Supporting Information

Ni-Catalyzed Reductive Addition of Alkyl Halides to Isocyanides

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**Experimental Section**

**Part 1. General Information**

Experiments were conducted under a nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. For product purification by flash column chromatography, silica gel (300–400 mesh) and petroleum ether (bp 60–90 °C) were used. NMR spectra were measured on 500 MHz instruments at room temperature. Reference peaks for chloroform in \(^1\)H NMR and \(^{13}\)C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using an Ion Spec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

The following chemicals were purchased and used as received: Zn (99.9%, powder), NiI\(_2\) (99.5%, Alfa Aesar), Ni(cod)\(_2\) (99%, Stream), NiCl\(_2\) (99.5%, Alfa Aesar), NiBr\(_2\) (99.5%, Alfa Aesar), Ni(acac)\(_2\) (99%, Alfa Aesar), Ni(ClO\(_4\))\(_2\)-6H\(_2\)O (99.5%, Alfa Aesar), 1,3-di-iso-propylimidazolium chloride (4, >97%, Alfa Aesar), 2,2’-bipyridine (5, Aldrich), DMA (99.8%, Super Dry, with molecular sieves), DMF (99.8%, Super Dry, with molecular sieves), 1,4-Dioxane (99.5%, Super Dry, with molecular sieves), MgCl\(_2\) (99%, Alfa Aesar), TBAI (99%, Aladdin), Isocyanides\(^1\) were synthesized according to the literature procedures.

**Part 2. Details of Optimization**

*A typical procedure for optimization reactions:* To a flame-dried Schlenk tube equipped with a stir bar was loaded 4-iodo-1-tosylpiperidine (54.8 mg, 0.15 mmol, 100%), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), cesium carbonate(77.4mg, 0.225mmol, 150%), ligand (20 mol%), and Ni catalyst (10 mol%). The tube was capped with a rubber septum, and it was degassed and refilled nitrogen (N\(_2\)) for three times. Isocyanide and solvent (1.0 mL) were added via syringe. The resulting reaction mixture was stirred for 12 hours under N\(_2\) atmosphere at 90 °C, and was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as a solid or oil.
**Table S1:** Screening of catalysts

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<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>Ni(COD)₂</td>
<td>27</td>
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<tr>
<td>2</td>
<td>NiI₂</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>NiBr₂</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>NiCl₂</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>Ni(acac)₂</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>Ni(ClO₄)₂·6H₂O</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>NiBr₂·glyme</td>
<td>&lt;10</td>
</tr>
<tr>
<td>8</td>
<td>NiCl₂·glyme</td>
<td>&lt;10</td>
</tr>
<tr>
<td>9</td>
<td>NiBr₂·diglyme</td>
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<td>10</td>
<td>Ni(OSO₂CF₃)₂</td>
<td>trace</td>
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<tr>
<td>11</td>
<td>NiCl₂·(Ph₂PCH₂CH₂PPh₂)</td>
<td>trace</td>
</tr>
<tr>
<td>12</td>
<td>NiCl₂·(PPh₃)₂</td>
<td>trace</td>
</tr>
<tr>
<td>13</td>
<td>none</td>
<td>trace</td>
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**Table S2:** Solvent screening

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<td>DMA</td>
<td>41%</td>
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<tr>
<td>2</td>
<td>DMF</td>
<td>25%</td>
</tr>
<tr>
<td>3</td>
<td>NMP</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>1,4-dioxane</td>
<td>50%</td>
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</tbody>
</table>

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Part 3. Phenanthridine Synthesis via Reductive Coupling

**General procedure** for Phenanthridine synthesis via reductive coupling of alkyl iodides with isocyanides: To a flame-dried Schlenk tube equipped with a stir bar was loaded alkyl iodides (0.15 mmol, 100%, if solid) and isocyanide (0.45 mmol, 300%, if solid), followed by addition of zinc power (29.4 mg, 0.45 mmol, 300%), Cesium carbonate (77.4 mg, 0.225 mmol, 150%). The tube was capped with a rubber septum, and it was evacuated and refilled nitrogen (N₂) three times through glove box. followed by addition of 1,3-dimethyl-1H-imidazol-3-ium chloride (4.6 mg, 0.03 mmol, 20%), NiI₂ (4.7 mg, 0.015 mmol, 10%) in glove box, alkyl iodides (0.15 mmol, 100%, if liquid) and isocyanide (0.45 mmol, 300%, if liquid) was added via syringe. 1,4-Dioxane (2.0 mL) was added via syringe. After the reaction mixture was allowed to stir for 12 hours under N₂ atmosphere at 90 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as a solid or oil

