Supporting Information

Direct arylation of phenanthroline derivatives via oxidative C–H/C–H cross-coupling: synthesis and discovery of excellent ligands

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz, a Varian Inova 400 MHz or a Bruker AMX-600. The $^1$H NMR (400 MHz or 600 MHz) chemical shifts were measured relative to CDCl$_3$ as the internal reference (CDCl$_3$: $\delta$ = 7.26 ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ as the internal standard (CDCl$_3$: $\delta$ = 77.16 ppm). High resolution mass spectra (HRMS) were recorded by ESI-TOF. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing for at least 24 h over CaH$_2$ (DMF), sodium (THF), and freshly distilled prior to use. All syntheses and manipulations were carried out under N$_2$ atmosphere.

II. Preparation and characterization of starting materials

(1) 6,7-Dihydro-3$^H$-1,4-diazepino[1,2,3,4-imn][1,10]phenanthroline-3,9(5$^H$)-dione (1a)$^1$

1,10-Phenanthroline monohydrate (10.0 g, 50.4 mmol) was dissolved in nitrobenzene (80.0 mL). 1,3-dibromopropane (26.0 mL, 253 mmol, 5.0 equiv) was then slowly added and the mixture was heated to 120 ºC with stirring. During the reaction, a crystalline product precipitated from the reaction mixture. After 4 h, the mixture was allowed to cool to room temperature and the crystalline product was collected by filtration. The mother liquor was concentrated by evaporating the solvent under reduced pressure, producing a second crop of crystalline material. The products were combined, washed with small amounts of toluene, and dried under vacuum for 24 h. The product was then dissolved in water (ca. 50.0 mL), the solution obtained was warmed to 80 ºC, and ethanol (ca. 300.0 mL) was slowly added with stirring until the precipitated material no longer dissolved in the mixture upon heating and stirring.

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The mixture was left to cool overnight and the crystals were collected to yield 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium dibromide (16.9 g, 88%).

\[ \text{[K}_3\text{Fe(CN)}_6 \text{]} \] (123.5 g, 375.0 mmol, 10.0 equiv) was dissolved in water (200.0 mL) and NaOH (56.4 g, 1.4 mol, 34 equiv) was gradually added with stirring. The flask was then placed in an ice/water bath. A solution of 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium dibromide (16.0 g, 41.9 mmol) in water (25.0 mL) was added dropwise, maintaining the temperature in the range 0–5 °C. The mixture was allowed to react for 2 h. It was then neutralised with 4 M HCl to pH 7–8 with simultaneous cooling and concentrated under reduced pressure. The resulting brown solid was crushed and subjected to Soxhlet extraction with refluxing CHCl₃ (4×500 mL). The solvent was evaporated from the combined organic layers to give 5.7 g of a brown crude product, which was adsorbed on silica (40 g) and subjected to chromatography (440 g of silica, prepared in CH₂Cl₂). Gradient elution from CH₂Cl₂ to CH₂Cl₂/2% MeOH gave 1a as pale yellow needles (4.0 g, 38%), multi-gram batches of 1a could be prepared relatively easily. ¹H NMR (400 MHz, CDCl₃): δ = 2.43-2.49 (m, 2H), 4.39 (s, 4H), 6.81 (d, \( J = 9.2 \text{ Hz} \), 2H), 7.37 (s, 2H), 7.72 (d, \( J = 9.6 \text{ Hz} \), 2H) ppm.

(2) 1-methyl-1,10-phenanthrolin-2(1H)-one (1b)

Under a stream of N₂, 1,10-phenanthroline (4.6 g, 25.5 mmol) was dissolved in nitrobenzene (70.0 mL). To the reaction mixture, methyl iodide (9.6 g, 63.8 mmol) was added dropwise at 35 °C for 24 h. The reaction mixture was cooled in an ice bath, filtered out. The resulting solids were sequentially washed with nitrobenzene, benzene, and ethanol, and evaporated under reduced pressure to give 7.4 g (yield: 90%) of the compound 1-methyl-1,10-phenanthrolinium iodide.

To a stirred aqueous solution of potassium ferricyanide (184.4 g, 140 mmol) (H₂O,
224.0 mL), 1-methyl-1,10-phenanthroline iodide (7.4 g, 23 mmol) and an aqueous solution of sodium hydroxide (13.9 g, 346 mmol NaOH was dissolved in 40.0 mL water) were alternately added in an ice bath (0-5 ºC) over 20 minutes. The resulting reaction mixture was stirred at room temperature for 3 h, filtered out. The resulting residue was washed with isopropyl ethyl acetate, and then dried to give 4.7 g (yield: 75%) of the compound 1b. ¹H NMR (400 MHz, CDCl₃): δ = 4.49 (s, 3H), 6.91 (d, J = 9.6 Hz, 1H), 7.48-7.52 (m, 1H), 7.54-7.59 (m, 2H), 7.78 (d, J = 9.2 Hz, 1H), 8.18 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.95 (dd, J = 4.0 Hz, 1.6 Hz, 1H) ppm.

III. Optimization of the oxidative cross-coupling of 6,7-dihydro-3H-1,4-diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione with benzene

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with palladium species (10-20 mol%), the oxidant (3-6 equiv), 1a (63.5 mg, 0.25 mmol), and the additive under N₂ atmosphere. The reaction mixture was stirred for 5 min at room temperature, and then heated at indicated temperature for the indicated time. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel to provide the desired product.

