Supporting Information

Rhodium(III)-Catalyzed Indole Synthesis at Room Temperature
Using the Transient Oxidizing Directing Group Strategy

Yaping Shang, Krishna Jonnada, Subhash Laxman Yedage, Hua Tu, Xiaofeng Zhang, Xin Lou, Shijun Huang, and Weiping Su*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academyof Sciences, Fuzhou 350002, China

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General Information. All reactions were carried out in dried glass wares under a dry nitrogen atmosphere using Schlenk technique. The air and moisture sensitive reagents were stored in a dry and nitrogen-filled glove box. All commercially available reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, Adamas-beta, Sinocompound and other commercial suppliers and used directly without further purification. All solvents used in the reactions were freshly distilled according to the standard methods and stored under a nitrogen atmosphere. Especially, Dichloromethane (CH$_2$Cl$_2$) and dichloroethane (DCE) were distilled over CaH$_2$ and stored under a nitrogen atmosphere. $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) and $^{19}$F NMR (377 MHz) spectra were recorded in CDCl$_3$ solutions using a Bruker AVANCE 400 spectrometer at 298 K. The chemical shifts (δ) were calibrated using TMS (0 ppm for $^1$H) and residual undeuterated solvent CHCl$_3$ (77.0 ppm for $^{13}$C). HRMS (High-Resolution Mass Spectra) were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (Instrument: Thermo Fisher Scientific LTQ FT Ultra, Operation Mode: DART Positive). Reactions were monitored by TLC and detected the target compound by the UV light (254 nm or 365 nm). The desired products were purified by flash chromatography using silica gel (300-400 mesh).

Preparation and data of substrates

3-Substituted N-Methyl Anilines and 1-(benzyloxy)-4-(prop-1-yn-1-yl)benzene are known compounds, but prepared by following the recently reported procedures.$^{1,2}$

Synthesis of 3-substituted N-Methyl Anilines$^1$

$$
\begin{align*}
\text{R} & \text{N}_2 & \text{NH}_2 & \text{[RuCp*Cl]_2} (0.5 \text{ mol\%}) \\
& & \text{dpePhos} (1.2 \text{ mol\%}) & \text{LitOBu} (5 \text{ mol\%}) \\
1^* & \text{MeOH} & & 100 \text{ °C, 24 h} \\
& & & R \text{NMe} \\
\end{align*}
$$
**General Procedure:** In a nitrogen-filled glovebox, a 100 mL Schlenk tube equipped with a magic stir bar was charged with aniline 1' (5.0 mmol), [RuCp*Cl₂]₂ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%), LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%). Then, the tube was fitted with a rubber septum and moved out of the glovebox. The methanol (5.0 mL) was added into the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. Finally, the reaction mixture was stirred at 100 °C for 24 hour. When finished, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel, washed with 60 mL of ethyl acetate. The organic layer was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product in 70–90 % yields.

**Synthesis of 3-(methoxymethyl)-N-methylaniline (1aa)**

![Structure of 3-(methoxymethyl)-N-methylaniline (1aa)](image)

This substrate was synthesized following the general procedure. The Schlenk tube was charged with 3-(methoxymethyl)aniline (0.6859 g, 5.0 mmol), [RuCp*Cl₂]₂ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 4), the product 1aa was obtained.

**Physical state:** colorless oil;

**¹H NMR** (400 MHz, CDCl₃): δ 7.15 (t, J = 7.7 Hz, 1H), 6.66 (d, J = 7.4 Hz, 1H), 6.59 (s, 1H), 6.53 (d, J = 8.0, 1.9 Hz, 1H), 4.39 (s, 2H), 3.72 (s, 1H), 3.37 (s, 3H), 2.81 (s, 3H);

**¹³C NMR** (100 MHz, CDCl₃): δ 149.5, 139.2, 129.1, 116.5, 111.7, 111.4, 74.9, 57.9, 30.6.

**Synthesis of 3-fluoro-N-methylaniline (1ab)**
This substrate was synthesized following the general procedure. The Schlenk tube was charged with 3-fluoroaniline (0.5556 g, 5.0 mmol), [RuCp*Cl₂]₂ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 2), the product 1ab was obtained.

**Physical state:** colorless oil;

**1H NMR** (400 MHz, CDCl₃): δ 7.1 (q, J = 8.0 Hz, 1H), 6.4 (ddd, J = 10.7, 8.3, 2.0 Hz, 2H), 6.3 (dt, J = 11.7, 2.1 Hz, 1H), 3.8 (s, 1H), 2.8 (s, 3H);

**19F NMR** (377MHz, CDCl₃): δ -113.07;

**13C NMR** (100 MHz, CDCl₃): δ 164.2 (d, J = 242.5 Hz), 151.1 (d, J = 10.8 Hz), 130.2 (d, J = 10.3 Hz), 108.3 (d, J = 2.2 Hz), 103.5 (d, J = 21.6 Hz), 98.9 (d, J = 25.3 Hz), 30.6.

**Synthesis of 3-iodo-N-methylaniline (1ae)**

This substrate was synthesized following the general procedure. The Schlenk tube was charged with 3-iodoaniline (1.0951 g, 5.0 mmol), [RuCp*Cl₂]₂ (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 2), the product 1ae was obtained.

**Physical state:** colorless oil;

**1H NMR** (400 MHz, CDCl₃): δ 7.00 (d, J = 7.7 Hz, 1H), 6.90 - 6.84 (m, 2H), 6.51 (d, J = 10.2 Hz, 1H), 3.68 (s, 1H), 2.76 (s, 3H);

**13C NMR** (100 MHz, CDCl₃): δ 150.4, 130.5, 125.9, 120.7, 111.7, 95.2, 30.4.
Synthesis of 3'-N-methylaminoacetophenone (1ah)

This substrate was synthesized following the general procedure. The Schlenk tube was charged with 3'-aminoacetophenone (0.6758 g, 5.0 mmol), [RuCp*Cl2]2 (0.0077 g, 0.025 mmol, 0.5 mol%), dpePhos (0.0323 g, 0.06 mmol, 1.2 mol%) and LiO'Bu (0.0200 g, 0.25 mmol, 5 mol%) in methanol (5.0 mL) and the reaction mixture was stirred at 100 °C for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 4), the product 1ah was obtained.

Physical state: colorless oil;

1H NMR (400 MHz, CDCl3): δ 7.28-7.25 (m, 2H), 7.18-7.17 (m, 1H), 6.80-6.77 (m, 1H), 3.93 (s, 1H), 2.86 (s, 3H), 2.56 (s, 3H);

13C NMR (100 MHz, CDCl3): δ 198.7, 149.4, 142.1, 137.6, 132.1, 129.2, 117.5, 117.2, 110.8, 30.5, 26.7.

Synthesis of 4-(benzyloxy)-N-(4-(2-chloroethoxy)benzyl)aniline (1ai)

1ai was prepared using the reported procedure [3] 4-benzyloxyaniline (1 g, 5 mmol), 4-(2-chloroethoxy)benzaldehyde (0.923 g, 5 mmol). The product 1ai was obtained as white solid in 72% yield (1.320 g).

Physical state: white solid;

1H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 6.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 (m, 3H), 6.88 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 2H), 4.98 (s, 2H), 4.22 (t, J = 5.9 Hz, 2H), 4.21(s, 2H), 3.81 (t, J = 5.9 Hz, 2H);

13C NMR (100 MHz, CDCl3):δ 157.6, 151.8, 142.1, 137.6, 132.1, 129.2, 128.6, 127.9, 127.6, 116.2, 114.9, 114.6, 70.9, 68.2, 49.0, 42.0;
HRMS (ESI): Caled for C_{22}H_{23}ClNO_2 ([M + H]^+) : 368.1412, found: 368.1409.

**Synthesis of 4-(ethylamino)phenyl acetate (1aj)**

A 50 mL Schlenk flask equipped with a magic stir bar was charged with 4-iodophenol (2.20 g, 10 mmol), ethyl amine (1.1 mL, 2 equiv.), CuI (0.19 g, 10 mol%), L-proline (0.2302 g, 20 mol%), K_2CO_3 (2.76 g, 2 equiv.) and DMSO (6 mL). The reaction mixture was stirred at 60 °C for 12 hours. After cooling down, the reaction mixture was diluted with 25 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (25 mL). The collected filtrate was washed with water (3×25 mL), and the organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with pentane/ethyl acetate (4:1) as eluent to afford p-ethylaminophenol as white solid (0.49 g, 36% yield). This newly obtained p-ethylaminophenol (274.4 mg, 2 mmol) was treated with t-butyl dicarbonate (0.048 mL, 1 equiv.) in THF (8 mL) at room temperature for 12 hours. Then, the solvent was removed under reduced pressure. The obtained residue was washed with hexane (10 mL x 3) and then dissolved in toluene (10 mL). To the resulting toluene solution, acetic anhydride (0.02 mL, 1 equiv.), sodium acetate (0.16 g, 1 equiv.) was added, and the reaction mixture was stirred at 110 °C for 12 hours. After cooling down, the reaction mixture was filtered through a pad of silica gel with several washings, and concentrated. The residue was dissolved in CH_2Cl_2 (6 mL) and then stirred with CF_3COOH (0.5 mL) at room temperature for 3 hours. Then the reaction mixture was neutralized with K_2CO_3 aqueous solution (0.5 M, 15 mL), extracted with ethyl estate (10 mL x 3). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give the product 1aj (215 mg, 60% yield).
Physical state: white solid;

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.91 - 6.85 (m, 2H), 6.56 (dd, $J = 8.8$ Hz, 2H), 3.11 (q, $J = 7.1$ Hz, 3H), 2.25 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 4H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.4, 146.4, 141.9, 122.1, 113.1, 38.8, 21.1, 14.8;

HRMS (ESI): Calcd for C$_{10}$H$_{14}$NO$_2$ ([M + H]$^+$) : 180.1019, found: 180.1018.

