Supporting Information

Rhodium-Catalyzed C–H Annulation of Nitrones with Alkynes: A Regiospecific Route to Unsymmetrical 2,3-Diaryl-Substitued Indoles**

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Supporting Information

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1. General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in an argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). NMR spectra were recorded on Bruker 400 MHz NMR spectrometer in the solvents indicated. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded at 400 MHz, 100 MHz and 377 MHz, respectively. The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for CDCl$_3$, 2.05 ppm for CD$_3$COCD$_3$). The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of CDCl$_3$ (77.16 ppm), CD$_3$COCD$_3$ (29.84 ppm) as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. HRMS data were obtained on Agilent Q-TOF 6540 and Agilent Accurate-Mass-Q-TOF MS 6520. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

2. Substrate Preparation

Alkynes and nitrones$^1$ (listed below) were synthesized according to the reported procedures.

2.1 General procedure for the preparation of nitrones

Nitroarene (1.0 equiv), aldehyde (1.1 equiv) and NH$_4$Cl (1.2 equiv) were dissolved in a 1:1 mixture of EtOH and water (2 mL/mmol of starting material) and cooled to 0 °C (ice bath). Then zinc powder (2.0 equiv) was added to the resulting mixture, and the reaction was allowed to warm to room temperature and stirred for 16 hours. The reaction mixture was filtered and washed with CH$_2$Cl$_2$. The filtrate was extracted with CH$_2$Cl$_2$ (4×50 mL) and the combined organic layer was washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure to give crude nitrones. Pure nitrones were obtained by recrystallization from ethyl acetate (cal. 65% yield).
2.2 General procedure for the preparation of alkynes

[Pd(PPh₃)Cl₂]₂ (2 mol%), CuI (4 mol%), Et₃N (2.0 equiv) and iodobenzene (1.1 equiv) were dissolved in 10.0 mL DMF and heated to 80 °C. Subsequently, phenylacetylene (1.0 equiv) was added to the resulting mixture by syringe, and the reaction was stirred under argon atmosphere for 10 h. After cooling to room temperature, the solvent was removed and extracted with CH₂Cl₂ (4×50 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, concentrated under reduced pressure to give crude alkyne. The residue was purified by silica gel flash chromatography using petroleum ether to afford the desired product.
3. General Procedure for Rh(III)-Catalyzed C–H Annulation of Nitrones with Alkynes

[Cp*RhCl₂]₂ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF₆ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)₂ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, nitrone (0.3 mmol, 1.2 equiv) was added followed by the alkyne (0.25 mmol, 1 equiv). The reaction mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product. Chromatography conditions: atmospheric pressure; eluent: petroleum ether/ethyl acetate, 50 mL of 100/0 (v/v), 450 mL of 20/1 (v/v).
4. Screening Reaction Conditions

Initial screening quickly identified [Cp*RhCl][2] as a good catalyst. Table S1 summarizes in-depth condition tuning for the reaction of nitrene 1a with 1,2-diphenylacetylene 2a.

![Screening Reaction Conditions Diagram]

Table S1. Screening reaction conditions.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive 1</th>
<th>Additive 2 (x eq.)</th>
<th>Solvent</th>
<th>t [°C]</th>
<th>3a : 4a</th>
<th>Yield of 3a[b]</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>AgSbF6</td>
<td>Cu(OAc)2 (2.0)</td>
<td>DCE</td>
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<td>3:1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>AgOTf</td>
<td>Cu(OAc)2 (2.0)</td>
<td>DCE</td>
<td>80</td>
<td>5:1</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>AgOTs</td>
<td>Cu(OAc)2 (2.0)</td>
<td>DCE</td>
<td>80</td>
<td>2:1</td>
<td>19</td>
</tr>
<tr>
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<td>AgNTf2</td>
<td>Cu(OAc)2 (2.0)</td>
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<td>80</td>
<td>3:1</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>AgSbF6</td>
<td>Cu(OAc)2 (2.0)</td>
<td>DCE</td>
<td>100</td>
<td>10:1</td>
<td>43</td>
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<td>3:1</td>
<td>31</td>
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<td>7</td>
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<td>Cu(OAc)2·H2O (2.0)</td>
<td>DCE</td>
<td>100</td>
<td>-</td>
<td>NR</td>
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<td>11</td>
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<tr>
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<td>-</td>
<td>NR</td>
</tr>
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<td>EDE</td>
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<td>25:1</td>
<td>53</td>
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<td>DCE/EDE = 1:1</td>
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<td>&gt;25:1</td>
<td>67; 40[d]</td>
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<tr>
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<td>DCE/EDE = 3:1</td>
<td>100</td>
<td>23:1</td>
<td>67; 41[d]</td>
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<tr>
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<td>Cu(OAc)2 (1.0)</td>
<td>DCE/EDE = 1:3</td>
<td>100</td>
<td>&gt;25:1</td>
<td>68; 43[d]</td>
</tr>
<tr>
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<td>Cu(OAc)2 (1.0)</td>
<td>DCE/EDE = 1:4</td>
<td>100</td>
<td>&gt;25:1</td>
<td>85; 81[c], 72[d]</td>
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<tr>
<td>20</td>
<td>AgSbF6</td>
<td>Cu(OAc)2 (1.0)</td>
<td>DCE/EDE = 1:5</td>
<td>100</td>
<td>25:1</td>
<td>74; 60[d]</td>
</tr>
</tbody>
</table>

