSbF₆ were used. **1.2 equiv of Ag₂CO₃ and 3.0 mL THF were used. n. r. = no reaction, DCE = 1,2-dichloroethane, THF = tetrahydrofuran, DMF = N,N-dimethylformamide.

Supplementary Methods
1. General Information

All manipulations were carried out under an N₂ atmosphere. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Indolyl aldehydes or ketones¹⁻³, alkynes⁴, [Cp*RhCl₂]₂⁵ and 7-(benzyloxy)-6-isopropyl-1H-indole⁶ were prepared according to the literature procedure. Solvents were dried by refluxing over CaH₂ (for DCE and DMF), P₂O₅ (for CH₃CN and CH₃CH₂CN), or sodium (for 1, 4-dioxane and THF), and freshly distilled prior to use. NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ¹H NMR (400 MHz) chemical shifts and the ¹³C NMR (100 MHz) chemical shifts were measured relative to CDCl₃ as the internal reference. High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI) or a Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E X-ray single crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected.

2. General procedure for the Rh-catalyzed tandem reaction of indolyl aldehydes or ketones with alkynes

General procedure for the reaction of indolyl aldehydes: A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl₂]₂ (5.4 mg, 8.75 μmol, 3.5 mol%), indolyl aldehyde (0.5 mmol), alkyne (0.25 mmol), AgSbF₆ (12.0 mg, 0.035 mmol, 14 mol%), Ag₂CO₃ (82.7 mg, 0.3 mmol) and THF (3.0 mL) under N₂. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH₂Cl₂, filtered through a celite pad, and washed with 10-20 mL of CH₂Cl₂. The combined organic phases were concentrated and the residue was purified by column chromatography on neutral alumina or silica gel to provide the desired product.

General procedure for the reaction of indolyl ketones: A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl₂]₂ (7.8 mg, 12.5 μmol, 5.0
mol%), alkyne (0.25 mmol), indolyl ketone (0.5 mmol), AgSbF₆ (17.2 mg, 0.05 mmol, 20 mol%), Ag₂CO₃ (137.9 mg, 0.5 mmol), H₂O (45 µL, 2.5 mmol) and THF (2.0 mL) under N₂. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH₂Cl₂, filtered through a celite pad, and washed with 10-20 mL of CH₂Cl₂. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel to provide the desired product.

1-Methyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (3a)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 1/1, v/v) afforded 3a as a pale yellow solid (38.5 mg, 46% yield). M.p.: 189-191 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.09 (s, 1H), 7.37-7.33 (m, 1H), 7.24-7.18 (m, 3H), 7.14-7.07 (m, 8H), 6.83 (d, J = 6.8 Hz, 1H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.2, 142.5, 141.7, 141.4, 140.1, 137.5, 131.2, 130.4, 128.9, 128.8, 128.01, 127.97, 127.4, 127.1, 126.9, 126.0, 124.6, 120.3, 104.7, 26.6. HRMS (ESI⁺): calcd for C₂₄H₁₇NNaO [M+Na]⁺ 358.1208, found 358.1205.

1,4,5-Triphenylbenzo[cd]indol-2(1H)-one (3b)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 5/1, v/v) afforded 3b as a pale yellow solid (66.5 mg, 67% yield). M.p.: 212-214 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) (s, 1H), 7.65-7.63 (m, 2H), 7.58 (t, J = 8.0 Hz,
2H), 7.45-7.40 (m, 3H), 7.34-7.32 (m, 3H), 7.25-7.18 (m, 7H), 7.05 (dd, \( J = 6.0 \) Hz, 1.6 Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 167.2, 143.0, 142.0, 141.2, 139.5, 137.4, 135.4, 131.2, 130.4, 129.6, 129.2, 128.9, 128.1, 128.0, 127.6, 127.51, 127.47, 127.0, 126.1, 125.3, 124.7, 120.8, 106.3. HRMS (ESI\(^+\)): calcd for C\(_{29}\)H\(_{20}\)NO [M+H]\(^+\) 398.1545, found 398.1548.

![1-Benzyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (3c)](image)

**1-Benzyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (3c)**

Purification by column chromatography on neutral alumina (petroleum ether/ether = 2/1, v/v) afforded 3c as a pale yellow solid (64.8 mg, 63% yield). M.p.: 176-178 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) (s, 1H), 7.32 (d, \( J = 7.6 \) Hz, 2H), 7.24-7.16 (m, 8H), 7.14-7.07 (m, 7H), 6.71 (d, \( J = 6.0 \) Hz, 1H), 5.10 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 168.0, 142.7, 141.8, 141.3, 139.1, 137.4, 137.0, 131.2, 130.4, 128.90, 128.88, 128.03, 127.97, 127.7, 127.6, 127.4, 127.3, 126.9, 125.7, 124.7, 120.3, 105.8, 44.2. HRMS (ESI\(^+\)): calcd for C\(_{30}\)H\(_{22}\)NO [M+H]\(^+\) 412.1701, found 412.1696.

![1-Isopropyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (3d)](image)

**1-Isopropyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (3d)**

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 3d as a pale yellow solid (55.4 mg, 61% yield). M.p.: 192-194 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) (s, 1H), 7.43-7.39 (m, 1H), 7.33-7.30 (m, 4H), 7.22-7.15 (m, 7H), 7.09 (d, \( J = 6.8 \) Hz, 1H), 4.99-4.88 (m, 1H), 1.61 (d, \( J = 7.2 \) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 167.6, 142.4, 141.6, 141.4, 138.3, 137.5, 131.2, 130.3, 129.0, 128.8, 127.99, 127.95, 127.4, 126.9, 126.8, 126.0, 124.8, 119.9,
106.7, 43.8, 20.9. HRMS (ESI⁺): calcd for C_{26}H_{22}NO [M+H]^+ 364.1701, found 364.1698.