**Synthesis of 1-(benzylxy)-4-(prop-1-yn-1-yl)benzene (2t)$^{2a}$**

![Reaction Scheme]

In a nitrogen-filled glovebox, a 150 mL Schlenk flask equipped with a magic stir bar was charged with 1-(benzylxy)-4-iodobenzene(3.1013 g, 10.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.1404 g, 0.2 mmol, 2 mol%), CuI (0.0381 g, 0.2 mmol, 2 mol%), $^n$Bu$_4$NF·3H$_2$O (3.1551 g, 1.0 equiv.). Then, the tube was fitted with a rubber septum and moved out of the glovebox. The trimethyl(prop-1-yn-1-yl)silane (2.2448 g, 2.0 equiv.), THF (60.0 mL), and Et$_3$N (6.0 mL) were added into the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. Finally, the reaction mixture was stirred at room temperature for 24 hours. When finished, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel, washed with 60 mL of ethyl acetate. The organic layer was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide product 2t.

Physical state: slight yellow solid;

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 - 7.26 (m, 7H), 6.86-6.82 (m, 2H), 4.97 (s, 2H), 1.98 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.1, 136.6, 132.7, 128.5, 127.9, 127.4, 116.4, 114.6, 84.2, 79.4, 69.8, 4.2.
Synthesis of 4-(prop-1-yn-1-yl)phenyl acetate (2u)

Under nitrogen flow, a 100 mL Schlenk flask equipped with a magic stir bar was charged with 4-iodophenol (2.20 g, 10 mmol), 1M solution of 1-propyne in THF (15 mL, 1.5 equiv.), Pd(PPh₃)₂Cl₂ (0.142 g, 4 mol%), CuI (0.181 g, 1 mol%), THF (10 mL) and triethyl amine (TFA) (25 mL). After the reaction mixture was stirred at room temperature for 3 hours, the solvent was removed under reduced pressure. The resultant residue was extracted with ethyl acetate (15 mL), and filtered through a pad of silica gel with washings. The filtrate is concentrated under reduced pressure to dark oil. The obtained dark oil was treated with acetic anhydride (1 mL) and sodium acetate (0.82 g) in toluene (15 mL) at 110 °C for 12 hours. The reaction mixture was filtered through a pad of silica gel with washings, concentrated. The residue was purified by flash chromatography on silica gel with pentane/ ethyl acetate (4:1) as eluent to provide the corresponding product 2u (1.22 g, 70% yield).

Physical state: slight cyan solid;

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H), 2.01 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 169.2, 149.9, 132.6, 121.7, 121.5, 86.0, 79.0, 21.0, 4.2.
Screening of the Reaction Conditions

Table S1. Optimization of the reaction conditions.\textsuperscript{a}

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<th>entry</th>
<th>solvent (1.0 mL)</th>
<th>additive</th>
<th>Ag salt (10 mol%)</th>
<th>Yield(%)\textsuperscript{b}</th>
</tr>
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<tr>
<td>1</td>
<td>DCM</td>
<td>-</td>
<td>AgSbF\textsubscript{6}</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>-</td>
<td>AgSbF\textsubscript{6}</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>1,4-dioxane</td>
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<td>AgSbF\textsubscript{6}</td>
<td>trace</td>
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<td>4</td>
<td>chlorobenzene</td>
<td>-</td>
<td>AgSbF\textsubscript{6}</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>CH\textsubscript{3}CN</td>
<td>-</td>
<td>AgSbF\textsubscript{6}</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>-</td>
<td>AgSbF\textsubscript{6}</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>tert-amyl alcohol</td>
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<td>AgSbF\textsubscript{6}</td>
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</tr>
<tr>
<td>8\textsuperscript{c}</td>
<td>DCM</td>
<td>-</td>
<td>-</td>
<td>24</td>
</tr>
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<td>DCM</td>
<td>-</td>
<td>AgBF\textsubscript{4}</td>
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<td>DCM</td>
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<tr>
<td>11</td>
<td>DCM</td>
<td>-</td>
<td>Ag\textsubscript{3}PO\textsubscript{4}</td>
<td>14</td>
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<tr>
<td>12</td>
<td>DCM</td>
<td>-</td>
<td>Ag\textsubscript{2}CO\textsubscript{3}</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>DCM</td>
<td>-</td>
<td>Ag\textsubscript{2}O</td>
<td>0</td>
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<tr>
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<td>DCM</td>
<td>LiOAc (1.0 equiv)</td>
<td>AgSbF\textsubscript{6}</td>
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<tr>
<td>15</td>
<td>DCM</td>
<td>NaOAc (1.0 equiv)</td>
<td>AgSbF\textsubscript{6}</td>
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</tr>
<tr>
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<td>DCM</td>
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<tr>
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<tr>
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<td>DCM</td>
<td>PivOH (0.5 equiv)</td>
<td>AgSbF\textsubscript{6}</td>
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<td>benzoic acid (0.5 equiv)</td>
<td>AgSbF\textsubscript{6}</td>
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<td>DCM</td>
<td>Substrate</td>
<td>AgSbF$_6$</td>
<td>Yield</td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
<td>------------------------------------------------</td>
<td>-----------</td>
<td>-------</td>
</tr>
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<td>22</td>
<td>DCM</td>
<td>2,4,6-trimethylbenzoic acid (50 mol%)</td>
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</tr>
<tr>
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<td>DCM</td>
<td>1-Adamantanecarboxylic acid (50 mol%)</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>24</td>
<td>DCM</td>
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<td>AgSbF$_6$</td>
<td>83</td>
</tr>
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<td>$m$-NO$_2$-PhCOOH (50 mol%)</td>
<td>AgSbF$_6$</td>
<td>38</td>
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<td>DCM</td>
<td>$p$-OMe-PhCOOH (50 mol%)</td>
<td>AgSbF$_6$</td>
<td>31</td>
</tr>
<tr>
<td>27</td>
<td>DCM</td>
<td>$p$-BuPhCOOH (50 mol%)</td>
<td>AgSbF$_6$</td>
<td>40</td>
</tr>
</tbody>
</table>

*a*Reaction Conditions: 1a (0.2 mmol), 2a (0.3 mmol), [Cp*RhCl]$_2$ (0.005 mmol, 2.5 mol%), Ag Salt (0.02 mmol, 10 mol%), additive (0.5 - 1.0 equiv.), iso-amyl nitrite (0.3 mmol), N$_2$ and solvent (1.0 mL) at room temperature for 24 h. *b*Yield of isolated product. *c*Cp*Rh(CH$_3$CN)$_3$[SbF$_6$]$_2$ (0.01 mmol, 5 mol) was used. *d*$t$-butyl nitrite (0.3 mmol) was used as oxidant.

**Experimental Procedures**

In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged [Cp*RhCl]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) or PivOH (0.0204 g, 1.0 equiv.), disubstituted alkynes (0.3 mmol) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then $N$-alkyl anilines (0.2 mmol) and dichloromethane (1.0 mL) were added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding product.
Product Characterization

1,2-Diphenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolone (3a)

3a (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3a was obtained in 83% yield (51.5 mg, slight yellow solid). ¹H NMR (400MHz, CDCl₃): δ 7.54 (d, J = 8.0 Hz, 1H), 7.29 – 7.23 (m, 7H), 7.18 (t, J = 7.1 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.0 Hz, 1H), 3.99 – 3.97 (m, 2H), 2.95 (t, J = 6.1 Hz, 2H), 2.13 (p, J = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) : δ 136.0, 135.6, 134.3, 131.8, 130.7, 129.7, 128.4, 128.2, 127.8, 125.3, 125.0, 122.0, 120.2, 119.1, 117.0, 114.4, 43.2, 25.1, 23.0. This compound has been known. [⁴ᵃ] Its NMR spectra are identical with the authorized ones.

1-Methyl-2,3-diphenyl-1H-indole (3b)

3b (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3b was obtained in 65% yield.
(37.0 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 7.9$ Hz, 1H), 7.41 – 7.14 (m, 13H), 3.65 (s, 3H). This compound has been known.$^{[4a]}$ Its NMR spectra are identical with the authorized ones.

1-Ethyl-2,3-diphenyl-1H-indole (3c)

3c (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-ethylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3c was obtained in 84% yield (50.0 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 7.9$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 1H), 7.39 – 7.12 (m, 12H), 4.12 (q, $J = 7.2$ Hz, 2H), 1.27 (t, $J = 7.2$ Hz, 3H). This compound has been known.$^{[4b]}$ Its NMR spectra are identical with the authorized ones.