6-(1-Tosylpiperidin-4-yl)phenanthridine (3a)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (54.9 mg, 0.132 mmol) 88% yield as a yellow solid

**¹H NMR (500 MHz, CDCl₃)**: δ 8.65 (d, J = 8.2 Hz, 1H), 8.52 (dd, J = 8.2, 1.4 Hz, 1H), 8.10 (dd, J = 21.7, 8.2 Hz, 2H), 7.80 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.67–7.58 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 4.00 (dt, J = 11.9, 3.6 Hz, 2H), 3.56–3.47 (m, 1H), 2.60 (td, J = 11.9, 2.5 Hz, 2H), 2.47 (s, 3H), 2.35 (qd, J = 12.0, 3.9 Hz, 2H), 2.13–2.05 (m, 2H).

**¹³C NMR (125 MHz, CDCl₃)**: δ 162.22, 143.60, 143.47, 133.29, 133.12, 130.17, 130.08, 129.65, 128.61, 127.89, 127.22, 126.60, 124.90, 124.33, 123.37, 122.86, 121.84, 46.57, 38.99, 30.53, 21.60.

**HRMS (ESI)**: calcd for C₂₅H₂₅N₂O₂S [M+H]⁺ 417.1631, found 417.1631.

**M.p.** 235 - 237°C.
2-Methyl-6-(1-tosylpiperidin-4-yl)phenanthidine (3b)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO2: 10% ethyl acetate in petroleum ether), this compound was obtained in (61.3 mg, 0.142 mmol) 95% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl3): δ 8.62 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.77 (t, J = 7.9, 1H), 7.74 (d, J = 8.3, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.52 (dd, J = 8.3, 1.9 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 3.99 (d, J = 11.9 Hz, 1H), 3.49 (ddd, J = 11.7, 7.8, 3.6 Hz, 1H), 2.61 (s, 3H), 2.60–2.55 (m, 2H), 2.47 (s, 3H), 2.33 (td, J = 11.6, 8.0 Hz, 2H), 2.15–2.00 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl3): δ 161.18, 143.47, 141.92, 136.40, 133.28, 132.87, 130.29, 129.79, 129.66, 127.89, 127.07, 124.85, 124.37, 123.18, 122.81, 121.47, 46.60, 38.90, 30.54, 21.97, 21.60.

HRMS (ESI): calcd for C$_{26}$H$_{27}$N$_2$O$_2$S [M]+ 431.1788; found : 431.1788.

M.p. 268 - 270°C.

8-Methoxy-2-methyl-6-(1-tosylpiperidin-4-yl)phenanthidine (3c)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO2: 10% ethyl acetate in petroleum ether), this compound was obtained in (44.2 mg, 0.096 mmol) 64% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl3): δ 8.54 (d, J = 9.5 Hz, 1H), 8.21 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.3 Hz, 1H), 7.42(s, 2H), 7.37 (d, J = 7.9 Hz, 2H), 3.98 (d, J = 13.5Hz, 2H), 3.94(s, 3H), 3.54–3.21 (m, 1H), 2.61 (d, J = 13.5 Hz, H), 2.59(s, 3H), 2.51–2.43 (s, 3H), 2.40–2.23 (m, 2H), 2.08 (d, J = 13.5 Hz, 2H)

$^{13}$C NMR (125 MHz, CDCl3): δ 160.29, 158.52, 143.45, 141.07, 136.46, 133.37, 129.74, 129.74, 129.33, 127.89, 127.16, 125.67, 124.51, 123.27, 120.96, 119.33, 106.29, 55.62, 46.52, 38.91, 30.38, 21.98, 21.60.

HRMS (ESI): calcd for C$_{27}$H$_{29}$N$_2$O$_3$S [M+H]$^+$ 461.1893; found: 461.1894.

