Supporting Information

Rhodium(III)-Catalyzed Oxidative [3+2] Annulation of 2-Acetyl-1-arylhydrazines with Maleimides: Synthesis of Pyrrolo[3,4-b]indole-1,3-diones

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1. General Information

All reactions were carried out under air atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C); DMSO-$d_6$ and CDCl$_3$ were used as the solvents. The chemical shifts are reported in ppm down field ($\delta$), the coupling constants $J$ are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. TLC was carried out on SiO$_2$ (silica gel 60F$_{254}$, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO$_2$ (silica gel 60, 200-300 mesh).

The starting materials 1a–1q$^{[1]}$, 2b–2n$^{[2]}$ were synthesized according the previous literatures. 2o–2s are commercially available.

2. General Procedure for the Rh(III)-Catalyzed Annulation Reaction

\[
\begin{array}{c}
\text{R}^1\text{HNHAc} \\
\text{N} \end{array} + \begin{array}{c}
\text{N} \\
\text{O} \end{array} \xrightarrow{\text{[Cp*RhCl]}_2 \text{ (2.5 mol%)}} \xrightarrow{\text{AgNTf$_2$ (15 mol%)}} \xrightarrow{\text{Ag$_2$CO$_3$ (2.0 equiv.)}} \xrightarrow{\text{DCE, 90 °C, 6 h, N$_2$}} \begin{array}{c}
\text{R}^1\text{N} \\
\text{O} \\
\text{NHAc} \\
\text{N} \end{array}
\]

A reaction flask was charged with a mixture of $N$-arylacetohydrazide (1) (0.2 mmol), maleimide (2) (0.4 mmol, 2.0 equiv.), [Cp*RhCl]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf$_2$ (7.8 mg, 0.02 mmol, 10 mol%), Ag$_2$CO$_3$ (110.2 mg, 0.4 mmol, 2.0 equiv.), and DCE (1.0 mL). The reaction mixture was stirred at 90 °C under N$_2$ atmosphere for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1) to give product 3.

3. Characterization Data of Products

$N$-(1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3aa)

![Diagram](3aa)

Yellow solid (54.3 mg, 85% yield), mp 286–288 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.82 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.54–7.50 (m, 3H), 7.46–7.41 (m, 4H), 2.19 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 169.8, 163.2, 159.6, 142.5, 138.9, 132.4, 129.3, 128.2, 128.0, 127.0, 125.0, 120.9, 118.0, 114.3, 112.4, 20.9; IR (KBr): 3227, 2923, 1769, 1716, 1487, 1360, 1195, 1133, 1078, 1002, 745, 690 (cm$^{-1}$); HRMS (EI) calcd for C$_{18}$H$_{13}$N$_3$O$_3$: 319.0992 [M$^+$]; found: 319.0994.

$N$-(7-methyl-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ba)

Yellow solid (54.3 mg, 85% yield), mp 286–288 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.82 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.54–7.50 (m, 3H), 7.46–7.41 (m, 4H), 2.19 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 169.8, 163.2, 159.6, 142.5, 138.9, 132.4, 129.3, 128.2, 128.0, 127.0, 125.0, 120.9, 118.0, 114.3, 112.4, 20.9; IR (KBr): 3227, 2923, 1769, 1716, 1487, 1360, 1195, 1133, 1078, 1002, 745, 690 (cm$^{-1}$); HRMS (EI) calcd for C$_{18}$H$_{14}$N$_3$O$_3$: 319.0995 [M$^+$]; found: 319.0948.
Yellow solid (61.1 mg, 92% yield), mp 274–276 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.77 (s, 1H), 7.64 (s, 1H), 7.51–7.48 (m, 3H), 7.42–7.39 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H), 2.17 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.7, 163.3, 159.5, 140.9, 138.6, 134.5, 132.5, 129.3, 128.7, 128.1, 127.9, 120.3, 119.1, 113.7, 112.1, 21.5, 20.9; IR (KBr): 3238, 2922, 1772, 1716, 1552, 1500, 1375, 1189, 1132, 1079, 733, 690 (cm–1); HRMS (EI) calcd for C9H3N3O6: 333.1113 [M]+; found: 333.1110.

N-(6-methyl-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ca)

Yellow solid (58.9 mg, 88% yield), mp 294–296 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.76 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.42–7.39 (m, 4H), 7.27 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.3, 159.6, 143.0, 138.2, 137.3, 132.5, 129.3, 128.1, 127.9, 126.8, 120.6, 116.8, 114.4, 111.9, 22.0, 20.9; IR (KBr): 3243, 2919, 1715, 1671, 1500, 1361, 1196, 1132, 1081, 810, 731, 690 (cm–1); HRMS (EI) calcd for C9H3N3O6: 333.1113 [M]+; found: 333.1103.

N-(5-methyl-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3da)

Yellow solid (57.6 mg, 86% yield), mp 303–305 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.89 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.43–7.40 (m, 3H), 7.32–7.28 (m, 1H), 7.23 (d, J = 4.0 Hz, 1H), 2.58 (s, 3H), 2.14 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 170.0, 163.2, 159.6, 140.8, 139.2, 132.4, 129.3, 128.1, 127.9, 124.9, 124.1, 119.6, 118.9, 114.3, 20.7, 17.3; IR (KBr): 3238, 2923, 1770, 1718, 1567, 1496, 1363, 1190, 1133, 1078, 742, 693 (cm–1); HRMS (EI) calcd for C9H3N3O6: 333.1113 [M]+; found: 333.1109.