1-Isopropyl-2,3-diphenyl-1H-indole (3d)

3d (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-isopropylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3d was obtained in 88% yield.
(55.3 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 8.3$ Hz, 1H), 7.35 − 7.10 (m, 12H), 4.56 − 4.51 (m, 1H), 1.60 (s, 3H), 1.59 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.5, 135.2, 134.6, 132.8, 131.1, 129.9, 128.3, 128.1, 128.0, 128.0, 125.3, 121.5, 119.9, 119.7, 115.1, 112.2, 47.8, 21.5. *This compound has been known.*$^{[4b]}$ Its NMR spectra are identical with the authorized ones.

1-Cyclohexyl-2,3-diphenyl-1H-indole (3e)

3e (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with $N$-cyclohexylaniline (0.0351g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3e was obtained in 70% yield (49.3 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.37 − 7.34 (m, 3H), 7.29 − 7.20 (m, 7H), 7.15 − 7.11 (m, 2H), 4.11 − 4.05 (m, 1H), 2.38 (q, $J = 12.1$, 11.0 Hz, 2H), 1.94 − 1.84 (m, 4H), 1.33 − 1.17 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.7, 135.3, 135.0, 132.8, 131.1, 129.9, 128.3, 128.0, 127.9, 125.3, 121.3, 119.8, 119.6, 115.1, 112.6, 56.4, 31.5, 26.2, 25.5; HRMS (ESI) Calcd for C$_{26}$H$_{26}$N ([M + H]$^+$): 352.2060, found: 352.2057.

1,2,3-Triphenyl-1H-indole (3f)

3f (0.2 mmol scale) was synthesized following the *general procedure*. The reaction was carried out with diphenylamine (0.0338g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%).
4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3f was obtained in 73% yield (50.7 mg, white solid). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 7.72 (d, \(J = 5.4\) Hz, 1H), 7.32 – 7.20 (m, 8H), 7.15 – 7.12 (m, 5H), 7.08 – 7.00 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.1, 137.9, 137.0, 134.9, 131.6, 131.2, 130.2, 129.0, 128.2, 127.9, 127.5, 127.3, 127.1, 125.9, 122.7, 120.9, 119.6, 116.7, 110.6. This compound has been known. \(^{[5]}\) Its NMR spectra are identical with the authorized ones.

![Benzyl-2,3-diphenyl-1H-indole (3g)](image)

1-Benzyl-2,3-diphenyl-1H-indole (3g)

3g (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-benzylaniline (0.0367 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}_2]\) (0.0031 g, 2.5 mol%), AgSbF\(_6\) (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3g was obtained in 83% yield (59.5 mg, white solid). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 8.9\) Hz, 1H), 7.34 (d, \(J = 7.1\) Hz, 2H), 7.27 – 7.13 (m, 14H), 6.98 (d, \(J = 6.8\) Hz, 2H), 5.25 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.0, 137.8, 136.9, 135.1, 131.7, 131.0, 129.9, 128.6, 128.3, 128.2, 128.1, 127.3, 127.1, 126.0, 125.5, 122.3, 120.4, 119.7, 115.6, 110.5, 47.5. This compound has been known. \(^{[5]}\) Its NMR spectra are identical with the authorized ones.
1-Allyl-2,3-diphenyl-1H-indole (3h)

3h (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-allylaniline (0.0266g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$)$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3h was obtained in 72% yield (44.6 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.80 (d, $J$ = 7.9 Hz, 1H), 7.38 – 7.16 (m, 13H), 5.99 - 5.89 (m, 1H), 5.17 (d, $J$ = 10.4 Hz, 1H), 4.99 (d, $J$ = 17.1 Hz, 1H), 4.65 (d, $J$ = 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.6, 136.8, 135.1, 133.7, 131.8, 131.0, 129.8, 128.3, 128.1, 127.2, 125.5, 122.2, 120.3, 119.7, 116.6, 115.4, 110.3 46.5; HRMS (ESI) Calcd for C$_{23}$H$_{20}$N ( [M + H]$^+$) : 310.1590, found : 310.1588.

3-(2,3-Diphenyl-1H-indol-1-yl)propanenitrile (3i)

3i (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 3-(phenylamino)-propanenitrile (0.0292g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$)$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3i was obtained in 55% yield (35.2 mg, white solid). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, $J$ = 7.9 Hz, 1H), 7.40 – 7.37 (m, 4H), 7.33 – 7.14 (m, 9H), 4.40 – 4.36 (m, 2H), 2.55 – 2.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.6, 135.8, 134.3, 130.9, 129.7, 128.8, 128.7, 128.2, 127.6, 125.8, 122.8, 121.0, 120.2, 116.9, 116.8, 109.2, 39.3, 18.0; HRMS (ESI)
Calcd for C_{23}H_{19}N_{2} ([M + H]^+) : 323.1543, found: 323.1543.

4,4,6,9-Tetramethyl-1,2-diphenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3j)

3j (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydro-2,2,4,7-tetramethylquinoline (0.0379g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3j was obtained in 71% yield (52.0 mg, pale yellow oil). $^1$H NMR (400MHz, CDCl$_3$): δ 7.33 – 7.10 (m, 7H), 7.01 – 6.93 (m, 4H), 6.79 – 6.76 (m, 1H), 3.20 – 3.19 (m, 1H), 2.04 (s, 3H), 1.89 – 1.76 (m, 2H), 1.45 (s, 3H), 1.40 (s, 3H), 1.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.0, 136.8, 134.8, 133.0, 132.2, 132.1, 131.6, 128.0, 127.8, 127.5, 127.2, 126.8, 125.7, 124.6, 123.8, 121.1, 118.2, 116.7, 56.4, 49.1, 30.2, 28.9, 26.7, 20.1, 18.6; HRMS (ESI) Calcd for C$_{27}$H$_{28}$N ([M + H]$^+$) : 366.2216, found : 366.2214.

1,2-Diphenyl-6,7-dihydrobenzo[6,7]azepino[3,2,1-bij]indole (3k)

3k (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with 5,6,11,11-a-tetrahydro-4aH-benzo[b][1]benzazepine(0.0395g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g,
0.3 mmol). The reaction mixture was stirred at 80 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3k was obtained in 75% yield (55.7 mg, white solid). This compound has been known. Its NMR spectra are identical with the authorized ones.

![9-Methyl-1,2-diaryl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3l)](image)

9-Methyl-1,2-diaryl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3l)

3l (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 7-methyl-1,2,3,4-tetrahydroquinoline (0.0294 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3l was obtained in 70% yield (45.7 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.17 (m, 10H), 7.10 – 7.06 (m, 1H), 6.76 (s, 1H), 3.97 (t, J = 5.6 Hz, 2H), 2.92 (t, J = 5.6 Hz, 2H), 2.37 (s, 3H), 2.15 – 2.11 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 135.9, 135.8, 132.8, 131.9, 130.6, 129.6, 129.6, 128.3, 128.1, 127.6, 125.2, 125.1, 121.6, 120.8, 116.4, 113.9, 43.0, 24.9, 23.1, 21.8; HRMS (ESI) Calcd for C₂₄H₂₂N ([M + H]+): 324.1747, found: 324.1744.

![8-Fluoro-4-methyl-1,2-diaryl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3m)](image)

8-Fluoro-4-methyl-1,2-diaryl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3m)

3m (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 6-fluoro-1,2,3,4-tetrahydro-2-methylquinoline (0.0330 g, 0.2
mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}_2]\) (0.0031g, 2.5 mol%), AgSbF\(_6\) (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and \(\text{iso-amyl nitrite} (0.0351g, 0.3 \text{ mmol})\). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product \(3\text{m}\) was obtained in 76% yield (52.0 mg, white solid). \(^1\text{H NMR} (400\text{MHz}, \text{CDCl}_3): \delta 7.38 - 7.20 (m, 10H), 7.12 (t, \(J = 7.2 \text{ Hz}, 1H\)), 6.78 (d, \(J = 9.6 \text{ Hz}, 1H\)), 4.60 -4.57 (m, 1H), 3.12 – 3.03 (m, 1H), 2.95 - 2.89 (m, 1H), 2.33 – 2.23 (m, 1H), 2.08 – 2.03 (m, 1H), 1.03 (d, \(J = 6.6 \text{ Hz}, 3H\)); \(^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3): \delta 158.8 (d, \(J = 234.1 \text{ Hz}\)), 137.1, 135.1, 131.8, 130.7, 129.9, 129.2, 128.5, 128.2, 125.3, 125.0 (d, \(J = 10.3 \text{ Hz}\)), 122.4 (d, \(J = 9.6 \text{ Hz}\)), 115.1 (d, \(J = 5.0 \text{ Hz}\)), 107.8 (d, \(J = 26.5 \text{ Hz}\)), 101.7 (d, \(J = 24.7 \text{ Hz}\)), 46.8, 28.2, 20.7 (d, \(J = 1.5 \text{ Hz}\)), 20.2; HRMS (ESI) Calcd for C\(_{24}\)H\(_{21}\)FN ([M + H]\(^+\)) : 342.1653, found : 342.1650.

