Supporting Information

Expeditious Synthesis of Phenanthridines through Pd/MnO$_2$-Mediated C-H Arylation/Oxidative Annulation Cascade from Aldehydes, Aryl Iodides and Amino Acid

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1. General information:

All commercial materials were used as received unless otherwise noted. Commercial reagents were purchased from Alfa Aesar, TCI, Energy Chemical, and used without further purification. $^1$H NMR spectra were recorded at 400 MHz or 500 MHz NMR spectrometers using TMS as an internal standard, $^{13}$C NMR spectra were recorded at 100 MHz or 125 MHz NMR spectrometers using CDCl$_3$ as an internal standard and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Melting points were measured on a hot-stage microscope (XT4-A) and are uncorrected. High resolution mass spectra (HRMS) were obtained on an APEXM Fourier transform mass spectrometry (APCI). EPR spectra were obtained using Bruker EMX plus6/1 X-band variable-temperature apparatus.

2. Optimization of reaction conditions

**Screening of Catalyst**

\[
\begin{align*}
\text{Cl-CHO} & \quad + \quad \text{Cl-CHO} \\
1a, \ 0.2 \text{ mmol} & \quad + \quad 2a, \ 1.5 \text{ eq} \\
\xrightarrow{[\text{Pd}] \ (10 \text{ mol\%)}, \text{L-tert-leucine} \ (1 \text{ eq}), \text{AgTFA} \ (2 \text{ eq}), \text{MnO}_2 \ (2 \text{ eq}), \text{AcOH} \ (4 \text{ eq}), \text{HFIP} \ (0.2 \text{ M}), 110 ^\circ \text{C}} \quad & \quad \text{Cl-N} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry$^a$</th>
<th>[Pd]</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N.R.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)$_2$</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>Pd(TFA)$_2$</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>Pd(acac)$_2$</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>PdCl$_2$</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>PdCl$_2$(CH$_3$CN)$_2$</td>
<td>27</td>
</tr>
<tr>
<td>7$^c$</td>
<td>Pd(OAc)$_2$</td>
<td>68</td>
</tr>
</tbody>
</table>
Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), [Pd] (0.02 mmol), AgTFA (0.4 mmol), MnO₂ (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. b Isolated yield by flash column chromatography. c 15 mmol% of Pd(OAc)₂.

### Screening of Amino Acid

![Chemical Reaction Diagram](image)

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Amine</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N.D.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>L-tert-leucine</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>L-alanine</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>L-aspartic acid</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>L-valine instead</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>L-isoleucine</td>
<td>12&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>Glycine</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>D,L-tert-leucine</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>L-tert-leucine</td>
<td>65&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>L-tert-leucine</td>
<td>57&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>AcNH₄</td>
<td>36&lt;sup&gt;e&lt;/sup&gt;, 42&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>t-BuNH₂</td>
<td>28&lt;sup&gt;e&lt;/sup&gt;, 34&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>BnNH₂</td>
<td>19&lt;sup&gt;e&lt;/sup&gt;, 14&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>AcNH₄</td>
<td>N.D.&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>15</td>
<td>t-BuNH₂</td>
<td>N.D.&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>16</td>
<td>BnNH₂</td>
<td>N.D.&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), Amino acid (0.2 mmol), Pd(OAc)₂ (0.02 mmol), AgTFA (0.4 mmol), MnO₂ (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> 1.2 equiv of L-tert-leucine. <sup>d</sup> 1.5 equiv of L-tert-leucine. <sup>e</sup> 30 mol% of L-tert-leucine was used. <sup>f</sup> 1
equiv of L-tert-leucine was used. \( \leq 10\% \) yield of B was obtained. $^h$ 0.2 mmol amine was used.

### Screening of Solvent

<table>
<thead>
<tr>
<th>Entry $^a$</th>
<th>Solvent</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HFIP</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>TFE</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>1,4-dioxane</td>
<td>N.D</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>N.D</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>N.D</td>
</tr>
<tr>
<td>7</td>
<td>MeOH</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>AcOH</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>DMSO</td>
<td>N.D.</td>
</tr>
<tr>
<td>11</td>
<td>HFIP/TFE (v/v = 1:1)</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$ Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), AgTFA (0.4 mmol), MnO$_2$ (0.4 mmol), AcOH (0.8 mmol), Solvent (1 mL), 110 °C, 24 h. $^b$ Isolated yield by flash column chromatography.
Screening of [Ag]

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} & \quad 1a, 0.2 \text{ mmol} & \quad + & \quad \text{I} & \quad 2a, 1.5 \text{ equiv} \\
\text{Pd(OAc)}_2 (10 \text{ mol\%}) & \quad \text{L-} & \quad \text{Acac} & \quad 1 \text{ eq} \quad \text{Pd(OAc)}_2 (0.02 \text{ mmol}) & \quad \text{[Ag]} (2 \text{ eq}) & \quad \text{MnO}_2 (2 \text{ eq}) \\
\text{L-tert-leucine} (1 \text{ eq}) & \quad \text{AcOH} (4 \text{ eq}) & \quad \text{HFIP} (0.2 \text{ M}) & \quad 110 \degree \text{C} & \quad \text{Cl} & \quad \text{3aa}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry (^a)</th>
<th>[Ag]</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>AgTFA</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>Ag$_2$CO$_3$</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>AgOAc</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>Ag$_2$O</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>AgNO$_3$</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>AgOTf</td>
<td>57</td>
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<tr>
<td>8</td>
<td>AgF</td>
<td>44</td>
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<tr>
<td>9</td>
<td>AgTFA</td>
<td>57(^c)</td>
</tr>
<tr>
<td>10</td>
<td>AgTFA</td>
<td>50(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Reactions conditons: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), [Ag] (0.4 mmol), MnO$_2$ (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 \degree C, 24 h. \(^b\) Isolated yield by flash column chromatography. \(^c\) 1.2 equiv of AgTFA. \(^d\) 1.5 equiv of AgTFA.

Screening of Oxidant

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} & \quad 1a, 0.2 \text{ mmol} & \quad + & \quad \text{I} & \quad 2a, 1.5 \text{ equiv} \\
\text{Pd(OAc)}_2 (10 \text{ mol\%}) & \quad \text{L-} & \quad \text{Acac} & \quad 1 \text{ eq} \quad \text{Pd(OAc)}_2 (0.02 \text{ mmol}) & \quad \text{AgTFA} (2 \text{ eq}) & \quad \text{Oxidant} (2 \text{ eq}) \\
\text{L-tert-leucine} (1 \text{ eq}) & \quad \text{AcOH} (4 \text{ eq}) & \quad \text{HFIP} (0.2 \text{ M}) & \quad 110 \degree \text{C} & \quad \text{Cl} & \quad \text{3aa}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry (^a)</th>
<th>Oxidant</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>N.D.</td>
</tr>
<tr>
<td>2</td>
<td>Mn(acac)$_2$</td>
<td>N.D.</td>
</tr>
<tr>
<td>3</td>
<td>Mn(OAc)$_2$·4H$_2$O</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>Mn(OAc)$_2$·2H$_2$O</td>
<td>61</td>
</tr>
<tr>
<td>Entry</td>
<td>Additive</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>1</td>
<td>/</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>AcOH</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>PivOH</td>
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</tr>
<tr>
<td>4</td>
<td>TFA</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>TsOH·H2O</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>o-ClC₆H₄COOH</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>o-CH₃C₆H₄COOH</td>
<td>52</td>
</tr>
<tr>
<td>8</td>
<td>PhCOOH</td>
<td>51</td>
</tr>
</tbody>
</table>

*Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)₂ (0.02 mmol), AgTFA (0.4 mmol), Oxidant (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h.

