Supporting Information

Rh/Cu-Catalyzed Multiple C-H, C-C and C-N Bonds Cleavage: Facile Synthesis of Pyrido[2,1-a]indoles from 1-(Pyridin-2-yl)-1H-indoles and γ-Substituted tert-Propargyl Alcohols

Ting Li, Zhen Wang, Mingliang Zhang, Hui-Jun Zhang, and Ting-Bin Wen*

Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P.R. China

<table>
<thead>
<tr>
<th>Content</th>
<th>Page number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General</td>
<td>2</td>
</tr>
<tr>
<td>2. Preparation of Starting Materials</td>
<td>3</td>
</tr>
<tr>
<td>3. General Procedure</td>
<td>13</td>
</tr>
<tr>
<td>4. Mechanism Studies</td>
<td>31</td>
</tr>
<tr>
<td>5. Proposed Mechanism for C-H alkynylation</td>
<td>36</td>
</tr>
<tr>
<td>6. References</td>
<td>37</td>
</tr>
<tr>
<td>7. X-ray Studies</td>
<td>38</td>
</tr>
<tr>
<td>8. NMR Spectra</td>
<td>51</td>
</tr>
</tbody>
</table>
1. General

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. All glassware was dried overnight at 110 °C prior to use. Chromatography was performed on 300-400 mesh silica gel. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained on Bruker En Apex ultra 7.0T FT-MS by the Public Instrument Platform of College of Chemistry and Chemical Engineering at Xiamen University.

$^1$H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d$_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration).

$^{13}$C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d$_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.
2. Preparation of Starting Materials

Compounds 1a-1o were prepared according to the known procedures.\textsuperscript{1}

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\textbf{1: 12}};
  \draw (0,0) rectangle (3,3);
  \node at (1.5,1.5) {\textbf{KOH (2.5 equiv)}};
  \node at (0,0) {\textbf{DMSO, N\textsubscript{2}, 130 \textdegree C, 36 h}};
  \draw (0,0) -- (1,1) -- (2,0);
  \draw (1,1) -- (2,2) -- (1,3) -- cycle;
  \draw (1,1) -- (1,2);
  \draw (2,0) -- (2,1);
  \draw (0,0) -- (1,0);
  \draw (1,1) -- (2,1);
  \draw (2,2) -- (3,2);
  \node at (1.5,1) {\textbf{R\textsubscript{1}}};
  \node at (2.5,1) {\textbf{R\textsubscript{2}}};
  \node at (1.5,2) {\textbf{Br}};
  \node at (1.5,3) {\textbf{N}};
  \node at (2.5,2) {\textbf{N}};
  \node at (1.5,0) {\textbf{H}};
  \node at (2.5,0) {\textbf{H}};
\end{tikzpicture}
\end{center}

3-methyl-1-(pyridin-2-yl)-1\textit{H}-indole (1a)

\textbf{1H NMR (500 MHz, CDCl\textsubscript{3})}: δ = 8.40 (m, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.60 (dt, J = 2.2 Hz, J = 8.6 Hz, 1H), 7.48 (m, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.32 (m, 1H), 7.24 (m, 1H), 7.11 (dt, J = 1.1 Hz, J = 7.4 Hz, 1H), 6.94 (m, 1H), 2.26 (s, 3H); \textbf{13C NMR (125 MHz, CDCl\textsubscript{3})}: δ = 152.5, 148.7, 138.2, 135.3, 131.0, 123.2, 123.1, 120.8, 119.3, 119.0, 114.7, 113.8, 113.1, 9.6 ppm. This compound is known and the spectroscopic date match those reported.\textsuperscript{1}

1-(pyridin-2-yl)-1\textit{H}-indole (1b)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.61$ (d, $J = 4.0$ Hz, 1H), 8.27 (d, $J = 8.2$ Hz, 1H), 7.83 (t, $J = 6.5$ Hz, 1H), 7.77 (d, $J = 3.4$ Hz, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.27 (t, $J = 7.3$ Hz, 1H), 7.19 (m, 1H), 6.77 (d, $J = 3.4$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 152.5, 148.9, 138.3, 135.1, 130.4, 126.0, 123.1, 121.2, 121.0, 120.0, 114.5, 113.0, 105.5$ ppm. This compound is known and the spectroscopic data match those reported.$^1$

5-methoxy-1-(pyridin-2-yl)-1$^H$-indole (1c)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.55$ (d, $J = 4.1$ Hz, 1H), 8.18 (d, $J = 8.8$ Hz, 1H), 7.80 (m, 1H), 7.70 (d, $J = 3.4$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.14 (m, 2H), 6.95 (dd, $J = 1.9$ Hz, $J = 8.8$ Hz, 1H), 6.67 (d, $J = 3.9$ Hz, 1H), 3.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 155.0, 152.6, 148.9, 138.4, 131.2, 130.2, 126.3, 119.7, 114.2, 113.9, 112.7, 105.4, 103.0, 55.8$ ppm; This compound is known and the spectroscopic data match those reported.$^1$

6-methyl-1-(pyridin-2-yl)-1$^H$-indole (1e)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.60 = (dd, J = 1.0$ Hz, $J = 4.8$ Hz, 1H), 8.17(d, $J = 8.6$ Hz, 1H), 7.81(m, 1H), 7.75(d, $J = 3.4$ Hz, 1H), 7.50 (br, 2H), 7.17(m, 2H), 6.69 (d, $J = 3.4$ Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 152.5, 148.8, 138.2, 133.3,$
5-chloro-1-(pyridin-2-yl)-1H-indole (1f)

\[
\begin{align*}
\text{1H NMR (500 MHz, CDCl}_3\text{): } & \delta = 8.59 (m, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 1.5 Hz, J = 6.8 Hz, 1H), 7.73 (d, J = 3.4 Hz, 1H), 7.64 (d, J = 2.0 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.27 (dd, J = 1.9 Hz, J = 8.8 Hz, 1H), 7.20 (dd, J = 4.5 Hz, J = 7.1 Hz, 1H), 6.67 (d, J = 3.9 Hz, 1H); \\
\text{13C NMR (125 MHz, CDCl}_3\text{): } & \delta = 152.3, 149.0, 138.5, 133.6, 131.5, 127.0, 126.8, 123.3, 120.4, 120.3, 114.4, 114.3, 105.0 ppm; \text{ This compound is known and the spectroscopic date match those reported.}^1
\end{align*}
\]

2-(2-methyl-1H-pyrrol-1-yl)pyridine (1h)

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{): } & \delta = 8.53 (m, 1H), 7.79 (m, 1H), 7.31 (dt, J = 0.9, 8.2 Hz, 1H), 7.20 (m, 1H), 7.09 (dd, J = 1.9, 3.0 Hz, 1H), 6.23 (t, J = 3.2 Hz, 1H), 6.07 (m, 1H), 2.45 (s, 3H), 2.25 (s, 3H); \\
\text{13C NMR (100 MHz, CDCl}_3\text{): } & \delta = 153.0, 148.8, 138.2, 129.2, 120.9, 120.3, 117.0, 110.2, 109.1, 14.2 ppm; \text{ This compound is known and the spectroscopic date match those reported.}^1
\end{align*}
\]

3-methyl-1-(4-methylpyridin-2-yl)-1H-indole (1i)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.42 (s, 1H), 8.25 (d, $J$ = 8.3 Hz, 1H), 7.69 (d, $J$ = 7.7 Hz, 1H), 7.57 (d, $J$ = 6.3 Hz, 1H), 7.54 (s, 1H), 7.33 (m, 3H), 2.46 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.5, 148.9, 139.0, 135.4, 130.9, 123.5, 123.1, 120.6, 119.1, 114.2, 113.8, 112.9, 17.8, 9.8 ppm; HRMS m/z (ESI) Calcd for C$_{15}$H$_{14}$N$_2$Na (M+Na)$^+$, 245.1049, found 245.1042.

3-methyl-1-(5-methylpyridin-2-yl)-1H-indole (1j)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.42 (dd, $J$ = 6.4, 11.8 Hz, 1H), 8.27 (dd, $J$ = 7.0, 11.8 Hz, 1H), 7.64 (d, $J$ = 7.5 Hz, 1H), 7.54 (s, 1H), 7.35 (m, 1H), 7.28 (m, 3H), 6.96 (d, $J$ = 8.2 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.8, 149.6, 148.5, 135.4, 131.0, 123.4, 123.1, 120.8, 120.7, 119.1, 114.7, 114.5, 113.1, 21.3, 9.7 ppm; HRMS m/z (ESI) Calcd for C$_{15}$H$_{14}$N$_2$Na (M+Na)$^+$, 245.1049, found 245.1042.