Table S1. Optimization of arylation reaction.ª

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Time (h)</th>
<th>Additive</th>
<th>Oxidant</th>
<th>ratio ³</th>
<th>yield (%)⁴</th>
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<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>24</td>
<td>PivOH</td>
<td>AgOAc</td>
<td>37/16</td>
<td>53</td>
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<tr>
<td>2</td>
<td>Pd(PPh₃)₄</td>
<td>24</td>
<td>PivOH</td>
<td>AgOAc</td>
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<td>43</td>
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<tr>
<td>3</td>
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<td>24</td>
<td>PivOH</td>
<td>AgOAc</td>
<td>30/9</td>
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<tr>
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<td>24</td>
<td>PivOH</td>
<td>AgOAc</td>
<td>32/12</td>
<td>44</td>
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<tr>
<td>5</td>
<td>Pd(acac)₂</td>
<td>24</td>
<td>PivOH</td>
<td>AgOAc</td>
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<td>Reaction</td>
<td>Ratio</td>
<td>Isolated Yield</td>
<td>Comments</td>
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<tr>
<td>6&lt;sup&gt;d&lt;/sup&gt; Pd(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; 24 PivOH AgOAc</td>
<td>32/14</td>
<td>46</td>
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<td>65</td>
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<td>8 - 24 PivOH AgOAc</td>
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<tr>
<td>9 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH AgOAc</td>
<td>43/40</td>
<td>83</td>
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<td>40/47</td>
<td>87</td>
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<td>11 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH Na&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
<td>39/19</td>
<td>58</td>
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<td>12 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH O₂ + TEMPO</td>
<td>-</td>
<td>n.r.</td>
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<td>13 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH Cu(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>trace</td>
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<tr>
<td>14 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH BQ + Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>trace</td>
<td></td>
<td></td>
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<tr>
<td>15 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 TFA Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>40/20</td>
<td>60</td>
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<td>41/17</td>
<td>58</td>
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<tr>
<td>17 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH (DMSO) Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>42/32</td>
<td>74</td>
<td></td>
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<tr>
<td>18&lt;sup&gt;e&lt;/sup&gt; Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>40/39</td>
<td>79</td>
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<tr>
<td>19&lt;sup&gt;f&lt;/sup&gt; Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 48 PivOH Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>32/48</td>
<td>80</td>
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<tr>
<td>20 Pd(TFA)&lt;sub&gt;2&lt;/sub&gt; 96 PivOH Ag&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>26/57</td>
<td>83</td>
<td></td>
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</table>

<sup>a</sup> Reactions were carried out by using 1a (0.25 mmol), [Pd] (20 mol%), oxidant (3.0 equiv), additive (4.0 equiv), in benzene (2a, 2.0 mL, 15–23 mmol, 60–90 equiv) under N<sub>2</sub> at 130 °C.<sup>b</sup> Ratio was determined after isolation and purification by flash silica gel chromatography.<sup>c</sup> Sum of the isolated yields of 3a and 4a.<sup>d</sup> [Pd] (10 mol%).<sup>e</sup> 110 °C.<sup>f</sup> 150 °C. n.r.: no reaction. PivOH = pivalic acid. TFA = trifluoroacetic acid. BQ = benzoquinone. DMSO = dimethyl sulfoxide. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

### IV. General procedure for the oxidative cross-coupling of phenanthroline derivatives with simple arenes

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 1 (0.25 mmol), Pd(TFA)<sub>2</sub> (16.6 mg, 0.05 mmol), Ag<sub>2</sub>CO<sub>3</sub> (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in arenes (2.0 mL, 15–23 mmol, 60–90 equiv). A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N<sub>2</sub>. The reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. The reaction mixture was then cooled to ambient temperature, diluted with 20.0 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (100-200 mesh) to provide the desired product 3.
and 4, respectively.

V. General procedure for the synthesis of unsymmetrical diarylated Phens

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 3 Pd(TFA)$_2$, Ag$_2$CO$_3$, PivOH, in arenes. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N$_2$. The reaction mixture was stirred for 5 min at room temperature, and then heated 130 ºC for 48 h. The reaction mixture was then cooled to ambient temperature, diluted with 20.0 mL of EtOAc, filtered through a celite pad, and washed with 10-20 mL of EtOAc, which was washed with brine. The aqueous layer was extracted with EtOAc and the combined organic layers was dried over anhydrous Na$_2$SO$_4$ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (100-200 mesh) to provide the desired product 5.

VI. General procedure for the preparation 2,9-dichloro-3,8-diaryl-1,10-phenanthrolines

Compound 4 (0.25 mmol) was suspended in POCl$_3$ (1.0 mL) and PCl$_5$ (104.1 mg, 0.5 mmol, 2 equiv) was added. The mixture was degassed and refluxed (120 ºC) under N$_2$ for 12 h. The excess POCl$_3$ was then distilled off under reduced pressure and the remaining material was decomposed with ice. The resulting suspension was neutralised with aqueous ammonia solution (30%) with simultaneous cooling. The brown precipitate was collected and dried under vacuum, and the mother liquor was extracted with CH$_2$Cl$_2$ (2×4 mL). Purification via silica gel column chromatography (Petroleum ether/CH$_2$Cl$_2$/EtOAc = 4/1/0.05-3/1/0.1, v/v/v) afforded the desired product 6.

VII. General procedure for the preparation 3,8-diaryl-1,10-phenanthrolines

A mixture of the 6 (0.25 mmol) in anhydrous THF (4.0 mL) was degassed by bubbling N$_2$ for few minutes. Then, PdCl$_2$(dppf) (18.3 mg, 0.025 mmol, 10 mol %), TMEDA (98.5 mg, 0.85 mmol, 3.4 equiv) and finally NaBH$_4$ (32.1 mg, 0.85 mmol, 3.4 equiv) were introduced in sequence. The mixture was stirred at heated at 70 ºC
under N₂ for 16 h. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried by anhydrous Na₂SO₄, the solvent was evaporated. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product 7.