*b Isolated yield by flash column chromatography. c 1.0 equiv of MnO₂. d 4.0 equiv of MnO₂.

Screening of Additive

![Diagram of reaction](image)
Screening of Temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>59</td>
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</tbody>
</table>

Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), AgTFA (0.4 mmol), MnO$_2$ (0.4 mmol), Additive (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. Isolated yield by flash column chromatography.

Screening of Reaction Time

Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), AgTFA (0.4 mmol), MnO$_2$ (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), Temp., 24 h. Isolated yield by flash column chromatography.
\[
\text{S8}
\]

\[
\text{C} \quad \text{H} \quad \text{O} + \quad \text{IPd(OAc)}_2(10 \text{ mol}%) \quad \text{L-tert-leucine} (1 \text{ eq}) \quad \text{AgTFA} (2 \text{ eq}), \text{MnO}_2 (2 \text{ eq}) \quad \text{AcOH} (4 \text{ eq}), \text{HFIP} (0.2 \text{ M}) \\
\text{Time, 110 °C}
\]

<table>
<thead>
<tr>
<th>Entry (^a)</th>
<th>Time (h)</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>48</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^a\) Reactions conditions: 1 (0.2 mmol), 2 (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)_2 (0.02 mmol), AgTFA (0.4 mmol), MnO_2 (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, Time. \(^b\) Isolated yield by flash column chromatography.

**Table S1 Optimization of reaction conditions \(^a\)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ag Salt</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Yield (%) (^b)</th>
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<tr>
<td>1</td>
<td>AgOAc</td>
<td>MnO_2</td>
<td>AcOH</td>
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</tr>
<tr>
<td>2</td>
<td>Ag_2CO_3</td>
<td>MnO_2</td>
<td>AcOH</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>Ag_2O</td>
<td>MnO_2</td>
<td>AcOH</td>
<td>21</td>
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<td>4</td>
<td>AgNO_3</td>
<td>MnO_2</td>
<td>AcOH</td>
<td>49</td>
</tr>
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<td>5</td>
<td>AgOTf</td>
<td>MnO_2</td>
<td>AcOH</td>
<td>57</td>
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<tr>
<td>6</td>
<td>AgF</td>
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<tr>
<td>8</td>
<td>AgTFA</td>
<td>MnO_2</td>
<td>AcOH</td>
<td>64(^c)</td>
</tr>
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<td>9</td>
<td>AgTFA</td>
<td>Mn(acac)_2</td>
<td>AcOH</td>
<td>N.D.</td>
</tr>
<tr>
<td>10</td>
<td>AgTFA</td>
<td>Mn(OAc)_2·4H_2O</td>
<td>AcOH</td>
<td>26</td>
</tr>
</tbody>
</table>
3. General procedure for synthesis of phenanthridine

A mixture of aldehyde substrates (1, 0.2 mmol), aryl iodide (2, 0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), Ag Sat (0.4 mmol), Oxidant (0.4 mmol), Additive (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. $^b$ Isolated yield by flash column chromatography. $^c$ Under argon atmosphere.

4. Gram-scale preparation of 3aa and competition experiment

$^a$ Reactions conditions: 1a (0.2 mmol), 2a (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)$_2$ (0.02 mmol), Ag Sat (0.4 mmol), Oxidant (0.4 mmol), Additive (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. $^b$ Isolated yield by flash column chromatography. $^c$ Under argon atmosphere.
A 75 mL Schlenk tube was charged with \( o \)-chlorobenzaldehyde 1a (8 mmol), 2a (12 mmol), L-\( \text{tert} \)-leucine (8 mmol) and Pd(OAc)\(_2\) (0.8 mmol), AgTFA (16 mmol), MnO\(_2\) (fresh) (16 mmol). The mixture was dissolved in 30 mL HFIP followed by addition of AcOH (32 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite\(^\circledR\) and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product 3aa (0.94 g, 55% isolated yield).

### 5. Control experiments

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \\
1a & \quad 0.2 \text{ mmol} \\
\text{I} & \quad \text{phenyl} \\
2a & \quad 0.3 \text{ mmol}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \\
1b & \quad 0.2 \text{ mmol} \\
\text{I} & \quad \text{phenyl} \\
2a & \quad 0.3 \text{ mmol}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \\
1c & \quad 0.2 \text{ mmol} \\
\text{I} & \quad \text{phenyl} \\
2a & \quad 0.3 \text{ mmol}
\end{align*}
\]

A 15 mL Schlenk tube was charged with \( o \)-chlorobenzaldehyde 1a (0.2 mmol), 2a (1.5 mmol), L-\( \text{tert} \)-leucine (1.0 mmol) and Pd(OAc)\(_2\) (0.02 mmol), AgTFA (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite\(^\circledR\) and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product A and B.

A 15 mL Schlenk tube was charged with biphenyl aldehyde A (0.2 mmol), L-\( \text{tert} \)-leucine (0.2 mmol) and Pd(OAc)\(_2\) (0.02 mmol), AgTFA (0.4 mmol), MnO\(_2\) (fresh) (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite\(^\circledR\) and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford product 3aa (0.94 g, 55% isolated yield).
afford the pure product 3aa (57% isolated yield).

A mixture of biphenyl aldehyde A (0.2 mmol), L-tert-leucine (0.2 mmol), MnO₂ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product 3aa (92% isolated yield).

A mixture of biphenyl aldehyde A (0.2 mmol), L-tert-leucine (0.2 mmol), AgTFA (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no 3aa was detected by TLC.

A mixture of biphenyl aldehyde A (0.2 mmol), L-tert-leucine (0.2 mmol), TEMPO (0.4 mmol), MnO₂ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no 3aa was detected by TLC.
A mixture of biphenyl aldehyde $\text{A}$ (0.2 mmol), L-\textit{tert}-leucine (0.2 mmol), BHT (0.4 mmol), MnO$_2$ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no 3aa was detected by TLC.

A mixture of biphenyl aldehyde $\text{A}$ (0.2 mmol), AcONH$_4$ (0.2 mmol), MnO$_2$ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product 3aa (90% isolated yield).

A mixture of biphenyl aldehyde $\text{A}$ (0.2 mmol), AcONH$_4$ (0.2 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no 3aa was detected by TLC.
A mixture of biphenyl aldehyde A (0.2 mmol), AcONH$_4$ (0.2 mmol), TEMPO (0.4 mmol), MnO$_2$ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no 3aa was detected by TLC.
6. GC-MS analysis

\[
\text{NH}_2 \quad \text{COOH} \quad \text{MnO}_2 \text{ (2 eq)} \quad \text{AcOH (4 eq), HFIP}
\]

\[110 \degree C, 12 \text{ h}\]

\[
\text{CN}
\]

Chemical Formula: C\textsubscript{7}H\textsubscript{3}N

Exact Mass: 103.04

detected by GC-MS
\[
\begin{align*}
\text{Cl-CHO} & \xrightarrow{\text{L-tert-leucine (1 eq)}} \text{Cl-N} + \text{Cl-NH} \\
& \text{MnO}_2 (2 \text{ eq}), \text{AcOH} (4 \text{ eq}) \\
& \text{HFIP, 110}^\circ \text{C, 12 h} \\
\text{Chemical Formula: } & C_{13}H_{10}ClN \\
\text{Exact Mass: } & 215.05 \\
\text{detected by GC-MS}
\end{align*}
\]
7. Deuteration Studies

A round-bottom flask equipped with a stir bar and a condenser was charged with $d_8$-tolune (99.9 atom % D) (1 g, 10 mmol), KMnO$_4$ (4 g, 25 mmol), Na$_2$CO$_3$ (0.26 g, 5 mmol), and H$_2$O (30 mL). The reaction mixture was refluxed for 8 h and then cooled to room temperature. The mixture was filtered through a pad of celite, and the filtrate was acidified with 12 M HCl and extracted with DCM (3 × 30 mL). The organic layer was washed with water and concentrated in vacuo. The crude product was recrystallized from water to give C$_6D_5CO_2H$ as white needle solid (0.64 g, 50% yield). Synthesis of C$_6D_5CO_2H$ was prepared using a similar procedure (P. Gandeepan, P. Rajamalli, C. Cheng, Angew. Chem. Int. Ed., 2016, 55, 4308–4311).