5-methyl-1-(5-methylpyridin-2-yl)-1H-indole (1k)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.26 (d, $J$ = 1.7 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.56 (d, $J$ = 3.4 Hz, 1H), 7.47 (dd, $J$ = 1.9, 8.3 Hz, 1H), 7.34 (s, 1H), 7.25 (d, $J$ = 8.3 Hz, 1H), 7.00 (d, $J$ = 8.6 Hz, 1H), 6.51 (d, $J$ = 3.5 Hz, 1H), 2.37 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 150.5, 149.0, 138.9, 133.4, 130.6, 130.3, 129.3, 126.1, 124.5, 120.8, 114.0, 112.4, 104.7, 21.4, 17.8 ppm; HRMS m/z (ESI) Calcd for C$_{15}$H$_{14}$N$_2$Na (M+Na)$^+$, 245.1049, found 245.1042.

5-chloro-1-(5-methylpyridin-2-yl)-1H-indole (1l)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.31 (dd, $J$ = 0.6, 1.6 Hz, 1H), 8.02 (d, $J$ = 8.9 Hz, 1H), 7.60 (d, $J$ = 3.5 Hz, 1H), 7.56 (dd, $J$ = 2.0, 8.0 Hz, 1H), 7.54 (d, $J$ = 2.1 Hz, 1H), 7.27 (d, $J$ = 8.3 Hz, 1H), 7.15 (dd, $J$ = 2.3, 8.9 Hz, 1H), 6.56 (dd, $J$ = 0.6, 3.4 Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 150.1, 149.0, 139.1, 133.5, 131.2, 130.0, 127.2, 126.6, 123.1, 120.4, 114.1, 114.0, 104.5, 17.8 ppm; HRMS m/z (ESI) Calcd for C$_{14}$H$_{11}$N$_2$ClNa (M+Na)$^+$, 265.0503, found 265.0505.

5-methoxy-1-(5-methylpyridin-2-yl)-1H-indole (1m)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 8.29 (dd, $J = 0.5, 1.5$ Hz, 1H), 8.00 (d, $J = 9.1$ Hz, 1H), 7.58 (d, $J = 3.4$ Hz, 1H), 7.53 (dd, $J = 2.3, 8.4$ Hz, 1H), 7.04 (d, $J = 2.5$ Hz, 1H), 6.85 (dd, $J = 2.5, 9.1$ Hz, 1H), 6.54 (d, $J = 3.2$ Hz, 1H), 3.80 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.9, 150.4, 148.9, 138.9, 130.9, 130.2, 129.3, 126.4, 113.8, 112.6, 104.8, 102.9, 55.8, 17.8 ppm; HRMS m/z (ESI) Calcd for C$_{13}$H$_{14}$N$_2$ONa (M+Na)$^+$, 261.0998, found 261.0991.

5-fluoro-1-(5-methylpyridin-2-yl)-1H-indole (1n)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 8.27 (s, 1H), 8.04 (dd, $J = 4.6, 9.1$ Hz, 1H), 7.58 (t, $J = 3.1$ Hz, 1H), 7.50 (t, $J = 5.7$ Hz, 1H), 7.22 (m, 2H), 6.92 (t, $J = 9.5$ Hz, 1H), 6.55 (m, 1H), 2.27 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 158.4 ($J_{CF} = 235.6$ MHz), 150.3, 148.9, 139.1, 131.7, 130.8 ($J_{CF} = 10.1$ MHz), 129.8, 127.4, 114.0, 113.9, 111.0 ($J_{CF} = 25.6$ MHz), 105.8 ($J_{CF} = 23.1$ MHz), 104.8 ($J_{CF} = 4.1$ MHz), 17.8 ppm; HRMS m/z (ESI) Calcd for C$_{14}$H$_{11}$N$_2$FNa (M+Na)$^+$, 249.0798, found 249.0799.

3-methyl-1-(6-methylpyridin-2-yl)-1H-indole (1o)
\[ \text{1H NMR (500 MHz, CDCl}_3): \delta = 8.18 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.59 \text{ (t, } J = 8.0 \text{ Hz, 1H)}, 7.53 \text{ (d, } J = 7.8 \text{ Hz, 1H)}, 7.45 \text{ (d, } J = 1.1 \text{ Hz, 1H)}, 7.23 \text{ (t, } J = 9.0 \text{ Hz, 1H)}, 7.16 \text{ (m, 2H)}, 6.90 \text{ (d, } J = 7.5 \text{ Hz, 1H)}, 2.55 \text{ (s, 3H), 2.31 (s, 3H); 13C NMR (125 MHz, CDCl}_3): \delta = 158.1, 152.0, 138.4, 135.4, 131.0, 123.3, 123.0, 120.6, 119.0, 118.8, 114.4, 113.2, 110.8, 24.4, 9.6 \text{ ppm. HRMS m/z (ESI) Calcd for C}_{15}H_{14}N_2Na (M+Na)^+: 245.1049, found 245.1042.} \]

Compounds 2a-2l were prepared according to the known procedures.\(^2\)-\(^3\)

\[
\text{R} \equiv + \overset{1)}{\text{CH}_3CO} \rightarrow \text{R} \equiv \overset{2)}{\text{CH}_3COH}
\]

R = Ar, Alkanyl

2-methyl-4-phenylbut-3-yn-2-ol (2a)

\[ \text{1H NMR (500 MHz, CDCl}_3): \delta = 7.34 \text{ (m, 2H)}, 7.21 \text{ (m, 3H)}, 2.16 \text{ (br, 1H)}, 1.54 \text{ (s, 6H); 13C NMR (125 MHz, CDCl}_3): \delta = 159.5, 133.0, 114.8, 113.8, 92.5, 81.9, 65.5, 55.2, 31.5 \text{ ppm. This compound is known and the spectroscopic date match those reported.}^2 \]

2-methyl-4-(p-tolyl)but-3-yn-2-ol (2b)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.19 (d, $J$ = 8.1 Hz, 2H), 6.97 (d, $J$ = 8.1 Hz, 2H), 2.21 (br, 1H), 1.49 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 138.3, 131.5, 129.0, 119.7, 93.2, 82.2, 65.6, 31.5, 21.4 ppm. This compound is known and the spectroscopic date match those reported.\textsuperscript{2}

4-(4-chlorophenyl)-2-methylbut-3-yn-2-ol (2d)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.25 (d, $J$ = 7.8 Hz, 2H), 7.19 (d, $J$ = 7.8 Hz, 2H), 2.20 (br, 1H), 1.53 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 134.2, 132.8, 128.5, 121.2, 94.7, 81.0, 65.5, 31.4. This compound is known and the spectroscopic date match those reported.\textsuperscript{2}

2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (2e)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.54 (m, 4H), 2.34 (br, 1H), 1.65 (s, 6H) ppm. This compound is known and the spectroscopic date match those reported.\textsuperscript{2}
4-((1,1'-biphenyl)-4-yl)-2-methylbut-3-yn-2-ol (2f)

![Chemical Structure of 2f]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.51 (d, $J$ = 7.9 Hz, 2H), 7.46 (d, $J$ = 7.9 Hz, 2H), 7.40 (d, $J$ = 7.9 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 2H), 7.27 (t, $J$ = 8.2 Hz, 3H), 1.99 (br, 1H), 1.56 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 141.0, 140.3, 132.0, 128.8, 127.6, 127.0, 126.9, 121.6, 94.4, 82.0, 65.7, 31.5 ppm. This compound is known and the spectroscopic date match those reported.$^2$

4-(4-methoxyphenyl)-2-methylbut-3-yn-2-ol (2g)

![Chemical Structure of 2g]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.26 (d, $J$ = 7.7 Hz, 2H), 6.73 (d, $J$ = 7.7 Hz, 2H), 3.71 (s, 3H), 2.32 (br, 1H), 1.55 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 159.5, 133.0, 114.8, 113.8, 92.5, 81.9, 65.5, 55.2, 31.5 ppm. This compound is known and the spectroscopic date match those reported.$^2$

4-(3-methoxyphenyl)-2-methylbut-3-yn-2-ol (2h)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.29 (m, 1H), 7.02 (m, 1H), 6.96 (m, 1H), 6.87 (m, 1H), 3.81 (s, 3H), 2.21 (br, 1H), 1.64 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.3, 129.3, 124.2, 123.8, 116.5, 114.9, 93.7, 82.1, 65.6, 55.3, 31.5 ppm. This compound is known and the spectroscopic data match those reported.$^2$

2-methyl-4-(thiophen-3-yl)but-3-yn-2-ol (2j)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.27 (m, 1H), 7.10 (m, 1H), 6.95 (m, 1H), 2.38 (br, 1H), 1.5347 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 129.9, 128.6, 125.3, 121.8, 93.5, 77.3, 65.6, 41.5 ppm. This compound is known and the spectroscopic data match those reported.$^2$

2-methyloct-3-yn-2-ol (2l)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 2.20 (m, 3H), 1.51 (s, 6H), 1.43 (m, 3H), 1.23 (br, 1H), 1.05 (br, 1H), 0.93 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 85.07, 82.58, 65.30, 31.77, 21.90, 18.25, 13.58 ppm. This compound is known and the spectroscopic data match those reported.$^2$
3. General Procedure

A mixture of 1-(pyridin-2-yl)-1\textit{H}-indole derivatives 1 (0.20 mmol), \( \gamma \)-substituted \textit{tert}-propargyl alcohols 2 (0.80 mmol), \([\text{RhCl(COD)}]_2\) (1.5 mol %), Cu(OAc)\(_2\) \( \cdot \) H\(_2\)O (88 mg, 0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for desired time (usually 6 h) until complete consumption of starting materials judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated, the residue was purified by chromatography (ethyl acetate/ hexane = 1/100 to 1/20) to afford the desired products 3.