VIII. General procedure for the preparation 2,3,8,9-tetraaryl-1,10-phenanthrolines

A mixture of the 6 (0.25 mmol) and aryl boronic acid (0.65 mmol, 2.6 equiv), K₂CO₃ (207.3 mg, 1.5 mmol, 6.0 equiv) were dissolved in toluene (2.0 mL)/DMF (2.0 mL). The solution was degassed and then Pd(PPh₃)₄ (28.9 mg, 0.025 mmol, 10 mol%) was rapidly added under a flow of N₂. The mixture was heated at 120 ºC with vigorous stirring for 20 h. It was then allowed to cool to room temperature. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried by anhydrous Na₂SO₄, the solvent was evaporated. Purification via silica gel column chromatography (Petroleum ether/CH₂Cl₂/EtOAc = 4/1/0.05-3/1/0.1, v/v/v) afforded the desired product 8.

IX. General procedure for direct arylation of benzene with aryl halides in the presence of a catalytic amount of Phens.

A mixture of aryl substituted Phen (10 mol% or 20 mol%), potassium t-butoxide (67.3 mg, 0.6 mmol), aryl halides (0.2 mmol) and benzene (2.4 mL, 27 mmol) in a 35 mL oven-dried pressure-resistant tube was stirred at 100 ºC for 24 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product 9.

X. General procedure for the Heck coupling reaction

A mixture of a iodobenzene (168.0 uL, 1.5 mmol), n-butyralcylate (427.5 uL, 3.0 mmol), 2.0×10⁻⁴ mmol/mL Pd(OAc)₂ (0.05 mL, 1.0×10⁻⁵ mmol), 1.0×10⁻⁴ mmol/mL ligand (0.1 mL, 1.0×10⁻⁵ mmol) and K₂CO₃ (414.5 mg, 3.0 mmol) in DMF (2.0 mL)
were allowed to react in a sealed tube at 130 °C for 10 h. After reaction, the volatiles were removed under reduced pressure. The residue was then dispersed in 20.0 mL CH₂Cl₂ and filtered. The organic phase was concentrated and passed through a silica gel column to afford the desired coupling product 10.

**XI. Experimental data for the described substances**

![Chemical structure of 2-Phenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3a)](attachment)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (33 mg, 40% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.50 (t, J = 6.0 Hz, 2H), 4.38 (s, 4H), 6.83 (d, J = 8.8 Hz, 1H), 7.37-7.47 (m, 5H), 7.76 (t, J = 8.4 Hz, 3H), 7.85 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 25.9, 45.9, 46.5, 122.6, 122.9, 123.0, 123.2, 128.4, 128.7, 129.0, 131.6, 132.0, 133.9, 135.9, 136.2, 139.1, 162.0, 162.9 ppm. HRMS (ESI⁺): calcd for C₂₁H₁₇N₂O₂ [M+H]⁺ 329.1290, found 329.1302.

![Chemical structure of 2,10-Diphenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4a)](attachment)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (47 mg, 47% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ
= 2.51-2.57 (m, 2H), 4.45 (s, 4H), 7.40-7.49 (m, 8H), 7.78 (d, J = 7.6 Hz, 4H), 7.87 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 45.5, 121.9, 122.0, 127.5, 127.7, 128.1, 130.4, 132.7, 135.1, 135.3, 161.1 ppm. HRMS (ESI⁺): calcd for C₂₇H₂₁N₂O₂ [M+H]⁺ 405.1603, found 405.1602.

2-(3,4-Dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3b)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 39% yield). M.p.: 224-226 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.32 (s, 3H), 2.34 (s, 3H), 2.49 (t, J = 6.2 Hz, 2H), 4.38 (s, 4H), 6.80 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.35-7.42 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.82 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.8, 20.0, 26.0, 45.9, 46.6, 122.5, 122.86, 122.89, 123.0, 123.3, 126.4, 129.8, 130.2, 131.4, 132.1, 133.5, 134.0, 135.5, 136.6, 137.5, 139.1, 162.1 ppm. HRMS (ESI⁺): calcd for C₂₃H₂₁N₂O₂ [M+H]⁺ 357.1603, found 357.1609.

2,10-Bis(3,4-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4b)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (53 mg, 46% yield). M.p.: 220-222 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.32 (s, 6H), 2.35 (s, 6H), 2.50-2.56 (m, 2H), 4.43 (s, 4H), 7.23 (d, J = 8.0 Hz,
2-(5,6,7,8-Tetrahydronaphthalen-2-yl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3c)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (38 mg, 40% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.84 (t, J = 3.0 Hz, 2H), 2.24-2.31 (m, 2H), 2.76 (t, J = 7.0 Hz, 2H), 2.82-2.85 (m, 2H), 2.98-2.99 (m, 2H), 4.44 (s, 4H), 7.07 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.26-7.28 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.70 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 23.3, 26.0, 27.3, 29.5, 29.6, 45.9, 46.5, 122.5, 122.75, 122.82, 122.9, 123.3, 126.1, 129.2, 129.7, 131.4, 132.0, 133.1, 134.1, 135.5, 137.2, 138.1, 139.1, 162.1, 162.9 ppm. HRMS (ESI⁺): calcd for C₂₅H₂₃N₂O₂ [M+H]⁺ 383.1760, found 383.1754.

