Supporting Information for:

**Rh-Catalyzed Oxidative C-H Activation/Annulation: Converting Anilines to Indoles with Molecular Oxygen as Sole Oxidant**

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1. General experiment details and materials

Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents were purchased from Alfa Aesar, and before use were dried and degassed by standard methods and stored under argon atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI) or Waters GCT Premier mass spectrometer (EI). Anilines used here are known compounds. 1,2-diphenylethyne and prop-1-ynylbenzene were purchased from Alfa Aesar. The other alkynes used here are known compounds and synthesized according to the reported methods.\(^1\) Cp*Rh(H\(_2\)O)\(_3\) (OTf)\(_2\), \(\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\text{(OAc)}_2\) and \(\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3\text{(SbF}_6)_2\), \([\text{RhCp}^*\text{Cl}_2]\)_2, used here are known compounds and synthesized according to the reported methods.\(^2\)
2. Optimization of the reaction conditions

Diphenylethyne 2a (71.3 mg, 0.4 mmol), [Rh] catalyst (0.02 mmol, 5 mol%), aniline 1a (55.0 µL, 0.6 mmol), solvent (2.0 mL) and Ac₂O (57.0 µL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at design temperature for 24 hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH₃OH (2.0 mL) were added to the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 3aa as a white solid.

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<th>Entry</th>
<th>[Rh] (5 mol%)</th>
<th>Additive</th>
<th>T/°C</th>
<th>Solvent</th>
<th>Yield (%) (^b)</th>
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\(^a\) General conditions: 1a (55.0 µL, 0.6 mmol), 2a (71.3 mg, 0.4 mmol), [Rh] catalyst (0.02 mmol, 5mol %), additive (0.6 mmol), solvents (2.0 mL), oxygen (1 atm), for 24 h, unless otherwise noted. \(^b\) Isolated yield. \(^c\) Under argon.
3. General procedure for the C-H activation/annulation

\[
\text{R}^1\text{NH}_2 + \text{R}^2_2 \xrightarrow{[\text{Rh}] / \text{O}_2 (1 \text{ atm})} \frac{\text{Ac}_2\text{O}, \text{t-AmOH}, 100 \degree\text{C, 24 h then NaOH}}{\text{R}^1\text{H}_2 \text{N} \text{R}^3} \xrightarrow{\text{R}^3} 3
\]

Alkynes \(2\) (0.4 mmol), \(\text{Cp}^*\text{Rh(H}_2\text{O})_3(\text{OTf})_2\) (11.8 mg, 0.02 mmol, 5 mol%), anilines \(1\) (0.6 mmol), \(\text{t-AmOH}\) (2.0 mL) and \(\text{Ac}_2\text{O}\) (57.0 µL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C or 40 °C for 24 hours. After cooling to room temperature, \(\text{NaOH}\) (48.0 mg, 1.2 mmol) and \(\text{CH}_3\text{OH}\) (2.0 mL) were added to the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1 – 5:1) to afford the desired products \(3\).
4. Experimental characterization data for products of 3.

2,3-Diphenyl-1H-indole (3aa): \(^3\)

The title compound was prepared according to the general procedure as a white solid, 90.3 mg, 84% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.13-7.17 (m, 1H), 7.21-7.45 (m, 12H), 7.67 (d, \(J = 7.68\), 1H), 8.18 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 110.9, 115.0, 119.7, 120.4, 122.7, 126.2, 127.7, 128.1, 128.5, 128.7, 130.1, 132.7, 134.0, 135.0, 135.9. HRMS (EI) calcd. for C\(_{20}\)H\(_{15}\)N [M]: 269.1204, found: 269.1205.

5-Methyl-2,3-diphenyl-1H-indole (3ba): \(^4\)

The title compound was prepared according to the general procedure as a white solid, 105.6 mg, 93% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.44 (s, 3H), 7.06-7.08 (m, 1H), 7.25-7.33 (m, 5H), 7.36-7.45 (m, 7H), 8.13 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.6, 110.6, 114.7, 119.3, 124.3, 126.2, 127.6, 128.1, 128.5, 128.7, 129.1, 129.8, 130.2, 132.9, 134.2, 134.2, 135.2; HRMS (ESI) calcd. for C\(_{21}\)H\(_{19}\)N [M+H]: 284.1434, found: 284.1436.