10-methyl-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-alindole (3aa)

![Structure of 3aa]

3aa: Yield: 78%; yellow solid, 64 mg; m.p: 152–154 °C.

\(^1\text{H NMR (500 MHz, CDCl}_3\)): \( \delta = 7.98 \) (d, \( J = 7.6 \) Hz, 2H), 7.73 (t, \( J = 7.5 \) Hz, 1H), 7.68-7.60 (m, 4H), 7.55 (s, 1H), 7.44 (t, \( J = 7.0 \) Hz, 2H), 7.37-7.30 (m, 2H), 7.21-7.19 (m, 2H), 7.03-6.97 (m, 4H), 6.52 (d, \( J = 8.5 \) Hz, 1H), 2.48 (s, 3H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\)): \( \delta = 150.0, 141.7, 141.4, 139.5, 138.3, 134.9, 133.7, 131.5, 130.7, 130.4, 129.2, 128.9, 128.5, 128.4, 128.2, 128.1, 127.8, 127.2, 126.1, 123.3, 120.6, 117.9, 114.4, 104.8, 101.8, 7.9 \) ppm; HRMS m/z (ESI) Calcd for C\(_{30}\)H\(_{23}\)N\(_2\) (M+H)\(^+\), 411.1856, found 411.1859.
10-methyl-8-(p-tolyl)-6-(2-(p-tolyl)pyridin-3-yl)pyrido[1,2-a]indole (3ab)

3ab: Yield: 66%; yellow solid, 58 mg; m.p: 207-209 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.89$ (d, $J = 8.3$ Hz, 2H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.62-7.56 (m, 4H), 7.51 (s, 1H), 7.30 (t, $J = 7.1$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.1 (d, $J = 8.4$ Hz, 2H), 6.95 (t, $J = 7.3$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 2H), 6.45 (d, $J = 8.7$ Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 150.0$, 141.7, 141.3, 138.0, 136.8, 136.7, 135.5, 134.9, 133.8, 131.5, 130.7, 130.3, 129.3, 129.1, 128.9, 128.6, 128.3, 127.9, 126.0, 123.2, 120.4, 117.8, 114.5, 104.1, 101.4, 21.2, 20.9, 7.9 ppm; HRMS m/z (ESI) Calcd for C$_{32}$H$_{27}$N$_2$ (M+H)$^+$, 439.2169, found 439.2172.

8-(4-ethylphenyl)-6-(2-(4-ethylphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ac)

3ac: Yield: 76%; yellow solid, 71 mg; m.p: 220-222 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.80$ (d, $J = 8.2$ Hz, 2H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.55-7.44 (m, 4H), 7.41 (s, 1H), 7.17 (m, 3H), 7.00 (d, $J = 8.1$ Hz, 2H), 6.85 (t, $J = 8.1$ Hz, 1H), 6.73 (d, $J = 8.1$ Hz, 2H), 6.37 (d, $J = 8.5$ Hz, 1H), 2.60 (q, $J = 7.6$ Hz, 2H), 2.36 (s, 3H), 2.32 (q, $J = 7.8$ Hz, 2H), 1.18 (q, $J = 7.6$ Hz, 3H), 0.95 (q, $J = 7.8$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 150.1$, 144.4, 143.1, 141.8, 141.3, 136.8, 135.8, 134.8,
133.8, 131.5, 130.6, 130.3, 129.2, 128.9, 128.3, 129.1, 127.9, 127.3, 126.1, 123.2, 120.3, 117.7, 114.5, 104.2, 101.3, 28.7, 28.3, 15.6, 15.2, 7.9 ppm; HRMS m/z (ESI) Calcd for C_{34}H_{31}N_{2} (M+H)^+, 467.2482, found 467.2484.

**8-(4-chlorophenyl)-6-(2-(4-chlorophenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ad)**

![Chemical structure of 3ad]

3ad: Yield: 67%; yellow solid, 64 mg; m.p: 202-204 °C.

^1H NMR (500 MHz, CDCl₃): δ = 7.93 (d, J = 8.9 Hz, 2H), 7.73 (t, J = 7.1 Hz, 1H), 7.68-7.62 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.53 (s, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.1 Hz, 2H), 7.00-6.96 (m, 3H), 6.41 (d, J = 8.6 Hz, 2H), 2.48 (s, 3H); ^13C NMR (125 MHz, CDCl₃): δ = 149.8, 140.3, 140.0, 137.9, 136.6, 134.7, 134.1, 133.4, 133.3, 131.5, 130.6, 130.5, 129.6, 129.2, 128.8, 128.7, 128.6, 128.0, 127.2, 123.4, 120.9, 118.2, 114.2, 105.0, 102.5, 7.9 ppm; HRMS m/z (ESI) Calcd for C_{30}H_{21}Cl₂N₂ (M+H)^+, 479.1076, found 479.1077.

**10-methyl-8-(4-(trifluoromethyl)phenyl)-6-(2-(4-(trifluoromethyl)phenyl)pyridin-3-yl)pyrido[1,2-a]indole (3ae)**

![Chemical structure of 3ae]

3ae: Yield: 41%; yellow solid, 45 mg; m.p: 192-194 °C.
$^1$H NMR (500 MHz, CDCl$_3$): δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 6.9$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.62 (m, 2H), 7.60 (m, 1H), 7.54 (m, 3H), 7.25 (t, $J = 7.2$ Hz, 1H), 7.17 (m, 4H), 6.91 (t, $J = 5.7$ Hz, 1H), 6.38 (d, $J = 8.6$ Hz, 1H), 2.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.8, 143.0, 141.3, 139.8, 134.6, 133.1, 132.8, 131.5, 130.8, 130.6, 129.3, 129.1, 128.9, 128.7, 126.1, 125.6, 125.5, 124.7, 123.7, 121.3, 118.5, 114.2, 106.3, 103.5, 7.9 ppm; HRMS m/z (ESI) Calcd for C$_{32}$H$_{20}$F$_6$N$_2$ (M+H)$^+$, 547.1603, found 547.1603.

8-((1,1'-biphenyl)-4-yl)-6-(2-((1,1'-biphenyl)-4-yl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3af)

3af: Yield: 76%; yellow solid, 85 mg; m.p: 215-217 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 8.07 (d, $J = 8.4$ Hz, 2H), 7.73 (t, $J = 8.0$ Hz, 1H), 7.68-7.62 (m, 4H), 7.62-7.55 (m, 5H), 7.44 (t, $J = 7.6$ Hz, 3H), 7.37 (t, $J = 6.3$ Hz, 3H), 7.32-7.27 (m, 3H), 7.24-7.20 (m, 3H), 6.97 (d, $J = 7.2$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 150.1, 142.0, 141.2, 140.9, 140.9, 140.8, 140.4, 140.1, 139.8, 138.5, 137.2, 134.9, 133.7, 132.9, 131.5, 130.6, 130.5, 129.3, 129.0, 128.9, 128.8, 128.6, 128.3, 127.9, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.5, 126.4, 123.3, 120.7, 118.0, 114.4, 104.8, 102.1, 8.0 ppm; HRMS m/z (ESI) Calcd for C$_{42}$H$_{31}$N$_2$ (M+H)$^+$, 563.2482, found 563.2476.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ag)
8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ag)

Yield: 74%; yellow solid, 70 mg; m.p: 165-167 °C.

\[ \text{H NMR (500 MHz, CDCl}_3\text{:} \quad \delta = 8.00 \ (d, \ J = 8.6 \text{ Hz, 2H}), \ 7.72 \ (t, \ J = 7.2 \text{ Hz, 1H}), \ 7.65-7.57 \ (m, \ 4H), \ 7.48 \ (s, \ 1H), \ 7.31 \ (t, \ J = 7.5 \text{ Hz, 1H}), \ 7.15 \ (d, \ J = 8.3 \text{ Hz, 2H}), \ 7.00-6.95 \ (m, \ 3H), \ 6.55 \ (d, \ J = 8.4 \text{ Hz, 2H}), \ 6.46 \ (d, \ J = 8.4 \text{ Hz, 1H}), \ 3.87 \ (s, \ 3H), \ 3.60 \ (s, \ 3H), \ 2.48 \ (s, \ 3H); \ \text{13C NMR (125 MHz, CDCl}_3\text{:} \quad \delta = 159.8, \ 158.7, \ 150.1, \ 141.4, \ 140.9, \ 134.8, \ 133.9, \ 132.0, \ 131.5, \ 131.0, \ 130.5, \ 130.3, \ 129.5, \ 129.2, \ 128.8, \ 127.8, \ 127.4, \ 123.2, \ 120.3, \ 117.7, \ 114.3, \ 114.0, \ 113.3, \ 103.3, \ 101.1, \ 55.3, \ 54.9, \ 7.9 \text{ ppm; HRMS m/z (ESI) Calcd for C}_{32}H_{27}N_{2}O_{2} (M+H)^{+}, \ 471.2067, \ \text{found 471.2064.}} \]