*aReaction conditions: 1a (0.25 mmol), 2a (0.3 mmol), [Cp*RhCl][2] (2.5 mol%), AgSbF6 (10 mol%), Cu(OAc)2 (0.25 mmol), 2.0 mL of solvent at 100 °C for 12 h unless otherwise stated. bYield of 3a was determined by GC analysis using naphthalene as an internal standard. cIsolated yield. dYield of PhCHO. EDE = 1,2-diethoxyethane.
GC-MS analysis of crude products:

To understand the reaction process, the reaction performed under the optimal reaction conditions (Table S1, entry 19) was directly subjected into GC-MS analysis. In addition to indole products 3a ($M = 299.4$) and 4a ($M = 299.4$), PhCHO ($M = 106.1$) and $p$-anisaldehyde ($M = 136.1$) were also detected. This result reveals that arylaldehyde is released as a byproduct from the reaction of nitrone with alkyne.
5. Characterization of Products

3a, 81% yield (85% yield, 2.5 mmol scale), yellow solid, mp 102–104 °C, Rf = 0.25 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, Acetone-d6) δ 10.49 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.50–7.34 (m, 7H), 7.28 (t, J = 7.0 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), 2.05 (d, J = 4.5 Hz, 1H); 13C NMR (100 MHz, Acetone-d6) δ 160.2, 137.3, 136.9, 135.3, 130.9, 130.4, 129.7, 129.4, 126.8, 126.2, 122.7, 120.6, 119.6, 114.8, 112.0, 111.97, 55.6; HRMS (ESI, m/z) calcd for C21H18NO [M + H]+ 300.1383, found 300.1383.

3b, 85% yield, white solid, mp 144–146 °C, Rf = 0.25 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, CDCl3) δ 8.09 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 27.4, 8.3 Hz, 4H), 7.37 (dd, J = 8.7, 4.3 Hz, 5H), 7.34–7.28 (m, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 136.3, 134.6, 132.4, 130.3, 129.5 (q, J = 32.5 Hz), 128.90, 128.87, 128.3, 126.9, 125.7 (q, J = 3.8 Hz), 124.2 (q, J = 271 Hz), 123.6, 120.9, 120.2, 116.8, 111.2; 19F NMR (377 MHz, CDCl3) δ -62.5; HRMS (ESI, m/z) calcd for C21H15F3N [M + H]+ 338.1151, found 338.1148.

3c, 72% yield, white solid, mp 165–166 °C, Rf = 0.3 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, CDCl3) δ 8.13 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.44–7.35 (m, 5H), 7.30 (m, 1H), 7.27–7.20 (m, 2H), 7.14 (dd, J = 11.4, 4.4 Hz, 2H), 7.11–7.05 (m, 1H), 6.98–6.91 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 163.0 (d, J = 246.1 Hz), 136.1, 134.9 (d, J = 8.3 Hz), 134.71, 132.73, 130.4, 130.3, 128.9, 128.8, 126.7, 123.9 (d, J = 2.9 Hz), 123.3, 120.75, 120.0, 116.0, 115.0 (d, J = 22.6 Hz), 114.8, 114.6, 111.1; 19F NMR (377 MHz, CDCl3) δ -112.2; HRMS (ESI, m/z) calcd for C20H15FN [M + H]+ 288.1183, found 288.1179.
3d, 88% yield, red solid, mp 173–175 °C, \( R_f = 0.3 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.33 \) (s, 1H), 8.13 (d, \( J = 8.8 \) Hz, 2H), 7.64 (d, \( J = 8.0 \) Hz, 1H), 7.53 (d, \( J = 8.8 \) Hz, 2H), 7.45 (d, \( J = 8.3 \) Hz, 1H), 7.43–7.33 (m, 5H), 7.30 (t, \( J = 7.5 \) Hz, 1H), 7.17 (t, \( J = 7.5 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 146.7, 139.3, 136.7, 134.3, 131.4, 130.3, 128.9, 128.4, 127.2, 124.2, 124.18, 121.2, 120.4, 118.4, 111.4; HRMS (ESI, m/z) calcd for \( \text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2 \) [M + H]\(^+\) 315.1128, found 315.1122.

3e, 65% yield, yellow oil, \( R_f = 0.35 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.17 \) (s, 1H), 7.64 (d, \( J = 7.9 \) Hz, 1H), 7.39 (dd, \( J = 11.4, 6.0 \) Hz, 4H), 7.33 (dd, \( J = 14.6, 4.5 \) Hz, 6H), 7.25 (dd, \( J = 12.5, 4.6 \) Hz, 1H), 7.17 (t, \( J = 7.5 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 136.1, 134.8, 132.9, 132.0, 131.8, 130.2, 129.7, 128.9, 128.8, 126.6, 123.2, 121.9, 120.8, 119.9, 115.8, 111.1; HRMS (ESI, m/z) calcd for \( \text{C}_{20}\text{H}_{15}\text{BrN} \) [M + H]\(^+\) 348.0382, found 349.0383.

3f, 75% yield, yellow oil, \( R_f = 0.4 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.60 \) (s, 1H), 7.57–7.53 (m, 3H), 7.47–7.37 (m, 4H), 7.33 (m, \( J = 7.0 \) Hz, 1H), 7.23–7.14 (m, 3H), 7.10 (t, \( J = 7.3 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 136.0, 135.0, 133.8, 133.3, 132.3, 130.7, 129.3, 128.9, 128.5, 128.4, 127.7, 126.6, 126.2, 126.1, 125.8, 125.4, 122.7, 120.5, 119.9, 116.8, 111.0; HRMS (ESI, m/z) calcd for \( \text{C}_{24}\text{H}_{18}\text{N} \) [M + H]\(^+\) 320.1434, found 320.1433.