8-Bromo-1,2-diphenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (3n)

3n (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 6-bromo-1,2,3,4-tetrahydroquinoline (0.0424 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}_2]\) (0.0031g, 2.5 mol%), AgSbF\(_6\) (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and \(\text{iso-amyl nitrite} (0.0351g, 0.3 \text{ mmol})\). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product \(3\text{n}\) was obtained in 71% yield (55.1 mg, white solid). \(^1\text{H NMR} (400\text{MHz}, \text{CDCl}_3): \delta 7.73 (d, \(J = 1.4 \text{ Hz}, 1H\)), 7.37 – 7.23 (m, 9H), 7.18 – 7.13 (m, 1H), 7.07 (s, 1H), 4.01 (t, \(J = 4.0 \text{ Hz}, 2H\)), 2.96 (t, \(J = 6.1 \text{ Hz}, 2H\)), 2.15 (p, \(J = 6.0 \text{ Hz}, 2H\)); \(^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3): \delta 136.8, 134.9, 132.9, 131.1, 130.6, 129.5, 128.4, 128.3, 128.0, 126.4, 125.6, 123.7, 122.0, 119.4, 114.0, 113.5, 43.1, 24.8, 22.7; HRMS (ESI) Calcd for C\(_{23}\)H\(_{19}\)BrN ([M +
5-Chloro-2,3-bis(4-isopropylphenyl)-1-methyl-1H-indole (3o)

3o (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 4-chloro-N-methylaniline (0.0283 g, 0.2 mmol), 1,2-bis(4-isopropylphenyl)acetylene (0.0787 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3o was obtained in 76% yield (61.0 mg, pale yellow oil). $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 7.74 (d, $J = 1.9$ Hz, 1H), 7.28 – 7.12 (m, 10H), 3.62 (s, 3H), 2.97 – 2.84 (m, 2H), 1.28 (d, $J = 6.9$ Hz, 6H), 1.25 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.8, 146.1, 138.9, 135.6, 131.9, 130.9, 129.5, 128.8, 128.2, 126.4, 126.3, 125.7, 122.0, 119.1, 114.5, 110.4, 33.9, 33.7, 31.1, 23.9, 23.9; HRMS (ESI) Calcd for C$_{27}$H$_{29}$ClN ([M + H]$^+$): 402.1983, found : 402.1981.

1,5-Dimethyl-2,3-diphenyl-1H-indole (3p)

3p (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methyl-p-toluidine (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel.
(petroleum ether/diethyl ether = 100:1), the product 3p was obtained in 78% yield (46.5 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.57 (s, 1H), 7.37 – 7.23 (m, 10H), 7.18 – 7.10 (m, 2H), 3.62 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.8, 135.8, 135.4, 132.0, 131.1, 129.9, 129.4, 128.3, 128.1, 127.9, 127.1, 125.4, 123.7, 119.1, 114.6, 109.3, 30.9, 21.5. This compound has been known.$^{[4a]}$ Its NMR spectra are identical with the authorized ones.

![Chemical structure of 7-Chloro-1-methyl-2,3-diphenyl-1H-indole (3q)](image)

7-Chloro-1-methyl-2,3-diphenyl-1H-indole (3q)

3q (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 2-chloro-N-methylaniline (0.0283 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3q was obtained in 76% yield (48.2 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.62 (d, $J = 8.0$ Hz, 1H), 7.37 – 7.14 (m, 11H), 7.02 (t, $J = 7.8$ Hz, 1H), 3.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.9, 134.5, 133.0, 131.4, 131.3, 130.2, 130.0, 128.4, 128.2, 128.2, 125.8, 123.9, 120.7, 118.3, 117.2, 115.9, 34.2; HRMS (ESI) Calcd for C$_{21}$H$_7$ClIN ( [M + H]$^+$) : 318.1044, found : 318.1042.

![Chemical structure of 7-Methoxy-1-methyl-2,3-diphenyl-1H-indole (3r)](image)

7-Methoxy-1-methyl-2,3-diphenyl-1H-indole (3r)

3r (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 2-methoxy-N-methylaniline (0.0274 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$
(0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3r was obtained in 66% yield (41.5 mg, white solid). Its NMR spectra are identical with the authorized ones. ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.22 (m, 10H), 7.15 (t, J = 6.6 Hz, 1H), 7.05 (t, J = 7.9 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 138.6, 135.4, 132.0, 131.3, 129.9, 129.1, 128.3, 128.0, 127.9, 127.1, 125.4, 120.4, 115.5, 112.4, 103.2, 55.6, 34.2. This compound has been known. [⁵] Its NMR spectra are identical with the authorized ones.

5-Methoxy-1-methyl-2,3-diphenyl-1H-indole (3s)

3s (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 4-methoxy-N-methylaniline (0.0274 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3s was obtained in 72% yield (45.0 mg, white solid). Its NMR spectra are identical with the authorized ones. ¹H NMR (400 MHz, CDCl₃): δ 7.37 - 7.33 (m, 3H), 7.29 - 7.24 (m, 8H), 7.16 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 138.3, 135.3, 132.7, 131.9, 131.0, 129.7, 128.3, 128.2, 127.9, 127.2, 125.4, 114.8, 112.4, 110.3, 101.2, 56.0, 31.0. This compound has been known. [⁴b] Its NMR spectra are identical with the authorized ones.
Methyl 1-methyl-2,3-diphenyl-1H-indole-7-carboxylate (3t)

3t (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with dimethyl anthranilate (0.0330 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}_2]_2\) (0.0031 g, 2.5 mol%), AgSbF_6 (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 3t was obtained in 71% yield (48.5 mg, white solid). \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.89 (d, \(J = 7.9\) Hz, 1H), 7.71 (d, \(J = 7.4\) Hz, 1H), 7.37 – 7.25 (m, 9H), 7.21 – 7.16 (m, 2H), 3.99 (s, 3H), 3.63 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 168.3, 140.5, 135.4, 134.6, 131.5, 131.2, 130.0, 129.6, 128.3, 128.2, 128.1, 125.9, 125.3, 123.8, 119.3, 116.3, 116.0, 52.2, 35.2; HRMS (ESI) Calcd for C\(_{23}\)H\(_{20}\)NO\(_2\) ([M + H\(^+\)]: 342.1489, found: 342.1486.

methyl 1-methyl-2,3-diphenyl-1H-indole-5-carboxylate (3u)

3u (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}_2]_2\) (0.0031 g, 2.5 mol%), AgSbF\(_6\) (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 3u was obtained in 85% yield (58.3 mg, white solid). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.52 (s, 1H), 8.00 (d \(J = 8.6\) Hz, 1H), 7.40 - 7.26 (m, 10H), 7.22-7.19 (m, 1H), 3.91 (s, 3H), 3.66 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 168.1, 139.6, 138.9, 134.3, 131.2, 131.0, 129.8, 128.4, 128.3, 126.6, 125.9, 123.5, 122.6, 122.1, 116.4, 109.2, 51.8, 31.1. This compound has been known,\(^{[4a]}\) Its NMR spectra are identical with the authorized ones.
1-Methyl-5-nitro-2,3-diphenyl-1H-indole (3v)

3v (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with N-methyl-4-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3v was obtained in 71% yield (46.6 mg, yellow solid). $^1$H NMR (400MHz, CDCl$_3$): δ 8.67 (d, $J = 2.1$ Hz, 1H), 8.16 (dd, $J = 9.0, 2.2$ Hz, 1H), 7.42 – 7.38 (m, 4H), 7.34 – 7.23 (m, 7H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.0, 140.6, 139.9, 133.4, 130.9, 130.5, 129.7, 128.8, 128.6, 128.5, 126.4, 126.4, 117.6, 117.4, 116.9, 109.5, 31.4; HRMS (ESI) Calcd for C$_{21}$H$_{17}$N$_2$O$_2$ ([M + H]$^+$) : 329.1284, found : 329.1285.

![Image of 1-Methyl-5-nitro-2,3-diphenyl-1H-indole (3v)]

1-Methyl-7-nitro-2,3-diphenyl-1H-indole (3w)

3w (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with N-methyl-2-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3w was obtained in 76% yield (50.0 mg, yellow solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.95 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.39 – 7.16 (m, 11H), 3.57 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 141.8, 136.7, 133.7, 132.0, 131.1, 130.5, 130.0, 129.2, 128.6, 128.5, 128.4, 126.4, 125.5, 119.9, 119.2, 116.6, 35.1; HRMS (ESI) Calcd for C$_{21}$H$_{17}$N$_2$O$_2$ ([M + H]$^+$) : 329.1285, found : 329.1282.
1-Methyl-2,3-diphenyl-1H-indole-5-carbonitrile (3x)

3x (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with 4-(methylamino)benzonitrile (0.0264 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 50 °C in DCE (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3x was obtained in 77% yield (47.5 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.09 (s, 1H), 7.50 – 7.22 (m, 12H), 3.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.7, 138.6, 133.6, 130.9, 130.6, 129.6, 128.6, 128.5, 128.4, 126.8, 126.2, 125.2, 124.9, 120.8, 115.8, 110.4, 102.9, 31.1. This compound has been known. Its NMR spectra are identical with the authorized ones.

1-Methyl-2,3-diphenyl-5-(trifluoromethyl)-1H-indole (3y)

3y (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 4-(methylamino)benzonitrile (0.0264 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3y was obtained in 78% yield (54.9 mg, yellow solid). ¹H NMR (400MHz, CDCl₃): δ 8.05 (s, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.39 – 7.38 (m, 3H), 7.32 – 7.28 (m, 6H), 7.24 – 7.20 (m, 1H), 3.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.4, 138.5, 133.6, 130.9, 130.6, 129.6, 128.6, 128.5, 128.4, 126.8, 126.2, 125.2, 124.9, 120.8, 115.8, 110.4, 102.9, 31.1.
134.2, 131.1, 131.0, 129.8, 128.5, 128.4, 128.4, 126.4, 126.1, 125.4 (q, J = 124.1 Hz), 122.5 (q, J = 31.7 Hz), 118.8 (q, J = 3.3 Hz), 117.3 (t, J = 4.3 Hz), 116.0, 109.8, 31.1. This compound has been known.\textsuperscript{[4a]} Its NMR spectra are identical with the authorized ones.