2,10-Bis(5,6,7,8-tetrahydronaphthalen-2-yl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4c)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (41 mg, 32% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ
= 1.85 (s, 8H), 2.49-2.56 (m, 2H), 2.82-2.86 (m, 8H), 4.42 (s, 4H), 7.16 (d, \( J = 8.0 \) Hz, 2H), 7.40 (s, 2H), 7.48 (d, \( J = 9.6 \) Hz, 2H), 7.51 (s, 2H), 7.82 (s, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 23.3, 23.4, 26.1, 29.5, 29.7, 46.4, 122.81, 122.83, 126.1, 129.2, 129.7, 131.2, 133.2, 133.7, 135.6, 137.2, 138.0, 162.2 \) ppm. HRMS (ESI\(^{+}\)): calcd for C\(_{35}\)H\(_{33}\)N\(_2\)O\(_2\) [M+H]\(^{+}\) 513.2542, found 513.2365.

2-(3,4-Difluorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3d)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH\(_2\)Cl\(_2\)/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (34 mg, 37% yield). M.p.: 219-221 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 2.47-2.53 \) (m, 2H), 4.38 (s, 4H), 6.82 (dd, \( J = 9.2 \) Hz, 3.2 Hz, 1H), 7.16-7.23 (m, 1H), 7.37-7.43 (m, 3H), 7.50-7.52 (m, 1H), 7.74 (d, \( J = 9.6 \) Hz, 1H), 7.86 (d, \( J = 17.6 \) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 25.8 \) (d, \( J = 3.0 \) Hz), 45.8, 46.6 (d, \( J = 6.0 \) Hz), 117.1, 117.3-117.6 (m), 118.2-118.4 (m), 122.5, 122.8, 122.9-123.1 (m), 123.3, 123.4, 123.9-124.0 (m), 125.2-125.3 (m), 126.36-126.40 (m), 127.9, 131.6, 132.0-132.1 (m), 136.5, 138.9-139.0 (m), 161.1 (d, \( J = 48 \) Hz), 162.8 ppm. HRMS (ESI\(^{+}\)): calcd for C\(_{21}\)H\(_{15}\)F\(_2\)N\(_2\)O\(_2\) [M+H]\(^{+}\) 365.1102, found 365.1104.

2,10-Bis(3,4-difluorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4d)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH\(_2\)Cl\(_2\)/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product
as a yellow solid (35 mg, 29% yield). M.p.: 220-222 °C. $^1$H NMR (400 MHz, CDCl$_3$):
$\delta = 2.54$ (s, 2H), 4.44 (s, 4H), 7.10-7.22 (m, 2H), 7.45 (s, 2H), 7.55-7.57 (m, 2H),
7.69-7.78 (m, 2H), 7.85-7.90 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 25.9$,
46.6 (d, $J = 4.0$ Hz), 117.2-117.6 (m), 118.3, 118.5, 122.5-122.8 (m), 123.0-123.4 (m),
123.9-124.1 (m), 125.2-125.3 (m), 126.40, 131.6-131.9 (m), 136.5, 139.0, 161.2 (d, $J$
= 47 Hz) ppm. HRMS (ESI$^+$): calcd for C$_{27}$H$_{17}$F$_4$N$_2$O$_2$ [M+H]$^+$ 477.1226, found
477.1262.

![Chemical structure of 2-(3,4-Dichlorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3e)]

2-(3,4-Dichlorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3e)

Following the general procedure, the reaction mixture was stirred for 5 min at room
temperature, and then heated at 130 °C for 48 h. Purification via silica gel column
chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product
as a yellow solid (38 mg, 38% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$
= 2.46-2.53 (m, 2H), 4.37 (s, 4H), 6.83 (d, $J = 9.6$ Hz, 1H), 7.38-7.44 (m, 2H), 7.52 (d,
$J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.74 (d, $J = 9.2$ Hz, 1H), 7.86 (s, 1H), 7.91
(s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 25.9$, 45.8, 46.6, 122.8, 123.01,
123.04, 123.2, 123.4, 128.3, 130.3, 130.8, 131.3, 131.8, 132.1, 132.6, 132.8, 135.8,
136.7, 138.9, 161.5, 162.8 ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{15}$Cl$_2$N$_2$O$_2$ [M+H]$^+$
397.0511, found 397.0541.

![Chemical structure of 2,10-Bis(3,4-dichlorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4e)]

2,10-Bis(3,4-dichlorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4e)

Following the general procedure, the reaction mixture was stirred for 5 min at room
temperature, and then heated at 130 °C for 48 h. Purification via silica gel column
chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 26% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.50-2.57 (m, 2H), 4.43 (s, 4H), 7.46 (s, 2H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.66 (d, $J$ = 8.0 Hz, 2H), 7.88 (s, 2H), 7.93 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 25.9, 46.6, 122.8, 123.4, 128.4, 130.4, 130.9, 131.4, 131.6, 132.7, 132.9, 135.8, 136.6, 161.5 ppm. HRMS (ESI$^+$): calcd for C$_{27}$H$_{17}$Cl$_4$N$_2$O$_2$ [M+H]$^+$ 543.0015, found 543.0053.

![Chemical Structure](image)

2-(3,5-Dimethylphenyl)-6,7-dihydro-3$H$-[1,4]diazepino[1,2,3,4-$lmn$][1,10]phenanthroline-3,9(5$H$)-dione (3f)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (32 mg, 36% yield). M.p.: 203-205 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.39 (s, 6H), 2.46-2.53 (m, 2H), 4.37 (s, 4H), 6.80 (d, $J$ = 9.6 Hz, 1H), 7.06 (s, 1H), 7.35-7.42 (m, 4H), 7.72 (d, $J$ = 9.6 Hz, 1H), 7.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.5, 26.0, 45.9, 46.5, 122.6, 122.8, 122.86, 122.94, 123.3, 126.8, 130.5, 131.5, 132.0, 134.3, 135.8, 136.0, 137.9, 139.1, 162.1, 162.9 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 357.1603, found 357.1618.