M.p. 287 - 289°C.
8-Methoxy-6-(1-tosylpiperidin-4-yl)phenanthridine (3d)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (48.8 mg, 0.110 mmol) 73% yield as a yellow solid.

1H NMR (500 MHz, CDCl₃): δ 8.57 (d, J = 9.7 Hz, 1H), 8.46–8.40 (m, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.77–7.71 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 6.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.04–3.96 (m, 2H), 3.95 (s, 3H), 3.63–3.27 (m, 1H), 2.61 (td, J = 11.8, 2.5 Hz, 2H), 2.48 (s, 3H), 2.34 (t, J = 12.4 Hz, 2H), 2.10s (d, J = 13.6 Hz, 2H).

13C NMR (125 MHz, CDCl₃): δ 161.34, 158.65, 143.45, 142.74, 133.39, 130.03, 129.66, 127.89, 127.64, 127.39, 126.67, 125.63, 124.57, 123.45, 121.33, 119.54, 106.38, 55.65, 46.49, 38.99, 30.38, 21.60.


M.p. 280-282°C.

8-Fluoro-6-(1-tosylpiperidin-4-yl)phenanthridine (3e)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (44.3 mg, 0.102 mmol) 68% yield as a yellow solid.

1H NMR (500 MHz, DMSO-d₆) δ 8.94 (dd, J = 9.2, 5.5 Hz, 1H), 8.74 (dd, J = 8.2, 1.4 Hz, 1H), 8.27 (dd, J = 10.7, 2.7 Hz, 1H), 8.01 (dd, J = 8.2, 1.4 Hz, 1H), 7.81 (td, J = 8.7, 2.6 Hz, 1H), 7.79–7.72 (m, 1H), 7.41–7.64 (m, 3H), 7.51 (d, J = 7.9 Hz, 2H), 3.79 (dd, J = 9.4, 5.9 Hz, 2H), 3.70 (dt, J = 10.2, 5.2 Hz, 1H), 2.57 (td, J = 11.3, 3.9 Hz, 2H), 2.45 (s, 3H), 2.18–1.86 (m, 4H).

13C NMR (125 MHz, DMSO-d₆) δ 163.14, 162.75, 160.80, 160.80, 143.92, 143.01, 133.02, 130.32, 130.11, 129.87, 129.79, 129.78, 128.11, 127.57, 126.56, 125.87, 125.82, 123.12, 123.00, 120.39, 120.20, 111.17, 110.99, 79.79, 79.44, 79.17, 46.45, 37.91, 30.80, 21.50


M.p. 178 - 180°C.
5-(1-tosylpiperidin-4-yl)benzo[i]phenanthridine (3f)

According to the general procedure. After purification of the crude material by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether).

This compound was obtained in (17.5 mg, 0.038 mmol) 25% yield as a yellow solid

\[ ^{1}H \text{ NMR (500 MHz, CDCl}_3\] \(\delta\) 8.57 (t, \(J = 8.7\) Hz, 2H), 8.42-8.39 (m, 1H), 8.15-8.08 (m, 1H), 8.04-7.98 (m, 1H), 7.80-7.72 (m, 2H), 7.70-7.60 (m, 3H), 7.38 (d, \(J = 8.7\) Hz, 2H), 4.03 (d, \(J = 8.4\) Hz, 2H), 3.97-3.88 (m, 1H), 2.65-2.45 (m, 7H), 2.07 (d, \(J = 10.1\) Hz, 2H)

\[ ^{13}C \text{ NMR (125 MHz, CDCl}_3\] \(\delta\) 161.57, 143.40, 133.56, 133.25, 129.66, 129.61, 129.01, 127.84, 126.66, 126.38, 122.83, 122.36, 11.74, 120.34, 46.49, 42.70, 31.69, 21.57


M.p. 295-297 ℃.

(4-(tert-butyl)Phenyl)(4-(2-methylphenanthridin-6-yl)piperidin-1-yl)methanone (3g)

This compound was obtained according to the general procedure.