3g, 71% yield, brown oil, \( R_f = 0.4 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.60 \) (s, 1H), 7.57–7.53 (m, 3H),
7.47 (dd, $J = 10.3$, 4.8 Hz, 2H), 7.43–7.37 (m, 3H), 7.22 (dd, $J = 8.1$, 1.0 Hz, 1H), 7.13–7.08 (m, 1H), 6.36 (dd, $J = 3.4$, 1.8 Hz, 1H), 6.33 (d, $J = 3.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.3, 141.5, 135.6, 134.8, 130.4, 129.0, 128.7, 127.1, 125.3, 123.1, 120.6, 119.7, 114.7, 112.0, 110.9, 106.9; HRMS (ESI, m/z) calcd for C$_{18}$H$_{14}$NS [M + H]$^+$ 276.0841, found 276.1021.

3h

3h, 63% yield, yellow oil, $R_f$ = 0.4 (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 7.57–7.53 (m, 3H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.41–7.35 (m, 3H), 7.22 (t, $J = 7.1$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 6.35 (dd, $J = 3.4$, 1.7 Hz, 1H), 6.33 (d, $J = 3.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.3, 141.5, 135.6, 134.8, 130.4, 128.9, 128.74, 127.1, 125.3, 123.1, 120.6, 119.7, 114.6, 112.0, 110.9, 106.9; HRMS (ESI, m/z) calcd for C$_{18}$H$_{14}$NO [M + H]$^+$ 260.1070, found 260.1067.

3i

3i, 81% yield, yellow solid, mp 188–190 °C, $R_f$ = 0.25 (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (s, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 6.9$ Hz, 3H), 7.38–7.20 (m, 6H), 7.14 (s, 1H), 6.93 (d, $J = 8.6$ Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 136.0, 133.8, 133.0, 131.3, 129.1, 128.8, 128.2, 127.7, 127.5, 122.8, 120.5, 119.8, 114.9, 114.2, 111.0, 55.4; HRMS (ESI, m/z) calcd for C$_{21}$H$_{18}$NO [M + H]$^+$ 300.1383, found 300.1378.

3j

3j, 80% yield, yellow oil, $R_f$ = 0.25 (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (s, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.59 (d, $J = 8.2$ Hz, 2H),
7.51 (d, \( J = 8.1 \) Hz, 2H), 7.41–7.28 (m, 6H), 7.24 (t, \( J = 7.5 \) Hz, 1H), 7.16 (t, \( J = 7.5 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 139.1, 136.0, 135.1, 132.3, 130.2, 129.0, 128.4, 128.3, 128.2, 128.0, 127.7, 124.6 (q, \( J = 270 \) Hz), 125.5 (q, \( J = 3.8 \) Hz), 123.1, 120.9, 119.4, 113.6, 111.2; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \( \delta \) -62.1; HRMS (ESI, m/z) calcd for C\(_{21}\)H\(_{15}\)F\(_3\)N [M + H]\(^+\) 338.1151, found 338.1148.

3k\(^8\), 75% yield, white solid, mp 165–166 °C, \( R_f = 0.35 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.14 (s, 1H), 7.61 (d, \( J = 7.9 \) Hz, 1H), 7.38–7.34 (m, 5H), 7.31–7.28 (m, 3H), 7.26–7.20 (m, 1H), 7.17–7.12 (m, 1H), 7.07–7.02 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 161.7 (d, \( J = 245.0 \) Hz), 135.9, 134.3, 132.6, 131.7 (d, \( J = 7.8 \) Hz), 131.1, 128.9, 128.8, 128.3, 127.9, 122.9, 120.7, 119.6, 115.6 (d, \( J = 21.2 \) Hz), 114.1, 111.1; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \( \delta \) -116.3; HRMS (ESI, m/z) calcd for C\(_{20}\)H\(_{15}\)FN [M + H]\(^+\) 288.1183, found 288.1179.

3l\(^7\), 80% yield, white solid, mp 146–149 °C, \( R_f = 0.3 \) (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.15 (s, 1H), 7.62 (d, \( J = 7.9 \) Hz, 1H), 7.42–7.28 (m, 10H), 7.23 (t, \( J = 12.5, 4.6 \) Hz, 1H), 7.15 (t, \( J = 7.5 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 136.0, 134.5, 133.7, 132.5, 132.1, 131.5, 129.0, 128.95, 128.6, 128.3, 128.1, 123.0, 120. 8, 119.5, 113.9, 111.1; HRMS (ESI, m/z) calcd for C\(_{20}\)H\(_{15}\)ClN [M + H]\(^+\) 304.0888, found 304.0885.

3m\(^7\), 70% yield, white solid, mp 170–171 °C, \( R_f = 0.4 \) (petroleum ether/ethyl acetate =
10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (s, 1H), 7.44 (d, $J$ = 8.1 Hz, 1H), 7.34–7.27 (m, 7H), 7.25–7.18 (m, 4H), 7.10 (t, $J$ = 7.1 Hz, 1H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.9, 136.0, 134.7, 133.9, 133.1, 131.7, 130.4, 129.8, 128.9, 127.6, 127.3, 126.9, 126.0, 122.8, 120.3, 120.2, 115.0, 110.9, 20.3; HRMS (ESI, m/z) calcd for C$_{21}$H$_{18}$N [M + H]$^+$ 284.1434, found 284.1426.