1-(Naphthalen-1-yl)-4,5-diphenyldibenzoc[de]indol-2(1H)-one (3e)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 3e as a pale yellow solid (61.5 mg, 55% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.35 (s, 1H), 8.03-7.98 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 4.4 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H) 7.36-7.33 (m, 4H), 7.26-7.22 (m, 7H), 6.58 (d, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.9, 143.1, 142.1, 141.3, 140.8, 137.5, 134.9, 131.8, 131.2, 130.6, 130.4, 129.5, 129.2, 129.1, 128.7, 128.09, 128.06, 127.8, 127.5, 127.04, 126.98, 126.74, 126.71, 125.9, 125.5, 124.9, 123.5, 120.6, 106.4. HRMS (ESI⁺): calcd for C_{33}H_{21}NNaO [M+Na]^+ 470.1521, found 470.1522.

1-(4-Chlorophenyl)-4,5-diphenyldibenzoc[de]indol-2(1H)-one (3f)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 3f as a pale yellow solid (79.8 mg, 74% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.28 (s, 1H), 7.57 (q, J = 9.2 Hz, 4H), 7.44-7.41 (m, 2H), 7.34-7.32 (m, 3H), 7.24-7.17 (m, 7H), 7.03 (dd, J = 5.6 Hz, 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.1, 143.2, 142.1, 141.1, 139.0, 137.3, 134.0,
133.0, 131.2, 130.4, 129.8, 129.3, 128.9, 128.09, 128.07, 127.8, 127.6, 127.3, 127.0, 125.0, 124.7, 121.0, 106.2. HRMS (ESI\(^+\)): calcd for \( \text{C}_{29}\text{H}_{18}\text{ClNNaO} \) [M+Na]\(^+\) 454.0975, found 454.0977.

1-(4-Methoxyphenyl)-4,5-diphenylbenzo[cd]indol-2(1H)-one (3g)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 1/1, v/v) afforded 3g as a pale yellow solid (68.3 mg, 64% yield). M.p.: 224-227 °C. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) 8.28 (s, 1H), 7.52 (d, \( J = 8.4 \) Hz, 2H), 7.43-7.37 (m, 2H), 7.33-7.32 (m, 3H), 7.24-7.18 (m, 7H), 7.10 (d, \( J = 8.8 \) Hz, 2H), 6.96 (d, \( J = 6.4 \) Hz, 1H), 3.90 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 167.5, 158.9, 142.9, 142.0, 141.3, 140.0, 137.5, 131.2, 130.4, 129.1, 128.9, 128.10, 128.05, 128.0, 127.7, 127.6, 127.5, 126.9, 125.5, 124.6, 120.6, 114.9, 106.0, 55.7. HRMS (ESI\(^+\)): calcd for \( \text{C}_{30}\text{H}_{22}\text{NO}_2 \) [M+H]\(^+\) 428.1651, found 428.1648.

8-Methyl-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3h)

Purification by column chromatography on silica gel (petroleum ether/ether = 6/1, v/v) afforded 3h as a pale yellow solid (69.9 mg, 68% yield). M.p.: 228-230 °C. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) 8.27 (s, 1H), 7.58-7.55 (m, 2H), 7.50-7.47 (m, 3H), 7.33-7.31 (m, 4H), 7.24-7.17 (m, 8H), 1.99 (s, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 168.4, 142.7, 141.3, 140.9, 137.6, 136.9, 136.2, 134.0, 131.2, 130.4, 129.5, 128.9, 128.6, 128.0, 127.9, 127.45, 127.43, 126.8, 125.2, 124.9, 120.7, 117.9, 17.9.

6-Methoxy-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3i)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 5/1, v/v) afforded 3i as a pale yellow solid (81.2 mg, 76% yield). M.p.: 185-187 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.26 (s, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.20-7.11 (m, 10H), 6.98 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.0, 154.3, 143.0, 142.4, 141.4, 140.2, 135.6, 132.8, 130.4, 130.3, 129.5, 127.9, 127.7, 127.2, 126.7, 126.6, 126.5, 126.0, 125.8, 125.3, 121.6, 107.6, 107.4, 56.1. HRMS (ESI⁺): calcd for C₃₀H₂₁NNaO₂ [M+Na]⁺ 450.1470, found 450.1474.

6-Benzylxy-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3j)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 1/1, v/v) afforded 3j as a pale yellow solid (88.1 mg, 70% yield). M.p.: 233-235 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.25 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.20-7.12 (m, 8H), 7.08-7.02 (m, 5H), 6.96 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 6.0 Hz, 2H), 6.77 (d, J = 7.6 Hz, 1H), 4.80 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 167.0, 153.2, 143.4, 142.5, 141.5, 140.1, 136.2, 135.6, 132.9, 130.4, 130.3, 129.6, 128.2, 127.9, 127.63, 127.58, 127.28, 127.26, 126.9, 126.7, 126.6, 126.0, 125.9, 125.3, 121.6, 108.6, 107.4, 71.0. HRMS (ESI⁺): calcd for C₃₆H₂₆NO₂ [M+H]⁺ 504.1964, found 504.1964.
6-Chloro-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3k)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 5/1, v/v) afforded 3k as a pale yellow solid (62.5 mg, 58% yield). M.p.: 208-210 °C. 
$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.25 (s, 1H), 7.60-7.56 (m, 4H), 7.45 (d, $J = 7.2$ Hz, 2H), 7.24-7.15 (m, 8H), 7.11-7.09 (m, 2H), 6.95 (d, $J = 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 166.7, 144.8, 142.9, 141.0, 138.8, 138.1, 134.9, 131.12, 131.08, 130.1, 129.7, 128.1, 127.8, 127.7, 127.4, 127.3, 126.9, 126.2, 126.01, 125.97, 125.8, 125.7, 107.1. HRMS (ESI$^+$): calcd for C$_{29}$H$_{19}$ClNO [M+H]$^+$ 432.1155, found 432.1154.