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ah)

Yield: 41%; yellow solid, 39 mg; m.p: 168-170 °C.

\[ \text{H NMR (500 MHz, CDCl}_3\text{:} \quad \delta = 7.74 \ (t, \ J = 6.1 \text{ Hz, 1H}), \ 7.67-7.60 \ (m, \ 4H), \ 7.65 \ (d, \ J = 7.7 \text{ Hz, 1H}), \ 7.51 \ (s, \ 2H), \ 7.33 \ (dd, \ J = 16.0, \ 8.1 \text{ Hz, 2H}), \ 6.99 \ (t, \ J = 8.3 \text{ Hz, 1H}), \ 6.91 \ (t, \ J = 7.6 \text{ Hz, 2H}), \ 6.80 \ (s, \ 1H), \ 6.75 \ (t, \ J = 7.3 \text{ Hz, 1H}), \ 6.57 \ (dd, \ J = 8.1, \ 2.2 \text{ Hz, 1H}), \ 6.48 \ (d, \ J = 8.6 \text{ Hz, 1H}), \ 3.87 \ (s, \ 3H), \ 3.37 \ (s, \ 3H), \ 2.47 \ (s, \ 3H); \ \text{13C NMR (125 MHz, CDCl}_3\text{:} \quad \delta = 160.0, \ 159.0, \ 150.7, \ 141.4, \ 140.8, \ 138.8, \ 133.1, \ 131.8, \ 130.8, \ 130.6, \ 129.6, \ 129.1, \ 128.9, \ 128.3, \ 123.8, \ 121.1, \ 120.9, \ 118.6, \ 118.2, \ 114.6, \ 114.4, \ 114.3, \ 113.0, \ 113.0.} \]
111.7, 105.5, 55.4, 54.9, 8.0 ppm; HRMS m/z (ESI) Calcd for C_{32}H_{27}N_{2}O_{2} (M+H)^{+}, 471.2067, found 471.2064.

10-methyl-8-(thiophen-3-yl)-6-(2-(thiophen-3-yl)pyridin-3-yl)pyrido[1,2-a]indole (3aj)

3aj: Yield: 76%; yellow solid, 64 mg; m.p: 184-186 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.86\) (d, \(J = 1.9\) Hz, 2H), 7.62-7.56 (m, 2H), 7.54-7.45 (m, 4H), 7.35 (s, 1H), 7.29 (dd, \(J = 5.0, 3.1\) Hz, 1H), 7.18 (t, \(J = 8.0\) Hz, 1H), 6.88 (dd, \(J = 3.0, 1.3\) Hz, 1H), 6.84-6.80 (m, 2H), 6.76 (dd, \(J = 5.0, 1.3\) Hz, 1H), 6.26 (d, \(J = 8.9\) Hz, 1H), 2.37(s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 150.4, 140.8, 139.6, 138.1, 135.9, 134.3, 133.3, 131.6, 130.5, 130.0, 129.3, 129.1, 128.2, 127.6, 126.3, 125.3, 125.1, 123.4, 123.2, 122.9, 122.7, 117.9, 114.3, 104.4, 102.0, 8.0 ppm; HRMS m/z (ESI) Calcd for C\(_{26}\)H\(_{19}\)N\(_{2}\)S\(_{2}\) (M+H)^{+}, 423.0984, found 423.0988.

8-butyl-6-(2-butylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3al)

3al: Yield: 41%; yellow solid, 30 mg; m.p: 135-137 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.71\) (d, \(J = 8.0\) Hz, 1H), 7.57 (dt, \(J = 8.4, 1.5\) Hz, 1H), 7.49 (d, \(J = 8.0\) Hz, 1H), 7.46-7.40 (m, 2H), 7.35 (t, \(J = 7.6\) Hz, 1H), 7.05 (s, 1H), 6.92 (t,
8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ba)

3ba: Yield: 61%; yellow solid, 48 mg; m.p: 144-147 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.00 (d, $J$ = 7.8 Hz, 2H), 7.77-7.70 (m, 2H), 7.66-7.61 (m, 3H), 7.60 (s, 1H), 7.45 (t, $J$ = 7.5 Hz, 2H), 7.37 (t, $J$ = 7.3 Hz, 1H), 7.28 (d, $J$ = 7.0 Hz, 1H), 7.15 (dd, $J$ = 5.6, 1.7 Hz, 2H), 7.02-6.95 (m, 4H), 6.65 (s, 1H), 6.53 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 150.0, 142.7, 141.3, 139.3, 137.9, 137.0, 134.7, 131.0, 130.6, 130.5, 129.2, 129.1, 128.5, 128.3, 128.2, 127.7, 127.2, 126.1, 123.7, 120.5, 119.9, 114.6, 106.4, 94.3 ppm; HRMS m/z (ESI) Calcd for C$_{29}$H$_{21}$N$_2$ (M+H)$^+$, 397.1699, found 397.1701.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)pyrido[1,2-a]indole (3bg)
3bg: Yield: 66%; yellow solid, 60 mg; m.p: 153-155 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.79-7.71$ (m, 2H), 7.70-7.64 (m, 3H), 7.63-7.56 (m, 3H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 8.5$ Hz, 1H), 6.96-6.91 (m, 2H), 6.76-6.75 (m, 2H), 6.69 (s, 1H), 6.60 (dd, $J = 8.3$, 1.6 Hz, 1H), 6.54 (d, $J = 8.5$ Hz, 1H), 3.90 (s, 3H), 3.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 160.1$, 158.9, 150.1, 142.6, 141.3, 140.8, 139.5, 137.0, 134.8, 131.1, 130.5, 129.6, 129.3, 129.2, 128.8, 128.3, 123.8, 120.9, 120.7, 120.1, 118.6, 114.7, 114.3, 114.2, 112.9, 111.7, 94.5, 55.4, 54.9 ppm; HRMS m/z (ESI) Calcd for C$_{31}$H$_{25}$N$_2$O$_2$ (M+H)$^+$, 457.1911, found 457.1919.

2-methoxy-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ca)

3ca: Yield: 68%; yellow solid, 58 mg; m.p: 159-161 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.03$ (d, $J = 7.2$ Hz, 2H), 7.79-7.72 (m, 2H), 7.66 (d, $J = 7.4$ Hz, 2H), 7.58 (s, 1H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.40 (t, $J = 6.8$ Hz, 1H), 7.20 (dd, $J = 5.0$, 2.0 Hz, 2H), 7.04 (dd, $J = 5.0$, 2.0 Hz, 4H), 6.65 (dd, $J = 9.3$, 2.5 Hz, 1H), 6.58 (s, 1H), 6.42 (d, $J = 9.2$ Hz, 1H), 3.86 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 156.7$, 149.5, 142.7, 141.3, 139.3, 138.0, 137.8, 134.6, 132.2, 130.6, 130.5, 129.2, 128.5, 128.4, 128.3, 128.2, 127.7, 127.2, 126.1, 124.2, 115.4, 111.1, 106.1, 100.4, 94.0, 55.3; HRMS (ESI) m/z Calcd for C$_{30}$H$_{23}$N$_2$O (M+H)$^+$, 427.1805, found 427.1802.

2-methoxy-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)pyrido[1,2-a]indole (3cg)
3cg: Yield: 78%; yellow solid, 76 mg; m.p: 159-161 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.99$ (d, $J = 8.9$ Hz, 2H), 7.72 (dt, $J = 8.1$, 1.7 Hz, 1H), 7.67 (d, $J = 1.7$ Hz, 1H), 7.61 (m, 2H), 7.49 (s, 1H), 7.09 (d, $J = 8.8$ Hz, 2H), 6.99 (m, 3H), 6.54 (m, 4H), 6.31 (d, $J = 9.2$ Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.63 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 160.0$, 158.8, 156.7, 149.7, 142.6, 141.0, 138.1, 134.7, 132.3, 131.9, 130.8, 130.6, 130.5, 129.5, 129.3, 127.9, 127.5, 124.3, 115.4, 114.0, 113.3, 110.8, 104.7, 100.4, 93.4, 55.4, 55.3, 55.0 ppm; HRMS (ESI) m/z Calcd for C$_{32}$H$_{27}$N$_2$O$_3$ (M+H)$^+$, 487.2016, found 487.2013.