6-Methyl-2,3-diphenyl-1H-indole (3ca): \(^5\)

The title compound was prepared according to the general procedure as a white solid, 80.1 mg, 71% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.34 (s, 3H), 6.86-6.88 (m, 1H), 7.03 (s, 1H), 7.13-7.19 (m, 4H), 7.23-7.27 (m, 4H), 7.31-7.33 (m, 2H), 7.45 (d, \(J = 8.14\), 1H), 7.86 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.7, 110.8, 114.8, 119.3, 122.2, 126.1, 126.6, 127.4, 128.0, 128.5, 128.6, 130.1, 132.6, 132.8, 133.4, 135.2, 136.3; HRMS (ESI) calcd. for C\(_{21}\)H\(_{18}\)N [M+H]: 284.1434, found: 284.1435.

5-tert-butyl-2,3-diphenyl-1H-indole (3da):

The title compound was prepared according to the general procedure as a white solid, 120.1 mg, 92% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.36 (s, 9H), 7.23-7.45 (m, 12H), 7.67 (s, 1H), 8.06 (br, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.0, 34.8, 110.5, 115.2, 115.4, 121.2, 126.2, 127.6, 128.3, 128.5, 128.7, 130.3, 133.0, 134.2, 134.5, 135.4, 143.6; HRMS (ESI) calcd. for C\(_{24}\)H\(_{23}\)NNa [M+Na]: 348.1710, found: 348.1723.
6-tert-butyl-2,3-diphenyl-1H-indole (3ea):

The title compound was prepared according to the general procedure as a white solid, 110.4 mg, 84% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.40 (s, 9H), 7.22-7.44 (m, 12H), 7.60 (d, $J$ = 8.4 Hz, 1H), 8.13 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 31.8, 34.9, 107.2, 114.9, 118.8, 119.2, 126.1, 126.5, 127.5, 128.1, 128.5, 128.7, 130.1, 133.0, 133.9, 135.3, 136.1, 146.4; HRMS (ESI) calcd. for C$_{126}$H$_{128}$N[M]$: 329.1418$, found: 329.1413.

5-Methoxy-2,3-diphenyl-1H-indole (3fa): $^5$

The title compound was prepared according to the general procedure as a white solid, 107.4 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.82 (s, 3H), 6.89 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.5 Hz, 1H), 7.12 (d, $J$ = 2.4 Hz, 1H), 7.25-7.33 (m, 5H), 7.36-7.44 (m, 6H), 8.12 (b, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.9, 101.3, 111.7, 113.0, 115.0, 126.2, 127.6, 128.1, 128.6, 128.7, 129.2, 130.1, 131.1, 132.8, 135.0, 135.2, 154.8; HRMS (ESI) calcd. for C$_{21}$H$_{18}$NO [M+H]: 300.1383 found: 300.1384.

4,6-Dimethoxy-2,3-diphenyl-1H-indole (3ga):

The title compound was prepared according to the general procedure as a white solid, 80.2 mg, 61% yield. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 3.60 (s, 3H), 3.80 (s, 3H), 6.17 (d, $J$ = 1.92 Hz, 1H), 6.56 (d, $J$ = 1.92 Hz, 1H), 7.19-7.29 (m, 10H), 11.36 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 54.9, 55.2, 86.8, 91.8, 112.2, 113.5, 125.7, 126.6, 127.2, 127.7, 128.2, 128.7, 131.1, 131.3, 131.6, 132.8, 136.4, 137.6, 154.4, 156.9; HRMS (ESI) calcd. for C$_{22}$H$_{20}$NO$_2$ [M+H]: 330.1489 found: 330.1491.

5,6-Dimethoxy-2,3-diphenyl-1H-indole (3ha): $^6$

The title compound was prepared according to the general procedure as a white solid, 100.7 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.89 (s, 3H), 3.94 (s, 3H), 6.94 (s, 1H), 7.09 (s, 1H), 7.28-7.44 (m, 10H), 8.10 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 55.7, 55.8, 94.9, 100.7, 113.3, 120.7, 125.9, 126.9, 127.7, 128.4, 128.7, 129.6, 130.6, 132.3, 132.8, 135.6, 145.1, 147.1. HRMS (EI) calcd. for C$_{22}$H$_{19}$NO$_2$ [M]: 329.1416 found: 329.1418.
2,3-Diphenyl-5-(trifluoromethoxy)-1H-indole (3ia):

The title compound was prepared according to the general procedure as a white solid, 110.0 mg, 78% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.98-7.01 (m, 1H), 7.17-7.29 (m, 11H), 7.42 (s, 1H), 8.13 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 110.5, 111.2, 114.3, 115.5, 116.0 (q, $J = 254$ Hz), 125.6, 127.1, 127.1, 127.5, 127.7, 128.0, 128.9, 131.0, 133.1, 133.2, 135.0, 142.6, 142.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.88. HRMS (EI) calcd. for C$_{21}$H$_{13}$F$_3$NO: [M]+: 353.1027, found: 353.1028.