After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (53.0 mg, 0.122 mmol) 81% yield as a yellow solid.

\[ ^{1}H \text{ NMR (500 MHz, CDCl}_3\] \(\delta\) 8.65 (d, \(J = 8.2\) Hz, 1H), 8.32 (s, 1H), 8.26 (d, \(J = 8.2\) Hz, 1H), 8.03 (d, \(J = 8.3\) Hz, 1H), 7.91-7.76 (m, 1H), 7.75-7.63 (m, 1H), 7.54 (dd, \(J = 8.3, 1.9\) Hz, 1H), 7.51–7.37 (m, 4H), 5.21–4.58 (m, 1H), 4.31–4.01 (m, 1H), 4.04–3.75 (m, 1H), 3.44–3.23 (m, 1H), 3.22–3.02 (m, 1H), 2.62 (s, 3H), 2.45–2.10 (s, 3H), 2.10–1.88 (m, 1H), 1.34 (s, 9H).

\[ ^{13}C \text{ NMR (125 MHz, CDCl}_3\] \(\delta\) 170.66, 161.58, 152.72, 141.98, 136.38, 133.45, 132.93, 130.31, 130.01, 129.73, 127.16, 126.92, 125.36, 125.04, 124.48, 123.25, 122.81, 121.53, 39.97, 34.81, 31.46, 31.28, 21.98.


M.p. 270 - 271 ℃.
3-(Phenanthridin-6-yl)butyl 4-methoxybenzoate (3h)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (52.8 mg, 0.136 mmol) 91% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl₃): δ 8.64 (d, $J = 8.3$ Hz, 1H), 8.53 (dd, $J = 8.3$, 1.4 Hz, 1H), 8.33 (d, $J = 8.3$ Hz, 1H), 8.15 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.80 (t, $J = 8.1$ Hz, 1H), 7.71 (t, $J = 8.1$ Hz, 1H), 7.68–7.59 (m, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.49 (dt, $J = 11.0$, 6.4 Hz, 1H), 4.35 (dt, $J = 11.1$, 6.4 Hz, 1H), 4.11 (q, $J = 6.9$ Hz, 1H), 3.84 (s, 3H), 2.94–2.65 (m, 1H), 2.41–2.16 (m, 1H), 1.55 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl₃): δ 166.35, 164.17, 163.17, 133.77, 131.14, 131.48, 130.11, 129.98, 128.49, 127.25, 126.36, 125.38, 124.98, 123.43, 122.85, 122.67, 121.86, 113.50, 63.59, 55.41, 34.68, 33.53, 20.83.

HRMS (ESI): calcd for C₂₅H₂₄NO₃ [M+H]$^+$ 386.1751; found: 386.1751.

M.p. 77 - 79°C.

3-(8-Methoxy-2-methylphenanthridin-6-yl)butyl 4-methoxybenzoate (3i)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 10% ethyl acetate in petroleum ether), this compound was obtained in (50.8 mg, 0.119 mmol) 79% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl₃): δ 8.53 (d, $J = 9.0$ Hz, 1H), 8.22 (s, 1H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 2.6$ Hz, 1H), 7.47 (d, $J = 8.4$, 2H), 7.41(dd, $J =$9.0, 2.6, 1H ), 6.85 (d, $J = 8.5$ Hz, 2H), 4.63–4.41 (m, 1H), 4.44–4.24 (m, 1H), 4.00 (q, $J = 7.2$ Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.84–2.67 (m, 1H), 2.60 (s, 3H), 2.29–2.17 (m, 1H), 1.55 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl₃): δ 166.35, 163.23, 162.22, 158.59, 141.28, 136.14, 131.50, 129.63, 129.20, 127.23, 126.32, 124.30, 123.34, 122.87, 120.99, 120.07, 113.48, 105.89, 63.56, 55.43, 55.41,
34.74, 33.45, 21.97, 20.51.

**HRMS (ESI):** calcd for C_{27}H_{28}NO_{4} [M+H]^+ 430.2013, found 430.2014.

**M.p.** 134 - 136°C.

3-(8-Methoxyphenanthridin-6-yl)butyl 4-methoxybenzoate (3j)

This compound was obtained according to the general procedure.

After purification of the crude material was performed by column chromatography (SiO_{2}: 10% ethyl acetate in petroleum ether), this compound was obtained in (44.2 mg, 0.107 mmol) 71% yield as a yellow solid.