7-Chloro-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3l)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 7/1, v/v) afforded 3l as a pale yellow solid (72.2 mg, 67% yield). M.p.: 243-244 °C. 
$^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.25 (s, 1H), 7.60 (d, $J = 4.4$ Hz, 4H), 7.46-7.44 (m, 1H), 7.47-7.43 (m, 1H), 7.38 (s, 1H), 7.35-7.34 (m, 3H), 7.22-7.16 (m, 7H), 7.01 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.0, 143.1, 142.4, 140.8, 140.6, 136.8, 135.2, 134.9, 131.1, 130.3, 129.8, 129.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.2, 126.1, 125.0, 123.3, 119.4, 107.7. HRMS (ESI$^+$): calcd for C$_{29}$H$_{18}$ClNO$_2$Na [M+Na]$^+$ 454.0975, found 454.0974.
Methyl 2-oxo-1,4,5-triphenyl-1,2-dihydrobenzo[cd]indole-7-carboxylate (3m)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 6/1, v/v) afforded 3m as a pale yellow solid (64.9 mg, 57% yield). M.p.: 208-210 °C.

1H NMR (400 MHz, CDCl3): δ (ppm) 8.37 (s, 1H), 8.23 (s, 1H), 7.65-7.58 (m, 5H), 7.46 (t, J = 7.2 Hz, 1H), 7.37-7.35 (m, 3H), 7.24-7.23 (m, 5H), 7.19-7.16 (m, 2H), 3.89 (s, 3H). 13C NMR (100 MHz, CDCl3): δ (ppm) 167.2, 166.9, 144.5, 142.9, 140.8, 139.9, 136.7, 135.1, 131.2, 130.3, 129.79, 129.77, 128.3, 128.21, 128.17, 127.9, 127.8, 127.2, 126.8, 126.2, 125.3, 124.5, 105.7, 52.6. HRMS (ESI⁺): calcd for C31H21NNaO3 [M+Na]⁺ 478.1419, found 478.1414.

3-Ethyl-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3n)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3n as a pale yellow solid (31.9 mg, 30% yield). M.p.: 225-227 °C.

1H NMR (400 MHz, CDCl3): δ (ppm) 7.66 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.25-7.19 (m, 7H), 7.15-7.10 (m, 4H), 7.06 (d, J = 7.2 Hz, 1H), 3.14 (q, J = 7.6 Hz, 2H), 1.16 (t, J = 7.6 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ (ppm) 167.5, 146.4, 144.2, 143.0, 139.0, 138.5, 138.0, 135.6, 130.8, 130.7, 129.5, 127.70, 127.66, 127.53, 127.50, 127.3, 127.0, 126.9, 126.2, 124.9, 121.4, 120.5, 106.0, 22.9, 15.4. HRMS (ESI⁺): calcd for C31H24NO [M+H]⁺ 426.1858, found 426.1856.
3-Methyl-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3o)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3o as a pale yellow solid (63.7 mg, 62% yield). M.p.: 203-204 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.64 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 8.0$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.26-7.19 (m, 7H), 7.16-7.13 (m, 2H), 7.08-7.04 (m, 3H), 2.68 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.9, 146.63, 146.61, 140.0, 139.3, 138.4, 137.9, 135.7, 130.8, 130.6, 129.5, 128.0, 127.62, 127.59, 127.5, 127.3, 127.1, 126.9, 126.3, 124.6, 122.0, 120.5, 106.0, 16.4. HRMS (ESI$^+$): calcd for C$_{30}$H$_{22}$NO $[M+H]^+$ 412.1701, found 412.1703.

3-Benzyl-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3p)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1, v/v) afforded 3p as a pale yellow solid (86.5 mg, 71% yield). M.p.: 221-223 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.68 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 8.0$ Hz, 2H), 7.45-7.37 (m, 2H), 7.25-7.19 (m, 4H), 7.16-7.08 (m, 6H), 7.05-7.04 (m, 3H), 6.87 (d, $J = 6.0$ Hz, 2H), 6.84-6.82 (m, 2H), 4.67 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.8, 144.6, 143.7, 142.0, 139.9, 138.6, 138.5, 137.8, 135.6, 131.2, 130.7, 129.5, 129.1, 128.02, 127.95, 127.6, 127.5, 127.4, 127.1, 126.9, 126.2, 125.8, 124.7, 122.3, 120.6, 106.1, 34.4. HRMS (ESI$^+$): calcd for C$_{36}$H$_{26}$NO $[M+H]^+$ 488.2014, found 488.2012.
3-Benzyl-7-chloro-1,4,5-triphenylbenzo[cd]indol-2(1H)-one (3q)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 13/1, v/v) afforded 3q as a pale yellow solid (79.5 mg, 61% yield). M.p.: 220-221 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.65-7.58 (m, 4H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.22-7.20 (m, 4H), 7.16-7.10 (m, 3H), 7.07-7.04 (m, 6H), 6.84 (d, $J = 6.8$ Hz, 2H), 6.80 (t, $J = 3.6$ Hz, 2H), 4.62 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.7, 144.8, 144.1, 142.2, 139.7, 139.6, 138.2, 137.2, 135.0, 134.2, 131.0, 130.6, 129.7, 129.1, 128.2, 128.0, 127.8, 127.71, 127.68, 127.3, 127.1, 126.2, 125.9, 123.4, 122.1, 119.2, 107.5, 34.4. HRMS (ESI$^+$): calcd for C$_{36}$H$_{25}$ClNO [M+H]$^+$ 522.1625, found 522.1631.

4,5-Bis(4-methoxyphenyl)-3-methyl-1-phenylbenzo[cd]indol-2(1H)-one (3r)