1,6-Dimethyl-2,3-diphenyl-1H-indole (3z)

3z (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N,3-dimethylaniline (0.0242 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (0.0031 g, 2.5 mol%), AgSbF\textsubscript{6} (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3z was obtained in 75% yield (44.6 mg, yellow solid). \textsuperscript{1H} NMR (400 MHz, CDCl\textsubscript{3}): δ 7.68 (t, J = 5.6 Hz, 1H), 7.33 – 7.13 (m, 11H), 7.02 (t, J = 6.1 Hz, 1H), 3.60 (s, 3H), 2.53 (s, 3H); \textsuperscript{13C} NMR (100 MHz, CDCl\textsubscript{3}): δ 137.7, 137.1, 135.4, 132.1, 132.0, 131.1, 129.8, 128.3, 128.1, 127.8, 125.4, 124.9, 121.9, 119.3, 114.9, 109.5, 30.8, 21.9. This compound has been known.\textsuperscript{[4a]} Its NMR spectra are identical with the authorized ones.

6-(Methoxymethyl)-1-methyl-2,3-diphenyl-1H-indole (3aa)

3aa (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 3-(methoxymethyl)-N-methylaniline (0.0302 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (0.0031 g, 2.5 mol%), AgSbF\textsubscript{6} (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography
on silica gel (petroleum ether/diethyl ether = 100:3), the product 3aa was obtained in 73% yield (47.9 mg, colorless oil). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, $J = 8.2$ Hz, 1H), 7.41 (s, 1H), 7.35 – 7.14 (m, 12H), 4.64 (s, 2H), 3.66 (s, 3H), 3.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.0, 137.4, 135.1, 132.3, 131.8, 131.1, 129.8, 128.3, 128.1, 128.0, 126.6, 125.5, 120.5, 119.5, 115.0, 109.0, 75.4, 57.8, 30.9; HRMS (ESI) Calcd for C$_{23}$H$_{22}$NO ([M + H]$^+$): 328.1696, found: 328.1694.

4-Fluoro-1-methyl-2,3-diphenyl-1H-indole (3ab)

3ab (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with 3-fluoro-N-methylaniline (0.0250 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3ab was obtained in 96% yield (57.6 mg, white solid). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.35 – 7.34 (m, 3H), 7.29 – 7.25 (m, 4H), 7.23 – 7.21 (m, 2H), 7.20 – 7.15 (m, 3H), 6.85 – 6.80 (m, 1H), 3.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.9 (d, $J = 248.9$ Hz), 139.8 (d, $J = 11.0$ Hz), 138.2 (d, $J = 1.5$ Hz), 134.8, 131.3, 131.2, 130.8 (d, $J = 2.6$ Hz), 128.3, 128.1, 127.4, 125.8, 122.2 (d, $J = 8.1$ Hz), 115.5 (d, $J = 18.1$ Hz), 113.5, 105.6, 105.5 (d, $J = 24.6$ Hz), 31.4; $^{19}$F NMR (377 MHz, CDCl$_3$): δ –117.83; HRMS (ESI) Calcd for C$_{21}$H$_{17}$NF ([M + H]$^+$): 302.1340, found: 302.1340.

6-Chloro-1-methyl-2,3-diphenyl-1H-indole (3ac)

3ac (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 3-chloro-N-methylaniline (0.0283 g, 0.2 mmol),
diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}]_2\) (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3ac was obtained in 80% yield (50.9 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.58 (d, $J = 8.5$ Hz, 1H), 7.30 – 7.27 (m, 4H), 7.23 – 7.21 (m, 2H), 7.18 – 7.16 (m, 4H), 7.11 – 7.03 (m, 2H), 3.53 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.2, 137.7, 134.6, 131.4, 131.0, 129.7, 128.4, 128.3, 128.2, 127.9, 125.8, 125.6, 120.7, 120.5, 115.2, 109.6, 31.0. This compound has been known.$^{[4a]}$ Its NMR spectra are identical with the authorized ones.

6-Bromo-1-methyl-2,3-diphenyl-1H-indole (3ad)

3ad (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 3-bromo-N-methylaniline (0.0372 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), \([\text{Cp}^*\text{RhCl}]_2\) (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3ad was obtained in 75% yield (54.4 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.62 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 1.4$ Hz, 1H), 7.39 – 7.36 (m, 3H), 7.31 – 7.23 (m, 7H), 7.19 – 7.15 (m, 1H), 3.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.2, 138.1, 134.6, 131.3, 131.0, 129.7, 128.4, 128.2, 125.9, 125.8, 123.3, 120.9, 115.5, 115.2, 112.6, 31.0. This compound has been known.$^{[4a]}$ Its NMR spectra are identical with the authorized ones.

6-Iodo-1-methyl-2,3-diphenyl-1H-indole (3ae)
3ae (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with 3-iodo-N-methylaniline (0.0466 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3ae was obtained in 65% yield (53.2 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.75 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.29 (dd, J = 6.6, 3.0 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.19 – 7.15 (m, 1H), 3.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.6, 137.9, 134.5, 131.2, 131.0, 129.7, 128.8, 128.4, 128.2, 126.3, 125.8, 121.2, 118.7, 115.2, 85.7, 77.2, 31.0; HRMS (ESI) Calcd for C₂₁H₁₇NI ([M + H]⁺): 410.0400, found: 410.0400.

![1-Methyl-2,3-diphenyl-6-(trifluoromethyl)-1H-indole (3af)](image)

3af (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methyl-3-(trifluoromethyl)aniline (0.0350 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3af was obtained in 76% yield (53.4 mg, colorless oil). ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.42 – 7.38 (m, 4H), 7.32 (dd, J = 6.8, 3.0 Hz, 2H), 7.28 – 7.27 (m, 4H), 7.22 – 7.18 (m, 1H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 136.2, 134.4, 131.1, 131.0, 129.8, 129.2, 128.5, 128.5, 128.3, 126.0, 125.3 (d, J = 275.7 Hz), 124.1 (d, J = 27.6 Hz), 119.9, 116.7 (q, J = 3.6 Hz), 115.5, 107.2 (q, J = 4.3 Hz), 31.1; HRMS (ESI) Calcd for C₂₂H₁₇F₃N ([M + H]⁺): 352.1308, found: 352.1306.
1-Methyl-6-nitro-2,3-diphenyl-1H-indole (3ag)

3ag (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with N-methyl-3-nitroaniline (0.0304 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:2), the product 3ag was obtained in 61% yield (40.1 mg, yellow solid). ∏H NMR (400 MHz, CDCl₃): δ 8.38 (d, J = 2.1 Hz, 1H), 8.04 (dd, J = 8.8, 2.1 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.34 – 7.23 (m, 7H), 3.76 (s, 3H); ∏C NMR (100 MHz, CDCl₃): δ 143.5, 142.9, 135.8, 133.6, 131.5, 130.7, 130.4, 129.7, 128.9, 128.6, 128.4, 126.3, 119.4, 116.2, 115.6, 106.7, 31.3; HRMS (ESI) Calcd for C₂₁H₁₇O₂N₂ ([M + H]⁺) : 329.1285, found : 329.1284.

1-(1-Methyl-2,3-diphenyl-1H-indol-6-yl)ethanone (3ah)

3ah (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with 1-(3-(methylamino)phenyl)ethanone (0.0298 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 3ah was obtained in 68% yield (44.2 mg, yellow solid). ∏H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1H), 7.79 (d, J = 1.1 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.34
- 7.30 (m, 2H), 7.27 (d, J = 4.8 Hz, 4H), 7.21 – 7.15 (m, 1H), 3.73 (s, 3H), 2.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.3, 141.6, 136.9, 134.4, 131.4, 131.2, 131.0, 130.7, 129.8, 128.6, 128.6, 128.4, 126.0, 120.8, 119.2, 115.6, 110.6, 31.2, 27.0; HRMS (ESI) Calcd for C$_{23}$H$_{20}$NO ([M + H]$^+$): 326.1539, found: 326.1540.