**^1H NMR (500 MHz, CDCl_{3}):** δ 8.54 (d, J = 9.1 Hz, 1H), 8.44 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.70–7.62 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.43 (dd, J = 9.0, 2.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 4.60–4.43 (m, 1H), 4.44–4.29 (m, 1H), 4.02 (q, J = 6.8 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.91–2.62 (m, 1H), 2.46–2.13 (m, 1H), 1.56 (d, J = 6.8 Hz, 3H).

**^13C NMR (125 MHz, CDCl_{3}):** δ 166.35, 163.29, 163.24, 158.72, 142.94, 131.50, 129.90, 127.50, 127.45, 126.42, 126.27, 124.34, 123.53, 122.83, 121.38, 120.29, 113.49, 105.96, 63.54, 55.46, 55.42, 34.74, 33.56, 20.56.

**HRMS (ESI):** calcd for C_{26}H_{26}NO_{4} [M+H]^+ 416.1856; found: 416.1855.

**M.p.** 104 - 106°C

3-(2-Methylphenanthridin-6-yl)butyl 4-methoxybenzoate (3k)

This compound was obtained according to the general procedure.

After purification of the crude material was performed by column chromatography (SiO_{2}: 10% ethyl acetate in petroleum ether), this compound was obtained in (56.8 mg, 0.142 mmol) 95% yield as a yellow solid.

**^1H NMR (500 MHz, CDCl_{3}):** δ 8.63 (d, J = 8.2 Hz, 1H), 8.48–8.15 (m, 2H), 8.04 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.78 (t, J = 8.2 Hz, 1H), 7.63 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.53 (dd, J = 8.4, 1.9 Hz, 1H), 6.85 (m, J = 8.4, 2H), 4.49 (dt, J = 10.9, 6.4 Hz, 1H), 4.34 (dt, J = 11.0, 6.3 Hz, 1H), 4.09 (q, J = 6.9 Hz, 1H), 3.84 (s, 3H), 2.75(dq, J = 13.0, 6.4 Hz, 1H), 2.62 (s, 3H), 2.26 (dq, J = 13.0, 6.4 Hz, 1H), 1.55 (d, J = 6.8 Hz, 3H).
\[ ^{13}C\text{ NMR (125 MHz, CDCl}_3\text{): } \delta 166.36, 163.21, 163.12, 142.07, 136.10, 132.92, 131.49, 130.18, 129.91, 129.68, 127.08, 125.34, 125.02, 123.24, 122.87, 122.63, 121.49, 113.49, 63.61, 55.41, 34.70, 33.70, 33.42, 21.96, 20.78. \]

HRMS (ESI): calcd for C\(_{26}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\) 400.1907; found: 400.1907.

M.p. 100-101°C.

6-(2,3-Dihydro-1H-inden-2-yl)phenanthridine (3l)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether), this compound was obtained in (29.2 mg, 0.099 mmol) 66% yield as a yellow solid. Purification of the crude material was performed by column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether)

\[ ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta 8.68 \text{ (dd, } J = 8.4, 1.1 \text{ Hz, 1H), 8.56 \text{ (dd, } J = 8.2, 1.4 \text{ Hz, 1H), 8.35 \text{ (dd, } J = 8.2, 1.1 \text{ Hz, 1H), 8.13 \text{ (d, } J = 8.1 \text{ Hz, 1H), 7.86 \text{ (ddd, } J = 8.3, 7.0, 1.3 \text{ Hz, 1H), 7.78–7.67 (m, 2H), 7.64 \text{ (ddd, } J = 8.3, 6.9, 1.4 \text{ Hz, 1H), 7.32 \text{ (dd, } J = 5.3, 3.3 \text{ Hz, 2H), 7.23 \text{ (dd, } J = 5.5, 3.2 \text{ Hz, 2H), 4.90–4.63 (m, 1H), 3.82 (dd, } J = 15.7, 9.1 \text{ Hz, 2H), 3.50 (dd, } J = 15.7, 8.6 \text{ Hz, 2H).} \]

\[ ^{13}C\text{ NMR (125 MHz, CDCl}_3\text{): } \delta 162.51, 142.82, 133.27, 130.36, 129.84, 128.66, 128.44, 127.37, 126.57, 126.49, 126.06, 125.30, 124.46, 123.66, 122.70, 121.90. \]

HRMS (ESI): calcd for C\(_{22}\)H\(_{17}\)N [M+H]\(^+\) 296.1434; found: 296.1434.