![3n](image)

3n, 72% yield, yellow oil, $R_f$ = 0.4 (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 10.63 (s, 1H), 7.96 (d, $J$ = 6.9 Hz, 1H), 7.82 (d, $J$ = 8.2 Hz, 1H), 7.60–7.44 (m, 4H), 7.39–7.34 (m, 1H), 7.17 (t, $J$ = 7.2 Hz, 3H). 7.10–7.05 (m, 1H); $^{13}$C NMR (100 MHz, Acetone-d$_6$) $\delta$ 137.6, 136.5, 134.7, 134.4, 133.3, 132.1, 130.1, 129.9, 129.6, 129.10, 129.06, 128.4, 127.2, 126.91, 126.86, 126.4, 126.2, 125.0, 120.8, 112.0, 116.8, 112.3; HRMS (ESI, m/z) calcd for C$_{24}$H$_{18}$N [M + H]$^+$ 320.1434, found 320.1424.

![3o](image)

3o, 81% yield, yellow oil, $R_f$ = 0.3 (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.53 (dd, $J$ = 17.6, 8.3 Hz, 4H), 7.42 (d, $J$ = 8.1 Hz, 1H), 7.32 (d, $J$ = 8.4 Hz, 2H), 7.25 (d, $J$ = 9.0 Hz, 1H), 7.16 (t, $J$ = 7.5 Hz, 1H), 6.95 (d, $J$ = 8.4 Hz, 2H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 136.5, 136.3, 132.1, 131.3, 129.4 (q, $J$ = 32.0 Hz), 129.1, 128.1, 126.3, 125.8 (q, $J$ = 3.8 Hz), 124.2 (q, $J$ = 270 Hz), 123.5, 120.8, 120.2, 116.6, 114.4, 111.2, 55.4; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.6; HRMS (ESI, m/z) calcd for C$_{22}$H$_{17}$F$_3$NO [M + H]$^+$ 368.1257, found 368.1253.

![3p](image)
3p. 85% yield, yellow oil, Rf = 0.25 (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.23 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.54 (q, J = 8.5 Hz, 4H), 7.43 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.7 Hz, 2H), 7.28 (dd, J = 7.1, 1.0 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 158.7, 136.5, 136.3, 132.1, 131.3, 129.3 \text{ (q, J = 32.0 Hz)}, 129.1, 128.1, 126.8, 125.8 \text{ (q, J = 3.7 Hz)}, 124.2 \text{ (q, J = 270 Hz)}, 123.5, 120.8, 120.2, 116.5, 114.4, 111.2, 55.4; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta -62.6\); HRMS (ESI, m/z) calcd for C\(_{22}\)H\(_{17}\)F\(_3\)NO [M + H]\(^+\) 368.1257, found 368.1250.

\[\text{3q. 74% yield, yellow oil, Rf = 0.3 (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.13 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.43–7.34 \text{ (m, 3H), 7.31 (d, J = 8.7 Hz, 2H), 7.26–7.19 (m, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 161.7 \text{ (d, J = 244.9 Hz)}, 159.5, 135.8, 134.3, 131.7 \text{ (d, J = 7.8 Hz), 131.3 \text{ (d, J = 3.4 Hz)}, 129.6, 128.9, 125.1, 122.6, 120.6, 119.4, 115.6 \text{ (d, J = 21.2 Hz), 114.4, 113.3, 111.0, 55.4; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta -116.3\); HRMS (ESI, m/z) calcd for C\(_{21}\)H\(_{17}\)F\(_3\)NO [M + H]\(^+\) 318.1289, found 318.1285.}\]

\[\text{3r. 78% yield, yellow solid, mp 165–166 °C, Rf = 0.25 (petroleum ether/ethyl acetate = 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.19 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.53 (q, J = 8.0 Hz, 4H), 7.42 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 17.3, 8.0 Hz, 3H), 7.21 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 2.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 161.5, 160.7, 135.8, 134.3, 131.7 \text{ (d, J = 7.8 Hz), 131.3 \text{ (d, J = 3.4 Hz)}, 129.6, 128.9, 125.1, 122.6, 120.6, 119.4, 115.6 \text{ (d, J = 21.2 Hz), 114.4, 113.3, 111.0, 55.4; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta -62.6\); HRMS (ESI, m/z) calcd for C\(_{22}\)H\(_{17}\)F\(_3\)N [M + H]\(^+\) 352.1308, found 352.1299.}\]
**3s**, 76% yield, colorless oil, R_f = 0.4 (petroleum ether/ethyl acetate = 10/1);^1^H NMR (400 MHz, CDCl_3) δ 8.21 (s, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.32–7.23 (m, 7H), 7.20 (d, J = 7.3 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.03 (s, 3H); ^13^C NMR (100 MHz, CDCl_3) δ 159.2, 138.0, 135.8, 134.9, 134.0, 131.8, 130.4, 129.9, 128.2, 127.2, 126.0, 125.7, 122.4, 120.2, 119.9, 114.4, 113.9, 110.7, 55.4, 20.3; HRMS (ESI, m/z) calcd for C_{22}H_{20}NO [M + H]^+ 314.1539, found 314.1540.