5-Fluoro-2,3-diphenyl-1H-indole (3ja):

The title compound was prepared according to the general procedure as a white solid, 87.3 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.93-6.98 (m, 1H), 7.25-7.39 (m, 12H), 8.14 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 104.5 (d, $J = 24$ Hz), 110.9 (d, $J = 27$ Hz), 111.6 (d, $J = 10$ Hz), 115.2 (d, $J = 5$ Hz), 126.5, 128.0, 128.2, 128.7, 128.8, 129.2 (d, $J = 10$ Hz), 130.0, 132.4 (d, $J = 4$ Hz), 134.7, 135.9, 157.4 (d, $J = 34$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -123.45. HRMS (EI) calcd. for C$_{20}$H$_{14}$FN: [M]+: 287.1110, found: 287.1098.

5-Chloro-2,3-diphenyl-1H-indole (3ka):

The title compound was prepared according to the general procedure as a white solid, 109.7 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 (dd, $J_1 = 8.6$ Hz, $J_2 = 2.04$ Hz, 1H), 7.27-7.34 (m, 5H), 7.35-7.41 (m, 6H), 7.62-7.63 (m, 1H), 8.21 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 111.9, 114.8, 119.2, 123.0, 126.2, 126.6, 128.1, 128.1, 128.7, 128.8, 129.9, 130.0, 132.2, 134.2, 134.4, 135.4. HRMS (EI) calcd. for C$_{20}$H$_{14}$ClN: [M]+: 303.0815, found: 303.0813.

4-Chloro-2,3-diphenyl-1H-indole (3la) and

6-Chloro-2,3-diphenyl-1H-indole (3la') (1.08:1, Determined by NMR):

The title compound was prepared according to the general procedure as a white solid, 59.2 mg, 49% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 (d, $J = 1.88$ Hz, 0.48H), 7.11 (d, $J = 1.88$ Hz, 0.52H), 7.27-7.41 (m, 11H), 7.54 (s, 0.51H), 7.57 (s, 0.49H), 8.19 (br, 0.95H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 110.8, 115.1, 120.6, 121.2,
126.5, 127.4, 128.0, 128.1, 128.4, 128.7, 128.8, 130.1, 132.2, 134.5, 134.6, 136.2; HRMS (EI) calcd. for C$_{20}$H$_{14}$ClN [M]: 303.0815, found: 303.0813.

5-Bromo-2,3-diphenyl-1H-indole (3ma):$^5$

The title compound was prepared according to the general procedure as a white solid, 125.9 mg, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24-7.33 (m, 6H), 7.38-7.41 (m, 6H), 7.77 (t, $J$ = 0.76 Hz, 1H), 8.24 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 112.3, 113.7, 114.7, 122.2, 125.5, 126.6, 128.1, 128.7, 128.8, 130.1, 130.6, 132.1, 134.3, 134.5, 135.2. HRMS (EI) calcd. for C$_{20}$H$_{14}$BrN [M]: 347.0310, found: 347.0308.

2,3-Diphenyl-1H-indole-5-carbonitrile (3ma):$^7$

The title compound was prepared according to the general procedure as a white solid, 36.0 mg, 31% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.33-7.49 (m, 10H), 7.52-7.55 (m, 1H), 7.61 (d, $J$ = 8.4 Hz, 1H), 7.90 (m, 1H), 12.21 (br, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 101.8, 112.8, 113.8, 120.5, 124.1, 124.7, 126.7, 127.7, 128.2, 128.3, 128.6, 128.8, 129.7, 131.4, 133.8, 136.6, 137.8; HRMS (ESI) calcd. for C$_{21}$H$_{15}$N$_2$ [M+H]: 295.1230, found: 295.1233.