3-methyl-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ea)

3ea: Yield: 74%; yellow solid, 61 mg; m.p: 192-194 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.87$ (d, $J = 7.4$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.46 (s, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.9$ Hz, 2H), 7.03 (m, 3H), 6.90 (m, 3H), 6.50 (s, 1H), 6.16 (s, 1H), 2.18 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 150.0$, 142.1, 141.4, 139.5, 138.0, 136.6, 134.8, 130.5, 130.4, 130.2, 129.5, 129.3, 128.9, 128.6, 128.3, 128.2, 128.1, 127.7, 127.2, 126.1, 125.5, 119.5, 114.7, 106.6, 94.2, 22.0 ppm; HRMS m/z (ESI) Calcd for C$_{30}$H$_{23}$N$_2$ (M+H)$^+$, 411.1856, found 411.1859.
2-chloro-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3fa)

3fa: Yield: 61%; yellow solid, 53 mg; m.p: 159-161 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.02$ (d, $J = 7.4$ Hz, 2H), 7.77 (t, $J = 7.4$ Hz, 1H), 7.73 (d, $J = 7.4$ Hz, 2H), 7.65 (m, 2H), 7.60 (s, 1H), 7.57 (d, $J = 1.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.1$ Hz, 1H), 7.11 (m, 2H), 7.01 (m, 3H), 6.91 (dd, $J = 1.8$, 9.1 Hz, 1H), 6.56 (s, 1H), 6.38 (d, $J = 9.0$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 150.0$, 143.4, 141.3, 139.1, 138.3, 137.7, 134.4, 132.0, 130.8, 130.7, 129.6, 129.2, 128.7, 128.6, 128.4, 128.3, 127.8, 127.6, 127.4, 126.3, 120.8, 119.1, 115.5, 106.3, 93.7 ppm; HRMS m/z (ESI) Calcd for C$_{29}$H$_{20}$ClN$_2$ (M+H)$^+$, 431.1310, found 431.1316.

3-methyl-7-phenyl-5-(2-phenylpyridin-3-yl)indolizine (3ha)

3ha: Yield: 61%; yellow solid, 44 mg; m.p: 135-137 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.84$ (dd, $J = 1.3$, 8.4 Hz, 2H), 7.56 (dd, $J = 1.0$, 7.5 Hz, 1H), 7.52 (dt, $J = 1.4$, 7.6 Hz, 1H), 7.47 (s, 1H), 7.44 (dd, $J = 1.0$, 7.5 Hz, 1H), 7.41 (dt, $J = 1.4$, 7.4 Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.15 (dd, $J = 1.8$, 8.2 Hz, 2H), 7.03 (m, 3H), 6.30 (d, $J = 3.7$ Hz, 1H), 6.27 (t, $J = 3.7$ Hz, 1H), 1.77 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 146.9$, 141.5, 139.8, 138.5, 137.7, 135.0, 134.3, 130.3, 129.5, 128.7, 128.4, 128.3, 127.8, 127.6, 127.4, 126.3, 120.8, 119.1, 115.5, 106.3, 93.7 ppm; HRMS m/z (ESI) Calcd for C$_{29}$H$_{20}$ClN$_2$ (M+H)$^+$, 431.1310, found 431.1316.
129.9, 129.7, 128.5, 128.4, 128.1, 127.4, 127.2, 126.8, 125.6, 121.5, 117.4, 107.4, 99.8, 14.9 ppm; HRMS m/z (ESI) Calcd for C_{26}H_{21}N_{2} (M+H)^+, 361.1699, found 360.1692.

7-(4-methoxyphenyl)-5-(2-(4-methoxyphenyl)pyridin-3-yl)-3-methylindolizine (3hg)

3hg: Yield: 66%; yellow solid, 56 mg; m.p: 154-156 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.6$ Hz, 2H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.38 (m, 3H), 7.09 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 6.28 (d, $J = 3.4$ Hz, 1H), 6.23 (d, $J = 3.4$ Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 1.73 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 159.4$, 158.8, 147.1, 141.1, 137.6, 134.9, 134.4, 132.3, 131.2, 130.4, 129.8, 129.6, 129.5, 126.9, 126.3, 121.3, 117.3, 114.0, 113.6, 106.3, 99.2, 55.3, 55.1, 14.8 ppm; HRMS m/z (ESI) Calcd for C$_{28}$H$_{25}$O$_2$N$_2$ (M+H)$^+$, 421.1911, found 421.1917.

10-methyl-6-(4-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ia)

3ia: Yield: 31%; yellow solid, 26 mg; m.p: 174-176 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.88$ (dd, $J = 1.9$, 8.1 Hz, 2H), 7.43 (m, 3H), 7.33 (m, 3H), 7.26 (t, $J = 8.1$ Hz, 1H), 7.06 (m, 2H), 6.89 (m, 3H), 6.70 (dd, $J = 1.5$, 8.7 Hz, 1H), 6.47 (s, 1H), 6.31 (d, $J = 8.7$ Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (125 MHz,
\[ \text{CDCl}_3: \delta = 149.4, 141.7, 141.6, 140.1, 138.4, 134.5, 133.3, 131.8, 131.5, 130.0, 129.8, 128.5, 128.4, 128.3, 128.0, 127.7, 127.0, 126.1, 123.4, 121.0, 118.0, 113.7, 104.7, 101.8, 31.4, 19.2, 7.9 \text{ ppm}; \]

HRMS m/z (ESI) Calcd for C\textsubscript{31}H\textsubscript{25}N\textsubscript{2} (M+H)\textsuperscript{+}, 425.2012, found 425.2008.

10-methyl-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ja)

![3ja](image)

3ja: Yield: 84%; yellow solid, 71 mg; m.p: 167-169 °C.

\[ ^1\text{H NMR (500 MHz, CDCl}_3): \delta = 7.90 (d, J = 7.6 \text{ Hz}, 2\text{H}), 7.51 (d, J = 7.9 \text{ Hz}, 1\text{H}), 7.45-7.41 (m, 3\text{H}), 7.38 (s, 1\text{H}), 7.34 (t, J = 7.6 \text{ Hz}, 2\text{H}), 7.28-7.17 (m, 2\text{H}), 7.08 (dd, J = 6.0, 2.5 \text{ Hz}, 2\text{H}), 6.95-6.81 (m, 4\text{H}), 6.43 (d, J = 8.3 \text{ Hz}, 1\text{H}), 2.40 (s, 3\text{H}), 2.36 (s, 3\text{H}); \]

\[ ^{13}\text{C NMR (125MHz, CDCl}_3): \delta = 150.4, 141.5, 139.4, 138.5, 138.2, 138.1, 134.4, 133.6, 131.5, 131.3, 130.6, 129.6, 128.9, 128.6, 128.4, 128.1, 127.7, 127.0, 126.2, 123.3, 120.6, 117.9, 114.6, 104.9, 101.9, 21.1, 7.9 \text{ ppm}; \]

HRMS m/z (ESI) Calcd for C\textsubscript{31}H\textsubscript{25}N\textsubscript{2} (M+H)\textsuperscript{+}, 425.2012, found 425.2008.

8-(4-ethylphenyl)-6-(2-(4-ethylphenyl)-5-methylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3jc)

![3jc](image)

3jc: Yield: 91%; yellow solid, 87 mg; m.p: 184-186 °C.
$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.84$ (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.42 (s, 3H), 7.35 (s, 1H), 7.18 (dd, $J = 4$, 9.7 Hz, 3H), 6.99 (d, $J = 7.59$ Hz, 2H), 6.87 (t, $J = 7.7$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 6.40 (d, $J = 8.5$ Hz, 1H), 2.61 (q, $J = 7.6$ Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 2.32 (q, $J = 7.8$ Hz, 2H), 1.19 (t, $J = 7.6$ Hz, 3H), 0.95 (q, $J = 7.8$ Hz, 3H); $^{13}$C NMR (125MHz, CDCl$_3$): $\delta = 150.3$, 144.4, 142.8, 141.8, 138.4, 137.8, 136.8, 135.8, 134.6, 133.8, 131.5, 131.1, 130.5, 129.6, 128.9, 128.3, 128.1, 127.2, 126.1, 123.2, 120.3, 117.7, 114.6, 104.2, 101.3, 28.7, 28.2, 21.1, 15.6, 15.2, 7.9; HRMS m/z (ESI) Calcd for C$_{35}$H$_{33}$N$_2$ (M+H)$^+$, 481.2638, found 481.2671.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3jg)

3jg: Yield: 86%; red solid, 83 mg; m.p: 222-225 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.99$ (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.39 (dd, $J = 7.9$, 9.4 Hz, 2H), 7.34 (d, $J = 9.4$ Hz, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.00 (d, $J = 8.9$ Hz, 2H), 6.87 (m, 3H), 6.42 (d, $J = 8.7$ Hz, 2H), 6.35 (d, $J = 8.9$ Hz, 1H), 3.77 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (125MHz, CDCl$_3$): $\delta = 159.9$, 158.6, 150.4, 141.5, 138.0, 137.7, 134.6, 133.9, 132.0, 131.6, 131.2, 131.1, 130.5, 129.6, 129.5, 128.9, 127.5, 123.2, 120.3, 117.7, 114.5, 114.0, 113.3, 103.4, 101.1, 55.5, 55.0, 21.1, 8.0 ppm; HRMS m/z (ESI) Calcd for C$_{33}$H$_{29}$N$_2$O$_2$ (M+H)$^+$, 485.2224, found 485.2221.