![Chemical Structure](image)

2,10-Bis(3,5-dimethylphenyl)-6,7-dihydro-3$H$-[1,4]diazepino[1,2,3,4-$lmn$][1,10]phenanthroline-3,9(5$H$)-dione (4f)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product.
as a yellow solid (44 mg, 38% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.40 (s, 12H), 2.51 (t, $J = 6.4$ Hz, 2H), 4.43 (s, 4H), 7.06 (s, 2H), 7.38 (s, 4H), 7.42 (s, 2H), 7.83 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 21.5, 26.0, 46.5, 122.8, 122.9, 126.8, 130.4, 131.3, 133.9, 136.0, 136.1, 137.9, 162.1 ppm. HRMS (ESI$^+$): calcd for C$_{31}$H$_{29}$N$_2$O$_2$ [M+H]$^+$ 461.2229, found 461.2241.

2-(4-Chloro-3,5-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (3g)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (36 mg, 37% yield). M.p.: 200-202 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.45 (s, 6H), 2.50 (t, $J = 6.4$ Hz, 2H), 4.37 (s, 4H), 6.82 (d, $J = 9.6$ Hz, 1H), 7.37-7.43 (m, 2H), 7.49 (s, 2H), 7.73 (d, $J = 9.6$ Hz, 1H), 7.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 21.0, 25.9, 45.8, 46.6, 122.7, 122.9, 123.0, 123.08, 123.13, 129.0, 131.5, 132.1, 133.1, 133.7, 135.4, 136.0, 136.3, 139.0, 161.9, 162.9 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{20}$ClN$_2$O$_2$ [M+H]$^+$ 391.1213, found 391.1214.

2,10-Bis(4-chloro-3,5-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4g)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (57 mg, 43% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.45 (s, 12H), 2.50-2.56 (m, 2H), 4.42 (s, 4H), 7.43 (s, 2H), 7.50 (s, 4H), 7.83 (s,
2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.0, 26.0, 46.5, 122.8, 123.0, 128.9, 131.3, 132.9, 133.8, 135.3, 136.1, 136.3, 161.9 ppm. HRMS (ESI$^+$): calcd for C$_{31}$H$_{27}$Cl$_2$N$_2$O$_2$ [M+H]$^+$ 529.1450, found 529.1453.

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (33 mg, 37% yield). M.p.: 158-160 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.24 (s, 3H), 2.35 (s, 3H), 2.46-2.52 (m, 2H), 4.38 (s, 4H), 6.85 (d, $J$ = 9.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.39 (s, 2H), 7.67 (s, 1H), 7.75 (d, $J$ = 9.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.7, 21.0, 25.9, 45.9, 46.4, 122.6, 122.8, 122.9, 123.0, 129.4, 130.3, 130.4, 131.9, 132.1, 133.8, 135.3, 135.8, 135.9, 137.6, 139.0, 161.8, 162.9 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 357.1603, found 357.1608.

2-(2,5-Dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-]lmn][1,10]phenanthroline-3,9(5H)-dione (3h)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (33 mg, 37% yield). M.p.: 158-160 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.24 (s, 3H), 2.35 (s, 3H), 2.46-2.52 (m, 2H), 4.38 (s, 4H), 6.85 (d, $J$ = 9.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.39 (s, 2H), 7.67 (s, 1H), 7.75 (d, $J$ = 9.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.7, 21.0, 25.9, 45.9, 46.4, 122.6, 122.8, 122.9, 123.0, 129.4, 130.3, 130.4, 131.9, 132.1, 133.8, 135.3, 135.8, 135.9, 137.6, 139.0, 161.8, 162.9 ppm. HRMS (ESI$^+$): calcd for C$_{23}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 357.1603, found 357.1608.

2,10-Bis(2,5-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-]lmn][1,10]phenanthroline-3,9(5H)-dione (4h)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (31 mg, 27% yield). M.p.: 98-100 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.25 (s, 6H), 2.36 (s, 6H), 2.51 (t, $J$ = 6.4 Hz, 2H), 4.44 (s, 4H), 7.13 (d, $J$ = 9.6 Hz, 4H), 7.19 (d, $J$ = 7.6 Hz, 2H), 7.40 (s, 2H), 7.69 (s, 2H) ppm. $^{13}$C NMR (100
Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a yellow solid (38 mg, 42% yield). M.p.: 219-221 °C. $^1$H NMR (400 MHz, CDCl$_3$): \( \delta = 2.46-2.53 \) (m, 2H), \( 4.38 \) (s, 4H), \( 6.84 \) (d, \( J = 9.2 \) Hz, 1H), \( 7.07-7.17 \) (m, 2H), \( 7.36-7.41 \) (m, 3H), \( 7.74 \) (d, \( J = 9.2 \) Hz, 1H), \( 7.89 \) (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): \( \delta = 25.8, 46.0, 46.6, 116.7-118.4 \) (m), \( 121.4, 122.3, 122.7, 123.1, 124.1, 128.1, 132.1, 132.3, 138.89, 138.92, 144.4, 155.1, 156.7, 157.3, 157.6, 161.1, 161.9 \) ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{15}$F$_2$N$_2$O$_2$ [M+H]$^+$ 365.1102, found 365.1105.