N-(6,7-dimethyl-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ea)

Yellow solid (63.6 mg, 92% yield), mp 309–310 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.72 (s, 1H), 7.61 (s, 1H), 7.52–7.48 (m, 2H), 7.42–7.37 (m, 4H), 2.38 (s, 3H), 2.36 (s, 3H), 2.16 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.9, 163.4, 159.6, 141.5, 137.7, 136.9, 134.3, 132.5, 129.3, 128.0, 127.9, 120.6, 117.2, 113.8, 112.1, 21.0, 20.7, 20.2; IR (KBr): 3216, 2921, 1769, 1717, 1499, 1359, 1196, 1136, 1078, 1056, 729, 683 (cm–1); HRMS (EI) calcd for C9H3N3O6: 347.1270 [M]+; found: 347.1265.

N-(7-(tert-butyl)-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3fa)

S-3
Yellow solid (66.3 mg, 88% yield), mp 223–225 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.80 (s, 1H), 7.75 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.53–7.49 (m, 3H), 7.42–7.40 (m, 3H), 2.18 (s, 3H), 1.37 (s, 9H). $^1$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.8, 163.4, 159.6, 147.9, 140.9, 132.5, 129.3, 128.1, 127.9, 125.6, 118.8, 116.3, 114.2, 112.0, 35.1, 31.8, 20.9. IR (KBr): 3279, 2928, 1774, 1720, 1500, 1363, 1197, 1143, 1078, 1044, 752, 694 (cm$^{-1}$); HRMS (EI) calcd for C$_{22}$H$_{21}$N$_3$O$_3$: 375.1583 [M]$^+$; found: 375.1573.

$N$-$(7$-butyl-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-$b$]-indol-4(1$H$)-yl)acetamide (3ga)

Yellow solid (64.4 mg, 86% yield), mp 252–254 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.86 (s, 1H), 7.63 (s, 1H), 7.53–7.49 (m, 3H), 7.42–7.39 (m, 3H), 7.37–7.34 (m, 1H), 2.17 (s, 3H), 1.65–1.57 (m, 2H), 1.33–1.27 (m, 2H), 0.91 (t, $J = 16.0$ Hz, 2H). $^1$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.7, 163.3, 159.6, 141.1, 139.5, 138.6, 132.5, 129.3, 128.1, 127.9, 119.8, 119.0, 113.8, 112.2, 35.2, 34.0, 22.1, 20.9, 14.3. IR (KBr): 3244, 2927, 1717, 1551, 1470, 1359, 1188, 1132, 1083, 750, 731, 690 (cm$^{-1}$); HRMS (EI) calcd for C$_{22}$H$_{21}$N$_3$O$_3$: 375.1583 [M]$^+$; found: 375.1581.

$N$-$(1,3$-dioxo-2,7-diphenyl-2,3-dihydropyrrolo[3,4-$b$]-indol-4(1$H$)-yl)acetamide (3ha)

Yellow solid (69.6 mg, 88% yield), mp 336–338 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.88 (s, 1H), 8.03 (s, 1H), 7.83 (dd, $J = 4.0$, 8.0 Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.54–7.48 (m, 4H), 7.44–7.38 (m, 4H), 2.20 (s, 3H). $^1$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.8, 163.1, 159.5, 142.0, 140.4, 139.4, 137.5, 132.4, 129.5, 129.3, 128.2, 128.0, 127.6, 126.5, 119.4, 118.5, 114.4, 113.0, 21.0, 14.3. IR (KBr): 3281, 2920, 1716, 1670, 1466, 1353, 1196, 1132, 1077, 1055, 748, 691 (cm$^{-1}$); HRMS (EI) calcd for C$_{24}$H$_{17}$N$_3$O$_3$: 395.1270 [M]$^+$; found: 395.1262.

$N$-$(1,3$-dioxo-2,5-diphenyl-2,3-dihydropyrrolo[3,4-$b$]-indol-4(1$H$)-yl)acetamide (3ia)

Yellow solid (42.5 mg, 54% yield), mp 278–280 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.24 (s, 1H), 8.03 (s, 1H), 7.83 (dd, $J = 4.0$, 8.0 Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.54–7.48 (m, 4H), 7.44–7.38 (m, 4H), 2.20 (s, 3H). $^1$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 168.8, 163.2, 159.5, 139.5, 138.8, 136.9, 132.4, 129.9, 129.3, 129.2, 128.3, 128.2, 128.0, 128.0, 124.7, 120.4, 120.0, 114.5, 20.0, 14.3. IR (KBr): 3266, 2920, 1773, 1719, 1483, 1357, 1196, 1132, 1077, 1043, 747, 703 (cm$^{-1}$); HRMS (EI) calcd for C$_{24}$H$_{17}$N$_3$O$_3$: 395.1270 [M]$^+$; found: 395.1264.
N-(7-methoxy-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ja)

Yellow solid (66.4 mg, 95% yield), mp 284–285 °C. 1H NMR (DMSO-d6, 400 MHz) δ 7.52–7.49 (m, 3H), 7.42–7.38 (m, 3H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.13 (dd, *J* = 2.0, 9.2 Hz, 1H), 3.84 (s, 3H), 2.16 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.3, 159.4, 157.7, 138.4, 137.4, 132.5, 129.3, 127.9, 119.6, 117.9, 113.5, 101.5, 56.2, 20.9; IR (KBr): 3242, 2917, 1716, 1551, 1492, 1363, 1181, 1133, 1077, 1043, 1021, 618 (cm⁻¹); HRMS (EI) calcd for C₁₉H₁₅N₃O₄: 349.1063 [M]+; found: 349.1055.