**3t**, 81% yield, brown solid, mp 217–220 °C, R_f = 0.25 (petroleum ether/ethyl acetate = 10/1);^1^H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 8.13 (d, J = 8.9 Hz, 2H), 7.45 (dd, J = 15.3, 8.1 Hz, 2H), 7.41–7.31 (m, 2H), 7.28 (d, J = 7.1, Hz, 1H), 7.17–7.11 (m, 1H), 7.04 (t, J = 7.4, 1H), 6.99 (d, J = 8.2 Hz, 1H), 3.55 (s, 3H); ^13^C NMR (100 MHz, CDCl_3) δ 157.3, 146.5, 140.0, 136.7, 132.5, 132.0, 129.4, 129.2, 127.3, 124.0, 123.1, 121.2, 120.9, 114.5, 111.6, 111.3, 100.1, 55.3; HRMS (ESI, m/z) calcd for C_{21}H_{17}N_{2}O_{2} [M + H]^+ 345.1234, found 345.1223.

**3u**, 82% yield, white solid, mp 180–183 °C, R_f = 0.4 (petroleum ether/ethyl acetate = 10/1);^1^H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.42 (d, J = 7.8 Hz, 3H), 7.36 (t, J = 7.5 Hz, 2H), 7.33–7.23 (m, 4H), 7.03 (d, J = 8.2 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H); ^13^C NMR (100 MHz, CDCl_3) δ 159.3, 135.6, 134.4, 134.3, 130.3, 129.8, 129.5, 129.3, 128.6, 126.2, 125.5, 124.1, 119.2, 114.3, 114.0, 110.6, 55.4, 21.7; HRMS (ESI, m/z) calcd for C_{22}H_{20}NO [M + H]^+ 314.1539, found 314.1532.
3v, 79% yield, colorless oil, $R_f = 0.4$ (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.75 (s, 1H), 7.37 (t, $J = 6.4$ Hz, 4H), 7.34–7.22 (m, 5H), 6.85 (d, $J = 8.7$ Hz, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.6, 135.4, 134.7, 134.5, 130.8, 130.2, 129.6, 128.8, 126.6, 125.3, 124.7, 122.1, 114.4, 113.9, 113.8, 112.3, 55.4; HRMS (ESI, m/z) calcd for C$_{21}$H$_{17}$BrNO [M + H]$^+$ 378.0488, found 378.0489.

3w, 80% yield, white solid, mp 220–223 ºC, $R_f = 0.35$ (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (s, 1H), 8.40 (s, 1H), 7.94 (dd, $J = 8.5$, 1.4 Hz, 1H), 7.41 (m, 5H), 7.33 (t, $J = 8.8$ Hz, 3H), 6.85 (d, $J = 8.7$ Hz, 2H), 4.37 (q, $J$ = 7.1 Hz, 2H), 3.80 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 159.6, 138.4, 135.4, 134.7, 130.3, 129.6, 128.8, 128.7, 126.8, 124.7, 124.0, 122.9, 122.5, 115.3, 114.4, 110.5, 60.8, 55.4, 14.6; HRMS (ESI, m/z) calcd for C$_{24}$H$_{22}$NO$_3$ [M + H]$^+$ 372.1594, found 372.1591.

3x, 80% yield, white solid, mp 151–153 ºC, $R_f = 0.3$ (petroleum ether/ethyl acetate = 10/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.55 (d, $J = 8.5$ Hz, 1H), 7.42–7.35 (m, 5H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.31–7.27 (m, 1H), 7.10 (dd, $J = 8.5$, 1.8 Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.5, 136.2, 134.8, 132.2, 130.1, 129.5, 128.7, 128.1, 127.6, 126.5, 124.8, 121.1, 120.5, 114.4, 114.3, 110.8, 55.4; HRMS (ESI, m/z) calcd for C$_{21}$H$_{17}$ClNO [M + H]$^+$ 334.0993, found 334.0988.
3y. 80% yield, white solid, mp 170–172 °C, Rf = 0.4 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, CDCl3) δ 8.40 (s, 1H), 7.43 (dd, J = 8.1, 1.2 Hz, 2H), 7.38–7.32 (m, 4H), 7.30–7.22 (m, 2H), 7.05 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 7.7 Hz, 1H), 3.98 (s, 3H), 3.79 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 159.3, 146.1, 135.6, 134.0, 130.2, 130.1, 129.6, 128.6, 126.3, 126.1, 125.4, 120.8, 114.6, 114.3, 112.4, 102.5, 55.6, 55.4; HRMS (ESI, m/z) calcd for C22H20NO2 [M + H]+ 330.1489, found 330.1493.

3z. 65% yield, red solid, mp 98–100 °C, Rf = 0.2 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, CDCl3) δ 8.31 (d, J = 8.8 Hz, 2H), 8.09 (s, 1H), 7.68 (dd, J = 12.5, 8.4 Hz, 3H), 7.39 (d, J = 8.1 Hz, 1H), 7.29–7.23 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 2.96–2.84 (m, 2H), 1.83–1.69 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 146.1, 135.6, 134.0, 130.2, 129.6, 128.6, 126.3, 126.1, 125.4, 120.8, 114.6, 114.3, 112.4, 102.5, 55.6, 55.4; HRMS (ESI, m/z) calcd for C17H17N2O2 [M + H]+ 281.1285, found 281.1280.