2,10-Bis(2,5-difluorophenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (4i)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (35 mg, 29% yield). M.p.: 230-232 °C. $^1$H NMR (400 MHz, CDCl$_3$): \( \delta = 2.51-2.57 \) (m, 2H), \( 4.44 \) (s, 4H), \( 7.06-7.17 \) (m, 4H), \( 7.40 \) (s, 2H), \( 7.45 \) (s, 2H), \( 7.92 \) (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): \( \delta = 25.9, 46.6, 116.7-117.2 \) (m), \( 118.1-118.4 \) (m), \( 122.7, 123.4, 124.7-125.0 \) (m), \( 127.9, 131.9, 139.0 \) (d, \( J = 4.0 \) Hz), \( 157.6, 158.7, 159.0, 161.1, 161.9 \) ppm. HRMS (ESI$^+$): calcd for C$_{21}$H$_{15}$F$_2$N$_2$O$_2$ [M+H]$^+$ 365.1102, found 365.1105.
1-Methyl-3-phenyl-1,10-phenanthroline-2(1H)-one (3j)

Following the general procedure, the reaction mixture was stirred for 5 min at room temperature, and then heated at 100 °C for 48 h. Purification via silica gel column chromatography (Petroleum ether/CH₂Cl₂/EtOAc = 30/10/1, v/v/v) afforded the desired product as a yellow solid (45 mg, 63% yield). M.p.: 145-147 °C. ¹H NMR (400 MHz, CDCl₃): δ = 4.56 (s, 3H), 7.40 (t, J = 7.2 Hz, 1H), 7.45-7.53 (m, 3H), 7.58 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.94 (s, 1H), 8.20 (dd, J = 8.0, 1.2 Hz, 1H), 8.97 (d, J = 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 38.6, 120.7, 121.9, 122.6, 127.1, 128.4, 129.1, 130.2, 132.9, 136.3, 136.8, 137.0, 137.5, 140.3, 147.4 ppm. HRMS (ESI⁺): calcd for C₁₉H₁₅N₂O [M+H]⁺ 287.1184, found 287.1183.

2-(3,4-Dimethylphenyl)-10-phenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-3,9(5H)-dione (5a)

Following the general procedure, 3b (89.0 mg, 0.25 mmol), Pd(TFA)₂ (16.6 mg, 0.05 mmol), Ag₂CO₃ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in benzene (2.0 mL, 22 mmol, 88 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (73 mg, 68% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.33 (s, 3H), 2.35 (s, 3H), 2.50-2.57 (m, 2H), 4.44 (s, 4H), 7.23 (d, J = 7.6 Hz, 1H), 7.42-7.43 (m, 3H), 7.45-7.52 (m, 3H), 7.59 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.83 (s,
1H), 7.86 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.7, 19.0, 25.0, 45.39, 45.40, 121.6, 121.9, 122.0, 125.4, 127.4, 127.6, 128.0, 128.7, 129.1, 130.2, 130.3, 132.4, 132.6, 132.7, 134.6, 135.1, 135.3, 135.5, 136.4, 161.0, 161.1 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 433.1916, found 433.1930.

2-(2,5-Difluorophenyl)-10-phenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-]lmn][1,10]phenanthroline-3,9(5H)-dione (5b)

Following the general procedure, 3i (36.4 mg, 0.1 mmol), Pd(TFA)$_2$ (6.6 mg, 0.02 mmol), Ag$_2$CO$_3$ (82.7 mg, 0.3 mmol), PivOH (40.8 mg, 0.4 mmol), in benzeen (1.0 mL, 11 mmol, 110 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (29.5 mg, 67% yield). M.p.: 226-228 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.51-2.57$ (m, 2H), 4.45 (s, 4H), 7.05-7.08 (m, 1H), 7.10-7.18 (m, 1H), 7.38-7.49 (m, 6H), 7.79 (d, $J = 7.2$ Hz, 2H), 7.87 (s, 1H), 7.91 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 26.0, 46.5, 46.6, 116.6, 116.7, 116.8-116.9$ (m), 117.1, 117.2, 118.1 (d, $J = 3.0$ Hz), 118.40 (d, $J = 3.0$ Hz), 122.2, 123.72 (d, $J = 4.0$ Hz), 123.4, 127.5, 128.5, 129.1, 131.5, 131.9, 134.1, 136.0, 136.2, 139.2 (d, $J = 4.0$ Hz), 161.2, 162.0 ppm. HRMS (ESI$^+$): calcd for C$_{27}$H$_{19}$F$_2$N$_2$O$_2$ [M+H]$^+$ 441.1415, found 441.1452.

2-(2,5-Difluorophenyl)-10-(3,4-dimethylphenyl)-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-]lmn][1,10]phenanthroline-3,9(5H)-dione (5c)

Following the general procedure, 3i (91 mg, 0.25 mmol), Pd(TFA)$_2$ (16.6 mg, 0.05 mmol), Ag$_2$CO$_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in
1,2-dimethylbenzene (2.0 mL, 16.6 mmol, 66 equiv). The reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (70 mg, 60% yield). M.p.: 106-108 °C. 

¹H NMR (400 MHz, CDCl₃): δ = 2.33 (s, 3H), 2.35 (s, 3H), 2.49-2.56 (m, 2H), 4.44 (s, 4H), 7.05-7.18 (m, 3H), 7.24 (d, J = 8.0 Hz, 1H), 7.39-7.43 (m, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.84 (s, 1H), 7.90 (s, 1H) ppm. 