N-(7-fluoro-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ka)

Yellow solid (58.0 mg, 82% yield), mp 266–268 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.86 (s, 1H), 7.68–7.61 (m, 2H), 7.53–7.49 (m, 2H), 7.43–7.37 (m, 4H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 162.7, 159.2, 142.0, 139.1, 132.3, 129.3, 128.2, 128.0, 119.1 (d, *J*C–F = 12.0 Hz), 115.7 (d, *J*C–F = 27.0 Hz), 114.2 (d, *J*C–F = 9.0 Hz), 113.9 (d, *J*C–F = 5.0 Hz), 106.1 (d, *J*C–F = 25.0 Hz), 20.9; IR (KBr): 3197, 2923, 1775, 1722, 1548, 1501, 1494, 1363, 1181, 1134, 1085, 747, 730, 673 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₂N₃O₃F: 337.0863 [M]+; found: 337.0855.

N-(7-chloro-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3la)

Yellow solid (55.5 mg, 83% yield), mp 250–252 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.88 (s, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55–7.49 (m, 3H), 7.43–7.40 (m, 3H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 162.7, 159.2, 141.0, 140.1, 132.3, 129.7, 129.3, 128.3, 128.0, 127.1, 120.1, 119.5, 114.3, 113.5, 20.9; IR (KBr): 3195, 2922, 1775, 1722, 1548, 1501, 1372, 1196, 1133, 1076, 750, 695 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₂N₃O₃Cl: 353.0567 [M]+; found: 353.0560.

N-(7-bromo-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ma)

Yellow solid (64.7 mg, 81% yield), mp 264–266 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.85 (s, 1H), 7.98 (s, 1H), 7.65–7.57 (m, 2H), 7.51–7.47 (m, 2H), 7.40–7.38 (m, 3H), 2.15 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 162.7, 159.2, 141.2, 139.9, 132.3, 129.7, 129.3, 128.3, 128.0, 123.1, 120.1, 117.6, 114.6, 113.4, 20.9; IR (KBr):
3198, 2918, 1764, 1718, 1500, 1371, 1194, 1133, 1079, 1058, 748, 691 (cm⁻¹); HRMS (EI) calcd for C₁₅H₁₃N₂O₄Br: 397.0062 and 399.0042 [M⁺]; found: 397.0055 and 399.0038.

*N-(7-iodo-1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3na)*

![Diagram](image1)

Yellow solid (76.7 mg, 82% yield), mp 319–321 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ 11.86 (s, 1H), 8.16 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.53–7.39 (m, 7H), 2.16 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 169.8, 162.8, 159.2, 141.6, 139.4, 135.1, 132.3, 129.1, 128.3 128.0, 120.7, 114.7, 113.0, 89.7, 20.9; IR (KBr): 3190, 2920, 1770, 1719, 1502, 1372, 1193, 1133, 1079, 1048, 748, 689 (cm⁻¹); HRMS (EI) calcd for C₁₅H₁₂N₂O₄Br: 444.9923 [M⁺]; found: 444.9914.

*N-(1,3-dioxo-2-phenyl-7-(trifluoromethyl)-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3oa)*

![Diagram](image2)

Yellow solid (47.3 mg, 61% yield), mp 198–200 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ 12.00 (s, 1H), 8.17 (s, 1H), 7.87–7.83 (m, 2H), 7.54–7.50 (m, 2H), 7.44–7.42 (m, 3H), 2.20 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 169.9, 162.7, 159.2, 143.9, 141.1, 132.3, 129.4, 128.6 (q, ¹JC-F = 282.8 Hz), 128.0, 125.7 (q, ²JC-F = 31.8 Hz), 123.6, 123.3 (q, ³JC-F = 3.3 Hz), 118.5 (q, ⁴JC-F = 3.8 Hz), 118.1, 114.9, 113.9, 20.9; IR (KBr): 3232, 2925, 1778, 1723, 1557, 1488, 1308, 1198, 1131, 1063, 745, 692 (cm⁻¹); HRMS (EI) calcd for C₁₇H₁₁F₃N₂O₄: 387.0831 [M⁺]; found: 387.0833.

*methyl 4-acetamido-1,3-dioxo-2-phenyl-1,2,3,4-tetrahydropyrrolo[3,4-b]indole-7-carboxylate (3pa)*

![Diagram](image3)

Yellow solid (48.9 mg, 65% yield), mp 218–220 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ 11.94 (s, 1H), 8.41 (s, 1H), 8.07 (dd, J = 1.6, 8.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.54–7.50 (m, 2H), 7.44–7.41 (m, 3H), 3.91 (s, 3H), 2.19 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 169.8, 166.5, 162.8, 159.2, 144.7, 140.8, 132.3, 129.4, 128.3, 128.0, 127.3, 126.3, 122.7, 118.3, 115.2, 112.9, 52.8, 20.9 IR (KBr): 3255, 2923, 1778, 1722, 1557, 1478, 1374, 1174, 1196, 1150, 752, 693 (cm⁻¹); HRMS (EI) calcd for C₁₉H₁₅N₃O₅: 377.1012 [M⁺]; found: 377.1006.

*N-(7,9-dioxo-8-phenyl-8,9-dihydrobenzo[g]pyrrolo[3,4-b]indol-10(7H)-yl)acetamide (3qa)*

![Diagram](image4)

Yellow solid (47.5 mg, 64% yield), mp 325–327 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ 12.36 (s, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.90–7.85 (m, 2H), 7.75–7.64 (m, 2H), 7.54–7.50 (m, 2H), 7.44–7.40 (m,
3H), 2.29 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 170.0, 163.3, 159.3, 136.9, 136.1, 132.7, 132.5, 130.0, 129.3, 128.2, 128.0, 127.9, 127.0, 126.5, 126.2, 126.0, 120.9, 118.9, 116.5, 115.8, 21.1; IR (KBr): 3231, 2920, 1765, 1718, 1501, 1360, 1197, 1133, 1062, 870, 744, 692 (cm⁻¹); HRMS (EI) calcd for C22H15N3O3: 369.1113 [M]+; found: 369.1110.