Figure S1. ORTEP drawing of product 3ma
Methyl 2,3-diphenyl-1H-indole-5-carboxylate (3oa):

The title compound was prepared according to the general procedure as a white solid, 79.1 mg, 60% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 3.83 (s, 3H), 7.33-7.50 (m, 10H), 7.54 (d, $J = 8.52$, 1H), 7.81-7.84 (m, 1H), 8.15 (d, $J = 1.36$ Hz, 1H), 12.03 (br); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 51.7, 111.5, 114.5, 121.1, 121.1, 123.0, 126.6, 127.7, 128.0, 128.2, 128.6, 128.8, 129.8, 131.8, 134.5, 135.8, 138.6, 167.1; HRMS (ESI) calcd. for C$_{22}$H$_{18}$NO$_2$ [M+H]: 328.1332, found: 328.1344.

2,3-Diphenyl-1H-benz[g]indole (3pa):

The title compound was prepared according to the general procedure as a white solid, 78.6 mg, 62% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.55 (m, 13H), 7.72 (d, $J = 8.68$, 1H), 7.91 (d, $J = 8.04$, 1H), 8.02 (d, $J = 8.16$, 1H), 8.87 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 116.9, 119.4, 119.5, 121.3, 121.5, 124.2, 124.6, 125.7, 126.4, 127.5, 128.1, 128.6, 128.8, 129.0, 130.3, 130.8, 132.5, 132.8, 135.0; HRMS (EI) calcd. for C$_{24}$H$_{19}$N [M]: 319.1361, found: 319.1365.

2,3-Di-p-tolyl-1H-indole (3ab):

The title compound was prepared according to the general procedure as a white solid, 96.0 mg, 81% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.23 (s, 3H), 2.28 (s, 3H), 6.99-7.13 (m, 6H), 7.18-7.26 (m, 5H), 7.56 (d, $J = 7.96$, 1H), 7.95 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.4, 110.9, 114.6, 119.7, 120.4, 122.5, 128.1, 129.0, 129.4, 129.5, 130.0, 130.1, 132.2, 134.1, 135.8, 135.9, 137.6; HRMS (ESI) calcd. for C$_{22}$H$_{20}$N [M+H]: 298.1590, found: 298.1595.

2,3-Bis(4-methoxyphenyl)-1H-indole (3ac):

The title compound was prepared according to the general procedure as a white solid, 111.8 mg, 85% yield. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 3.77 (s, 3H), 3.79 (s, 3H), 6.93-7.04 (m, 5H), 7.11-7.15 (m, 1H), 7.25-7.28 (m, 2H), 7.39-7.44 (m, 4H), 11.39 (br, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.2, 55.3, 110.7, 113.8, 114.0, 114.2, 119.5, 120.2, 122.3, 125.3, 127.6,
129.0, 129.3, 131.2, 133.7, 135.7, 158.7, 159.1; HRMS (ESI) calcd. for C_{22}H_{20}NO_{2} [M+H]: 330.1489, found: 330.1487.

2,3-Bis(4-fluorophenyl)-1H-indole (3ad):\(^5\)

The title compound was prepared according to the general procedure as a white solid, 93.0 mg, 76% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.98-7.08 (m, 4H), 7.13-7.17 (m, 1H), 7.21-7.26 (m, 1H), 7.31-7.39 (m, 5H), 7.60 (d, \(J = 8.00\) Hz, 1H), 8.12 (br, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 111.0, 114.0, 115.5, 115.7 (d, \(J = 7\) Hz), 116.0, 119.5, 120.7, 122.9, 128.6, 129.9, 130.0 (d, \(J = 8\) Hz), 131.5 (d, \(J = 8\) Hz), 133.2, 135.8, 160.4, 161.2 (d, \(J = 246\) Hz), 162.9 (d, \(J = 244\) Hz); \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -116.2, -113.3; HRMS (EI) calcd. for C\(_{20}\)H\(_{13}\)F\(_2\)N [M]: 305.1013, found: 305.1008.

2,3-Bis(4-bromophenyl)-1H-indole (3ae):\(^5\)

The title compound was prepared according to the general procedure as a white solid, 128.4 mg, 75% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 (t, \(J = 7.84\) Hz, 1H), 7.24-7.29 (m, 5H), 7.40-7.51 (m, 5H), 7.61 (d, \(J = 7.96\) Hz, 1H), 8.18 (br, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 111.1, 114.3, 119.5, 120.4, 120.9, 122.1, 123.3, 128.4, 129.7, 131.3, 131.7, 131.9, 132.1, 133.1, 133.7, 136.0. HRMS (EI) calcd. for C\(_{20}\)H\(_{13}\)Br\(_2\)N [M]: 424.9415, found: 424.9426.