$[^2H_5]$-Benzyl alcohol (0.45 g; 4 mmol) in CH$_2$Cl$_2$ (2 mL) was slowly dropped into the solution of pyridinium chlorochromate (Sigma-Aldrich) (1.5 g; 6 mmol) and CH$_2$Cl$_2$ (12 mL). The mixture which turned quickly from orange to black was stirred for 1.5 h. Diethyl ether (20 mL) was added, and the residue was further extracted with diethyl ether (3 × 10 mL) until the gummy residue became granular solid. The combined extracts were passed through dry Florisil® (Sigma-Aldrich) (10 g), and the solvent was removed by N$_2$ gas to obtain $[^2H_5]$-benzaldehyde (80% yield, 85.1% purity) (L. Li, B. Zhou, Y.-H. Wang, C. Shu, Y.-F. Pan, X. Lu, L.-W. Ye, Angew. Chem. Int. Ed., 2015, 54, 8245 –8249).

A sealed tube with magnetic stir bar was charged with $[^2H_5]$- benzaldehyde (0.3 mmol), NCS (0.45 mmol, 60.0 mg), Pd(OAc)$_2$ (0.03 mmol, 6.7 mg), T (0.09 mmol, 12.3 mg), and AgTFA (0.03 mmol, 6.6 mg) in air, followed by DCE (3.0 mL) and TFA (3.0 mmol, 342.0 mg). The reaction mixture was stirred at 60 °C for 24 hours. Upon completion, the reaction mixture was quenched by sat. NaHCO$_3$ (aq) (30 mL), and extracted with DCM for 3 times. The combined organic layers were washed with water (50 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The crude residue was purified by column
chromatography on silica gel using petroleum ether/EtOAc (50:1) as eluent to afford the 

A 15 mL Schlenk tube was charged with o-chlorobenzaldehyde 1a (0.1 mmol), [D₄]-1a (0.1 
mmol), 2a (1.5 mmol), L-tert-leucine (1.0 mmol) and Pd(OAc)₂ (0.02 mmol), AgTFA (0.4 
mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 
mmol). The reaction mixture was stirred for 3 hours at 110 °C. After that it was filtered 
through a short pad of Celite® and washed with ethyl acetate. The solvent was then 
evaporated under reduced pressure and the crude was purified by column chromatography 
on silica gel to afford the pure arylation product, and the KIE was determined by ¹H NMR.

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \\
\text{H₄/D₄} & \quad \text{I} \\
\text{1a/[D₄]-1a} & \quad \text{2a, 1.5 eq} \\
\text{Pd(OAc)₂ (10 mol%)} & \quad \text{AgTFA (2 eq), AcOH (4 eq)} \\
\text{L-tert-leucine (1 eq)} & \quad \text{HFIP (0.2 M), 110 °C, 3 h} \\
\text{A/[D₃]-A} & \quad K_{1H}/K_D = 3.7
\end{align*}
\]
A 15 mL Schlenk tube was charged with [D₄]-1a (0.2 mmol), L-tert-leucine (1.0 mmol) and Pd(OAc)₂ (0.02 mmol), AgTFA (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the aldehyde was recovered by column chromatography on silica gel and characterized by ¹H NMR.
A mixture of biphenyl aldehyde A (0.1 mmol), [D₅]-A (0.1 mmol), L-tert-leucine (0.2 mmol), MnO₂ (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 3 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure phenanthridine product, and the KIE was determined by ¹H NMR.

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \quad \text{D₅/H₅} \\
\text{A/[D₅]-A} & \quad \xrightarrow{\text{MnO₂ (2 eq)}} \quad \text{L-tert-leucine (1 eq)} \\
\text{AcOH (4 eq), HFIP (0.2 M)} & \quad 110 ^\circ \text{C, 3 h} \\
\text{Cl} & \quad \text{N} \quad \text{D₄/H₄} \\
\text{3aa/[D₄]-3aa} & \quad K_w/K_D = 1.5
\end{align*}
\]
8. Proposed mechanism (Scheme S1)
Analytic Data of Products

7-fluorophenanthridine (3ba)

White solid. Isolated yield: 66%. Melting point: 90-91 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.61 (s, 1H), 8.57-8.55 (m, 1H), 8.39 (d, $J$ = 8.2 Hz, 1H), 7.83-7.78 (m, 2H), 7.73-7.70 (m, 1H), 7.38-7.34 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 160.6 ($J_{F-C}$ = 254.0 Hz), 146.8 ($J_{F-C}$ = 6.8 Hz), 144.9, 134.7 ($J_{F-C}$ = 3.2 Hz), 131.9 ($J_{F-C}$ = 8.9 Hz), 130.8, 129.7, 128.0, 123.5 ($J_{F-C}$ = 2.1 Hz), 122.9, 118.2 ($J_{F-C}$ = 4.3 Hz), 116.5 ($J_{F-C}$ = 13.9 Hz), 112.6 ($J_{F-C}$ = 19.4 Hz). HRMS (APCI) calcd for C$_{13}$H$_9$FN (M+H$^+$): 198.0713, found: 198.0712.

7-chlorophenanthridine (3aa)

White solid. Isolated yield: 66%. Melting point: 95-96 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.73 (s, 1H), 8.53-8.48 (m, 2H), 8.21 (d, $J$ = 8.1 Hz, 1H), 7.79-7.76 (m, 1H), 7.74-7.68 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 150.0, 144.8, 134.7, 134.2, 131.3, 130.7, 129.7, 128.4, 128.0, 123.5, 123.46, 122.8, 121.3. HRMS (APCI) calcd for C$_{13}$H$_9$ClN (M+H$^+$): 214.0418, found: 214.0416.

7-bromophenanthridine (3ca)

White solid. Isolated yield: 55%. Melting point: 151-152 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.70 (s, 1H), 8.57 (t, $J$ = 8.7 Hz, 2H), 8.39 (d, $J$ = 8.1 Hz, 1H), 7.92 (d, $J$ = 7.6 Hz, 1H), 7.80 (t, $J$ = 7.2 Hz, 1H), 7.73-
7.66 (m, 2H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 152.6, 144.8, 135.0, 132.1, 131.7, 130.7, 129.8, 128.0, 124.7, 124.5, 123.4, 122.7, 122.0. \(\text{HRMS (APCI)}\) calcd for C\(_{13}\)H\(_9\)BrN (M+H\(^+\)): 257.9912, found: 257.9910.

7-methylphenanthridine (3da)

\[
\text{H}_3\text{C} \implies \text{N} \\
\text{Ar} \implies \text{Ar}
\]

White solid. Isolated yield: 31%. Melting point: 72-73 °C.

\(\text{^1H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.57 (s, 1H), 8.60 (d, \(J = 8.1\) Hz, 1H), 8.50 (d, \(J = 8.3\) Hz, 1H), 8.21-8.19 (m, 1H), 7.77-7.73 (m, 2H), 7.70-7.67 (m, 1H), 7.51-7.50 (m, 1H), 2.89 (s, 3H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 150.7, 144.5, 137.0, 133.2, 131.1, 130.4, 129.2, 129.0, 127.4, 125.3, 124.7, 122.8, 120.4, 19.3. \(\text{HRMS (APCI)}\) calcd for C\(_{14}\)H\(_{12}\)N (M+H\(^+\)): 194.0964, found: 194.0961.