5-(benzyloxy)-2-(4-(benzyloxy)phenyl)-1-(4-(2-chloroethoxy)benzyl)-3-methyl-1H-indole (3ai)

3ai was synthesized following the general procedure with slight modifications. The reaction was carried out with 4-(benzyloxy)-N-(4-(2-chloroethoxy)benzyl)aniline 1ai (0.0736g, 0.2 mmol), 1-((benzyloxy)methyl)-4-(prop-1-yn-1-yl)benzene (0.0709 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), PivOH (0.0102 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 80°C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), the product 3ai was obtained in 47% yield (55.2 mg, white solid). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.50 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 6.6$ Hz, 2H), 7.44 – 7.32 (m, 6H), 7.24 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 2.4$ Hz, 1H), 7.07 (d, $J = 8.8$ Hz, 1H), 7.02 (d, $J = 8.6$ Hz, 2H), 6.93 – 6.84 (m, 3H), 6.77 (d, $J = 8.7$ Hz, 2H), 5.14 (s, 2H), 5.13 (s, 2H), 5.10 (s, 2H), 4.17 (t, $J = 5.9$ Hz, 2H), 3.78 (t, $J = 5.9$ Hz, 2H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.7, 157.3, 153.4, 138.5, 137.9, 136.9, 132.2, 131.8, 131.6, 129.2, 128.8, 128.7, 128.2, 127.9, 127.8, 127.7, 127.5, 124.7, 114.9, 114.8, 112.4, 111.0, 108.6, 102.5, 71.1, 70.2, 68.1, 47.2, 42.1, 9.7; HRMS (ESI) Calcd for C$_{38}$H$_{35}$ClNO$_3$ ([M + H]$^+$): 588.2300, found: 588.2301.
1-(4-(2-(azepan-1-yl)ethoxy)benzyl)-5-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-methyl-1H-indole (3ai-2)

A solution of 3ai (50 mg, 0.085 mmol), azepane (100 µL, 0.86 mmol) in acetonitrile (2 mL) was stirred at 90°C over night. The reaction mixture was neutralized with Na2CO3 aqueous and extracted with EtOAc. The crude product was purified by silica gel column chromatography using gradient eluent of EtOAc/hexane to EtOAc, the product 3ai-2 was obtained in 92% yield (50.9 mg, white solid). 1H NMR (400 MHz, CDCl3): δ 7.48-7.46 (m, 4H), 7.45 – 7.37 (m, 4H), 7.37 – 7.32 (m, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.13 (m, 3H), 6.81 (dd, J = 8.8, 2.4 Hz, 1H), 6.74 (s, 4H), 5.16 (s, 2H), 5.15 (s, 2H), 5.12 (s, 2H), 3.91 (t, J = 6.1 Hz, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.63 (m, 4H), 2.16 (s, 3H), 1.58 – 1.46 (m, 8H); 13C NMR (100 MHz, CDCl3): δ 158.1, 156.6, 152.6, 137.8, 136.9, 131.5, 131.3, 128.8, 128.5, 128.0, 127.9, 127.7, 127.6, 127.4, 123.8, 111.9, 111.2, 107.6, 102.1, 69.8, 69.4, 55.1, 54.4, 46.1, 3.10, 9.5; HRMS (ESI) Calcd for C44H47N2O3 ([M + H]+) : 651.3581, found: 651.3582.

Zindoxifene (3aj)

3aj (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 4-(ethylamino)phenyl acetate (0.0358g, 0.2 mmol), 4-(prop-1-yn-1-yl)phenyl acetate (0.0523 g, 0.3 mmol), [Cp*RhCl2]2 (0.0031g, 2.5 mol%), AgSbF6 (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at 40 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 3aj was obtained in 67% yield (47.2 mg, white solid). 1H NMR (400 MHz, CDCl3): δ 7.36 (d, J = 8.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.94 (dd, J = 8.7, 2.3 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.31 (s, 6H), 2.18 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 170.6, 169.4, 150.5, 144.1, 137.5, 134.0, 131.5, 129.8, 128.9, 121.7,
This compound has been known. Its NMR spectra are identical with the authorized ones.

1-Methyl-2,3-di-p-tolyl-1H-indole (4a)

4a (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), 1,2-di-p-tolylethyne (0.0619 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4a was obtained in 79% yield (49.2 mg, white solid). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, J = 7.9 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.29 – 7.13 (m, 8H), 7.09 – 7.05 (m, 2H), 3.59 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 137.6, 137.3, 134.8, 132.3, 130.9, 129.7, 129.1, 129.0, 128.9, 127.1, 121.9, 120.0, 119.6, 114.7, 109.4, 30.8, 21.3, 21.1. This compound has been known. Its NMR spectra are identical with the authorized ones.

2,3-Bis(4-ethylphenyl)-1-methyl-1H-indole (4b)

4b (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), 1,2-bis(4-ethylphenyl)ethyne (0.0703 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room
temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4b was obtained in 86% yield (58.5 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.79 (d, $J = 7.9$ Hz, 1H), 7.35 – 7.33 (m, 1H), 7.27 – 7.13 (m, 8H), 7.09 (d, $J = 8.0$ Hz, 2H), 3.60 (s, 3H), 2.68 – 2.58 (m, 4H), 1.26 – 1.20 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 143.9, 141.1, 137.6, 137.2, 132.5, 131.0, 129.7, 129.2, 127.8, 127.6, 127.1, 121.9, 119.9, 119.6, 114.7, 109.4, 30.8, 28.6, 28.5, 15.3, 15.3. This compound has been known. It's NMR spectra are identical with the authorized ones.

2,3-Bis(4-isopropylphenyl)-1-methyl-1H-indole (4c)

4c (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), 1,2-bis(4-isopropylphenyl)ethyne (0.0787 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4c was obtained in 80% yield (58.8 mg, white solid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.80 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.28 – 7.10 (m, 10H), 3.61 (s, 3H), 2.95 – 2.83 (m, 2H), 1.28 – 1.23 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.5, 145.6, 137.6, 137.2, 132.6, 131.0, 129.6, 129.3, 127.1, 126.3, 126.1, 121.9, 119.9, 119.7, 114.7, 109.4, 33.8, 33.7, 30.9, 24.0, 23.9; HRMS (ESI) Calcd for C$_{27}$H$_{30}$N ( [M + H]$^+$) : 368.2373, found : 368.2370.
1-Ethyl-2,3-bis(3-fluorophenyl)-1H-indole (4d)

4d (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-ethylaniline (0.0242 g, 0.2 mmol), 1,2-bis(3-fluorophenyl)ethyne (0.0643 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4d was obtained in 68% yield (45.4 mg, brown oil). ¹H NMR (400MHz, CDCl₃): δ 7.70 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.15 – 7.10 (m, 2H), 7.04 – 6.88 (m, 5H), 6.81 – 6.76 (m, 1H), 4.05 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.8 (d, J = 244.5 Hz), 162.6 (d, J = 247.3 Hz), 161.5 (d, J = 19.9 Hz), 137.2 (d, J = 8.4 Hz), 136.1, 136.0 (d, J = 2.2 Hz), 134.0 (d, J = 8.1 Hz), 130.2 (d, J = 8.5 Hz), 129.6 (d, J = 8.8 Hz), 126.9, 126.8 (d, J = 3.0 Hz), 125.4 (d, J = 2.7 Hz), 122.6, 120.5, 119.6, 117.8 (d, J = 21.6 Hz), 116.3 (d, J = 21.5 Hz), 115.5 (d, J = 21.0 Hz), 114.7 (d, J = 2.5 Hz), 112.5 (d, J = 21.1 Hz), 109.9, 38.7, 15.3; HRMS (ESI) Calcd for C₂₂H₁₉F₂N ([M + H]⁺) 334.1402, found : 334.1399.

1-Ethyl-2,3-di-m-tolyl-1H-indole (4e)

4e (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with N-ethylaniline (0.0242 g, 0.2 mmol), 1,2-di-m-tolylethyne (0.0619 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4e was obtained in 75% yield (48.8 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.72 (d, J = 7.9 Hz, 1H),
7.29 (d, \(J = 8.2\) Hz, 1H), 7.17 – 6.94 (m, 9H), 6.84 (d, \(J = 7.3\) Hz, 1H), 3.98 (q, \(J = 7.1\) Hz, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 1.14 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 137.8, 137.4, 137.4, 136.0, 135.2, 132.2, 131.5, 130.4, 128.8, 128.2, 128.2, 127.9, 127.3, 126.9, 126.1, 121.8, 119.9, 119.8, 109.7, 38.6, 21.5, 21.4, 15.3; HRMS (ESI) Calcd for C\(_{24}\)H\(_{24}\)N ([M + H]\(^+\)) : 326.1903, found : 326.1901.

1-Ethyl-2,3-bis(4-methoxyphenyl)-1\(H\)-indole (4f)

4f (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with \(N\)-ethylaniline (0.0242 g, 0.2 mmol), 1,2-bis(4-methoxyphenyl)ethyne (0.0715 g, 0.3 mmol), [Cp*RhCl\(_2\)]\(_2\) (0.0031g, 2.5 mol%), AgSbF\(_6\) (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4f was obtained in 84% yield (60.1 mg, colorless solid). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta 7.76 \text{ (d, } J = 7.9 \text{ Hz, 1H), 7.37 \text{ (d, } J = 8.2 \text{ Hz, 1H), 7.25 – 7.08 \text{ (m, 6H), 6.86 \text{ (d, } J = 8.7 \text{ Hz, 2H), 6.79 \text{ (d, } J = 8.8 \text{ Hz, 2H), 4.06 \text{ (q, } J = 7.1 \text{ Hz, 2H), 3.74 \text{ (s, 3H), 3.71 \text{ (s, 3H), 1.22 \text{ (t, } J = 7.2 \text{ Hz, 3H); }}^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 159.3, 157.4, 136.6, 135.9, 132.1, 130.7, 127.7, 127.7, 127.8, 124.4, 121.7, 119.8, 119.5, 114.6, 113.8, 113.5, 109.6, 55.1, 55.0, 38.4, 15.3. This compound has been known.\^8\) Its NMR spectra are identical with the authorized ones.