5. 85% yield, white solid, Rf = 0.1 (petroleum ether/ethyl acetate = 10/1); 1H NMR (400 MHz, Acetone-d6) δ 7.97 (d, J = 9.1 Hz, 2H), 7.72 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7, 1.1 Hz, 1H), 7.40–7.32 (m, 3H), 7.31–7.23 (m, 5H), 7.21–7.13 (m, 3H), 6.96–6.90 (m, 2H), 3.81 (s, 3H); 13C NMR (100 MHz, Acetone-d6) δ 197.4, 177.4, 163.2, 156.9, 143.9, 139.8, 138.7, 133.3, 131.9, 130.1, 129.6, 129.1, 129.0, 128.5, 128.3, 127.4, 126.5, 124.5, 122.2, 114.9, 78.8, 55.8. HRMS (ESI, m/z) calcd for C28H22NO2 [M + H]+ 404.1645, found 404.1660.
6. Control Experiments

(1) $\text{1a-d$_5$} + \text{2a} \xrightarrow{\text{Standard Conditions, 12 h}} \text{3a-d$_5$}$

(2) $\text{1a} + \text{CH$_3$COOD (1.5 eq)} \xrightarrow{\text{Standard Conditions, 2 h}} \text{3a (C-phenyl)}$

(3) $\text{1a} + \text{2a} + \text{CH$_3$COOD (1.5 eq)} \xrightarrow{\text{Standard Conditions, 5 h}} \text{3a-d'$_n$} (N-phenyl)$

(4) $\text{1a} + \text{2a} \xrightarrow{\text{Standard Conditions}} \text{3a} + \text{3a-d$_5$} \xrightarrow{\text{Standard Conditions}} \text{3a} + \text{3a-d$_5$}$

(5) $\text{1a} + \text{1a-d$_5$} + \text{2a} \xrightarrow{\text{Standard Conditions, 5 h}} \text{3a} + \text{3a-d$_5$}$

(6) $\text{1a-d$_4$} + \text{2a} \xrightarrow{\text{Standard Conditions, 5 h}} \text{3a} + \text{3a-d$_5$}$
Scheme S1. Summary of control experiments
Scheme S1-1. Reaction of 2a with 1a-\textit{d}_5

This reaction was performed following the “General Procedure”, only except that 1a-\textit{d}_5 was used as nitrone. Compared with the \textsuperscript{1}H NMR spectra of 3a, the deuterium atom was completely transferred into the product (>99% deuterium incorporation).

Scheme S1-2. Reaction of 1a with CH\textsubscript{3}COOD

The 1a (0.25 mmol) and CH\textsubscript{3}COOD (0.375 mmol, 1.5 equiv) was stirred under standard reaction conditions. After reaction for 2 h, the resulting mixture was purified by chromatography and subjected into \textsuperscript{1}H NMR analysis. Compared with the \textsuperscript{1}H
NMR spectra of 1a, 1.14 protons were missing in product 1a-d_
. That is, 0.5 H at 8.53 ppm and 0.64 H at 7.91 ppm, respectively. This result suggests that the C–H cleavage of nitrone is reversible.

Scheme S1-3. Influence of external deuterium source

This reaction was performed following the “General Procedure”, only except that CH₃COOD was added into the model reaction. Compared with the ¹H NMR spectra of 3a, no deuteration on the indole ring was observed while 23% deuteration at the meta-positions of the methoxyl group was observed. This result indicates an irreversible C–H insertion step on the indole ring under the reaction conditions.

Note: The chemical shifts of protons on the indole ring were determined according to the following information:
(1). The comparison of $^1$H NMR spectra of $3a$ with $3a-d_6$ suggests that the chemical shifts of protons on the indole ring are 7.08 ppm, 7.15 ppm, 7.46 ppm (1H NMR spectra: Scheme S1-1 vs Scheme S1-3) and 7.55 ppm.

(2). Decrease of proton number in 7.36~7.49 ppm (Scheme S1-6) suggests that the proton in this area is the on the 4-position of indole ring (~7.46 ppm).

(3). Therefore, the protons at the 5-, 6- and 7-positions are 7.08 ppm, 7.15 ppm and 7.55 ppm. All these protons can be clearly recognized in the $^1$H NMR spectra. However, the detailed chemical shifts of individual protons cannot be assigned. Therefore, the KIE values were determined by the information of these three protons (7.08 ppm, 7.15 ppm and 7.55 ppm).

Scheme S1-4. Independent reactions

\[
\begin{align*}
1a + 2a & \quad \text{Standard Conditions} \\
1a-d_5 + 2a & \quad \text{Standard Conditions} \\
\text{mix} & \quad 3a + 3a-d_5
\end{align*}
\]
Two separate dried Schlenk tubes were charged with \([\text{Cp}^*\text{RhCl}_2]\) \((0.00625 \text{ mmol, 3.9 mg, 2.5 mol\%})\), \(\text{AgSbF}_6\) \((0.025 \text{ mmol, 8.6 mg, 10 mol\%})\), \(\text{Cu(OAc)}_2\) \((0.25 \text{ mmol, 45.4 mg, 1.0 equiv})\). Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, 1a \((0.3 \text{ mmol, 1.5 equiv})\) or 1a-d5 \((0.3 \text{ mmol, 1.5 equiv})\) was added followed by 2a \((0.25 \text{ mmol, 1 equiv})\). The two reaction mixtures were stirred side by side at 100 °C for 3 or 5 h. After cooling to the room temperature, the solvent was removed under reduced pressure and the residues of the two reactions were combined and purified together by silica gel chromatography using PE/EA to give the mixture of 3a and 3a-d5. A KIE value of 2.6 or 3.3 was obtained on the basis of \(^1\text{H}\) NMR analysis.
Scheme S1-5. Intermolecular competitive reactions

$\text{[Cp}^\ast\text{RhCl}_2]_2$ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF$_6$ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)$_2$ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighed in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 min to afford a light yellow clear solution. After which time, 1a (0.3 mmol) and 1a-$d_5$ (0.3 mmol) were added followed by alkyne 2a (0.25 mmol, 1 equiv). The reaction mixture was stirred at 100 °C for 5 h. Then, the solvent was evaporated and the crude product was directly purified by silica gel column chromatography to give the mixture of 3a and 3a-$d_5$. A KIE value of 3.8 was obtained on the basis of $^1$H NMR analysis.
Scheme S1-6. Intramolecular competitive reaction