8-chlorophenanthridine (3ea)

\[
\text{Cl} \implies \text{N} \\
\text{Ar} \implies \text{Ar}
\]

White solid. Isolated yield: 57%. Melting point: 84-85 °C.

\(\text{^1H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.21 (s, 1H), 8.53 (t, \(J = 8.0\) Hz, 2H), 8.19 (d, \(J = 8.15\) Hz, 1H), 8.03-8.02 (m, 1H), 7.81-7.75 (m, 2H), 7.72-7.69 (m, 1H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 152.7, 144.8, 133.7, 132.0, 131.3, 130.7, 129.5 128.2, 128.0, 127.6, 124.2, 124.0, 122.5. \(\text{HRMS (APCI)}\) calcd for C\(_{13}\)H\(_9\)ClN (M+H\(^+\)): 214.0418, found: 214.0415.

8-bromophenanthridine (3fa)

\[
\text{Br} \implies \text{N} \\
\text{Ar} \implies \text{Ar}
\]

White solid. Isolated yield: 53%. Melting point: 72-73 °C.

\(\text{^1H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.20 (s, 1H), 8.52 (d, \(J = 9.2\) Hz, 1H), 8.46 (d, \(J = 8.8\) Hz, 1H), 8.20-8.18 (m, 2H), 7.94-7.9 (m, 1H), 7.79-7.76 (m, 1H),
7.72-7.68 (m, 1H). ¹³C NMR (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 152.6, 144.7, 134.6, 131.6, 131.4, 130.7, 129.5, 128.0, 127.9, 124.2, 124.0, 122.5, 121.7. HRMS (APCI) calcd for C₁₃H₉BrN (M+H⁺): 257.9912, found: 257.9908.

8-(trifluoromethyl)phenanthridine (3ga)

![Chemical structure of 8-(trifluoromethyl)phenanthridine (3ga)]

White solid. Isolated yield: 41%. Melting point: 118-119 °C.

¹H NMR (500 MHz, CDCl₃, TMS as the internal standard): δ 9.39 (s, 1H), 8.76 (d, J = 8.6 Hz, 1H), 8.63 (d, J = 8.1 Hz, 1H), 8.38 (s, 1H), 8.29 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.7 Hz, 1H), 7.86 (t, J = 7.4 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, CDCl₃ as the internal standard): δ 153.1, 145.2, 134.7, 130.4, 130.0, 129.5 (J_F-C = 33.1 Hz), 127.8, 126.8 (J_F-C = 3.1 Hz), 126.2 (J_F-C = 4.2 Hz), 125.6, 125.3, 123.2, 123.1, 122.6. HRMS (APCI) calcd for C₁₄H₉F₃N (M+H⁺): 248.0681, found: 248.0678.

8-methylphenanthridine (3ha)

![Chemical structure of 8-methylphenanthridine (3ha)]

White solid. Isolated yield: 57%. Melting point: 139-140 °C.

¹H NMR (500 MHz, CDCl₃, TMS as the internal standard): δ 9.21 (s, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.48 (d, J = 8.35 Hz, 1H), 8.18-8.16 (m, 1H), 7.80 (s, 1H), 7.73-7.64 (m, 3H), 2.59 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 153.8, 144.5, 137.9, 133.2, 130.4, 128.6, 128.56, 127.4, 127.0, 124.6, 122.5, 122.2, 21.9. HRMS (APCI) calcd for C₁₄H₁₂N (M+H⁺): 194.0964, found: 194.0960.

8-methoxyphenanthridine (3ia)

![Chemical structure of 8-methoxyphenanthridine (3ia)]

White solid. Isolated yield: 46%. Melting point: 92-93 °C.

¹H NMR (500 MHz, CDCl₃, TMS as the internal standard): δ 9.24 (s, 1H), 8.52 (t, J = 9.6
Hz, 2H), 8.17 (d, $J = 7.85$ Hz, 1H), 7.71-7.65 (m, 2H), 7.34 (d, $J = 8.7$ Hz, 1H), 7.39 (s, 1H), 4.00 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 159.3, 153.3, 144.0, 128.1, 127.6, 127.4, 124.7, 124.0, 122.5, 122.2, 108.3, 56.0. HRMS (APCI) calcd for C$_{14}$H$_{12}$NO (M+H$^+$): 210.0913, found: 210.0911.

Phenanthridine (3ja)

![Phenanthridine (3ja)](image)

White solid. Isolated yield: 36%. Melting point: 93-94 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.29 (s, 1H), 8.61-8.57 (m, 2H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.86(t, $J = 8.0$ Hz, 1H), 7.77-7.67 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 153.6, 144.5, 132.6, 131.1, 130.2, 128.8, 128.7, 127.5, 127.1, 126.4, 124.1, 122.3, 121.9; HRMS (APCI) calcd for C$_{13}$H$_{10}$N (M+H$^+$): 180.0807, found: 180.0804.

9-chlorophenanthridine (3ka)

![9-chlorophenanthridine (3ka)](image)

White solid. Isolated yield: 30%. Melting point: 89-90 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.27 (s, 1H), 8.59 (d, $J = 1.5$ Hz, 1H), 8.52-8.50 (m, 1H), 8.26 (d, $J = 8.1$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.83-7.79 (m, 1H), 7.76-7.69 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 153.1, 145.1, 137.9, 134.1, 130.7, 130.6, 139.8, 128.6, 127.8, 125.0, 123.4, 122.6, 121.1. HRMS (APCI) calcd for C$_{13}$H$_9$ClN (M+H$^+$): 214.0418, found: 214.0416.

9-methylphenanthridine (3la)

![9-methylphenanthridine (3la)](image)
White solid. Isolated yield: 30%. Melting point: 88-89 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.24 (s, 1H), 8.58-8.56 (m, 1H), 8.40 (s, 1H), 8.18-8.16 (m, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.75-7.72 (m, 1H), 7.68-7.65 (m, 1H), 7.55-7.53 (m, 1H), 2.66 (s, 3H). **13C NMR** (100 MHz, CDCl₃, CDCl₃ as the internal standard): δ 153.3, 144.6, 132.7, 130.1, 128.7, 128.6, 126.9, 124.6, 124.0, 122.2, 121.6, 22.5. **HRMS** (APCI) calcd for C₁₄H₁₂N (M+H⁺): 194.0964, found: 194.0961.

7-phenylphenanthridine (3jaa)

![7-phenylphenanthridine](image)

White solid. Isolated yield: 43%. Melting point: 195-196 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.36 (s, 1H), 8.66-8.64 (m, 2H), 8.19-8.17 (m, 1H), 7.91-7.88 (m, 1H), 7.78-7.75 (m, 1H), 7.72-7.69 (m, 1H), 7.65-7.63 (m, 1H), 7.55-7.48 (m, 5H). **13C NMR** (100 MHz, CDCl₃, CDCl₃ as the internal standard): δ 151.9, 144.1, 142.3, 138.9, 133.0, 130.4, 130.3, 130.1, 128.81, 128.8, 128.5, 128.0, 127.2, 124.0, 123.99, 122.4, 121.2. **HRMS** (APCI) calcd for C₁₉H₁₄N (M+H⁺): 256.1120, found: 256.1117.