Purification by column chromatography on silica gel (toluene/ether = 50/1, v/v) afforded 3r as a pale yellow solid (67.1 mg, 57% yield). M.p.: 236-238 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.63 (dd, $J = 8.8$ Hz, 1.6 Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 2H), 7.41 (tt, $J = 7.2$ Hz, 1.6 Hz, 1H), 7.37-7.33 (m, 1H), 7.27 (d, $J = 9.6$ Hz, 1H), 7.08-7.02 (m, 3H), 6.98-6.95 (m, 2H), 6.80 (d, $J = 8.4$ Hz, 4H), 3.802 (s, 3H), 3.795 (s, 3H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 168.0, 158.5, 158.3, 143.7, 143.5, 140.5, 138.3, 135.7, 132.0, 131.7, 131.6, 130.3, 129.5, 127.8, 127.4, 127.3, 126.3, 124.6, 121.8, 120.6, 113.5, 113.2, 105.8, 55.29, 55.28, 16.5. HRMS (ESI$^+$):
3-Benzyl-1-phenyl-4,5-dip-tolylbenzo[cd]indol-2(1H)-one (3s)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) afforded 3s as a pale yellow solid (77.3 mg, 60% yield). M.p.: 198-199 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.67 (d, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 8.0$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.24 (dd, $J = 8.8$ Hz, 2.0 Hz, 1H), 7.08-6.98 (m, 8H), 6.94 (d, $J = 7.6$ Hz, 2H), 6.87-6.85 (m, 2H), 6.76 (d, $J = 7.6$ Hz, 2H), 4.64 (s, 2H), 2.31 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.8, 144.7, 143.7, 142.3, 140.1, 138.5, 136.5, 136.3, 135.63, 135.61, 134.9, 131.0, 130.6, 129.5, 129.1, 128.32, 128.25, 128.2, 127.9, 127.8, 127.3, 126.2, 125.7, 124.7, 122.1, 120.7, 106.0, 34.4, 21.4. HRMS (ESI$^+$): calcd for C$_{38}$H$_{30}$NO $[M+H]^+$ 516.2327, found 516.2320.

3-Benzyl-5-ethyl-6-methoxy-1,4-diphenylbenzo[cd]indol-2(1H)-one (3t)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1, v/v) afforded 3t as a pale yellow solid (62.2 mg, 53% yield). M.p.: 78-79 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.65 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 8.0$ Hz, 2H), 7.41-7.32 (m, 4H), 7.05-7.00 (m, 4H), 6.96 (d, $J = 6.8$ Hz, 2H), 6.78-6.75 (m, 3H), 4.49 (s, 2H), 3.98 (s, 3H), 3.01 (q, $J = 7.2$ Hz, 2H), 1.06 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR
1-Phenyl-4,5-dim-tolylbenzo[cd]indol-2(1H)-one (4a)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 5/1, v/v) afforded 4a as a pale yellow solid (63.8 mg, 60% yield). M.p.: 178-179 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.27 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 2H), 7.58 (t, $J$ = 8.4 Hz, 2H), 7.44-7.40 (m, 3H), 7.16-7.02 (m, 9H), 2.39 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.3, 143.0, 141.9, 139.4, 138.4, 137.1, 136.5, 135.5, 134.5, 131.1, 130.2, 129.6, 129.4, 128.82, 128.80, 128.7, 127.8, 127.4, 126.1, 125.1, 124.6, 120.9, 106.1, 21.4, 21.3. HRMS (ESI$^+$): calcd for C$_{31}$H$_{23}$NNaO [M+Na]$^+$ 448.1677, found 448.1680.

1-Phenyl-4,5-dip-tolylbenzo[cd]indol-2(1H)-one (4b)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 5/1, v/v) afforded 4a as a pale yellow solid (63.8 mg, 60% yield). M.p.: 178-179 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.27 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 2H), 7.58 (t, $J$ = 8.4 Hz, 2H), 7.44-7.40 (m, 3H), 7.16-7.02 (m, 9H), 2.39 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.3, 143.0, 141.9, 139.4, 138.4, 137.1, 136.5, 135.5, 134.5, 131.1, 130.2, 129.6, 129.4, 128.82, 128.80, 128.7, 127.8, 127.4, 126.1, 125.1, 124.6, 120.9, 106.1, 21.4, 21.3. HRMS (ESI$^+$): calcd for C$_{31}$H$_{23}$NNaO [M+Na]$^+$ 448.1677, found 448.1680.
= 8.0 Hz, 2H), 7.44-7.41 (m, 3H), 7.21 (t, \(J = 7.6\) Hz, 1H), 7.14-7.01 (m, 7H), 6.95 (d, \(J = 7.2\) Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) 167.3, 143.1, 142.0, 141.2, 139.5, 137.6, 137.5, 137.4, 135.5, 131.8, 131.1, 129.6, 129.2, 128.7, 128.3, 128.2, 127.84, 127.77, 127.7, 127.6, 127.5, 127.4, 126.1, 125.1, 124.6, 120.9, 106.2, 21.54, 21.49. HRMS (ESI\(^+\)): calcd for C\(_{31}\)H\(_{24}\)NO \([M+H]\)^+ 426.1858, found 426.1861.

**4,5-Bis(4-methoxyphenyl)-1-phenylbenzo[cd]indol-2(1H)-one (4c)**

Purification by column chromatography on silica gel (toluene/ether = 25/1, v/v) afforded 4c as a pale yellow solid (60.6 mg, 53% yield). M.p.: 230-232 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.26 (s, 1H), 7.63 (d, \(J = 8.0\) Hz, 2H), 7.57 (t, \(J = 8.0\) Hz, 2H), 7.44-7.38 (m, 3H), 7.16-7.10 (m, 4H), 7.02 (dd, \(J = 6.0\) Hz, 1.6 Hz, 1H), 6.89 (d, \(J = 8.4\) Hz, 2H), 6.79 (d, \(J = 8.8\) Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) 167.3, 159.0, 158.5, 142.6, 141.7, 139.5, 135.5, 133.8, 132.4, 131.5, 129.8, 129.6, 129.5, 128.7, 127.8, 127.4, 126.1, 125.0, 124.6, 120.8, 113.6, 106.1, 55.4, 55.3. HRMS (ESI\(^+\)): calcd for C\(_{31}\)H\(_{24}\)NO\(_3\) [M+H]\(^+\) 458.1756, found 458.1758.
4,5-Bis(4-fluorophenyl)-1-phenylbenzo[cd]indol-2(1H)-one (4d)
Purification by column chromatography on neutral alumina (petroleum ether/ether = 3/1, v/v) afforded 4d as a pale yellow solid (79.0 mg, 73% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.23 (s, 1H), 7.64-7.56 (m, 4H), 7.46-7.41 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.20-7.17 (m, 2H), 7.15-7.11 (m, 2H), 7.07-7.03 (m, 3H), 6.97-6.93 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.0, 163.6, 163.2, 161.1, 160.8, 141.9, 141.1, 139.6, 137.08, 137.05, 135.4, 133.20, 133.17, 132.83, 132.75, 132.0, 131.9, 129.7, 129.2, 127.6, 127.3, 126.1, 125.6, 124.8, 120.4, 115.5, 115.4, 115.24, 115.15, 106.5. HRMS (ESI$^+$): calcd for C$_{29}$H$_{17}$F$_2$NNaO [M+Na]$^+$ 456.1176, found 456.1173.