M.p. 201 - 203°C.

6-(2,3-Dihydro-1H-inden-2-yl)-2-methylphenanthridine (3m)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO\(_2\): 5% ethyl acetate in petroleum ether), this compound was obtained in (29.7 mg, 0.096 mmol) 64% yield as a yellow solid.

\[ ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta 8.66 \text{ (d, } J = 8.2 \text{ Hz, 1H), 8.38–8.25 (m, 2H), 8.03 (d, } J = 8.3 \text{ Hz, 1H), 7.83 (ddd, } J = 8.2, 6.9, 1.3 \text{ Hz, 1H), 7.70 (ddd, } J = 8.2, 6.9, 1.2 \text{ Hz, 1H), 7.54 (dd, } J = 8.3, 1.9 \text{ Hz, 1H),} \]

S10
7.31 (dd, $J = 5.4$, 3.3 Hz, 2H), 7.23 (dd, $J = 5.5$, 3.2 Hz, 2H), 4.91–4.60 (m, 1H), 3.81 (dd, $J = 15.7$, 9.2 Hz, 2H), 3.49 (dd, $J = 15.8$, 8.7 Hz, 2H), 2.63 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.47, 143.02, 141.98, 136.35, 133.08, 130.35, 130.09, 129.83, 127.23, 126.51, 126.04, 125.51, 124.52, 123.53, 122.71, 121.61.


M.p 220 - 221 ℃.

6-(2,3-Dihydro-1H-inden-2-yl)-8-methoxyphenanthridine (3n)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether), this compound was obtained in (28.3 mg, 0.087 mmol) 58% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.58 (d, $J = 9.1$ Hz, 1H), 8.46 (d, $J = 8.0$ Hz, 1H), 8.10 (s, 1H), 7.64–7.60 (m, 3H), 7.48 (dd, $J = 9.1$, 2.7 Hz, 1H), 7.35–7.29 (m, 2H), 7.26–7.20 (m, 2H), 4.71–4.67 (m, 1H), 3.89 (s, 3H), 3.79 (dd, $J = 15.9$, 8.8 Hz, 2H), 3.53 (dd, $J = 16.0$, 8.9 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.84, 158.68, 142.88, 130.46, 130.16, 129.85, 127.62, 126.55, 124.49, 124.35, 123.75, 121.38, 120.62, 114.04, 114.78, 106.38, 55.38, 44.23, 38.69.

HRMS (ESI): calcd for C$_{23}$H$_{20}$NO [M+H]$^+$ 326.1539; found: 326.1539.


3-(phenanthridin-6-yl)propyl benzoate (3o)

According to the general procedure. After purification of the crude material was performed by column chromatography (SiO$_2$: 5% ethyl acetate in petroleum ether). This compound was obtained in (19.4 0.057 mmol) 38% yield as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (d, $J = 8.2$Hz, 1H), 8.54 (d, $J = 8.2$Hz, 1H), 8.27 (d, $J = 8.2$Hz, 1H), 8.14 (d, $J = 8.2$Hz, 1H), 8.02 (d, $J = 8.2$Hz, 1H), 7.83(t, $J = 7.8$Hz, 1H), 7.75-7.60 (m, 3H), 7.55 (t, $J = 7.8$Hz, 1H), 7.42 (t, $J = 8.2$Hz, 2H), 4.56 (t, $J = 6.3$Hz, 2H), 3.57(t, $J = 7.6$, 2H), 2.55-2.45 (m,2H)

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.66, 160.69, 132.97, 132.87, 130.33, 129.57, 128.71, 128.33,
127.43, 126.55, 125.96, 125.21, 123.69, 122.60, 121.95, 64.91, 32.26, 27.80.

**HRMS (ESI)**: calcd for C_{23}H_{20}NO_{2}[M+H]^+ 342.1416; found: 342.1416.

**M.p.** 146-148°C.

6-(tert-Butyl)phenanthridine (3p)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), this compound was obtained in (22.1 mg, 0.090 mmol) 60% yield as a yellow liquid.

**{1H NMR (500 MHz, CDCl₃)}**: δ 8.70 (d, J = 8.3 Hz, 1H), 8.64 (d, J = 8.5 Hz, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.68–7.58 (m, 2H), 1.75 (s, 9H).