9-chloro-7-phenylphenanthridine (3kaa)

![9-chloro-7-phenylphenanthridine](image)

White solid. Isolated yield: 31%. Melting point: 120-121 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.29 (s, 1H), 8.60 (d, J = 2.0 Hz, 1H), 8.55 (d, J = 7.9 Hz, 1H), 8.18-8.16 (m, 1H), 7.80-7.77 (m, 1H), 7.73-7.70 (m, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.57-7.50 (m, 5H). **13C NMR** (100 MHz, CDCl₃, CDCl₃ as the internal standard): δ 151.3, 144.4, 144.1, 137.5, 136.7, 134.4, 130.2, 130.1, 129.5, 129.2,
128.7, 128.5, 127.5, 123.0, 122.5, 122.4, 120.8. **HRMS** (APCI) calcd for C$_{19}$H$_{13}$ClN (M+H$^+$): 290.0731, found: 290.0728.

**9-methyl-7-phenylphenanthridine (3laa)**

![Structure of 9-methyl-7-phenylphenanthridine](image)

White solid. Isolated yield: 36%. Melting point: 174-175 °C.

**$^1$H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.30 (s, 1H), 8.63-8.61 (m, 1H), 8.43 (s, 1H), 8.17-8.15(m, 1H), 7.76-7.72 (m, 1H), 7.69-7.66 (m, 1H), 7.54-7.47 (m, 6H), 2.68 (s, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 151.7, 144.3, 142.1, 140.8, 138.9, 133.2, 130.6, 130.3, 130.0, 128.7, 128.5, 127.9, 126.9, 123.9, 122.4, 122.2, 120.9, 22.4. **HRMS** (APCI) calcd for C$_{20}$H$_{16}$N (M+H$^+$): 270.1277, found: 270.1274.

**7-bromo-9-fluorophenanthridine (3ma)**

![Structure of 7-bromo-9-fluorophenanthridine](image)

White solid. Isolated yield: 42%. Melting point: 161-162 °C.

**$^1$H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.64 (s, 1H), 8.45 (d, $J$ = 9.0 Hz, 1H), 8.24-8.21 (m, 2H), 7.84-7.81 (m, 1H), 7.75-7.72 (m, 2H).

**$^{13}$C NMR** (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 163.3 ($J_{F-C}$ = 253.9 Hz), 151.8, 144.9, 136.4 ($J_{F-C}$ = 9.6 Hz), 130.6 ($J_{F-C}$ = 42.8 Hz), 128.1, 125.8 ($J_{F-C}$ = 11.0 Hz), 122.9 ($J_{F-C}$ = 4.2 Hz), 122.8, 121.9, 121.7, 121.49, 107.3 ($J_{F-C}$ = 21.9 Hz). **HRMS** (APCI) calcd for C$_{13}$H$_8$FBrN (M+H$^+$): 275.9818, found: 275.9815.

**7-bromo-9-methylphenanthridine (3na)**

---

s27
White solid. Isolated yield: 43%. Melting point: 145-146 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.60 (s, 1H), 8.50-8.49 (m, 1H), 8.29 (s, 1H), 8.19-8.17 (m, 1H), 7.77-7.73 (m, 2H), 7.68-7.65 (m, 1H), 2.59 (s, 3H).

**13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 152.2, 144.7, 142.6, 134.8, 133.6, 130.5, 129.6, 127.8, 124.2, 123.2, 122.8, 122.6, 121.7, 22.5. **HRMS** (APCI) calcd for C₁₄H₁₁BrN (M+H⁺): 272.0069, found: 272.0064.

7,10-dichlorophenanthridine (3oa)

White solid. Isolated yield: 30%. Melting point: 188-189 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.81 (d, J = 8.6 Hz, 1H), 9.78 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.84 (t, J = 7.2 Hz, 2H), 7.73 (t, J = 8.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H). **13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 150.0, 145.9, 134.7, 133.5, 131.4, 130.9, 130.3, 130.1, 128.5, 127.6, 126.6, 125.3, 122.8. **HRMS** (APCI) calcd for C₁₃H₈Cl₂N (M+H⁺): 248.0028, found: 248.0025.

7,9-dichlorophenanthridine (3pa)

White solid. Isolated yield: 57%. Melting point: 157-158 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.62 (s, 1H), 8.41-8.39 (m, 2H), 8.19 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.70-7.66 (m, 2H). **13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 149.4, 145.1, 137.2, 135.4, 135.2, 130.8, 130.4, 128.7, 128.3, 122.8, 122.4, 121.9, 121.1. **HRMS** (APCI) calcd for C₁₃H₈Cl₂N
(M+H\(^+\)): 248.0028, found: 248.0024.

**7,8-dichlorophenanthridine (3qa)**

![7,8-dichlorophenanthridine](image)

Yellow solid. Isolated yield: 60%. Melting point: 135-136 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.77 (s, 1H), 8.55-8.53 (m, 1H), 8.49 (d, \(J = 8.8\) Hz, 1H), 8.25-8.23 (m, 1H), 7.89 (d, \(J = 8.9\) Hz, 1H), 7.83-7.80 (m, 1H), 7.76-7.72 (m, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 149.7, 144.6, 133.0, 132.5, 132.0, 130.8, 130.0, 128.4, 124.7, 123.0, 122.6, 121.1. HRMS (APCI) calcd for C\(_{13}\)H\(_8\)Cl\(_2\)N (M+H\(^+\)): 248.0028, found: 248.0025.

**8,9-dimethoxyphenanthridine (3ra)**

![8,9-dimethoxyphenanthridine](image)

White solid. Isolated yield: 18%. Melting point: 172-173 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.15 (s, 1H), 8.44 (d, \(J = 10.3\) Hz, 1H), 8.17-8.15 (m, 1H), 7.88 (s, 1H), 7.72-7.62 (m, 2H), 7.35 (s, 1H), 4.14 (s, 3H), 4.07 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 153.3, 152.2, 150.4, 144.4, 130.5, 128.6, 128.2, 127.0, 124.2, 122.2, 122.1, 108.2, 102.2, 56.6, 56.5. HRMS (APCI) calcd for C\(_{15}\)H\(_{14}\)NO\(_2\) (M+H\(^+\)): 240.1019, found: 240.0115.

**[1,3]dioxolo[4,5-j]phenanthridine (3sa)**

![[1,3]dioxolo[4,5-j]phenanthridine](image)

White solid. Isolated yield: 22%. Melting point: 144-145 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 8.98 (s, 1H), 8.30 (d, \(J = 7.9\) Hz, 1H), 8.15 (d, \(J = 7.9\) Hz, 1H), 7.83 (s, 1H), 7.66-7.58 (m, 2H), 7.21 (s, 1H), 6.18 (s,
2H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 152.1, 151.6, 148.6, 143.5, 130.8, 129.6, 128.5, 127.2, 124.6, 123.2, 122.3, 105.9, 102.4, 100.2. HRMS (APCI) calcd for C$_{14}$H$_{10}$NO$_2$ (M+H$^+$): 224.0706, found: 224.0703.

**10-bromo-[1,3]dioxolo[4,5-i]phenanthridine (3ta)**

Yellow solid. Isolated yield: 40%. Melting point: 225-226 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.51 (s, 1H), 8.83 (d, $J$ = 8.0 Hz, 1H), 8.16 (d, $J$ = 8.2 Hz, 1H), 7.76 (t, $J$ = 7.2 Hz, 1H), 7.66 (t, $J$ = 7.2 Hz, 1H), 7.55 (s, 1H), 6.36 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 152.6, 149.3, 144.6, 143.0, 130.0, 129.8, 127.6, 127.0, 121.3, 120.5, 119.8, 116.7, 114.9, 103.1. HRMS (APCI) calcd for C$_{14}$H$_{9}$BrNO$_2$ (M+H$^+$): 301.9811, found: 301.9810.