N-(1,3-dioxo-2-p-tolyl)-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ab)

Yellow solid (58.7 mg, 88% yield), mp 282−284 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.81 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.53−7.49 (m, 1H), 7.45−7.41 (m, 1H), 7.32−7.27 (m, 4H), 2.36 (s, 3H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.4, 159.7, 142.5, 138.9, 137.7, 129.8, 127.9, 127.0, 125.0, 120.9, 118.8, 114.2, 112.4, 21.2, 20.9; IR (KBr): 3189, 2917, 1768, 1720, 1485, 1394, 1195, 1140, 1074, 924, 745, 617 (cm⁻¹); HRMS (EI) calcd for C19H15N3O3: 333.1113 [M]+; found: 333.1110.

N-(1,3-dioxo-2-(m-tolyl)-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ac)

Yellow solid (61.7 mg, 93% yield), mp 240−242 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.82 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53−7.49 (m, 1H), 7.45−7.37 (m, 2H), 7.24−7.19 (m, 3H), 2.36 (s, 3H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.3, 159.6, 142.5, 138.9, 138.8, 132.3, 129.1, 128.9, 128.4, 127.0, 125.1, 125.0, 120.9, 118.8, 114.2, 112.4, 21.3, 20.9; IR (KBr): 3253, 2920, 1772, 1718, 1499, 1395, 1350, 1195, 1133, 1057, 741, 635 (cm⁻¹); HRMS (EI) calcd for C19H15N3O3: 333.1113 [M]+; found: 333.1110.

N-(2-(3,4-dimethylphenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ad)

Yellow solid (59.8 mg, 86% yield), mp 258−260 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.82 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.53−7.49 (m, 1H), 7.45−7.41 (m, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.17 (s, 1H), 7.12−7.09 (m, 1H), 2.26 (s, 6H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.4, 159.7, 142.5, 138.9, 137.3, 136.6, 136.0, 130.2, 130.1, 128.9, 127.0, 125.4, 125.0, 120.9, 118.8, 114.2, 112.4, 20.9, 19.8, 19.5; IR (KBr): 3259, 2920, 1772, 1717, 1499, 1395, 1196, 1133, 1076, 1021, 742, 631 (cm⁻¹); HRMS (EI) calcd for C20H17N3O3: 347.1270 [M]+; found: 347.1261.

N-(2-(3,5-dimethylphenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ae)
Yellow solid (54.7 mg, 79% yield), mp 261–263 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.82 (s, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 1H), 7.53–7.49 (m, 1H), 7.45–7.41 (m, 1H), 7.05–7.01 (m, 3H), 2.31 (s, 6H), 2.18 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 169.8, 163.3, 159.6, 142.5, 138.9, 138.5, 132.2, 129.7, 127.0, 125.6, 125.0, 120.9, 118.8, 114.2, 112.4, 21.2, 20.9; IR (KBr): 3255, 2922, 1773, 1720, 1486, 1362, 1195, 1134, 1076, 742, 688 (cm$^{-1}$); HRMS (EI) calcd for C$_{20}$H$_{17}$N$_3$O$_3$: 347.1270 [M]$^+$; found: 347.1261.

N-(2-(4-methoxyphenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3af)

Yellow solid (65.7 mg, 94% yield), mp 247–249 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.80 (s, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.52–7.48 (m, 1H), 7.45–7.41 (m, 1H), 7.05 (d, $J$ = 8.0 Hz, 2H), 3.80 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 169.8, 163.6, 159.9, 159.1, 142.4, 138.9, 129.5, 126.9, 125.0, 124.9, 120.9, 118.8, 114.6, 114.2, 112.4, 55.8, 20.9; IR (KBr): 3203, 2924, 1768, 1713, 1487, 1395, 1196, 1141, 1076, 1042, 740, 616 (cm$^{-1}$); HRMS (EI) calcd for C$_{19}$H$_{15}$N$_3$O$_4$: 349.1063 [M]$^+$; found: 349.1052.

N-(2-[(1,1'-biphenyl]-4-yl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ag)

Yellow solid (68.6 mg, 87% yield), mp 286–288 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 11.86 (s, 1H), 7.86 (d, $J$ = 8.0 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.0 Hz, 2H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.52–7.39 (m, 7H), 2.20 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 169.8, 163.2, 159.5, 142.5, 139.9, 139.9, 138.9, 131.8, 129.5, 128.3, 128.2, 127.6, 127.3, 127.1, 125.0, 121.0, 118.9, 114.3, 112.4, 21.0; IR (KBr): 3246, 2918, 1772, 1717, 1487, 1393, 1195, 1140, 1076, 1009, 740, 698 (cm$^{-1}$); HRMS (EI) calcd for C$_{23}$H$_{17}$N$_3$O$_3$: 349.1063 [M]$^+$; found: 349.1260.

Methyl 4-(4-acetamido-1,3-dioxo-3,4-dihydropyrrolo[3,4-b]indol-2(1H)-yl)benzoate (3ah)
Yellow solid (48.6 mg, 64% yield), mp 268–270 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.85 (s, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.62–7.59 (m, 3H), 7.54–7.51 (m, 1H), 7.46–7.43 (m, 1H), 3.88 (s, 3H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 166.2, 162.7, 159.0, 142.6, 138.8, 136.8, 130.2, 128.6, 127.3, 127.2, 125.1, 121.0, 118.8, 114.4, 112.5, 52.7, 20.9; IR (KBr): 3359, 3194, 2922, 1776, 1730, 1677, 1361, 1196, 1133, 1058, 750, 632 (cm⁻¹); HRMS (EI) calcld for C₅H₅N₃O: 377.1012 [M⁺]; found: 377.1010.