2-Phenyl-3-p-tolyl-1H-indole (3af) and 3-Phenyl-2-p-tolyl-1H-indole (3af\(^+\)) (1.14:1, Determined by NMR):\(^8\)

The title compound was prepared according to the general procedure as a white solid, 90.0 mg, 79% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.31 (s, 1.36H), 2.36 (s, 1.64H), 7.07-7.44 (m, 12H), 7.65 (d, \(J = 7.92\) Hz, 1H), 8.08 (br, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.3, 110.8, 119.6, 119.8, 120.4, 122.5, 122.7, 126.2, 127.6, 128.0, 128.1, 128.5, 128.7, 128.8, 129.3, 129.4.
130.0, 130.2, 132.0, 132.8, 134.2, 135.8, 135.9, 137.6; HRMS (ESI) calcd. for C_{21}H_{18}N [M+H]: 284.1434, found: 284.1436.

**2-(4-Bromophenyl)-3-phenyl-1H-indole (3ag) and 3-(4-Bromophenyl)-2-phenyl-1H-indole (3ag') (1:1 Determined by NMR):**

![Chemical Structure](image)

The title compound was prepared according to the general procedure as a white solid, 86.6 mg, 62% yield. 

$^1\text{H NMR} (400 \text{ MHz, CDCl}_3)$ $\delta$

7.13-7.18 (m, 1H), 7.23-7.50 (m, 11H), 7.63-7.67 (m, 1H), 8.17 (br, 0.48H), 8.24 (br, 0.45H); $^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3)$ $\delta$

111.0, 111.0, 113.8, 115.7, 119.4, 119.8, 120.2, 120.6, 120.7, 121.8, 122.9, 123.1, 126.5, 128.0, 128.2, 128.4, 128.7, 128.9, 129.6, 130.1, 131.6, 131.7, 131.9, 132.4, 132.8, 134.1, 134.4, 134.7, 135.9, 136.0; HRMS (ESI) calcd. for C_{20}H_{18}N_{2}Br [M+NH}_4$: 365.0648, found: 365.0634.

**2-(4-Bromophenyl)-3-phenyl-1H-indole (3ah):**

The title compound was prepared according to the general procedure as a white solid, 124.0 mg, 77% yield. $^1\text{H NMR} (400 \text{ MHz, CDCl}_3)$ $\delta$

7.08-7.12 (m, 1H), 7.20-7.38 (m, 7H), 7.58 (d, $J = 7.96$ Hz, 1H), 7.66 (s, 1H), 7.72 (s, 2H), 8.21 (br, 1H); $^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3)$ $\delta$

111.2, 117.9, 120.3, 120.7 (heptet, $J = 4$ Hz), 121.1, 121.7 (q, $J = 271$ Hz), 124.0, 127.3, 127.7, 128.6, 129.0, 130.0, 130.5, 131.5 (q, $J = 33$ Hz), 133.7, 134.8, 136.4; $^{19}\text{F NMR} (376 \text{ MHz, CDCl}_3)$ $\delta$ -63.2; HRMS (EI) calcd. for C_{22}H_{13}F_{6}N [M]: 405.0952, found: 405.0945.

**3-Methyl-2-phenyl-1H-indole (3ai):**

The title compound was prepared according to the general procedure as a white solid, 43.0 mg, 52% yield. $^1\text{H NMR} (400 \text{ MHz, DMSO-d}_6)$ $\delta$

2.43 (s, 3H), 7.01-7.05 (m, 1H), 7.10-7.14 (m, 1H), 7.35-7.39 (m, 2H), 7.50-7.55 (m, 3H), 7.68-7.70 (m, 2H), 11.17 (br, 1H); $^{13}\text{C
NMR (100 MHz, DMSO-\textit{d}_6) \delta 9.8, 106.7, 111.0, 118.4, 118.5, 121.5, 126.9, 127.5, 128.7, 129.4, 133.1, 133.7, 135.9; HRMS (ESI) calcd. for C_{15}H_{16}N [M+H]: 208.1121, found: 208.1125.