**benzo[k]phenanthridine (3ua)**

White solid. Isolated yield: 25%. Melting point: 75-76 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.35 (s, 1H), 9.19 (d, $J$ = 8.1 Hz, 1H), 9.10 (d, $J$ = 8.3 Hz, 1H), 8.34-8.32 (m, 1H), 7.08-7.793 (m, 3H), 7.82-7.73 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 153.0, 147.0, 135.6, 131.6, 130.7, 129.41, 129.4, 129.2, 128.6, 128.5, 128.2, 127.4, 127.3, 127.2, 125.6, 125.5, 125.0. HRMS (APCI) calcd for C$_{17}$H$_{12}$N (M+H$^+$): 230.0964, found: 230.0961.

**7-chloro-1-fluorophenanthidine (3ab)**
White solid. Isolated yield: 45%. Melting point: 122-123 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.79 (s, 1H), 8.97-8.95 (m, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.81-7.71 (m, 3H), 7.46-7.42 (m, 1H).

**13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 160.8 (J_F-C = 253.7 Hz), 151.1, 146.7 (J_F-C = 2.0 Hz), 134.1, 132.7 (J_F-C = 4.8 Hz), 132.0 (J_F-C = 1.7 Hz), 129.3 (J_F-C = 10.6 Hz), 128.9, 126.8 (J_F-C = 3.5 Hz), 126.2 (J_F-C = 23.3 Hz), 123.9, 114.5 (J_F-C = 23.9 Hz), 113.5 (J_F-C = 9.1 Hz). **HRMS** (APCI) calcd for C₁₃H₈ClFN (M+H⁺): 232.0323, found: 232.0321.

**1,7-dichlorophenanthridine (3ac)**

White solid. Isolated yield: 41%. Melting point: 145-146 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.82-9.80 (m, 2H), 8.18-8.17 (m, 1H), 7.79-7.75 (m, 3H), 7.66 (t, J = 7.7 Hz, 1H).

**13C NMR** (100 MHz, CDCl₃, CDCl₃ as the internal standard): δ 150.5, 146.7, 133.7, 133.7, 131.4, 131.0, 130.4, 130.3, 128.7, 128.6, 125.3, 124.1, 121.1. **HRMS** (APCI) calcd for C₁₃H₈Cl₂N (M+H⁺): 248.0028, found: 248.0024.

**7-chloro-3-methylphenanthridine (3ad)**

White solid. Isolated yield: 65%. Melting point: 115-116 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard) δ 9.74 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.05 (s, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.71-7.69 (m, 1H), 7.57-7.55 (m, 1H), 2.62 (s, 3H).

**13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard) δ 149.2, 143.3, 140.7, 135.2, 134.6, 132.2, 130.3, 129.1, 128.2, 123.0, 122.6, 121.4, 121.2, 22.0. **HRMS** (APCI) calcd for C₁₄H₁₁ClN (M+H⁺): 228.0574, found: 228.0571.
7-chloro-3-methoxyphenanthridine (3ae)

White solid. Isolated yield: 53%. Melting point: 149-150 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard) $\delta$ 9.71 (s, 1H), 8.43 (t, $J = 8.8$ Hz, 2H), 7.71 (t, $J = 8.0$ Hz, 1H), 7.65-7.61 (m, 2H), 7.35-7.33 (m, 1H), 4.00 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard) $\delta$ 160.9, 150.5, 146.6, 135.0, 134.3, 131.4, 127.3 124.0, 122.8, 120.8, 119.2, 117.6, 110.3, 56.0. HRMS (APCI) calcd for C$_{14}$H$_{11}$ClNO (M+H$^+$): 244.0523, found: 244.0522.

7-chloro-3-fluorophenanthridine (3af)

White solid. Isolated yield: 65%. Melting point: 84-85 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.77 (s, 1H), 8.57-8.54 (m, 1H), 8.47 (d, $J = 8.0$ Hz, 1H), 7.92-7.89 (m, 1H), 7.79 (t, $J = 7.9$ Hz, 1H), 7.73 (d, $J = 7.3$ Hz, 1H), 7.51-7.47 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 163.4 (d, $J = 248.5$ Hz), 151.1, 134.7 ($J_{F,C} = 3.2$ Hz), 132.1, 128.4 (2C), 124.9 ($J_{F,C} = 9.5$ Hz), 123.2, 121.1 (2C), 120.3 ($J_{F,C} = 1.8$ Hz), 117.4 ($J_{F,C} = 23.8$ Hz), 114.9 ($J_{F,C} = 20.6$ Hz). HRMS (APCI) calcd for C$_{13}$H$_8$ClFN (M+H$^+$): 232.0323, found: 232.0320.

7-chloro-3-(trifluoromethyl)phenanthridine (3ag)

White solid. Isolated yield: 64%. Melting point: 224-225 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.83 (s, 1H), 8.67 (d, $J = 8.7$ Hz, 1H), 8.56 (d, $J = 7.8$ Hz, 1H), 8.54 (s, 1H), 7.93-7.91 (m, 1H), 7.87-7.81 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 151.4, 144.1, 134.6, 133.9, 132.0, 131.5 ($J_{F,C} = 33.0$ Hz), 129.6, 128.3 ($J_{F,C} = 4.1$ Hz), 125.8, 125.4, 124.1, 123.9 ($J_{F,C} = 4.6$ Hz), 123.2, 121.6. HRMS (APCI) calcd for C$_{14}$H$_8$ClF$_3$N (M+H$^+$): 282.0291, found:
methyl 7-chlorophenanthridine-3-carboxylate (3ah)

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{COOCH}_3 \\
\text{Cl} & \quad \text{Cl}& \quad \text{Cl}
\end{align*}
\]

White solid. Isolated yield: 57%. Melting point: 198-199 °C.

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.81 (s, 1H), 8.89 (s, 1H), 8.61-8.55 (m, 2H), 8.31 (d, \(J = 8.5\) Hz, 1H), 7.82-7.78 (m, 2H), 4.03 (s, 3H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 167.0, 151.0, 144.4, 134.5, 134.1, 132.8, 131.7, 131.2, 129.5, 127.9, 126.7, 124.2, 123.1, 121.8, 52.9. \text{HRMS (APCI)} calcd for C\(_{15}\)H\(_{11}\)ClO\(_2\)N (M+H\(^+\)): 272.0472, found: 272.0468.

7-chloro-2-fluorophenanthridine (3ai)

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{F} \\
\text{Cl} & \quad \text{Cl}& \quad \text{Cl}
\end{align*}
\]

White solid. Isolated yield: 36%. Melting point: 167-168 °C.

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard): \(\delta\) 9.78 (s, 1H), 8.51 (d, \(J = 7.8\) Hz, 1H), 8.32 (d, \(J = 8.4\) Hz, 1H), 7.81-7.75 (m, 2H), 7.68-7.63 (m, 1H), 7.51-7.48 (m, 1H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 159.2 (d, \(J_{F,C} = 254.0\) Hz), 150.3, 134.6, 134.5, 134.1 (\(J_{F,C} = 2.8\) Hz), 131.9, 129.1, 128.0 (\(J_{F,C} = 8.5\) Hz), 125.5, 123.8, 121.6, 118.4 (d, \(J_{F,C} = 4.5\) Hz), 114.7 (d, \(J_{F,C} = 19.1\) Hz). \text{HRMS (APCI)} calcd for C\(_{13}\)H\(_8\)ClF\(_2\)N (M+H\(^+\)): 232.0323, found: 232.0325.