N-(2-(4-cyanophenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ai)

Yellow solid (30.7 mg, 45% yield), mp 288–290 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.86 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.67–7.60 (m, 3H), 7.55–7.51 (m, 1H), 7.47–7.43 (m, 1H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 162.4, 158.8, 142.6, 138.7, 136.7, 133.4, 127.9, 127.3, 125.2, 121.0, 119.0, 118.8, 114.4, 112.5, 110.1, 20.9; IR (KBr): 3214, 2921, 2231, 1774, 1727, 1684, 1338, 1197, 1133, 740, 635 (cm⁻¹); HRMS (EI) calcld for C₁₇H₁₅N₃O₇: 344.0909 [M⁺]; found: 344.0912.

N-(2-(4-nitrophenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3aj)

Yellow solid (43.7 mg, 60% yield), mp 290–292 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.88 (s, 1H), 8.36 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 12.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.55–7.51 (m, 1H), 7.47–7.43 (m, 1H), 2.19 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 162.3, 158.8, 146.0, 142.6, 138.8, 138.4, 127.6, 127.4, 125.2, 124.6, 121.1, 118.8, 140.5, 112.5, 20.9; IR (KBr): 3220, 2918, 1776, 1724, 1495, 1328, 1196, 1124, 1077, 1020, 748, 627 (cm⁻¹); HRMS (EI) calcld for C₁₈H₁₂N₄O₆: 364.0808 [M⁺]; found: 364.0819.

N-(2-(4-fluorophenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ak)

Yellow solid (60.2 mg, 86% yield), mp 265–267 °C. 1H NMR (DMSO-d6, 400 MHz) δ 11.83 (s, 1H), 7.84 (d, J = 4.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53–7.41 (m, 4H), 7.37–7.32 (m, 2H), 2.18 (s, 3H); 13C NMR (DMSO-d6, 100 MHz) δ 169.8, 163.2, 161.6 (d, J_C,F = 243.0 Hz), 159.5, 142.5, 138.9, 130.2 (d, J_C,F = 9.0 Hz), 128.7 (d, J_C,F = 3.0 Hz), 127.0, 125.0, 120.9, 118.8, 116.2 (d, J_C,F = 23.0 Hz), 114.3, 112.4, 20.9; IR (KBr): 3180, 2924, 1772, 1722, 1511, 1487, 1395, 1196, 1141, 1100, 1062, 744, 631 (cm⁻¹); HRMS (EI) calcld for C₉H₈FNO₃: 337.0863 [M⁺]; found: 337.0873.

N-(2-(4-chlorophenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3al)
Yellow solid (61.8 mg, 87% yield), mp 275–277 °C. \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 11.84 (s, 1H), 7.84 (d, \(J = 8.0\) Hz, 1H), 7.62–7.56 (m, 3H), 7.53–7.50 (m, 1H), 7.47–7.42 (m, 3H), 2.18 (s, 3H); \(^1^3\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 169.8, 162.9, 159.3, 142.5, 138.8, 132.6, 131.3, 129.6, 129.3, 127.1, 125.0, 121.0, 118.8, 114.3, 112.4, 20.9; IR (KBr): 3217, 2920, 1771, 1722, 1492, 1395, 1196, 1134, 1056, 1016, 741, 634 (cm\(^{-1}\)); HRMS (EI) calcd for C\(_{18}\)H\(_{12}\)N\(_3\)O\(_3\)Cl: 353.0567 [M]\(^+\); found: 353.0558.

**N-(2-(4-bromophenyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3am)**

Yellow solid (68.3 mg, 86% yield), mp 290–292 °C. \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 11.84 (s, 1H), 7.84 (d, \(J = 8.0\) Hz, 1H), 7.71 (d, \(J = 12.0\) Hz, 2H), 7.61 (d, \(J = 12.0\) Hz, 1H), 7.53–7.49 (m, 1H), 7.45–7.38 (m, 3H), 2.18 (s, 3H); \(^1^3\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 169.8, 162.9, 159.2, 142.5, 138.8, 132.3, 131.8, 129.8, 127.1, 125.0, 121.0, 118.8, 114.3, 112.4, 20.94; IR (KBr): 3211, 2923, 1772, 1722, 1488, 1396, 1196, 1133, 1073, 1010, 741, 633 (cm\(^{-1}\)); HRMS (EI) calcd for C\(_{18}\)H\(_{12}\)N\(_3\)O\(_3\)Br: 397.0062 and 399.0042 [M]\(^+\); found: 397.0059 and 399.0040.

**N-(2-(naphthalen-1-yl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3an)**

Yellow solid (59.8 mg, 81% yield), mp 252–254 °C. \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 11.84 (s, 1H), 8.11–8.06 (m, 2H), 7.88 (d, \(J = 8.0\) Hz, 1H), 7.66–7.53 (m, 6H), 7.48–7.45 (m, 1H), 2.18 (s, 3H); \(^1^3\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 169.8, 163.9, 160.2, 142.5, 139.0, 134.3, 131.2, 129.9, 129.0, 128.8, 128.5, 127.6, 127.1, 127.0, 126.1, 125.1, 121.0, 119.0, 114.6, 112.5, 21.0; IR (KBr): 3279, 2923, 1772, 1719, 1487, 1399, 1196, 1134, 1076, 1046, 743, 621 (cm\(^{-1}\)); HRMS (EI) calcd for C\(_{22}\)H\(_{15}\)N\(_3\)O\(_3\): 369.1113 [M]\(^+\); found: 369.1120.