**{13C NMR (125 MHz, CDCl₃)}**: δ 166.67, 142.96, 134.04, 130.28, 129.28, 128.40, 128.28, 126.48, 125.96, 124.33, 123.44, 123.00, 121.62, 40.22, 31.24.

**HRMS (ESI)**: calcd for C_{17}H_{18}N [M+H]^+ 236.1434, found 236.1433.

6-(tert-Butyl)-2-methylphenanthridine (3q)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), this compound was obtained in (15.7 mg, 0.063 mmol) 42% yield as a yellow liquid.

**{1H NMR (500 MHz, CDCl₃)}**: δ 8.68 (d, J = 8.3 Hz, 1H), 8.62 (d, J = 8.5 Hz, 1H), 8.31 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.68–7.59 (m, 1H), 7.53 (dd, J = 8.3, 1.9 Hz, 1H), 2.62 (s, 3H), 1.75 (s, 9H).

**{13C NMR (125 MHz, CDCl₃)}**: δ 165.64, 141.27, 136.18, 133.82, 130.08, 130.02, 129.05, 128.23, 125.78, 124.40, 123.23, 122.95, 121.28, 40.09, 31.24, 22.02.

**HRMS (ESI)**: calcd for C_{18}H_{20}N [M]^+ 250.1590; found: 250.1590.

6-(tert-Butyl)-8-methoxy-2-methylphenanthridine (3r)

This compound was obtained according to the general procedure. After
purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), this compound was obtained in (23.0 mg, 0.083 mmol) 55% yield as a yellow solid.

Purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether)

\[ \text{H NMR (500 MHz, CDCl₃):} \delta 8.58 \text{ (d, } J = 9.1 \text{ Hz, 1H)}, 8.22 \text{ (s, 1H)}, 8.04-7.92 \text{ (m, 2H)}, 7.46 \text{ (dd, } J = 8.2, 1.8 \text{ Hz, 1H)}, 7.40 \text{ (dd, } J = 9.1, 2.6 \text{ Hz, 1H)}, 3.99 \text{ (s, 3H)}, 2.60 \text{ (s, 3H)}, 1.74 \text{ (s, 9H).}
\]

\[ \text{C NMR (125 MHz, CDCl₃):} \delta 164.71, 157.15, 140.52, 136.25, 129.97, 129.12, 128.04, 125.55, 124.42, 123.31, 120.78, 118.94, 109.63, 55.47, 39.95, 30.09, 22.01
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M.p. 127 - 129°C.

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6-(But-3-en-1-yl)phenanthridine (3s)

This compound was obtained according to the general procedure. After purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether), this compound was obtained in (21.2 mg, 0.093 mmol) 62% yield as a yellow solid. Purification of the crude material was performed by column chromatography (SiO₂: 1% ethyl acetate in petroleum ether)

\[ \text{H NMR (500 MHz, CDCl₃):} \delta 8.65 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 8.55 \text{ (dd, } J = 8.2, 1.3 \text{ Hz, 1H)}, 8.27 \text{ (dd, } J = 8.1, 1.2 \text{ Hz, 1H)}, 7.87 \text{ (ddd, } J = 8.3, 6.9, 1.3 \text{ Hz, 1H)}, 7.73 \text{ (dddd, } J = 8.2, 7.0, 5.6, 1.3 \text{ Hz, 2H)}, 7.65 \text{ (ddd, } J = 8.3, 7.1, 1.4 \text{ Hz, 1H)}, 6.14-5.95 \text{ (m, 1H)}, 5.15 \text{ (dd, } J = 17.1, 1.7 \text{ Hz, 1H)}, 5.04 \text{ (dd, } J = 10.1, 1.6 \text{ Hz, 1H)}, 3.63-3.36 \text{ (m, 2H)}, 2.89-2.49 \text{ (m, 2H).}
\]

\[ \text{C NMR (125 MHz, CDCl₃):} \delta 161.52, 137.64, 133.19, 131.16, 129.01, 128.70, 127.65, 126.88, 126.53, 124.94, 123.73, 122.65, 122.01, 115.43, 34.76, 33.39
\]


M.p. 110-112°C.
II. Spectral Data for New Compounds
iii. References