¹³C NMR (100 MHz, CDCl₃, except for C-F carbons because of the low solubility of 6c in CDCl₃): δ = 19.8, 20.0, 29.8, 46.4, 46.6, 116.8-117.0 (m), 117.1 (d, J = 2.0 Hz), 117.2 (d, J = 2.0 Hz), 118.0, 118.1 (d, J = 3.0 Hz), 118.4 (d, J = 3.0 Hz), 122.0, 123.1 (d, J = 4.0 Hz), 123.5, 126.5, 127.3, 129.8, 130.2, 131.3, 131.8, 133.5, 134.2, 135.5, 136.6, 137.6, 139.18, 139.22, 161.2, 162.1 ppm. HRMS (ESI⁺): calcd for C₂₉H₂₃F₂N₂O₂ [M+H]⁺ 469.1728, found 469.1727.

![Chemical Structure](image)

2-(3,5-Dimethylphenyl)-10-phenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-lmn][1, 10]phenanthroline-3,9(5H)-dione (5d)

Following the general procedure, 3f (35.6 mg, 0.1 mmol), Pd(TFA)₂ (6.6 mg, 0.02 mmol), Ag₂CO₃ (82.7 mg, 0.3 mmol), PivOH (40.8 mg, 0.4 mmol), in benzeen (1.0 mL, 11 mmol, 110 equiv). The reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (28 mg, 65% yield). M.p.: >119-121 °C. 

¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 6H), 2.50-2.57 (m, 2H), 4.44 (s, 4H), 7.06 (s, 1H), 7.39 (s, 2H), 7.41-7.42 (m, 3H), 7.47 (t, J = 7.2 Hz, 2H), 7.78 (d, J = 6.8 Hz, 2H), 7.84 (s, 1H), 7.86 (s, 1H) ppm. 

¹³C NMR (100 MHz, CDCl₃): δ = 21.5, 26.0, 46.4, 122.7, 122.91, 122.94, 126.8, 128.4, 128.7, 129.1, 129.8, 130.4, 131.3, 131.4, 133.6, 134.0, 135.9, 136.06, 136.09, 136.3, 137.9, 162.0, 162.1 ppm. HRMS (ESI⁺): calcd for C₂₉H₂₅N₂O₂...
2-(2,5-Dimethylphenyl)-10-phenyl-6,7-dihydro-3H-[1,4]diazepino[1,2,3,4-\textit{lmn}][1,10]phenanthroline-3,9(5H)-dione (5e)

Following the general procedure, 3h (89.0 mg, 0.25 mmol), Pd(TFA)$_2$ (16.6 mg, 0.05 mmol), Ag$_2$CO$_3$ (206.8 mg, 0.75 mmol), PivOH (102.1 mg, 1 mmol), in benzeen (2.0 mL, 22 mmol, 88 equiv). the reaction mixture was stirred for 5 min at room temperature, and then heated at 130 °C for 48 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (76.7 mg, 71% yield). M.p.:170-172 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.26 (s, 3H), 2.36 (s, 3H), 2.50-2.56 (m, 2H), 4.44 (s, 4H), 7.13 (d, $J$ = 9.6 Hz, 2H), 7.19 (d, $J$ = 7.6 Hz, 1H), 7.38-7.49 (m, 5H), 7.69 (s, 1H), 7.79 (d, $J$ = 7.2 Hz, 2H), 7.88 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.7, 21.1, 26.1, 46.4, 46.5, 122.6, 122.85, 122.90, 122.93, 128.4, 128.7, 129.1, 129.4, 130.3, 130.5, 131.5, 131.7, 133.7, 133.9, 135.3, 135.6, 136.0, 136.1, 136.3, 137.7, 161.9, 162.1 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 433.1916, found 433.1930 ppm.

2,9-Dichloro-3,8-diphenyl-1,10-phenanthroline (6a)

Following the general procedure, the mixture was degassed and refluxed (120 °C) under N$_2$ for 12 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (76 mg, 76% yield). M.p.: 233-235 °C. $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ = 7.49-7.55 (m, 6H), 7.60 (d, $J$ = 7.2 Hz, 4H), 7.86 (s, 2H), 8.22 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 126.7, 128.1, 128.5, 128.7, 129.8, 137.4, 139.1, 143.7, 150.8 ppm. HRMS (ESI$^+$): calcd for C$_{24}$H$_{15}$Cl$_2$N$_2$ [M+H]$^+$ 401.0612, found 401.0644.
2,9-Dichloro-3,8-bis(3,4-dimethylphenyl)-1,10-phenanthroline (6b)

Following the general procedure, compound 4b (130 mg, 0.28 mmol) was suspended in POCl₃ (1.1 mL) and PCl₅ (116.6 mg, 0.56 mmol, 2.0 equiv) was added. The mixture was degassed and refluxed (120 °C) under N₂ for 12 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (93 mg, 73% yield). M.p.: 240-242 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.27 (s, 12H), 7.18 (d, J = 9.2 Hz, 4H), 7.24 (s, 2H), 7.74 (s, 2H), 8.09 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.8, 20.0, 126.6, 127.2, 128.1, 129.8, 130.8, 134.9, 136.9, 137.4, 138.9, 143.6, 150.9 ppm. HRMS (ESI⁺): calcd for C₂₈H₂₃Cl₂N₂ [M+H]⁺ 457.1238, found 457.1241.