**N-(2-methyl-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ao)**

Yellow solid (44.3 mg, 86% yield), mp 249–251 °C. \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 11.72 (s, 1H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.54 (d, \(J = 8.0\) Hz, 1H), 7.47–7.37 (m, 1H), 2.95 (s, 3H), 2.16 (s, 3H); \(^1^3\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 169.7, 164.4, 160.7, 142.2, 139.4, 126.6, 124.7, 120.7, 118.7, 114.3, 112.3, 24.1, 20.9; IR
(KBr); 3157, 2918, 1767, 1718, 132, 1361, 1193, 1133, 1012, 752, 731, 631 (cm$^{-1}$); HRMS (EI) calcd for C$_{13}$H$_{11}$N$_{3}$O$_{3}$: 257.0800 [M]$^+$; found: 257.0798.

N-(2-benzyl-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ap)

Yellow solid (50.7 mg, 76% yield), mp 224−226 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.74 (s, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.57 (d, $J$ = 12.0 Hz, 1H), 7.49−7.45 (m, 1H), 7.42−7.38 (m, 1H), 7.36−7.25 (m, 5H), 4.68 (s, 2H), 2.16 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.8, 164.1, 160.4, 142.4, 139.0, 137.7, 129.1, 127.8, 127.8, 126.8, 124.9, 120.8, 118.8, 114.2, 112.4, 41.1, 20.9; IR (KBr): 3207, 2920, 1770, 1711, 1487, 1337, 1196, 1132, 1077, 1056, 735, 682 (cm$^{-1}$); HRMS (EI) calcd for C$_{19}$H$_{15}$N$_{3}$O$_{3}$: 333.1113 [M]$^+$; found: 333.1123.

N-(2-cyclohexyl-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3aq)

Yellow solid (49.5 mg, 76% yield), mp 206−208 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.67 (s, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.52 (d, $J$ = 12.0 Hz, 1H), 7.47−7.43 (m, 1H), 7.40−7.37 (m, 1H), 3.88−3.82 (m, 1H), 2.15 (s, 3H), 2.05−1.97 (m, 2H), 1.79 (d, $J$ = 12.0 Hz, 2H), 1.71 (d, $J$ = 8.0 Hz, 1H), 1.35−1.11 (m, 4H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.7, 164.2, 160.5, 142.3, 138.8, 126.6, 124.7, 124.7, 120.7, 118.7, 114.0, 112.3, 50.4, 30.4, 26.1, 25.4, 20.9; IR (KBr): 3275, 2933, 1764, 1707, 1487, 1399, 1196, 1133, 1044, 1020, 742, 631 (cm$^{-1}$); HRMS (EI) calcd for C$_{18}$H$_{19}$N$_{3}$O$_{3}$: 325.1426 [M]$^+$; found: 325.1419.

N-(2-(tert-butyl)-1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3ar)

Yellow solid (34.7 mg, 79% yield), mp 246−248 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.62 (s, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.51 (d, $J$ = 8.0 Hz, 1H), 7.47−7.43 (m, 1H), 7.39−7.36 (m, 1H), 2.14 (s, 3H), 1.59 (s, 9H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 169.7, 165.6, 161.6, 142.4, 138.5, 126.6, 124.6, 120.7, 118.5, 114.0, 112.2, 57.5, 29.5, 20.9; IR (KBr): 3241, 2918, 1762, 1706, 1484, 1398, 1195, 1132, 1077, 998, 743, 637 (cm$^{-1}$); HRMS (EI) calcd for C$_{16}$H$_{17}$N$_{3}$O$_{3}$: 299.1270 [M]$^+$; found: 299.1264.

N-(1,3-dioxo-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3as)

Yellow solid (23.4 mg, 48% yield), mp 299−301 °C. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.66 (s, 1H), 10.54 (s, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.53 (d, $J$ = 8.0 Hz, 1H), 7.47−7.44 (m, 1H), 7.40−7.36 (m, 1H), 2.14 (s, 3H); $^{13}$C
NMR (DMSO-\text{d}_6, 100 MHz) $\delta$ 169.7, 165.4, 161.8, 142.5, 139.7, 126.6, 124.6, 120.8, 118.6, 115.4, 112.2, 20.9; IR (KBr): 3218, 2920, 1769, 1723, 1485, 1400, 1195, 1133, 1045, 996, 742, 638 (cm$^{-1}$); HRMS (EI) calcd for C$_{12}$H$_7$N$_2$O: 243.0644 [M]$^+$; found: 243.0645.

4. Synthesis of 4-Amino-2-phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (4) and 2-Phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (5)

Following the procedure reported by Liu, a 25 mL Schlenk tube was charged with a mixture of N-(1,3-dioxo-2-phenyl-2,3-dihydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (3aa, 63.9 mg, 0.2 mmol), 4 M HCl (2.0 mL), and THF (2 mL). The mixture was then sealed with a Teflon-lined cap and heated to 80 °C for 12 h. After cooling to room temperature, the reaction was quenched by saturated aqueous solution of sodium bicarbonate (10 mL). Concentrated and the aqueous layer was extracted with CH$_2$Cl$_2$ until no obvious fluorescence of the aqueous phase was observed under a UV lamp. The combined organic extract was dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford 4-amino-2-phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (4) as a yellow solid in 78% yield (43.3 mg).

4-Amino-2-phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (4)

Yellow solid (43.3 mg, 78% yield), mp 145–147 °C. $^1$H NMR (DMSO-\text{d}_6, 400 MHz) $\delta$ 7.76 (d, $J$ = 12.0 Hz, 2H), 7.54–7.45 (m, 3H), 7.42–7.35 (m, 4H), 6.45 (s, 2H); $^{13}$C NMR (DMSO-\text{d}_6, 100 MHz) $\delta$ 156.6, 153.3, 137.0, 132.3, 126.0, 122.5, 121.2, 119.1, 117.6, 113.7, 112.1, 106.5, 104.8, 100.0; IR (KBr): 3395, 1766, 1707, 1560, 1409, 1348, 1196, 1133, 1077, 1020, 749, 691 (cm$^{-1}$); HRMS (EI) calcd for C$_{12}$H$_7$N$_2$O: 277.0851 [M]$^+$; found: 277.0859.