3-Benzyl-2-phenyl-1H-indole (3aj) and
2-benzyl-3-phenyl-1H-indole (3aj') (12:1 Determined by NMR):^8

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\text{The title compound was prepared according to}
\]
the general procedure as a white solid, 57.2 mg, 50% yield. \( ^1 \text{H NMR (400 MHz, DMSO-\textit{d}_6)} \delta \]
4.19 (s, 0.15H), 4.24 (s, 1.85H), 6.94-6.98 (m, 0.92H), 7.01-7.04 (m, 0.09H), 7.09-7.18 (m, 3.84H), 7.22-7.27 (m, 1.91H), 7.29-7.31 (m, 0.17H), 7.35-7.41 (m, 2.83H), 7.46-7.50 (m, 2.07H), 7.53-7.55 (m, 0.09H), 7.60-7.62 (m, 1.93H), 7.66-8.24 (m, 0.28H), 11.22 (br, 0.07H), 11.33 (br, 0.90); \( ^{13} \text{C NMR (100 MHz, DMSO-\textit{d}_6)} \delta \]
29.9, 109.7, 111.2, 118.7, 118.8, 121.6, 125.7, 127.4, 127.5, 127.9, 128.3, 128.6, 128.7, 128.8, 132.7, 134.9, 136.1, 141.5; HRMS (ESI) calcd. for C_{21}H_{18}N [M+H]: 284.1428, found: 284.1434.
5. Mechanistic studies

5.1 Rh/O₂ catalytic system catalyzed aerobic C-H activation

Following our general procedure: 1,2-diphenylethylene 2a (71.3 mg, 0.4 mmol), Cp*Rh(H₂O)₃(OTf)₂ (11.8 mg, 0.02 mmol, 5 mol%), acetanilide (81.1 mg, 0.6 mmol), t-AmOH (2.0 mL) and AcOH (35 µL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C for 24 hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH₃OH (2.0 mL) were added into the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 3aa in 85% yield (91.2 mg).

5.2 Substrate Competition Experiments

Following our general procedure: 1,2-diphenylethylene 2a (71.3 mg, 0.4 mmol), Cp*Rh(H₂O)₃(OTf)₂ (11.8 mg, 0.02 mmol, 5 mol%), p-toluidine 1b, (32.2 mg, 0.3 mmol), 4-chloroaniline 1k (38.3 mg, 0.3 mmol), t-AmOH (2.0 mL) and Ac₂O (57.0 µL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C for two hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH₃OH (2.0 mL) were added into the reaction mixture, and then stirred...
at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired products 3ba (24.5% yield) and 3ka (11.1% yield), respectively.

5.3 Synthesis of aniline (D₅-1a⁺):⁹

**Synthesis of D₅-nitrobenzene:**

Concentrated nitric acid (12.0 mL) and concentrated sulfuric acid (13.6 mL) were mixed together in a 250 mL round-bottom flask held in 30-50 °C. Benzene-d₆ (10.0 mL, 112 mmol) was added drop-wise at 80 °C and the mixture was allowed to stir at 60 °C for an additional 45 minutes. Then the reaction mixture was poured into ice-water (100 mL) and extracted with DCM (3×50 mL). The combined organic layer was washed with ice water (2×50 mL), sat. aq. NaHCO₃ solution (2×50 mL), brine (2×40 mL), and dried with anhydrous Na₂SO₄ for 24 hours. After distilling, faint yellow oil of D₅-nitrobenzene was obtained in 81 % yield, (11.7 g).

**Synthesis of D₅-aniline (D₅-1a⁺):**

D₅-nitrobenzene (2.55 g), Pd/C (200 mg), MeOH (5 mL) were added to a teflon tube which was placed in an autoclave. Then the autoclave was purged and charged with H₂
at 3 atm. The reaction mixture was stirred at room temperature for 16 hours, and then H$_2$ was carefully released. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the colorless oil desired product D$_5$-aniline in 92% yield (1.8 g).

5.4 Experimental detail for determination of the intramolecular KIE

Following our general procedure: 1,2-diphenylethyne (71.3 mg, 0.4 mmol), Cp*Rh(H$_2$O)$_3$(OTf)$_2$ (11.8 mg, 0.02 mmol, 5 mol%), D$_5$-aniline (29.4 mg, 0.3 mmol), aniline (27.5 mg, 0.3 mmol), t-AmOH (2.0 mL) and Ac$_2$O (57.0 µL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of O$_2$, and then stirred at 100°C for two hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH$_3$OH (2.0 mL) were added into the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired products 3aa (23.1% yield) and 3aa’ (6.6% yield), respectively.
6. References
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7. Copies for $^1$H NMR and $^{13}$C NMR of the indole products
ZGY-130902-8-HNMR

3ia

$\text{F}_3\text{CO}$

7.5 7.4 7.3 7.2 7.1 7.0 ppm

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

S-34
3oa
S-55
11-10-ZhangCY-HNMR

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\text{Ph} \quad + \quad \text{D}_5 \quad \text{Ph} \\
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S-73