![Chemical structure of 4d](image)

4,5-Bis(4-chlorophenyl)-1-phenylbenzo[cd]indol-2(1H)-one (4e)
Purification by column chromatography on neutral alumina (petroleum ether/ether = 3/1, v/v) afforded 4e as a pale yellow solid (74.4 mg, 64% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.22 (s, 1H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 2H), 7.46-7.42 (m, 2H), 7.34 (d, $J = 8.4$ Hz, 3H), 7.24 (d, $J = 8.8$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 7.06 (d, $J = 6.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.0, 143.1, 142.4, 140.8, 140.6, 136.8, 135.2, 134.9, 131.1, 130.3, 129.8, 129.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.2, 126.1, 125.0, 123.3, 119.4, 107.7. HRMS (ESI$^+$): calcd for C$_{29}$H$_{17}$Cl$_2$NNaO [M+Na]$^+$ 488.0585, found 488.0590.
4,5-Bis(4-bromophenyl)-1-phenylbenzo[cd]indol-2(1H)-one (4f)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 4f as a pale yellow solid (78.8 mg, 57% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.21 (s, 1H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.46-7.39 (m, 4H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 7.06-7.03 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 166.9, 141.4, 140.6, 139.8, 139.6, 136.0, 135.2, 132.7, 131.9, 131.6, 131.5, 129.7, 129.4, 129.0, 127.6, 127.1, 126.1, 125.8, 124.8, 122.2, 121.7, 120.3, 106.6. HRMS (ESI$^+$): calcd for C$_{29}$H$_{18}$Br$_2$NO [M+H]$^+$ 553.9755, found 553.9755.

5-Ethyl-1,4-diphenylbenzo[cd]indol-2(1H)-one (4g)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 4g as a pale yellow solid (49.8 mg, 57% yield). M.p.: 143-145 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.05 (s, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.62-7.54 (m, 4H), 7.52-7.38 (m, 7H), 7.04 (d, $J = 7.2$ Hz, 1H), 3.10 (q, $J = 7.6$ Hz, 2H), 1.26 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.3, 144.7, 142.3, 141.7, 140.1, 135.5, 129.5, 129.4, 128.7, 128.6, 128.4, 127.54, 127.50, 127.3, 126.1, 125.0, 123.6, 118.8, 106.1, 23.0, 16.7. HRMS (ESI$^-$): calcd for C$_{25}$H$_{20}$NO [M+H]$^-$ 350.1545, found 350.1546.
5-Ethyl-6-methoxy-1,4-diphenylbenzo[cd]indol-2(1H)-one (4h)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 4h as a pale yellow solid (63.5 mg, 67% yield). M.p.: 157-158 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.05 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.48-7.35 (m, 6H), 6.96 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.99 (s, 3H), 3.24 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.1, 154.7, 146.3, 143.0, 142.2, 135.7, 132.9, 129.54, 129.47, 128.3, 128.0, 127.3, 127.1, 126.4, 126.0, 123.4, 121.6, 106.9, 106.2, 56.0, 25.5, 16.7. HRMS (ESI$^+$): calcd for C$_{26}$H$_{22}$NO$_2$ [M+H]$^+$ 380.1651, found 380.1651.

5-Cyclopropyl-6-methoxy-1,4-diphenylbenzo[cd]indol-2(1H)-one (4i)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 3/1, v/v) afforded 4i as a pale yellow solid (53.8 mg, 55% yield). M.p.: 176-177 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.16 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 4.00 (s, 3H), 2.57-2.50 (m, 1H), 0.85 (d, J = 8.0 Hz, 2H), 0.21 (d, J = 5.6 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 166.9, 154.7, 144.31, 144.27, 142.9, 135.7, 132.6, 130.0, 129.5, 128.3, 128.2, 127.1, 127.0, 126.0, 125.8, 124.5, 124.2, 106.9, 106.4, 56.0, 16.4, 11.7. HRMS (ESI$^+$): calcd for C$_{27}$H$_{21}$NNaO$_2$ [M+Na]$^+$ 414.1470, found 414.1470.
6-Methoxy-1-phenyl-4,5-dipropylbenzo[cd]indol-2(1H)-one (4j)

Purification by column chromatography on neutral alumina (petroleum ether/ether = 4/1, v/v) afforded 4j as a pale yellow solid (49.4 mg, 55% yield). M.p.: 135-137 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.05 (s, 1H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 8.0$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 3.97 (s, 3H), 3.33 (t, $J = 8.0$ Hz, 2H), 2.89 (t, $J = 8.0$ Hz, 2H), 1.75-1.63 (m, 4H), 1.11 (t, $J = 7.2$ Hz, 3H), 1.05 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 167.3, 154.5, 144.6, 141.5, 135.8, 132.8, 129.5, 127.9, 127.0, 126.1, 125.7, 123.6, 122.0, 106.2, 105.8, 56.0, 36.1, 33.0, 25.6, 25.3, 15.0, 14.4. HRMS (ESI$^+$): calcd for C$_{24}$H$_{26}$NO$_2$ [M+H]$^+$ 360.1964, found 360.1960.