2,7-dichlorophenanthridine (3aj)

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}& \quad \text{Cl}
\end{align*}
\]

White solid. Isolated yield: 47%. Melting point: 161-162 °C.

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\), TMS as the internal standard) \(\delta\) 9.74 (s, 1H), 8.52 (d, \(J = 2.8\) Hz, 1H), 8.49 (d, \(J = 8.4\) Hz, 1H), 8.30 (d, \(J = 8.5\) Hz, 1H), 7.82-7.77 (m, 2H), 7.68-7.63 (m, 1H), 7.52-7.49 (m, 1H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\), CDCl\(_3\) as the internal standard): \(\delta\) 167.0, 151.0, 144.4, 134.5, 134.1, 132.8, 131.7, 131.2, 129.5, 127.9, 126.7, 124.2, 123.1, 121.8, 52.9. \text{HRMS (APCI)} calcd for C\(_{15}\)H\(_{11}\)ClO\(_2\)N (M+H\(^+\)): 272.0472, found: 272.0468.
Hz, 1H), 8.48-8.45 (m, 1H), 8.16 (d, J = 10.9 Hz, 1H), 7.82-7.72 (m, 3H). 13C NMR (125 MHz, CDCl₃, CDCl₃ as the internal standard) δ 150.3, 143.2, 134.5, 134.0, 133.8, 132.2, 131.7, 130.3, 129.1, 124.6, 123.8, 122.5, 121.3. HRMS (APCI) calcd for C₁₃H₈Cl₂N (M+H⁺): 248.0028, found: 248.0025.

7-chloro-2-(trifluoromethyl)phenanthridine (3ak)

[Chemical structure image]

White solid. Isolated yield: 63%. Melting point: 136-137 °C.

1H NMR (500 MHz, CDCl₃, TMS as the internal standard): δ 9.77 (s, 1H), 8.76 (s, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.81-7.75 (m, 2H). 13C NMR (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 152.1, 146.1, 134.6, 134.3, 132.1, 131.7, 129.6 (Jₑ-C = 32.3 Hz), 129.3, 125.7 (Jₑ-C = 3.4 Hz), 125.6, 123.8, 123.4, 123.1, 121.2, 120.6 (Jₑ-C = 4.6 Hz). HRMS (APCI) calcd for C₁₄H₈ClF₃N (M+H⁺): 282.0291, found: 282.0289.

7-chloro-2-methylphenanthridine (3al)

[Chemical structure image]

White solid. Isolated yield: 58%. Melting point: 147-148 °C

1H NMR (500 MHz, CDCl₃, TMS as the internal standard) δ 9.69 (s, 1H), 8.51 (d, J = 7.9 Hz, 1H), 8.33 (s, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.75-7.69 (m, 2H), 7.62-7.60 (m, 1H), 7.64 (s, 3H). 13C NMR (125 MHz, CDCl₃, CDCl₃ as the internal standard) δ 149.1, 143.1, 138.0, 134.5, 134.2, 131.5, 131.1 130.4, 128.3, 123.7, 123.3, 122.4, 121.3, 22.4. HRMS (APCI) calcd for C₁₄H₁₁ClN (M+H⁺): 228.0574, found: 228.0572.

7-chloro-4-fluorophenanthridine (3ai')
White solid. Isolated yield: 37%. Melting point: 159-160 ºC.

**1H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.72 (s, 1H), 8.43 (d, $J$ = 7.9 Hz, 1H), 8.32-8.29 (m, 1H), 8.19-8.16 (m, 1H), 7.84-7.78 (m, 2H), 7.58-7.54 (m, 1H).

**13C NMR** (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 162.0 ($J_{F-C}$ = 247.3 Hz), 149.0, 141.1, 134.5, 134.2 ($J_{F-C}$ = 4.0 Hz), 132.7 ($J_{F-C}$ = 9.1 Hz), 131.7, 129.2, 125.0 ($J_{F-C}$ = 7.7 Hz), 123.6, 121.4, 118.9 ($J_{F-C}$ = 24.1 Hz), 107.8 ($J_{F-C}$ = 23.5 Hz). HRMS (APCI) calcd for C$_{13}$H$_8$ClFN (M+H$^+$): 232.0323, found: 232.0322.

**4,7-dichlorophenanthridine (3aj')**

White solid. Isolated yield: 31%. Melting point: 167-168 ºC.

**1H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.88 (s, 1H), 8.54-8.49 (m, 2H), 7.90 (d, $J$ = 7.6 Hz, 1H), 7.82-7.76 (m, 2H), 7.63 (d, $J$ = 7.8 Hz, 1H).

**13C NMR** (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 150.7, 141.1, 135.1, 134.6, 134.6, 131.9, 130.2, 129.1, 127.9, 125.3, 123.7, 121.8, 121.5; HRMS (APCI) calcd for C$_{13}$H$_8$Cl$_2$N (M+H$^+$): 248.0028, found: 248.0026.

**2,4,7-trichlorophenanthridine (3am)**

White solid. Isolated yield: 76%. Melting point: 199-200 ºC.

**1H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.86 (s, 1H), 8.46-8.45 (m, 2H), 7.89 (d, $J$ = 2.2 Hz, 1H), 7.85-7.81 (m, 2H).

**13C NMR** (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 150.8, 139.6, 136.0, 134.8, 133.6, 132.3, 130.4, 129.8, 125.9, 123.9, 121.6, 121.5. HRMS (APCI) calcd for C$_{13}$H$_7$Cl$_3$N (M+H$^+$): 281.9638, found: 281.9635.
7-chloro-2,4-dimethylphenanthridine (3an)

White solid. Isolated yield: 46%. Melting point: 129-130 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.73 (s, 1H), 8.51 (d, $J$ = 7.6 Hz, 1H), 8.20 (s, 1H), 7.73-7.68 (m, 2H), 7.48 (s, 1H), 2.85 (s, 3H), 2.59 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 147.3, 141.6, 137.7, 137.0, 134.4, 133.8, 131.9, 130.4, 127.6, 123.0, 122.9, 121.1, 119.8, 22.0, 18.4. HRMS (APCI) calcd for C$_{15}$H$_{13}$ClN (M+H$^+$): 242.0731, found: 242.0728.

2,3,7-trichlorophenanthridine (3ao)

White solid. Isolated yield: 65%. Melting point: 184-185 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.75 (s, 1H), 8.63 (s, 1H), 8.42 (d, $J$ = 8.8 Hz, 1H), 8.33 (s, 1H), 7.82-7.77 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 151.4, 143.8, 134.7, 134.0, 133.4, 132.5, 132.0, 131.8, 129.3, 124.3, 123.7, 123.1, 121.2. HRMS (APCI) calcd for C$_{13}$H$_7$Cl$_3$N (M+H$^+$): 281.9638, found: 281.9636.

7-chloro-2,3-dimethylphenanthridine (3ap)

White solid. Isolated yield: 40%. Melting point: 162-163 °C.

$^1$H NMR (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.66 (s, 1H), 8.48 (d, $J$ = 8.1 Hz, 1H), 8.28 (s, 1H), 7.96 (s, 1H), 7.72-7.65 (m, 2H), 2.53 (s, 3H), 2.51 (s, 3H). $^{13}$C NMR
(125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 149.1, 143.7, 139.5, 137.6, 134.5, 134.2, 131.0, 130.5, 127.8, 123.3, 122.8, 121.5, 121.1, 20.9, 20.6. **HRMS** (APCI) calcd for C$_{15}$H$_{13}$ClN (M+H$^+$): 242.0731, found: 242.0728.