Following the procedure reported by Zheng, a reaction vial with a stirring bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$[dF(CF$_3$)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4’-di-tert-butyl-2,2’-bipyridine] (4.6 mg, 0.004 mmol, 2 mol%), 4-amino-2-phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (4, 0.2 mmol, 55.5 mg) and methanol : acetonitrile (1:1, 2 mL). The solution was sealed with a Teflon-lined cap and heated to 40 °C under the irradiation of a 5 W blue LED at a wavelength of 465 nm for 4 h. When the reaction was complete, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford 2-phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (5) as a yellow solid in 76% (39.9 mg).

2-Phenylpyrrolo[3,4-b]indole-1,3(2H,4H)-dione (5)
Yellow solid (39.9 mg, 76% yield), mp 318–320 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 13.16 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.52–7.47 (m, 2H), 7.43–7.32 (m, 5H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 164.0, 161.3, 142.5, 140.7, 132.9, 129.2, 127.9, 127.8, 126.0, 123.9, 121.0, 120.6, 115.4, 115.0; IR (KBr): 3214, 2918, 1773, 1692, 1468, 1358, 1083, 1051, 744, 691, 640 (cm$^{-1}$); HRMS (EI) calcd for C$_{16}$H$_{10}$N$_2$O$_2$: 262.0742 [M]$^+$; found: 262.0739.

5. Synthesis of N-ethyl-2-phenyl-2,3-dihydropyrrolo[3,4-$b$]indol-4(1H)-amine (6)

Following the procedure reported by Luo,$^5$ a solution of 3aa (63.9 mg, 0.2 mmol) in THF (2 mL) was cooled down to 0 °C before the addition of sodium borohydride (22.7 mg, 0.6 mmol). It was kept under stirring at the same temperature for 10 minutes and, subsequently, BF$_3$·Et$_2$O (85.2 mg, 0.6 mmol) was added dropwise. Once the addition was performed, the temperature was allowed to slowly increase until achieving room temperature. Then, the mixture was stirred for overnight. When the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 8:1) to afford N-ethyl-2-phenyl-2,3-dihydropyrrolo[3,4-$b$]indol-4(1H)-amine (6) as a yellow oil in 81% yield (44.9 mg).

N-ethyl-2-phenyl-2,3-dihydropyrrolo[3,4-$b$]indol-4(1H)-amine (6)

Yellow oil (44.9 mg, 81% yield). $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 10.44 (s, 1H), 8.11 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.37–7.33 (m, 2H), 7.27–7.23 (m, 1H), 7.20–7.16 (m, 1H), 7.08–7.05 (m, 1H), 6.70 (t, $J = 4.0$ Hz, 1H), 6.33 (t, $J = 4.0$ Hz, 1H), 5.01 (d, $J = 4.0$ Hz, 1H), 3.14–3.11 (m, 2H), 1.05 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 163.8, 141.7, 140.2, 135.0, 129.3, 124.9, 123.4, 122.8, 121.7, 121.5, 119.7, 110.9, 108.0, 53.22, 46.06, 13.45.; IR (neat): 3399, 2925, 1601, 1563, 1503, 1408, 1315, 1249, 1195, 1132, 1076, 1020 (cm$^{-1}$); HRMS (EI) calcd for C$_{18}$H$_{19}$N$_3$: 277.1579 [M]$^+$; found: 277.1586.

6. Control Experiments

(1) Intermediate 7 trapping experiments
A reaction flask was charged with a mixture of $1a$ (30.0 mg, 0.2 mmol), $2a$ (69.3 mg, 0.4 mmol, 2.0 equiv.), [$Cp^*\text{RhCl}_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf$_2$ (7.8 mg, 0.02 mmol, 10 mol%), Ag$_2$CO$_3$ (110.2 mg, 0.4 mmol, 2.0 equiv.) and DCE (1.0 mL). The reaction mixture was stirred at 90 °C for 10 min under N$_2$ condition, and then was rapidly cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 8:1 to 3:1) to give intermediate 7 (13.6 mg, 46%) and 3aa (8.3 mg, 13%).

1-(Phenyldiazenyl)ethan-1-one (7)\(^6\)

Red oil (13.6 mg, 46% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.89 (d, $J = 8.0$ Hz, 2H), 7.57–7.51 (m, 3H), 2.43 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 188.6, 151.5, 133.6, 129.4, 123.7, 21.3.

(2) Conversion of intermediate 7 to 3aa

A reaction flask was charged with a mixture of $[Cp^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf$_2$ (7.8 mg, 0.02 mmol, 10.0 mol%), Ag$_2$CO$_3$ (55.1 mg, 0.2 mmol, 1.0 equiv.) and DCE (1.0 mL). The reaction was stirred at 90 °C under N$_2$ for 6 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to afford product 3aa (53.0 mg, 83%).

(3) Intermediate 8 trapping experiments

A reaction flask was charged with a mixture of $1a$ (30.0 mg, 0.2 mmol), $2a$ (69.3 mg, 0.4 mmol, 2.0 equiv.), $[Cp^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf$_2$ (7.8 mg, 0.02 mmol, 10 mol%), Ag$_2$CO$_3$ (55.1 mg, 0.2 mmol, 1.0 equiv.) and DCE (1.0 mL). The reaction mixture was stirred at 90 °C for 6 h under N$_2$ condition. The solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 1:1) to give intermediate 8 (58.5 mg, 91%).