Scheme S1-6. Intramolecular competitive reaction

$	ext{[Cp}^*\text{RhCl}_2\text{]}_2$ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF$_6$ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)$_2$ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighed in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 min to afford a light yellow clear solution. After which time, 1a-\textit{d}_1 (0.3 mmol, 1.2 equiv) was added followed by alkyne 2a (0.25 mmol, 1 equiv). The reaction mixture was stirred at 100 °C for 5 h. Then, the solvent was evaporated and the crude product was directly purified by silica gel column chromatography to give the mixture of 3a-\textit{d}_1 and 3a-\textit{d}_1'. A KIE value of 4.0 was obtained on the basis of $^1$H NMR analysis.
Scheme S1-7. Competition reaction between 1u and 1w

\[ \text{[Cp*RhCl}_2\text{]} (0.00625 \text{ mmol, 3.9 mg, 2.5 mol%}) \text{, AgSbF}_6 (0.025 \text{ mmol, 8.6 mg, 10 mol%}) \text{ and Cu(OAc)}_2 (0.25 \text{ mmol, 45.4 mg, 1.0 equiv}) \] were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, 1u (0.3 mmol, 1.2 equiv) and 1w (0.3 mmol, 1.2 equiv) were added followed by diphenylacetylene 2a (0.25 mmol, 1.0 equiv). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude products. Product ratio of 3u and 3w was determined by HPLC analysis (3u/3w = 2.9/1).
3u: $t = 35.082 \text{ min}, A_{3u}/A_{IS} = 2.524, f = 0.358, \text{LC yield (3u)} = 57.6\%$

3w: $t = 28.945 \text{ min}, A_{3w}/A_{IS} = 1.245, f = 0.297, \text{LC yield (3w)} = 19.9\%$

Ratio of LC yield: $3u/3w = 2.9/1$

Scheme S1-8. Reaction with unsymmetrical alkyne

$[\text{Cp}^*\text{RhCl}_2]_2$ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF$_6$ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)$_2$ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes.
After which time, 1aa (0.3 mmol, 1.2 equiv) was added followed by the unsymmetrical alkyne 2ij (0.25 mmol, 1.0 equiv). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, the solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude product. Product ratio of 3i and 3j was determined by HPLC analysis (3i/3j = 5.5/1)

3i: t = 20.362 min, A$_{3i}$/A$_{IS}$ = 0.3438, f = 1.416, LC yield (3i) = 33%

3j: t = 13.328 min, A$_{3j}$/A$_{IS}$ = 0.0655, f = 1.650, LC yield (3j) = 6%

Ratio of LC yield: 3i/3j = 5.5/1

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[ Cp*RhCl$_2$]$_2$ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF$_6$ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)$_2$ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, 1aa (0.3 mmol, 1.2 equiv) was added followed by the
unsymmetrical alkyne 2am (0.25 mmol, 1.0 equiv). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, the solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude product. Product ratio of 4a and 3m was determined by HPLC analysis (4a/3m = 1.5/1)

4a: t = 49.930 min, A₄ₐ/ₐ₃ לעבוד = 1.1955, f = 0.506, LC yield (4a) = 45%

3m: t = 32.688 min, A₃ₐ/ₐ₃avors = 0.9106, f = 0.5423, LC yield (3m) = 31%

Ratio of LC yield: 4a/3m = 1.5/1

[Cp*RhCl₂]₂ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF₆ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)₂ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes.
After which time, 1d (0.3 mmol, 1.2 equiv) was added followed by the unsymmetrical alkyne 2az (0.25 mmol, 1.0 equiv). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, the solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude product. Product ratio of 1d and 3z was determined by HPLC analysis (3z/3d = 2.3/1)

3z: t = 29.086 min, A_{3z}/A_{IS} = 2.0457, f = 0.245, LC yield (3z) = 36%

3d: t = 31.981 min, A_{3d}/A_{IS} = 0.7452, f = 0.315, LC yield (3d) = 16%

Ratio of LC yield: 3z/3d = 2.3/1

<table>
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<th>Height</th>
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<td>0.7941</td>
<td>2530.65845</td>
<td>48.58513</td>
<td>15.1124</td>
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</table>

**Conclusion:** The results of the reactions with unsymmetrical alkynes suggest that the nitrones react preferentially on the positively polarized or less hindered alkynyl atom.
Scheme S1-9. Reaction with stoichiometric amount of Rh(III)

\[
\begin{array}{c}
\text{H} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{Ph} \\
\text{Ph}
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \xrightarrow{\text{[Cp*RhCl}_2\text{] (0.5 equiv) AgSbF}_6\text{ (2.0 equiv)}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

\[[\text{Cp*RhCl}_2\text{]} (0.125 \text{ mmol, 77.3 mg, 0.5 equiv}), \text{AgSbF}_6 (0.5 \text{ mmol, 171.8 mg, 2.0 equiv})\] were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, \(1\text{a} (0.3 \text{ mmol, 1.2 equiv})\) was added followed by diphenylacetylene \(2\text{a} (0.25 \text{ mmol, 1.0 equiv})\). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, the solvent was evaporated and washed by 5% aq. HCl and 5% aq. NaHCO\(_3\), then extracted with CH\(_2\)Cl\(_2\) (4 × 50 mL). The combined organic layer was washed with brine, dried over Na\(_2\)SO\(_4\). The solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude product. Indole \(4\text{a}\) was obtained in 80% LC yield and no \(3\text{a}\) was detected. In the case of 50 mol% [Rh] (0.25 equiv [Cp*RhCl\(_2\)]\(_2\)), \(4\text{a}\) was obtained in 35% yield and no \(3\text{a}\) was detected.