3. Synthesis of priolines
1-Benzyl-7-(benzyloxy)-6-isopropyl-1H-indole (8)

7-(Benzyloxy)-6-isopropyl-1H-indole (7, 2.65 g, 10.0 mmol) in 30 mL of DMF was treated with a suspension of NaH (0.80 g, 20.0 mmol, 60% dispersion in mineral oil) in small portions at room temperature. The reaction mixture was stirred at room temperature for 1 h, followed by the addition of BnBr (3.56 mL, 30.0 mmol). The reaction mixture was heated at 60 °C overnight. The reaction mixture was cooled, diluted with EtOAc, washed with H2O and saturated aqueous NaCl, and dried over Na2SO4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ether = 20/1, v/v) to provide 1-benzyl-7-(benzyloxy)-6-isopropyl-1H-indole 8 as brown oil (2.98 g, 84% yield). 1H NMR (400 MHz, CDCl3): δ (ppm) 7.52 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.40-7.35 (m, 3H), 7.32 (d, J = 7.2 Hz, 2H), 7.26-7.24 (m, 3H), 7.09 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.00-6.98 (m, 3H), 6.56-6.54 (m, 1H), 5.61 (s, 2H), 4.84 (s, 2H), 3.61-3.50 (m, 1H), 1.33 (dd, J = 7.2 Hz, 2.0 Hz, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm) 142.2, 139.3, 137.4, 135.0, 129.8, 129.4, 129.3, 128.7, 128.6, 128.0, 127.34, 127.27, 126.6, 118.6, 117.5, 102.7, 77.0, 51.3, 26.0, 24.7. HRMS (ESI+): calcd for C25H26NO [M+H]+ 356.2014, found 356.2017.

1-(1-Benzyl-7-(benzyloxy)-6-isopropyl-1H-indol-3-yl)ethanone (9)

A Schlenk tube with a magnetic stir bar was charged with Pd(OAc)2 (188.1 mg, 0.84 mmol), 1,10-phenanthroline (302.52 mg, 1.68 mmol), 1-benzyl-7-(benzyloxy)-6-isopropyl-1H-indole 8 (2.98 g, 8.4 mmol), H2O (3.36 mL), CH3COOH (5.04 mL) and acetonitrile (20 mL) under air. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 36 h. The reaction mixture was cooled, diluted with EtOAc, washed with H2O and saturated aqueous NaCl, and dried over Na2SO4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/
EtOAc = 5/1, v/v) to provide 1-(1-benzyl-7-(benzyloxy)-6-isopropyl-1H-indol-3-yl)ethanone 9 as a white solid (2.24 g, 67% yield). M.p.: 110-111 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 8.21 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.39-7.36 (m, 3H), 7.31-7.28 (m, 6H), 7.02-6.99 (m, 2H), 5.61 (s, 2H), 4.83 (s, 2H), 3.57-3.47 (m, 1H), 2.49 (s, 3H), 1.32 (d, J = 6.8 Hz, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm) 193.1, 142.2, 137.7, 136.94, 136.90, 136.1, 130.2, 129.0, 128.7, 128.2, 127.9, 127.3, 127.2, 126.7, 121.9, 119.1, 118.0, 77.5, 52.0, 27.8, 26.1, 24.5. HRMS (ESI+): calcd for C27H28NO2 [M+H]+ 398.2120, found 398.2116.

1-Phenyl-8-(benzyloxy)-7-isopropyl-3-methyl-4,5-diphenylbenzo[cd]indol-2(1H)-one (10a)

According to the general procedure, purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 12/1, v/v) afforded 10a as a pale yellow solid (75.9 mg, 53% yield). M.p.: 194-196 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.42-7.37 (m, 3H), 7.32 (d, J = 7.2 Hz, 5H), 7.24-7.17 (m, 8H), 7.14-7.12 (m, 3H), 7.03 (d, J = 6.8 Hz, 2H), 5.35 (s, 2H), 4.79 (s, 2H), 3.43-3.34 (m, 1H), 2.64 (s, 3H), 1.20 (d, J = 6.8 Hz, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm) 169.2, 145.9, 142.7, 142.2, 139.5, 139.0, 138.9, 138.3, 138.0, 136.7, 130.8, 130.7, 128.7, 128.6, 128.3, 127.9, 127.52, 127.48, 127.34, 127.27, 127.2, 127.0, 126.7, 125.4, 124.8, 121.9, 118.1, 77.7, 45.0, 27.4, 24.4, 16.4. HRMS (ESI+): calcd for C41H36NO2 [M+H]+ 574.2746, found 574.2748.
1-Benzyl-8-(benzyloxy)-5-ethyl-7-isopropyl-3-methyl-4-phenylbenzo[cd]indol-2(1H)-one (10b)

According to the general procedure, purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 12/1, v/v) afforded 10b as a pale yellow solid (52.5 mg, 40% yield). M.p.: 147-149 °C. \( ^{1} \mathrm{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) 7.59 (s, 1H), 7.49 (t, \( J = 7.6 \) Hz, 2H), 7.44-7.36 (m, 4H), 7.32-7.27 (m, 4H), 7.24-7.18 (m, 5H), 5.30 (s, 2H), 4.77 (s, 2H), 4.50-3.41 (m, 1H), 2.85 (q, \( J = 7.6 \) Hz, 2H), 2.48 (s, 3H), 1.36 (d, \( J = 6.8 \) Hz, 6H), 1.17 (t, \( J = 7.6 \) Hz, 3H). \( ^{13} \mathrm{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) (ppm) 169.3, 145.5, 143.7, 142.4, 140.1, 139.2, 138.6, 138.3, 138.6, 129.6, 128.6, 128.67, 128.6, 128.3, 128.1, 127.3, 127.2, 127.1, 125.7, 124.1, 120.6, 115.9, 77.6, 44.9, 27.4, 24.6, 23.6, 16.38, 16.36. HRMS (ESI\(^{+}\)): calcd for C\(_{37}\)H\(_{36}\)NO\(_2\) [M+H]\(^{+}\) 526.2746, found 526.2743.