N-(1,3-dioxo-2-phenyl-2,3,3a,8b-tetrahydropyrrolo[3,4-b]indol-4(1H)-yl)acetamide (8)

White solid (46.2 mg, 72% yield). Because intermediate 8 is a racemate, the NMR spectra is complex. 8 is identified by GC-MS.

GC-MS Spectra of intermediate 8

① GC spectrum
(4) Conversion of intermediate 8 to 3aa

A reaction flask was charged with a mixture of 8 (64.3 mg, 0.20 mmol), Ag₂CO₃ (55.1 mg, 0.2 mmol, 1.0 equiv.)
and DCE (1.0 mL). The reaction was stirred at 90 °C under N₂ for 6 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to afford product 3aa (59.4 mg, 93%).

(5) H/D exchange experiment

![Chemical diagram]

A reaction flask was charged with a mixture of [Cp*RhCl₂]: (3.1 mg, 0.005 mmol, 2.5 mol %), AgNTf₂: (7.8 mg, 0.02 mmol, 10.0 mol %), Ag₂CO₃: (110.2 mg, 0.4 mmol, 2.0 equiv.), 1a (0.20 mmol), 2a (0.4 mmol, 2.0 equiv.), CD₃COOD (64.1 mg, 1.0 mmol, 5.0 equiv.) and DCE (1.0 mL). The reaction was stirred at 90 °C under N₂ for 1 h, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford 3aa (23.0 mg, 36%). The result was observed by ¹H NMR determination.

![NMR spectrum]

(6) Experiment of deuterium kinetic isotope effect

![Chemical diagram]

A reaction flask was charged with a mixture of [Cp*RhCl₂]: (3.1 mg, 0.005 mmol, 2.5 mol %), AgNTf₂: (7.8 mg, 0.02 mmol, 10.0 mol %), Ag₂CO₃: (110.2 mg, 0.4 mmol, 2.0 equiv.), 1a (0.20 mmol) and 1a-d₅ (0.20 mmol), 2a (0.4 mmol, 2.0 equiv.) and DCE (1.0 mL). The reaction was stirred at 90 °C under N₂ for 1 h, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by
column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford 3aa and 3aa-d₄ (40.3 mg, 32%). A 2.1 of KIE was observed by ¹H NMR determination.

7. References:

8. X-ray Analysis of 3ma

**Figure S1.** The X-ray structure of product 3ma.

CCDC No. 1890966 (3ma) contains the supplementary crystallographic data for this paper. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data request/cif.

- **Empirical formula**: C\textsubscript{18}H\textsubscript{13}BrN\textsubscript{3}O\textsubscript{3}
- **Formula weight**: 319.32
- **Temperature**: 296(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Triclinic
- **Space group**: P1
- **Unit cell dimensions**:
  - a = 4.7205(5) Å, \(\alpha = 96.527(7)^\circ\)
  - b = 12.4967(14) Å, \(\beta = 94.459(7)^\circ\)
  - c = 15.6365(17) Å, \(\gamma = 94.614(7)^\circ\)
- **Volume**: 909.94(17) Å\textsuperscript{3}
- **Z**: 1
- **Density (calculated)**: 1.466 Mg/m\textsuperscript{3}
- **Absorption coefficient**: 2.281 mm\textsuperscript{-1}
- **F(000)**: 403
- **Crystal size**: 0.24 x 0.29 x 0.26 mm\textsuperscript{3}
- **Theta range for data collection**: 1.65 to 27.51°
- **Index ranges**: -5 \(\leq h \leq 6\), -16 \(\leq k \leq 16\), -20 \(\leq l \leq 18\)
- **Reflections collected**: 7610
- **Independent reflections**: 5706 [R(int) = 0.0434]
- **Completeness to theta = 25.00**: 97.1 %
- **Absorption correction**: None
- **Refinement method**: Full-matrix least-squares on \(F^2\)
- **Data / restraints / parameters**: 5706/1513/451
- **Goodness-of-fit on \(F^2\)**: 1.039
- **indices \([I > 2\delta (I)]\)**:
  - R1 = 0.1009, wR2 = 0.3084
- **R indices (all data)**:
  - R1 = 0.1331, wR2 = 0.3443
- **Largest diff. peak and hole**: 1.381 and -1.340 e.Å\textsuperscript{-3}
9. Copies of $^1$H and $^{13}$C NMR Spectra of Products

$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^{1}$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^{1}$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-\textit{d}_6

$^{13}$C NMR, 100 MHz, DMSO-\textit{d}_6

\textbf{3fa}
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$_d_6$

$^{13}$C NMR, 100 MHz, DMSO-$_d_6$
$^{1}H$ NMR, 400 MHz, DMSO-$d_6$

$^{13}C$ NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

13C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
\[ ^1H \text{NMR, 400 MHz, DMSO-}d_6 \]

\[ ^{13}C \text{NMR, 100 MHz, DMSO-}d_6 \]

[Chemical structures and spectra shown]
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^{1}H$ NMR, 400 MHz, DMSO-$d_{6}$

$^{13}C$ NMR, 100 MHz, DMSO-$d_{6}$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^{13}$C NMR, 100 MHz, DMSO-$d_6$
$^1$H NMR, 400 MHz, DMSO-$d_6$


$^{13}$C NMR, 100 MHz, DMSO-$d_6$


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1H NMR, 400 MHz, DMSO-d₆

13C NMR, 100 MHz, DMSO-d₆
$^1$H NMR, 400 MHz, DMSO-$d_6$

$^13$C NMR, 100 MHz, DMSO-$d_6$