1-Ethyl-2,3-bis(3-(trifluoromethoxy)phenyl)-1\(H\)-indole (4g)

4g (0.2 mmol scale) was synthesized following the general procedure. The reaction
was carried out with N-ethylaniline (0.0242 g, 0.2 mmol), 1,2-bis(3-(trifluoromethoxy)phenyl)ethyne (0.1039 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4g was obtained in 78% yield (72.6 mg, colorless solid). ¹H NMR (400MHz, CDCl₃): δ 7.68 (d, J = 8.0 Hz, 1H), 7.35 (dd, J = 13.9, 8.0 Hz, 2H), 7.24 – 7.11 (m, 7H), 6.97 (s, 1H), 6.93 (d, J = 7.9 Hz, 1H), 4.05 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.3 (q, J = 1.9 Hz), 136.8, 136.3, 135.8, 133.7, 130.1, 129.5, 129.3, 127.9, 126.8, 123.5, 122.8, 122.0, 120.9, 120.7, 120.4 (q, J = 256.7 Hz), 119.5, 118.2, 114.7, 110.1, 38.8, 15.3; HRMS (ESI) Calcd for C₂₄H₁₈F₆NO₂ ([M + H]+): 466.1236, found: 466.1233.

![Chemical Structure](image)

1,2-Bis(4-(tert-butyl)phenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4h)

4h (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,2-bis(4-(tert-butyl)phenyl)ethyne (0.0872 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the product 4h was obtained in 85% yield (71.7 mg, white solid). ¹H NMR (400MHz, CDCl₃): δ 7.54 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.22 – 7.17 (m, 6H), 6.98 – 6.95 (m, 1H), 6.86 (d, J = 6.8 Hz, 1H), 3.95 – 3.92 (m, 2H), 2.91 (t, J = 5.9 Hz, 2H), 2.10 – 2.05 (m,
2H), 1.25 (s, 9H), 1.23 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.6, 147.7, 135.9, 134.3, 132.7, 130.3, 129.1, 128.9, 125.2, 125.0, 121.8, 120.0, 118.9, 117.2, 43.2, 34.6, 34.4, 31.4, 31.3, 25.1, 23.0; HRMS (ESI) Calcd for C$_{31}$H$_{36}$N ( [M + H]$^+$) : 422.2842, found : 422.2839.

1,2-Bis(3-methoxyphenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4i)

4i (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,2-bis(3-methoxyphenyl)ethyne (0.0715 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4i was obtained in 75% yield (55.4 mg, brown oil). $^1$H NMR (400MHz, CDCl$_3$): δ 7.54 (d, $J$ = 8.0 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.08 (t, $J$ = 7.9 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.89 – 6.76 (m, 6H), 6.62 (dd, $J$ = 7.9, 2.2 Hz, 1H), 3.98 – 3.95 (m, 2H), 3.60 (s, 3H), 2.92 (t, $J$ = 6.0 Hz, 2H), 2.10 (p, $J$ = 6.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.4, 159.4, 136.9, 135.9, 134.3, 133.0, 129.4, 129.1, 124.9, 123.1, 122.1, 122.0, 120.3, 119.2, 117.1, 116.2, 114.7, 114.4, 113.5, 111.4, 55.2, 55.0, 43.2, 25.0, 22.9; HRMS (ESI) Calcd for C$_{25}$H$_{34}$NO$_2$ ( [M + H]$^+$) : 370.1802, found : 370.1803.

1,1'-(5,6-Dihydro-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diyl)bis(3,1-phenylene)dieth
anone (4j)

4j (0.2 mmol scale) was synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1,1’-(ethyne-1,2-diylbis(3,1-phenylene))diethanone (0.0787 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:10), the product 4j was obtained in 70% yield (55.1 mg, white solid). 

1H NMR (400MHz, CDCl₃): δ 7.98 – 7.93 (m, 3H), 7.77 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.34 (t, J = 7.7 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.0 Hz, 1H), 4.09 (t, J = 5.7 Hz, 2H), 3.05 (t, J = 6.1 Hz, 2H), 2.52 (s, 3H), 2.45 (s, 3H), 2.26 – 2.21 (m, 2H); 13C NMR (100 MHz, CDCl₃): δ 198.1, 197.5, 137.2, 137.1, 135.7, 135.1, 135.0, 134.4, 134.1, 131.9, 130.2, 129.6, 128.9, 128.6, 127.7, 125.2, 124.6, 122.2, 120.7, 119.6, 116.6, 114.0, 43.1, 26.5, 26.4, 24.9, 22.8; HRMS (ESI) Calcd for C₂₇H₂₄NO₂ ( [M + H]⁺) : 394.1802, found : 394.1798.

1-(4-Ethylphenyl)-2-(p-tolyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4k)

2-(4-Ethylphenyl)-1-(p-tolyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4k’)

4k and 4k’(0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1-ethyl-4-(p-tolylethynyl)benzene (0.0661 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash
chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4k and 4k’) were obtained in 73% yield (1 : 1 determined by $^1$H NMR, 51.3 mg, viscous liquid). $^1$H NMR (400MHz, CDCl$_3$): δ 7.53 (dd, $J = 7.5$, 5.9 Hz, 2H), 7.20 – 7.15 (m, 8H), 7.11 (t, $J = 8.2$ Hz, 4H), 7.04 – 6.97 (m, 6H), 6.89 (d, $J = 6.6$ Hz, 2H), 3.99 (q, $J = 5.2$ Hz, 4H), 2.96 (t, $J = 6.1$ Hz, 4H), 2.64 – 2.59 (m, 2H), 2.58 – 2.53 (m, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 2.14 (p, $J = 6.0$ Hz, 4H), 1.21 – 1.19 (m, 3H), 1.18 – 1.15 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 143.7, 140.9, 137.5, 135.9, 135.8, 134.6, 134.2, 132.9, 132.7, 130.6, 130.5, 129.5, 129.1, 128.9, 127.8, 127.6, 125.1, 121.9, 121.8, 120.0, 118.9, 117.1, 117.0, 114.1, 114.0, 43.1, 43.0, 28.6, 28.5, 25.1, 23.0, 21.3, 21.1, 15.3, 15.2; HRMS (ESI) Calcd for C$_{26}$H$_{26}$N ([M + H]$^+$) : 352.2060, found 352.2057.

1-(4-Bromophenyl)-2-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4l)
2-(4-Bromophenyl)-1-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (4l’)

4l and 4l'(0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 1-bromo-4-(phenylethynyl)benzene (0.0771 g, 0.3 mmol), [Cp*RhCl$_2$]$_2$ (0.0031g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4l and 4l’) were obtained in 77% yield (1 : 1 determined by $^1$H NMR, 59.8 mg, colorless oil). $^1$H NMR (400MHz, CDCl$_3$): δ 7.52 – 7.47 (m, 2H), 7.38 (d, $J = 7.1$ Hz, 2H), 7.29 – 7.18 (m, 11H), 7.11 – 7.09 (m, 5H), 7.03 – 6.98 (m, 2H), 6.90 (d, $J = 7.0$ Hz, 2H), 3.96 – 3.94 (m, 4H), 2.94 (t, $J = 5.9$ Hz, 4H), 2.11 (p, $J = 6.1$, 5.6 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.2, 135.2, 134.6, 134.5, 134.4, 134.3, 132.2, 131.6, 131.4, 131.3, 131.1, 130.7, 130.6, 129.7, 128.5, 128.3, 128.0, 125.6, 124.9,
124.6, 122.11, 122.07, 122.01, 120.5, 120.4, 119.4, 119.3, 119.0, 117.1, 116.7, 114.9, 113.2, 43.2, 43.1, 25.0, 25.0, 22.9, 22.9; HRMS (ESI) Calcd for C_{23}H_{19}BrN ([M + H]^{+}) : 388.0695, found 388.0694.

1-Methyl-2-phenyl-3-(4-(trimethylsilyl)phenyl)-1H-indole (4m)

1-Methyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)-1H-indole (4m’)

4m and 4m’ (0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with N-methylaniline (0.0214 g, 0.2 mmol), trimethyl(4-(phenylethynyl)phenyl)silane (0.0751 g, 0.3 mmol), [Cp*RhCl_2]_2 (0.0031 g, 2.5 mol%), AgSbF_6 (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4m and 4m’) were obtained in 70% yield (1.2 : 1 determined by ^1H NMR, 49.8 mg, colorless oil). ^1H NMR (400MHz, CDCl_3): δ 7.83 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1X1.2 H), 7.51 (d, J = 7.8 Hz, 1+ 1X1.2 H), 7.42 – 7.26 (m, 9 + 9X1.2 H), 7.19 – 7.15 (m, 2 + 2X1.2 H), 3.65 (s, 3X1.2 H), 3.63 (s, 3H), 0.28 (s, 9X1.2 H), 0.25 (s, 9H); ^13C NMR (100 MHz, CDCl_3): δ 140.2, 137.8, 137.7, 137.4, 137.3, 135.6, 135.2, 133.2, 133.19, 132.1, 132.0, 131.2, 130.3, 129.9, 129.0, 128.4, 128.2, 128.0, 127.0, 126.9, 125.5, 122.1, 120.2, 119.8, 119.6, 115.1, 115.0, 109.5, 31.0, 30.9, -1.0, -1.1; HRMS (ESI) Calcd for C_{24}H_{26}NSi ([M + H]^{+}) : 356.1829, found 356.1827.
1-Isopropyl-2-phenyl-3-(4-(trimethylsilyl)phenyl)-1H-indole (4n)