1-Benzyl-8-(benzyloxy)-7-isopropyl-3-methyl-4,5-dipropylbenzo[cd]indol-2(1H)-one (10c)

According to the general procedure, purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 12/1, v/v) afforded 10c as a pale yellow solid (30.3 mg, 24% yield). M.p.: 138-139 °C. \( ^{1} \mathrm{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) 7.52 (s, 1H), 7.40-7.35 (m, 3H), 7.29-7.24 (m, 4H), 7.22-7.16 (m, 3H), 5.28 (s, 2H), 4.74 (s, 2H), 3.45-3.40 (m, 1H), 3.12-3.08 (m, 2H), 2.88 (s, 3H), 2.86-2.82 (m, 2H), 1.78-1.68 (m, 2H), 1.62-1.55 (m, 2H), 1.35 (d, \( J = 6.8 \) Hz, 6H), 1.16-1.09 (m, 6H). \( ^{13} \mathrm{C} \) NMR
A solution of 10a (86.0 mg, 0.15 mmol) and anisole (324.4 mg, 3.0 mmol) in trifluoroacetic acid (5.0 mL) was heated at reflux under N2 for 3 days. The solvent and excess anisole were removed under vacuum. The residue was dissolved in EtOAc, and NEt3 was added with stirring. Water was then added, and the organic layer was washed with brine, dried MgSO4 and concentrated to yield a solid residue, which was recrystallized from EtOH to provide 8-hydroxy-7-isopropyl-3-methyl-4,5-diphenylbenzo[cd]indol-2(1H)-one 11a as a pale yellow solid (42.5 mg, 72% yield). M.p.: > 250 °C. 1H NMR (400 MHz, DMSO-d6): δ (ppm) 9.69 (s, 1H), 9.64 (s, 1H), 7.23-7.16 (m, 6H), 7.10-7.04 (m, 4H), 6.84 (s, 1H), 2.43 (s, 3H), 1.23 (s, 1H), 1.12 (d, J = 6.4 Hz, 6H). 13C NMR (100 MHz, DMSO-d6): δ (ppm) 168.1, 141.8, 141.3, 139.8, 139.2, 137.7, 136.7, 136.9, 136.2, 130.4, 130.3, 127.6, 127.3, 126.8, 126.4, 125.2, 121.7, 121.1, 118.7, 115.6, 27.6, 22.7, 15.5. HRMS (ESI–): calcd for C27H24NO2 [M+H]+ 394.1807, found 394.1800.

5-Ethyl-8-hydroxy-7-isopropyl-3-methyl-4-phenylbenzo[cd]indol-2(1H)-one (11b)
A solution of 10b (78.8 mg, 0.15 mmol) and anisole (324.4 mg, 3.0 mmol) in trifluoroacetic acid (5.0 mL) was heated at reflux under N2 for 3 days. The solvent
and excess anisole were removed under vacuum. The residue was dissolved in EtOAc, and NEt₃ was added with stirring. Water was then added, and the organic layer was washed with brine, dried MgSO₄ and concentrated to yield a solid residue, which was recrystallized from EtOH to provide 8-hydroxy-7-isopropyl-3-methyl-4,5-diphenylbenzo[c,d]indol-2(1H)-one 11b as a pale yellow solid (35.2 mg, 68% yield). M.p.: 237-238 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.83 (s, 1H), 9.93 (s, 1H), 7.59 (s, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 6.8 Hz, 2H), 3.56-3.46 (m, 1H), 2.86 (q, J = 7.6 Hz, 2H), 2.56 (s, 3H), 1.35 (d, J = 6.8 Hz, 6H), 1.16 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.9, 145.6, 141.5, 140.48, 140.45, 140.0, 139.2, 130.0, 128.7, 127.2, 126.4, 121.6, 119.6, 117.6, 116.6, 28.6, 23.7, 23.1, 17.1, 16.6. HRMS (ESI⁺): calcd for C₂₃H₂₄NO₂ [M+H]+ 346.1807, found 346.1808.

![Chemical structure of 8-hydroxy-7-isopropyl-3-methyl-4,5-diphenylbenzo[c,d]indol-2(1H)-one 11b]

8-Hydroxy-7-isopropyl-3-methyl-4,5-dipropylbenzo[c,d]indol-2(1H)-one (11c)

A solution of 10c (50.5 mg, 0.10 mmol) and anisole (216.3 mg, 2.0 mmol) in trifluoroacetic acid (3.0 mL) was heated at reflux under N₂ for 3 days. The solvent and excess anisole were removed under vacuum. The residue was dissolved in EtOAc, and NEt₃ was added with stirring. Water was then added, and the organic layer was washed with brine, dried MgSO₄ and concentrated to yield a solid residue, which was recrystallized from EtOH to provide 8-hydroxy-7-isopropyl-3-methyl-4,5-diphenylbenzo[c,d]indol-2(1H)-one 11c as a pale yellow solid (18.2 mg, 56% yield). M.p.: 218-220 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.54 (s, 1H), 9.54 (s, 1H), 7.53 (s, 1H), 3.56-3.53 (m, 1H), 3.11 (s, 2H), 2.85 (s, 2H), 1.75-1.70 (m, 4H), 1.40 (d, J = 6.8 Hz, 6H), 1.14 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.0, 143.6, 140.9, 140.3, 138.5, 138.0, 125.5.

4. ^18O-Labeling experiments

4.1. Preparation of ^18O-1n

A flame-dried Schlenk tube with a magnetic stir bar was charged with Pd(OAc)\textsubscript{2} (22.5 mg, 0.1 mmol), 2,2'-bipyridine (18.7 mg, 0.12 mmol), D-(-)-camphorsulfonic acid (D-CSA) (348.5 mg, 1.5 mmol), 1-phenyl-1H-indole (193.1 mg, 1.0 mmol), H\textsubscript{2}^{18}O (200 µL, 10.0 mmol), and propionitrile (1.5 mL) under N\textsubscript{2}. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 36 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of ethyl acetate, filtered through a celite pad, and washed with 10-20 mL of ethyl acetate. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) to provide the desired (151.9 mg, 61% yield). HRMS analysis showed that the abundance of ^18O in 1n was 82% (For HRMS spectrum of ^18O-1n, see Supplementary Fig. 44).