2-methyl-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ka)
3ka: Yield: 88%; yellow solid, 75 mg; m.p: 161-163 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.00$ (dd, $J = 2.0, 8.2$ Hz, 2H), 7.59 (s, 1H), 7.55 (s, 2H), 7.52 (s, 1H), 7.45 (m, 3H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.18 (m, 2H), 7.02 (m, 3H), 6.83 (dd, $J = 1.5, 8.7$ Hz, 1H), 6.59 (s, 1H), 6.43 (d, $J = 8.7$ Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H);

$^{13}$C NMR (125MHz, CDCl$_3$): $\delta$ 150.1, 142.6, 139.4, 138.5, 138.1, 138.0, 137.2, 134.5, 133.4, 131.4, 131.2, 130.5, 129.6, 128.6, 128.4, 128.2, 127.7, 127.6, 127.0, 126.2, 122.4, 119.5, 114.3, 106.4, 93.8, 21.5, 21.1 ppm; HRMS m/z (ESI) Calcd for C$_{31}$H$_{25}$N$_2$ (M+H)$^+$, 425.2012, found 425.2008.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-2-methylpyrido[1,2-a]indole (3kg)

3kg: Yield: 84%; yellow solid, 81 mg; m.p: 187-189 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 8.8$ Hz, 2H), 7.38 (m, 3H), 7.33 (s, 1H), 7.29 (s, 1H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.66 (dd, $J = 1.2, 8.8$ Hz, 1H), 6.41 (m, 3H), 6.23 (d, $J = 8.6$ Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H);

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 159.0, 157.6, 149.3, 141.3, 137.0, 136.7, 136.4, 133.3, 132.3, 130.9, 130.5, 130.2, 129.7, 129.5, 128.5, 128.4, 126.6, 126.5, 121.2, 118.3, 113.3, 113.0, 112.3, 104.0, 92.3, 54.4, 54.0, 20.5, 20.1 ppm; HRMS m/z (ESI) Calcd for C$_{33}$H$_{29}$N$_2$O$_2$ (M+H)$^+$, 485.2224, found 484.2226.
2-chloro-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3la)

3la: Yield: 74%; yellow solid, 66 mg; m.p: 171-173 °C.

\[ \text{\( \delta \) 7.93 (d, } J = 7.5 \text{ Hz, 2H), 7.47 (s, 1H), 7.44 (m, 4H), 7.36 (t, } J = 7.5 \text{ Hz, 2H), 7.28 (t, } J = 7.5 \text{ Hz, 1H), 6.99 (m, 2H), 6.87 (m, 3H), 6.80 (dd, } J = 2.0, 9.0 \text{ Hz, 1H), 6.43 (s, 1H), 6.28 (d, } J = 9.0 \text{ Hz, 1H), 2.42 (s, 3H); \] \[ \text{\( \delta \) 150.2, 143.4, 139.0, 138.4, 138.3, 138.2, 137.7, 134.0, 132.0, 131.5, 130.5, 129.6, 128.7, 128.6, 128.2, 127.8, 127.5, 127.2, 126.3, 120.7, 119.0, 115.6, 106.3, 93.7, 21.1 ppm; HRMS m/z (ESI) Calcd for C\text{3}0\text{H}\text{2}2\text{ClN}\text{2} \text{(M+H)}^+, 445.1466, \text{found 445.1472.} \]

2-chloro-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)pyrido[1,2-a]indole (3lg)

3lg: Yield: 84%; yellow solid, 85 mg; m.p: 187-189 °C.

\[ \text{\( \delta \) 7.92 (d, } J = 9.0 \text{ Hz, 2H), 7.44 (d, } J = 1.5 \text{ Hz, 1H), 7.43 (d, } J = 1.5 \text{ Hz, 1H), 7.39 (t, } J = 5.5 \text{ Hz, 3H), 6.92 (m, 4H), 6.78 (dd, } J = 2.0, 9.0 \text{ Hz, 1H), 6.41 (m, 3H), 6.23 (d, } J = 8.9 \text{ Hz, 1H), 3.78 (s, 3H), 3.51 (s, 3H), 2.42 (s, 3H); \] \[ \text{\( \delta \) 160.3, 158.7, 150.3, 143.2, 138.4, 137.9, 134.0, 132.1, 131.5, 93.7 ppm; HRMS m/z (ESI) Calcd for C\text{3}0\text{H}\text{2}2\text{ClN}\text{2} \text{(M+H)}^+, 473.1801, \text{found 473.1807.} \]
131.4, 130.5, 130.4, 129.6, 127.7, 127.5, 120.5, 118.9, 115.6, 114.1, 114.0, 113.3, 104.8, 93.1, 55.4, 55.0, 21.1 ppm; HRMS m/z (ESI) Calcd for C$_{32}$H$_{27}$ClN$_2$O$_2$ (M+H)$^+$, 505.1677, found 505.1674.

2-methoxy-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)pyrido[1,2-a]indole (3mg)

![Structural diagram of 3mg]

3mg: Yield: 79%; yellow solid, 79 mg; m.p: 188-190 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.89 (d, $J = 8.8$ Hz, 2H), 7.43 (dd, $J = 1.2$, 7.9 Hz, 1H), 7.38 (m, 3H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.3$ Hz, 2H), 6.48 (dd, $J = 2.4$, 9.1 Hz, 1H), 6.43 (m, 3H), 6.23 (d, $J = 9.1$ Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.52 (s, 3H), 2.41 ppm; HRMS m/z (ESI) Calcd for C$_{33}$H$_{29}$N$_2$O$_3$ (M+H)$^+$, 501.2173, found: 501.2171.

2-fluoro-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3na)

![Structural diagram of 3na]

3na: Yield: 74%; yellow solid, 63 mg; m.p: 186-189 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.94 (d, $J = 7.3$ Hz, 2H), 7.48 (s, 1H), 7.44 (m, 3H), 7.37 (t, $J = 7.4$ Hz, 2H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.11 (dd, $J = 2.1$, 9.2 Hz, 1H), 6.99 (m, 1H), 7.04 (m, 3H), 5.31 (s, 1H), 4.16 (dd, $J = 8.3$, 10.0 Hz, 1H), 4.13 (dd, $J = 7.9$, 10.0 Hz, 1H), 4.10 (dd, $J = 8.3$, 10.0 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.54 (s, 3H), 2.44 ppm; HRMS m/z (ESI) Calcd for C$_{33}$H$_{29}$FNI$_2$O$_3$ (M+H)$^+$, 504.2145, found: 504.2144.
2H), 6.87 (m, 3H), 6.60 (dt, J = 2.4, 9.0 Hz, 1H), 6.47 (s, 1H), 6.33 (dd, J = 4.4, 9.3 Hz, 1H), 2.44 (s, 3H);\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 159.8 (J = 240.8 MHz), 150.2, 143.3, 139.0, 138.5, 138.4, 138.3, 137.7, 134.1, 131.9 (J = 11.0 MHz), 131.5, 130.5, 129.6, 128.6, 128.5, 128.2, 127.7, 127.1, 126.3, 125.8, 115.7 (J = 9.6 MHz), 109.0 (J = 25.4 MHz), 106.1, 104.2 (J = 23.5 MHz), 94.2 (J = 4.5 MHz), 21.2 ppm; HRMS m/z (ESI) Calcd for C\textsubscript{30}H\textsubscript{22}FN\textsubscript{2} (M+H)\textsuperscript{+}, 429.1762, found 429.1766.