1-Isopropyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)-1H-indole (4n’)

4n and 4n’ (0.2 mmol scale) were synthesized following the general procedure. The reaction was carried out with N-isopropylaniline (0.0242 g, 0.2 mmol), trimethyl(4-(phenylethynyl)phenyl)silane (0.0751 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butybenzoic acid (0.0178 g, 50 mol%) and iodo-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at room temperature in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:1), the inseparable products (4n and 4n’) were obtained in 74% yield (1.5 : 1 determined by ¹H NMR, 56.8 mg, pale yellow oil). ¹H NMR (400MHz, CDCl₃): δ 7.82 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1X1.5 H), 7.63 (d, J = 8.3 Hz, 1 + 1X1.5 H), 7.50 (d, J = 7.8 Hz, 1 + 1X1.5 H), 7.40 – 7.24 (m, 8 + 8X1.5 H), 7.15 – 7.10 (m, 3 + 3X1.5 H), 4.59 – 4.48 (m, 1 + 1X1.5 H), 1.61 – 1.58 (m, 6 + 6X1.5 H), 0.28 (s, 9X1.5 H), 0.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 140.2, 137.6, 137.5, 136.6, 135.7, 135.3, 134.6, 133.2, 133.1, 133.0, 132.9, 131.2, 131.1, 130.3, 130.0, 129.9, 129.1, 128.4, 128.2, 128.1, 128.0, 127.9, 125.4, 125.3, 121.4, 120.1, 119.9, 119.7, 115.1, 115.0, 112.3, 112.2, 47.8, 21.5, 21.4, -1.0, -1.1; HRMS (ESI) Calcd for C₂₆H₃₀NSi ([M + H]⁺): 384.2142, found 384.2140.

Methyl 1,3-dimethyl-2-phenyl-1H-indole-5-carboxylate (4o)

4o (0.2 mmol scale) was synthesized following the general procedure with slight
modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 1-phenyl-1-propyne (0.0348 g, 0.3 mmol), [Cp*RhCl₂](0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4o was obtained in 52% yield (29.1 mg, white solid). ^1H NMR (400 MHz, CDCl₃): δ 8.38 (d, J = 1.2 Hz, 1H), 7.96 (dd, J = 8.6, 1.7 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.38 (m, 3H), 7.31 (d, J = 8.6 Hz, 1H), 3.95 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H); ^13C NMR (100 MHz, CDCl₃): δ 168.4, 139.6, 138.9, 131.4, 130.5, 128.4, 128.1, 128.0, 123.1, 121.8, 120.9, 110.1, 108.8, 51.8, 31.1, 9.3; HRMS (ESI) Calcd for C₁₈H₁₈O₂N ([M + H]^+): 280.1332, found: 280.1332.

Methyl 3-ethyl-1-methyl-2-phenyl-1H-indole-5-carboxylate (4p)

4p (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 1-phenyl-1-butyne (0.0391 g, 0.3 mmol), [Cp*RhCl₂](0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4p was obtained in 70% yield (41.1 mg, white solid). ^1H NMR (400 MHz, CDCl₃): δ 8.42 (d, J = 1.4 Hz, 1H), 7.95 (dd, J = 8.6, 1.6 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.39 – 7.37 (m, 2H), 7.32 (d, J = 8.6 Hz, 1H), 3.95 (s, 3H), 3.59 (s, 3H), 2.73 (q, J = 7.5 Hz, 2H), 1.23 (d, J = 7.6 Hz, 3H); ^13C NMR (100 MHz, CDCl₃): δ 168.4, 139.6, 138.5, 131.6, 130.5, 128.4, 128.2, 127.0, 123.0, 122.0, 120.9, 116.9, 108.9, 51.8, 31.0, 17.7, 16.1; HRMS (ESI) Calcd for C₁₉H₂₀O₂N ([M + H]^+): 294.1489, found: 294.1488.
Methyl 2,3-dibutyl-1-methyl-1H-indole-5-carboxylate (4q)

4q (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 5-decyne (0.0415 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 80 °C in DCM (1.0 mL) for 24 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:3), the product 4q was obtained in 73% yield (44.0 mg, colorless oil). ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 1.3 Hz, 1H), 7.85 (dd, J = 8.6, 1.6 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H), 2.75 – 2.70 (m, 4H), 1.64 – 1.52 (m, 4H), 1.48 – 1.36 (m, 4H), 0.95 (q, J = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 168.5, 139.2, 138.4, 127.4, 122.0, 121.2, 120.4, 113.3, 108.1, 51.7, 33.7, 32.3, 29.8, 24.3, 24.2, 22.9, 22.7, 14.0, 13.9; HRMS (ESI) Calcd for C₁₉H₂₈O₂N ([M + H]+): 302.2115, found: 302.2115.

Methyl 2-acetyl-1-methyl-3-phenyl-1H-indole-5-carboxylate (4r)

4r (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), 4-phenyl-3-butyn-2-one (0.0433 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 60 °C in DCM (1.0 mL) for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:6), the product 4r was obtained in 43% yield (26.4 mg, sight yellow solid). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (d, J =
1.3 Hz, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.45 – 7.42 (m, 2H), 7.37 (d, J = 8.6 Hz, 1H), 3.96 (s, 3H), 3.53 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.4, 168.0, 147.5, 139.0, 131.6, 130.2, 129.9, 128.9, 126.1, 125.4, 124.9, 124.7, 116.7, 109.3, 51.9, 31.0, 30.2; HRMS (ESI) Calcd for C$_{19}$H$_{18}$O$_3$N ([M + H]$^+$) : 308.1281, found : 308.1281.

Dimethyl 1-methyl-3-phenyl-1H-indole-2,5-dicarboxylate (4s)

4s (0.2 mmol scale) was synthesized following the general procedure with slight modifications. The reaction was carried out with methyl 4-(methylamino)benzoate (0.0330 g, 0.2 mmol), methyl phenylpropiolate (0.0481 g, 0.3 mmol), [Cp*RhCl$_2$](2) (0.0031 g, 2.5 mol%), AgSbF$_6$ (0.0069 g, 10 mol%), PivOH (0.0204 g, 1.0 equiv.) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The reaction mixture was stirred at 60 °C in DCM (1.0 mL) for 48 h. After concentration and purification by flash chromatography on silica gel (petroleum ether/diethyl ether = 100:6), the product 4s was obtained in 58% yield (37.5 mg, sight yellow solid). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.93 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.45 – 7.38 (m, 3H), 3.96 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.9, 165.0, 148.3, 139.2, 130.8, 130.2, 129.2, 128.2, 125.9, 124.7, 124.2, 124.0, 109.5, 106.1, 51.9, 50.9, 31.1; HRMS (ESI) Calcd for C$_{19}$H$_{18}$O$_4$N ([M + H]$^+$) : 324.123., found : 324.1230.
Mechanistic Studies

Experiment to Probe the Intermediate.

In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), 4-tert-butylbenzoic acid (0.0356 g, 0.2 mmol) and iso-amyl nitrite (0.0351 g, 0.3 mmol) and dichloromethane (1.0 mL). The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the isolated product 5a (100% yield).

![Chemical Reaction Diagram]

Experiments to Identify the Role of Benzoic Acid

(1) In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%), 4-tert-butylbenzoic acid (0.0178 g, 50 mol%) and iso-amyl nitrite (0.0351 g, 0.3 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then dichloromethane (1.0 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 6 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel. The product 3a was obtained in 43% yield.

(2) In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged 1,2,3,4-tetrahydroquinoline (0.0266 g, 0.2 mmol), diphenylacetylene (0.0535 g, 0.3 mmol), [Cp*RhCl₂]₂ (0.0031 g, 2.5 mol%), AgSbF₆ (0.0069 g, 10 mol%).
tube was fitted with a rubber septum and moved out of the glove box. Then dichloromethane (1.0 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature for 24 h. when the reaction finished, the reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel, the product 3a was obtained in 15% yield.

\[ \begin{align*}
\text{N} & \quad + \quad \text{Ph} \quad \text{Ph} \\
\text{NO} & \quad 0.2 \text{ mmol} & \quad \text{1.5 eq} \\
5a & & \\
\end{align*} \]

\[ \begin{align*}
[\text{OP}^\dagger\text{RhCl}]_2 & \quad (2.5\text{ mol}%) \\
\text{AgSbF}_6 & \quad (10\text{ mol}%) \\
\text{CH}_2\text{Cl}_2 & \quad (1\text{ mL}) , \text{N}_2, \text{ rt} \\
\end{align*} \]

\[ \begin{align*}
3a
\end{align*} \]

with 4-tBuPhCO_2H (1 eq): 6 h, 43%
without 4-tBuPhCO_2H: 24 h, 15%

References

NMR Spectra of Substrates and Products

1aa

1aa
1ab

1ab
2u

3a
3g

3h
$3h$

$3i$
3t

3u
3aa

![NMR Spectrum of 3aa](image)

3ab

![NMR Spectrum of 3ab](image)
3ah

3ah
4p

MeO₂C

Et

Ph

Me

4p

MeO₂C

Et

Ph

Me

S105