4.2. Synthesis of ^18O-3n from ^18O-1n

A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl\textsubscript{2}]\textsubscript{2} (7.8 mg, 12.5 µmol), ^18O-1n (124.6 mg, 0.50 mmol), diphenyl acetylene 2a (44.5 mg,
0.25 mmol), AgSbF<sub>6</sub> (17.2 mg, 0.05 mmol), Ag<sub>2</sub>CO<sub>3</sub> (137.9 mg, 0.5 mmol) and THF (2.0 mL) under N<sub>2</sub>. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 10-20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide 27.6 mg of 3n in 26% yield. HRMS analysis showed that the abundance of O in 3n was 64%, indicating that the oxygen of the carbonyl group in 3n originated from the initial material 1n (For HRMS spectrum of 18O-3n obtained from 18O-1n, see Supplementary Fig. 45). The lower abundance of O in 3n than in 1n probably attributed to trace amounts of H<sub>2</sub>O in the reaction system.

### 4.3. The reaction of 1n with 2a in the presence of H<sub>2</sub>O

A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl<sub>2</sub>] (7.8 mg, 12.5 µmol), 1-(1-phenyl-1H-indol-3-yl)propan-1-one 1n (124.6 mg, 0.50 mmol), diphenyl acetylene 2a (44.5 mg, 0.25 mmol), AgSbF<sub>6</sub> (17.2 mg, 0.05 mmol), Ag<sub>2</sub>CO<sub>3</sub> (137.9 mg, 0.50 mmol), H<sub>2</sub>18O (50.0 µL), and THF (2.0 mL) under N<sub>2</sub>. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 10-20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide 3n (62.7 mg, 59% yield). HRMS analysis showed that the abundance of O in 3n was 83%, suggesting that H<sub>2</sub>O might participate in the reaction (For HRMS
4.4. Oxygen scrambling experiment of 1n with H$_2^{18}$O

A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl$_2$]$_2$ (7.8 mg, 12.5 µmol), 1-(1-phenyl-1H-indol-3-yl)propan-1-one 1n (124.6 mg, 0.50 mmol), AgSbF$_6$ (17.2 mg, 0.05 mmol), Ag$_2$CO$_3$ (137.9 mg, 0.50 mmol), H$_2$^{18}O (50.0 µL, 2.5 mmol), and THF (2.0 mL) under N$_2$. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH$_2$Cl$_2$, filtered through a celite pad, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) to provide 108.4 mg of 1n. HRMS analysis showed that the abundance of $^{18}$O in 1n was 69%, demonstrating the oxygen scrambling between 1n and H$_2^{18}$O (Supplementary Fig. 47).

4.5. Oxygen scrambling experiment of 3n with H$_2^{18}$O

A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl$_2$]$_2$ (7.8 mg, 12.5 µmol), 3-ethyl-1,4,5-triphenylbenzo[cd]indol-2(1H)-one 3n (106.3 mg, 0.25 mmol), AgSbF$_6$ (17.2 mg, 0.05 mmol), Ag$_2$CO$_3$ (137.9 mg, 0.50 mmol), H$_2$^{18}O (50.0 µL, 2.5 mmol), and THF (2.0 mL) under N$_2$. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The
mixture was then cooled to ambient temperature, diluted with 10 mL of CH$_2$Cl$_2$, filtered through a celite pad, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide 99.9 mg of 3n. The abundance of $^{18}$O in 3n was 4% as determined by HRMS, indicating that the oxygen scrambling between 3n and H$_2^{18}$O did not occur under the current catalytic system (Supplementary Fig. 48).

5. Detection of the reaction intermediates

5.1. Detection of the intermediate E’ by HRMS

A flame-dried Schlenk tube with a magnetic stir bar was charged with [Cp*RhCl$_2$]$_2$ (5.4 mg, 8.75 µmol), N-phenyl-indolyl-3-carbaldehyde 1b (110.5 mg, 0.50 mmol), diphenyl acetylene 2a (44.5 mg, 0.25 mmol), AgSbF$_6$ (12.0 mg, 0.035 mmol), Ag$_2$CO$_3$ (82.7 mg, 0.30 mmol) and THF (2.0 mL) under N$_2$. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 2 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH$_2$Cl$_2$, filtered through a celite pad, and washed with 10-20 mL of CH$_2$Cl$_2$. The combined organic phases were evaporated to afford the crude product, which was analyzed by HRMS. As shown in Figure S6, a peak at m/z 400.1707 was observed and identified as the intermediate E’ (Supplementary Fig. 49). Unfortunately, the attempt to isolate E’ from the reaction mixture failed probably due to its rapid dehydration.

5.2. The reaction of 2-methyl substituted indole 1u with 2a

As shown in Figure S6, a peak at m/z 400.1707 was observed and identified as the intermediate E’ (Supplementary Fig. 49). Unfortunately, the attempt to isolate E’ from the reaction mixture failed probably due to its rapid dehydration.
A flame-dried Schlenk tube with a magnetic stir bar was charged with \([\text{Cp}^*\text{RhCl}_2]_2\) (7.8 mg, 12.5 µmol), 1-(2-methyl-1-phenyl-1\textit{H}-indol-3-yl)propan-1-one \textit{1u} (131.6 mg, 0.50 mmol), diphenyl acetylene \textit{2a} (44.5 mg, 0.25 mmol), AgSbF\textsubscript{6} (17.2 mg, 0.05 mmol), Ag\textsubscript{2}CO\textsubscript{3} (137.9 mg, 0.50 mmol), H\textsubscript{2}O (45.0 µL, 2.5 mmol) and THF (2.0 mL) under N\textsubscript{2}. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 120 °C for 24 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH\textsubscript{2}Cl\textsubscript{2}, filtered through a celite pad, and washed with 10-20 mL of CH\textsubscript{2}Cl\textsubscript{2}. The combined organic phases were concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v). The benzo-fused oxindole \textit{3n} was obtained in 35% yield (37.2 mg). However, the desired indol-2-ol \textit{5} was not obtained. We suspected that \textit{3n} might be obtained through the dehydration of \textit{5} and subsequent oxidation of the exocyclic double bond of the resulting benzo-fused dihydroindole\textsuperscript{8}.

**Supplementary References**