**4-chlorobenzo[\textit{a}]phenanthridine (3aq)**

![Structure of 4-chlorobenzo[\textit{a}]phenanthridine](image)

White solid. Isolated yield: 35%. Melting point: 147-148 °C

**$^1$H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.86 (s, 1H), 9.00-8.97 (m, 2H), 8.14-8.12 (m, 1H), 8.07-8.05 (m, 2H), 7.79-7.67 (m, 4H). **$^{13}$C NMR** (125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 149.4, 144.8, 134.7, 134.0, 133.9, 130.8, 130.7, 129.9, 129.3, 128.6, 128.1, 127.7, 127.2, 127.1, 126.0, 124.9, 120.4. **HRMS** (APCI) calcd for C$_{17}$H$_{11}$ClN (M+H$^+$): 264.0574, found: 264.0571.

**6-chlorothieno[2,3-\textit{c}]isoquinoline (3ar)**

![Structure of 6-chlorothieno[2,3-\textit{c}]isoquinoline](image)

Yellow solid. Isolated yield: 20%. Melting point: 94-95 °C.

**$^1$H NMR** (500 MHz, CDCl$_3$, TMS as the internal standard): $\delta$ 9.56 (s, 1H), 8.19-8.17 (m, 1H), 7.83 (d, $J$ = 5.9 Hz, 1H), 7.70-7.64 (m, 3H). **$^{13}$C NMR** (100 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 156.9, 146.6, 133.7, 133.3, 130.7, 126.94, 126.9, 122.9, 121.9, 199.7. **HRMS** (APCI) calcd for C$_{11}$H$_7$ClNS (M+H$^+$): 219.9982, found: 219.9978.

**2,4-dichloro-7-methylphenanthridine (3dm)**

![Structure of 2,4-dichloro-7-methylphenanthridine](image)

White solid. Isolated yield: 55%. Melting point: 171-172 °C.
**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.63 (s, 1H), 8.43 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 1.7 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 2.87 (s, 3H).

**13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 151.4, 139.4, 137.4, 135.7, 132.8, 132.0, 131.9, 130.5, 129.5, 126.9, 125.5, 121.5, 120.6, 19.1.

**HRMS** (APCI) calcd for C_{14}H_{10}Cl₂N (M+H⁺): 262.0184, found: 262.0182.

**methyl 7,10-dichlorophenanthridine-3-carboxylate (3nh)**

![methyl 7,10-dichlorophenanthridine-3-carboxylate](image)

White solid. Isolated yield: 57%. Melting point: 177-178 °C.

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 9.86 (d, J = 9.0 Hz, 1 H), 9.83 (s, 1H), 8.90 (d, J = 2 Hz, 1H), 8.32-8.30 (m, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.72 (t, J = 8.3 Hz, 1H), 4.04 (s, 3H).

**13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 166.8, 150.9, 145.7, 135.0, 133.7, 132.6, 131.3, 131.0, 130.8, 129.5, 127.3, 126.9, 126.0, 125.9, 52.9.

**HRMS** (APCI) calcd for C_{15}H_{10}Cl₂O₂N (M+H⁺): 306.0083, found: 306.0081.

**3-chloro-[1,1'-biphenyl]-2-carbaldehyde (A)**

![3-chloro-[1,1'-biphenyl]-2-carbaldehyde](image)

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 10.06 (s, 1H), 7.49-7.48 (m, 2H), 7.44-7.42 (m, 3H), 7.33-7.29 (m, 3H); **13C NMR** (125 MHz, CDCl₃, CDCl₃ as the internal standard): δ 191.6, 147.0, 138.4, 134.9, 133.1, 132.3, 130.6, 128.9, 128.7.

**1-chloro-9H-fluoren-9-one (B)**

![1-chloro-9H-fluoren-9-one](image)

**1H NMR** (500 MHz, CDCl₃, TMS as the internal standard): δ 7.69 (d, J = 7.4 Hz, 1H), 7.54-7.49 (m, 2H), 7.45-7.38 (m, 2H), 7.35-7.32 (m, 1H), 7.23-7.21 (m, 1H); **13C NMR**
(125 MHz, CDCl$_3$, CDCl$_3$ as the internal standard): $\delta$ 191.2, 146.9, 143.0, 135.6, 135.1, 134.3, 133.2, 131.4, 130.1, 129.9, 124.9, 120.8, 119.1.
Copies of $^1$H, $^{13}$C Spectra

7-fluorophenanthridine (3ba)

![Spectral Diagram]

- Chemical structure and spectral data for 7-fluorophenanthridine (3ba) are shown.
- The diagram includes proton (H) and carbon (C) resonances with corresponding chemical shifts.

---

S40
7-chlorophenanthridine (3aa)
7-bromophenanthridine (3ca)
8-chlorophenanthridine (3ea)
8-bromophenanthridine (3fa)
8-(trifluoromethyl)phenantridine (3ga)
8-methylphenanthridine (3ha)

![Chemical Structure](image)

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8-methoxyphenanthridine (3ia)
Phenanthridine (3ja)
9-chlorophenanthridine (3ka)
9-methylphenanthridine (3la)
7-phenylphenanthridine (3jaa)
9-methyl-7-phenylphenanthridine (3kaa)
7-bromo-9-fluorophenanthridine (3ma)
7-bromo-9-methylphenanthridine (3na)
7,10-dichlorophenanthridine (3oa)
7,9-dichlorophenanthridine (3pa)
7,8-dichlorophenanthridine (3qa)
8,9-dimethoxyphenanthridine (3ra)

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[1,3]dioxolo[4,5-j]phenanthridine (3a)

![Chemical structure of [1,3]dioxolo[4,5-j]phenanthridine (3a)](image)
10-bromo-[1,3]dioxolo[4,5-i]phenanthridine (3ta)
benzo[k]phenanthridine (3ua)
7-chloro-1-fluorophenanthridine (3ab)
1,7-dichlorophenanthridine (3ac)
7-chloro-3-methylphenanthridine (3ad)
7-chloro-3-methoxyphenanthridine (3ae)
7-chloro-3-(trifluoromethyl)phenanthridine (3ag)
methyl 7-chlorophenanthridine-3-carboxylate (3ah)
7-chloro-2-fluorophenanthridine (3ai)
2,7-dichlorophenanthridine (3aj)
7-chloro-2-(trifluoromethyl)phenanthridine (3ak)

[Chemical structure image]

[Spectrum image]
7-chloro-2-methylphenanthridine (3a1)
7-chloro-4-fluorophenanthridine (3ai')
4,7-dichlorophenantridin (3aj')
2,4,7-trichlorophenanthridine (3am)
7-chloro-2,4-dimethylphenanthridine (3an)
2,3,7-trichlorophenanthridine (3ao)
7-chloro-2,3-dimethylphenanthridine (3ap)
4-chlorobenzo[a]phenanthridine (3aq)
6-chlorothieno[2,3-c]isoquinoline (3ar)
2,4-dichloro-7-methylphenanthridine (3dm)
methyl 7,10-dichlorophenanthridine-3-carboxylate (3nh)
3-chloro-[1,1'-biphenyl]-2-carbaldehyde (A)

![Chemical structure image]

**NMR Spectra**

**1H (ppm)**

- 10.0594
- 7.4809
- 7.4878
- 7.4927
- 7.4970
- 7.5006
- 7.5037
- 7.5079
- 7.5122
- 7.5165
- 7.5208
- 7.5251
- 7.5294

**13C (ppm)**

- 77.1853
- 77.4394
- 77.6941
- 128.7300
- 128.8816
- 130.0153
- 130.5938
- 132.3108
- 133.1098
- 134.9213
- 138.3526
- 146.9819
- 191.5595

**Remarks**

- All values are approximate and may vary slightly depending on the experimental conditions.

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S85
1- chloro-9H-fluoren-9-one (B)