6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-10-methyl-8-phenylpyrido[1,2-a]indole (3jga) and 8-(4-methoxyphenyl)-10-methyl-6-(5-methyl-2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3jag)

![Chemical structure](image)

3jga and 3jag: 1 : 1.1, Yield: 36%.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) = 7.95 (d, J = 7.6 Hz, 2.2H), 7.84 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H), 3.49 (s, 3.3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) = 159.8, 158.6, 150.4, 150.1, 141.6, 141.5, 139.5, 138.4, 138.3, 138.1, 138.0, 137.7, 134.7, 134.5, 133.9, 133.6, 131.9, 131.5, 131.4, 131.2, 131.0, 130.5, 130.4, 129.6, 129.5, 128.9, 128.8, 128.6, 128.4, 128.1, 127.7, 127.4, 126.9, 126.1, 123.2, 123.1, 120.5, 120.2, 117.8, 117.7, 114.5, 114.4, 114.0, 113.3, 104.8, 103.3, 101.7, 101.0, 55.3, 55.0, 21.1, 21.0, 7.9, 7.8 ppm; HRMS m/z (ESI) Calcd for C\textsubscript{32}H\textsubscript{27}ON\textsubscript{2} (M+H)\textsuperscript{+}, 455.2118, found 455.2119.
3-methyl-1-(6-methylpyridin-2-yl)-2-(phenylethynyl)-1H-indole (3oa)

3oa: Yield: 61%; colorless solid, 39 mg; m.p: 150-152 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.3$ Hz, 1H), 7.76 (t, $J = 7.7$ Hz, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.44-7.42 (m, 2H), 7.34-7.30 (m, 3H), 7.29 (t, $J = 7.3$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 2.66 (s, 3H), 2.53 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 158.0, 150.9, 137.9, 136.6, 131.0, 128.6, 128.3, 128.2, 124.4, 123.2, 121.2, 121.0, 120.8, 119.1, 118.5, 116.6, 112.1, 98.2, 81.5, 24.3, 9.9; HRMS m/z (ESI) Calcd for C$_{23}$H$_{18}$N$_2$Na (M+Na)$^+$, 345.1362, found 345.1367.
4. Mechanism Studies

4.1 Stoichiometric reactions of 2a with [RhCl(COD)]₂ and Cu(OAc)₂·H₂O

\[
\text{Ph} = \text{OH} \quad \text{[RhCl(COD)]₂ (1.5 mol %)} \quad \text{PhMe, air, 125 °C, 24 h} \quad \text{No Reaction} \quad (1)
\]

A mixture of 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.80 mmol), [RhCl(COD)]₂ (1.5 mol %, 0.024 mmol) and toluene (2 ml) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 24 h. Only trace amount of 4a was detected by TLC.

\[
\text{Ph} = \text{OH} \quad \text{Cu(OAc)₂·H₂O} \quad \text{PhMe, air, 125 °C, 2 h} \quad (\text{Ph} = \text{OH})_2 \quad 4a \quad 96\% \quad (2)
\]

A mixture of 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.80 mmol), Cu(OAc)₂·H₂O (80 mg, 0.40 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 2 h, which was then filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (hexane) to afford the desired products 4a in 96% isolated yield.

4.2 Stoichiometric reactions of 1a with [RhCl(COD)]₂ in the presence of Cu(OAc)₂·H₂O

\[
[\text{RhCl(COD)}]_2 + \text{Cu(OAc)₂·H₂O} + \text{PhMe, air, 125 °C, 24 h} \quad \text{Rh(III)-complex 5} \quad (3)
\]
A mixture of $[\text{RhCl(COD)}]_2$ (0.2 mmol), Cu(OAc)$_2$·H$_2$O (200 mg, 1 mmol), 1-(pyridin-2-yl)-1H-indole 1a (208 mg, 1 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 24 h, which was then concentrated. The residue was purified by chromatography (methanol/ethyl acetate/hexane = 1/20/100) to afford the desired product 5 in 85% isolated yield. 5: Yield: 85%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.72 (d, $J$ = 5.5 Hz, 2H), 7.87 (m, 2H), 7.79 (m, 2H), 7.59 (d, $J$ = 7.9 Hz, 2H), 7.06 (d, $J$ = 7.7 Hz, 2H), 6.96 (m, 6H), 1.98 (s, 3H), 1.26 (s, 3H) ppm; The poor solubility of complex 5 prevented $^{13}$C-$^1$H NMR characterization.

### 4.3 Stoichiometric reactions of complex 6 with 2a and copper phenylacetylide 6

A mixture of 5 (0.2 mmol), 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.22 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 10 h. No reaction took place as detected by TLC.

A mixture of 5 (0.2 mmol), 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.22 mmol), Cu(OAc)$_2$·H$_2$O (0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an
air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for for 10 h until complete consumption of 2a judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products 3aa in 28% isolated yield based on complex 5.

A mixture of 5 (0.2 mmol), PhC≡CCu 6 (1.0 mmol), Cu(OAc)₂·H₂O (0.44 mmol), HOAc (0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for for 16 h, which was then filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products 3aa in 34% isolated yield.

4.4 catalytic activity of complex 5

A mixture of 1-(pyridin-2-yl)-1H-indole 1a (0.20 mmol), 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.80 mmol), 5 (1.5 mol %), Cu(OAc)₂·H₂O (88 mg, 0.44 mmol) and toluene (2 mL) was added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for about 10 h until complete consumption of 1a judged by TLC. Then the reaction mixture was filtered through a short plug of silica
gel, washed with ethyl acetate and concentrated, the residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products 3aa in 68% isolated yield.

4.5 Cross Reactions between 1b, 1j, and 2a

A mixture of 1-(pyridin-2-yl)-1H-indole 1b (0.10 mmol), 3-methyl-1-(5-methylpyridin-2-yl)-1H-indole 1j (0.10 mmol), 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.80 mmol), [RhCl(COD)]2 (1.5 mol%), Cu(OAc)2·H2O (88 mg, 0.44 mmol) and toluene (2 mL) was added to a Schlenk tube. Then the mixture was stirred at 125 °C (bath temperature, preheated) under air for 8 h until complete consumption of 1b and 1j judged by TLC. The reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The resulting residue was purified by chromatography to afford 3ba in 30% isolated yield (ethyl acetate/hexane = 1/150) and 3ja in 52% isolated yield (ethyl acetate/hexane = 1/30).
4.6 Cross Reactions between 1j, 2a, and 2g

A mixture of 3-methyl-1-(5-methylpyridin-2-yl)-1H-indole 1j (0.20 mmol), 2-methyl-4-phenyl-3-butyn-2-ol 2a (0.40 mmol), 4-(4-methoxyphenyl)-2-methylbut-3-yn-2-ol 2g (0.40 mmol), [RhCl(COD)]_2 (1.5 mol %), Cu(OAc)\_2\cdot H_2O (88 mg, 0.44 mmol) and toluene (2 mL) were added to a Schlenk tube. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 8 h until complete consumption of 1j judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography to afford 3ja in 10% isolated yield (ethyl acetate/hexane = 1/200), 3jga and 3jag as a mixture in 36% isolated yield (ethyl acetate/hexane = 1/50), and 3jg in 32% isolated yield (ethyl acetate/hexane = 1/20).
5. Proposed mechanism for C-H alkynylation

It is worthy to note that blocking the C-6 position of the pyridine directing group with a Me group (substrate 1o) suppressed formation of the corresponding pyrido[2,1-a]indole product and only the the alkynylation product 3oa was isolated. Probably, the steric hindrance of the Me group at the C-6 position prevented the further transformation of 3oa. Isolation of 3oa indicated that the alkynylation step was possibly involved in the catalytic cycle for the formation of pyrido[2,1-a]indoles 3. Thus it is reasonable to believe that the catalytic reactions start with the direct C-H alkynylation of substrates 1, which then proceed to undergo a series of transformations to afford the target products finally.

Scheme S1. Proposed mechanism for the C-H alkynylation.

A proposed mechanism for the C-H alkynylation is shown in Scheme S1. Initially, the reaction of [RhCl(COD)]₂ with Cu(OAc)₂·H₂O leads to formation of active metalating agent I. Then, substrate 1a could react with complex I to generate intermediate II through chelation with pyridyl nitrogen and subsequent C-H activation of the alkene. Meanwhile, copper phenylacetylide was generated from the reaction of 2a with Cu(OAc)₂·H₂O via β-carbon elimination. Transmetalation of the alkynl group from Cu to Rh generated the
Rh(III) species III. Intermediate III could undergo a reductive elimination to yield the desired alkynylation product and extruded Rh(I), which could be reoxidized by Cu(II) to the catalytically active species I to complete the catalytic cycle. Cu(II) might also regenerate from Cu(I) with O₂ in the air. Meanwhile, copper phenylacetylide generated in situ could undergo Glaser coupling to afford conjugate diyne 4a as a byproduct. The alkynylation product 3aa could react with another 2a to yield pyrido[2,1-a]indole skeleton.

Unfortunately, our further attempt to detect or isolate other intermediates from the reaction mixtures failed. The mechanistic details for the further transformation of the alkynylation product to give the pyrido[2,1-a]indole skeleton are unclear yet.