Scheme S1-10. Reaction with catalytic amount of Cu(OAc)\(_2\)

\[
\begin{array}{c}
\text{H} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{Ph} \\
\text{Ph}
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \xrightarrow{\text{[Cp*RhCl}_2\text{] (2.5 mol%) AgSbF}_6\text{ (10 mol%) Cu(OAc)}_2\text{ (x equiv), 100 °C}}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \quad \text{byproduct}
\]

Five separate dried Schlenk tubes were charged with [Cp*RhCl\(_2\)]\(_2\) (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF\(_6\) (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)\(_2\) (10 mol%, 20 mol%, 30 mol%, 40 mol% and 50 mol% respectively) in the glove box. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, \(1\text{a} (0.3 \text{ mmol, 1.2 equiv})\) was added followed by diphenylacetylene \(2\text{a} (0.25 \text{ mmol, 1.0 equiv})\). The reaction mixture was stirred at 100 °C for 12 h. After cooling to the room temperature, the
solvent was evaporated and 50 mg of naphthalene (internal standard) was added into the crude product. Product ratio of 3a and 4a was determined by HPLC analysis. Detailed information is shown in Table S2.

Table S2. Ratio of 3a and 4a with catalytic amount of Cu(OAc)$_2$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>x eq.</th>
<th>Yield of 3a (%)$^a$</th>
<th>Ratio of 3a/4a$^b$</th>
<th>Yield of PhCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(OAc)$_2$</td>
<td>10%</td>
<td>42.6</td>
<td>20:1</td>
<td>30.1</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OAc)$_2$</td>
<td>20%</td>
<td>54.3</td>
<td>23:1</td>
<td>41.2</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)$_2$</td>
<td>30%</td>
<td>57.5</td>
<td>20:1</td>
<td>43.3</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OAc)$_2$</td>
<td>40%</td>
<td>61.4</td>
<td>17:1</td>
<td>46.5</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OAc)$_2$</td>
<td>50%</td>
<td>55.0</td>
<td>&gt;25:1</td>
<td>40.2</td>
</tr>
</tbody>
</table>

$^a$Yield of 3a was determined by HPLC using naphthalene as an internal standard. $^b$Ratio of 3a/4a was determined by HPLC analysis using naphthalene as an internal standard.

Scheme S1-11. Isolation of intermediate 5 and its further transformation to 3a

[Cp*RhCl$_2$]$_2$ (0.00625 mmol, 3.9 mg, 2.5 mol%), AgSbF$_6$ (0.025 mmol, 8.6 mg, 10 mol%) and Cu(OAc)$_2$ (0.25 mmol, 45.4 mg, 1.0 equiv) were weighted in the glove box and placed in a dried Schlenk tube. Then 2.0 mL of solvent (DCE/EDE = 1/4, v/v) was added. The resulting mixture was stirred at room temperature for 30 minutes. After which time, 1a (0.3 mmol, 1.2 equiv) was added followed by diphenylacetylene 2a (0.25 mmol, 1.0 equiv). The reaction mixture was stirred at 100 °C for 1 h. After cooling to the room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford desired product. The product was isolated in 85% yield. $^1$H and $^{13}$C NMR analysis was performed using Acetone-$d_6$ as solvent, the results are shown below.
7. Possible Pathway for 4a

On the basis of our mechanistic studies, a plausible mechanistic pathway for the formation of 4a is proposed (Scheme S2). The reaction follows the similar pathway of 3a to generate intermediate D. Competitive tautomerization between D and D' may occur in the reaction. In the case of 3a, the copper salt probably acts as a Lewis acid to coordinate carbonyl group to preferably generate intermediate D (Main text, Scheme 4), and then releases the Rh catalyst in a transmetalation event (Main text, Scheme 4, intermediate E). However, in the absence of copper salt (e.g. Main text,
Scheme 3f; Scheme S1-9), intermediate D’ is preferred. Then, intramolecular nucleophilic attack of oxygen to imino moiety furnishes intermediate E’. By heating at 100 °C, it rearranges to intermediate F’, followed by elimination of ArCHO to generate rhodium-indole complex. Finally, acid/base workup (in the case of stoichiometric reaction with Rh catalyst) or protonation provides 4a.
8. Crystal Structure of Product

CCDC 1041488
9. References


9. Copies of NMR and HRMS Spectra

$^1$H NMR (400 MHz, Acetone-$d_6$)
$^{13}$C NMR (100 MHz, Acetone-$d_6$)
$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

**3d**
$^1$H NMR (400 MHz, CDCl$_3$)
^13C NMR (100 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

S52
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, Acetone-$d_6$)
$^{13}$C NMR (100 MHz, Acetone-d$_6$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

- 159.60
- 135.42
- 134.47
- 134.47
- 130.15
- 129.55
- 128.80
- 128.80
- 126.57
- 126.57
- 125.27
- 125.27
- 122.08
- 122.08
- 114.38
- 114.38
- 113.93
- 113.93
- 113.77
- 113.77
- 112.32
- 112.32
- 77.48
- 77.16
- 77.16
- 76.84
- 76.84
- 55.42

3v
$^1$H NMR (400 MHz, CDCl$_3$)

3w

EtOOC

Ph
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)