6. References
7. X-ray studies

7.1 X-ray Crystal Structures of 3af

The data (CCDC1032403) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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7.2 X-ray Crystal Structures of 3ag

The data (CCDC1032402) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S2: Crystallographic Details for 3ag

<table>
<thead>
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<th>Complex NO.</th>
<th>3ag</th>
</tr>
</thead>
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<tr>
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<td>C&lt;sub&gt;32&lt;/sub&gt; H&lt;sub&gt;26&lt;/sub&gt; N&lt;sub&gt;2&lt;/sub&gt; O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
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<td>formula weight</td>
<td>470.55</td>
</tr>
<tr>
<td>temperature, K</td>
<td>173(2)</td>
</tr>
<tr>
<td>radiation (Mo Kα), Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>18.889(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>7.1199(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>18.6541(19)</td>
</tr>
<tr>
<td>α, °</td>
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</tr>
<tr>
<td>β, °</td>
<td>104.646(11)</td>
</tr>
<tr>
<td>γ, °</td>
<td>90</td>
</tr>
<tr>
<td>V, Å&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2427.3(5)</td>
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<tr>
<td>Z</td>
<td>4</td>
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<td>d&lt;sub&gt;calc&lt;/sub&gt;, g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
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<td>abs coeff, mm&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>θ range, °</td>
<td>3.07 to 25.99</td>
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<tr>
<td>indep reflns</td>
<td>10153 / 4763 [R(int) = 0.0611]</td>
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<td>data-restraints-params</td>
<td>4763 / 2 / 325</td>
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<td>GOF on F&lt;sup&gt;2&lt;/sup&gt;</td>
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<tr>
<td>final R (I &gt; 2σ(I))</td>
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<td>R indices (all data)</td>
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<tr>
<td>peak and hole, e.Å&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.685 and -0.615</td>
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7.3 X-ray Crystal Structures of 3ia

The data (CCDC1032405) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S3: Crystallographic Details for 3la

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</tr>
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<td>radiation (Mo K(\alpha)), Å</td>
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</tr>
<tr>
<td>crystal system</td>
<td>Triclinic</td>
</tr>
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<td>space group</td>
<td>P-1</td>
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<td>a, Å</td>
<td>8.8053(4)</td>
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<td>b, Å</td>
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<tr>
<td>c, Å</td>
<td>12.0975(13)</td>
</tr>
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<td>(\alpha), °</td>
<td>67.401(9)</td>
</tr>
<tr>
<td>(\beta), °</td>
<td>89.113(7)</td>
</tr>
<tr>
<td>(\gamma), °</td>
<td>83.151(6)</td>
</tr>
<tr>
<td>(V), Å(^3)</td>
<td>1100.51(16)</td>
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<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>(d_{\text{calc}}), g cm(^{-3})</td>
<td>1.343</td>
</tr>
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<td>abs coeff, mm(^{-1})</td>
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</tr>
<tr>
<td>(F(000))</td>
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<tr>
<td>(\theta) range, °</td>
<td>3.42 to 26.00</td>
</tr>
<tr>
<td>indep reflns</td>
<td>8275 / 4304 [R(int) = 0.0340]</td>
</tr>
<tr>
<td>data-restraints-params</td>
<td>4304 / 0 / 298</td>
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<tr>
<td>GOF on (F^2)</td>
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</tr>
<tr>
<td>final (R(I &gt; 2\sigma(I)))</td>
<td>(R_1 = 0.0630), w(R_2 = 0.1664)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.0764), w(R_2 = 0.1778)</td>
</tr>
<tr>
<td>peak and hole, e.Å(^{-3})</td>
<td>0.758 and -0.815</td>
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7.4 X-ray Crystal Structures of 3jga

The data (CCDC1032406) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
### Table S4: Crystallographic Details for 3iga

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<td>temperature, K</td>
<td>173(2)</td>
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<tr>
<td>radiation (Mo Kα), Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.9489(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>17.1959(6)</td>
</tr>
<tr>
<td>c, Å</td>
<td>14.4905(8)</td>
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<tr>
<td>α, °</td>
<td>90</td>
</tr>
<tr>
<td>β, °</td>
<td>109.121(6)</td>
</tr>
<tr>
<td>γ, °</td>
<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>2342.26(19)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>d_{calcd}, g cm⁻³</td>
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</tr>
<tr>
<td>abs coeff, mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>960</td>
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<tr>
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<td>0.15 x 0.14 x 0.11</td>
</tr>
<tr>
<td>θ range, °</td>
<td>3.42 to 26.00</td>
</tr>
<tr>
<td>indep reflns</td>
<td>8275 / 4304 [R(int) = 0.0340]</td>
</tr>
<tr>
<td>data-restraints-params</td>
<td>4304 / 0 / 298</td>
</tr>
<tr>
<td>GOF on F²</td>
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<tr>
<td>final R (I &gt; 2σ(I))</td>
<td>R₁ = 0.0630, wR₂ = 0.1664</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0764, wR₂ = 0.1778</td>
</tr>
<tr>
<td>peak and hole, e.Å⁻³</td>
<td>0.758 and -0.815</td>
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</tbody>
</table>
7.6 X-ray Crystal Structures of complex 5

The data (CCDC1032404) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S5: Crystallographic Details for 5

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<td>C\textsubscript{30} H\textsubscript{25} N\textsubscript{4} O\textsubscript{2} Rh \cdot 0.3 CH\textsubscript{2}Cl\textsubscript{2}</td>
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<tr>
<td>formula weight</td>
<td>601.93</td>
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<td>temperature, K</td>
<td>173(2)</td>
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<tr>
<td>radiation (Mo K(\alpha)), Å</td>
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</tr>
<tr>
<td>crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.6401(19)</td>
</tr>
<tr>
<td>b, Å</td>
<td>11.069(2)</td>
</tr>
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<td>c, Å</td>
<td>12.562(3)</td>
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<td>(\alpha), °</td>
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<td>(\beta), °</td>
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<tr>
<td>(\gamma), °</td>
<td>83.72(3)</td>
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<td>1295.6(4)</td>
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<tr>
<td>Z</td>
<td>2</td>
</tr>
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<td>(d_{\text{calc}}), g cm(^{-3})</td>
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<tr>
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<td>3.30 to 26.00</td>
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<tr>
<td>indep reflns</td>
<td>16782 / 4565 [R(int) = 0.0616]</td>
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<td>data-restraints-params</td>
<td>4565 / 0 / 362</td>
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<tr>
<td>GOF on (F^2)</td>
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<tr>
<td>final (R (I &gt; 2\sigma(I)))</td>
<td>(R_1 = 0.0505), (wR_2 = 0.1225)</td>
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<td>(R_1 = 0.0727), (wR_2 = 0.1693)</td>
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</table>
Table S6: Bond lengths [Å] and angles [deg] for 5.

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<td>Rh(1)-N(4)</td>
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<td>C(2)-C(9)</td>
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<td>N(4)-C(111)</td>
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<td>N(3)-C(108)</td>
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<td>N(4)-C(115)</td>
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<td>C(4)-C(5)</td>
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<td>C(5)-C(6)</td>
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<td>Bond angles [deg]</td>
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<td>117.3(6)</td>
<td>C(13)-C(12)-C(11)</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle (°)</td>
<td>Bond</td>
</tr>
<tr>
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<td>-----------</td>
<td>-----------------------------</td>
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<td>C(104)-C(103)-C(108)</td>
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<td>C(7)-C(8)-N(1)</td>
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<td>C(14)-C(13)-C(12)</td>
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<td>C(103)-C(108)-N(3)</td>
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<td>O(1)-C(31)-Rh(1)</td>
<td>60.2(3)</td>
<td>N(4)-C(111)-C(112)</td>
</tr>
<tr>
<td>C(41)-C(31)-Rh(1)</td>
<td>177.8(6)</td>
<td>C(111)-C(112)-C(113)</td>
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<td>C(102)-C(101)-N(3)</td>
<td>106.0(6)</td>
<td>C(114)-C(113)-C(112)</td>
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<td>C(102)-C(101)-Rh(1)</td>
<td>141.8(5)</td>
<td>C(113)-C(114)-C(115)</td>
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<td>N(3)-C(101)-Rh(1)</td>
<td>112.2(4)</td>
<td>N(4)-C(115)-N(3)</td>
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<td>109.2(6)</td>
<td>N(4)-C(115)-C(114)</td>
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<tr>
<td>C(101)-C(102)-C(109)</td>
<td>127.7(6)</td>
<td>N(3)-C(115)-C(114)</td>
</tr>
<tr>
<td>C(103)-C(102)-C(109)</td>
<td>123.1(5)</td>
<td></td>
</tr>
</tbody>
</table>
8. NMR Spectra

TL20130911-9 1H CDCl3

1a

TL20130911-9 13C CDCl3

1a

51
2d

\[
\text{Cl} - \text{C} = \text{C} - \text{OH}
\]

2d

\[
\text{Cl} - \text{C} = \text{C} - \text{OH}
\]
Chemical structure and NMR spectra of compound 2j.
3ae
**H-H COSY**

![H-H COSY spectrum](image)

**HSQC**

![HSQC spectrum](image)