2,9-Dichloro-3,8-bis(2,5-difluorophenyl)-1,10-phenanthroline (6c)

Following the general procedure, compound 4i (140 mg, 0.29 mmol) was suspended in POCl₃ (1.2 mL) and PCl₅ (120.7 mg, 0.58 mmol, 2.0 equiv) was added. The mixture was degassed and refluxed (120 °C) under N₂ for 12 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (94 mg, 69% yield). M.p.: 240-242 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.27 (s, 12H), 7.18 (d, J = 9.2 Hz, 4H), 7.24 (s, 2H), 7.74 (s, 2H), 8.09 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃, except for C-F carbons because of the low solubility of 6c in CDCl₃): δ = 117.2-118.3 (m), 125.8, 126.4, 127.7, 130.5, 131.6, 137.3, 139.0, 143.4, 144.7, 151.5, 152.3 ppm. HRMS (ESI⁺): calcd for C₂₄H₁₁Cl₂F₄N₂ [M+H]⁺ 473.0235, found 473.0263.
3,8-Diphenyl-1,10-phenanthroline (7a)

Following the general procedure, the mixture was stirred at heated at 70 °C under N₂ for 16 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a white solid (71 mg, 86% yield). M.p.: 189-191 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (t, J = 7.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 4H), 7.78 (d, J = 7.2 Hz, 4H), 7.86 (s, 2H), 8.38 (d, J = 2.4 Hz, 2H), 9.44 (d, J = 2.4 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 127.2, 127.7, 128.5, 128.6, 129.4, 133.5, 135.9, 137.7, 145.3, 149.7 ppm. HRMS (ESI⁺): calcd for C₂₄H₁₇N₂ [M+H]⁺ 333.1392, found 333.1390.

![chemical structure of 7a](image)

3,8-Bis(3,4-dimethylphenyl)-1,10-phenanthroline (7b)

Following the general procedure, the mixture was stirred at heated at 70 °C under N₂ for 16 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 10/1/1, v/v/v) afforded the desired product as a white solid (82 mg, 85% yield). M.p.: 140-142 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.35 (s, 6H), 2.39 (s, 6H), 7.31 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.56 (s, 2H), 7.95 (s, 2H), 8.51 (s, 2H), 9.55 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.7, 20.1, 125.0, 127.5, 128.5, 129.0, 130.9, 134.0, 134.6, 136.8, 137.99, 138.01, 148.6 ppm. HRMS (ESI⁺): calcd for C₂₈H₂₅N₂ [M+H]⁺ 389.2018, found 389.2011.

![chemical structure of 7b](image)

2,3,8,9-Tetraphenyl-1,10-phenanthroline (8a)

Following the general procedure, the mixture was heated at 120 °C with vigorous stirring for 20 h. Purification via silica gel column chromatography (CH₂Cl₂/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a white solid (111 mg, 92% yield). M.p.: 212-214 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.27 (s, 6H),
7.33 (s, 10H), 7.61 (d, J = 6.8 Hz, 4H), 7.89 (s, 2H), 8.31 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 126.8, 127.6, 127.9, 128.1, 128.3, 128.6, 129.9, 130.8, 136.3, 138.5, 140.0, 144.4, 157.8 ppm. HRMS (ESI$^+$): calcd for C$_{36}$H$_{25}$N$_2$ [M+H]$^+$ 485.2018, found 485.2029.

3,8-Bis(3,4-dimethylphenyl)-2,9-diphenyl-1,10-phenanthroline (8b)

Following the general procedure, the mixture was heated at 120 ºC with vigorous stirring for 20 h. Purification via silica gel column chromatography (CH$_2$Cl$_2$/EtOAc/acetone = 20/1/1, v/v/v) afforded the desired product as a yellow solid (126 mg, 93% yield). M.p.: 124-126 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.22 (s, 6H), 2.26 (s, 6H), 6.90 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 7.06-7.09 (m, 6H), 7.17 (t, J = 7.2 Hz, 2H), 7.40 (d, J = 4.4 Hz, 4H), 7.91 (d, J = 6.0 Hz, 2H), 8.31 (d, J = 7.2 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.6, 19.9, 126.9, 127.3, 127.7, 128.2, 128.3, 129.7, 130.4, 130.9, 136.2, 136.3, 136.66, 136.72, 136.8, 136.9, 138.8, 157.4 ppm. HRMS (ESI$^+$): calcd for C$_{40}$H$_{33}$N$_2$[M+H]$^+$ 541.2644, found 541.2642.

Biphenyl (9a)

Following the general procedure, the mixture was stirred at heated at 100 ºC for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a white solid (28.6 mg, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.43 (t, J = 6.8 Hz, 2H), 7.53 (t, J = 7.2 Hz, 4H), 7.69 (d, J = 7.6 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 127.3, 127.4, 128.9, 141.4 ppm.
4-Methoxybiphenyl (9b)
Following the general procedure, the mixture was stirred at heated at 100 °C for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as a white solid (34.2 mg, 93% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 3.86\) (s, 3H), 6.99 (d, \(J = 8.4\) Hz, 2H), 7.31 (t, \(J = 7.4\) Hz, 1H), 7.43 (t, \(J = 7.6\) Hz, 2H), 7.55 (t, \(J = 8.4\) Hz, 4H) ppm.

![Image of 4-Methoxybiphenyl (9b)](MeO)

3-Methoxybiphenyl (9c)
Following the general procedure, the mixture was stirred at heated at 100 °C for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as yellow oil (32.7 mg, 89% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 3.89\) (s, 3H), 6.93 (d, \(J = 8.0\) Hz, 1H), 7.16 (s, 1H), 7.21 (d, \(J = 8.0\) Hz, 1H), 7.36-7.40 (m, 2H), 7.46 (t, \(J = 7.6\) Hz, 2H), 7.62 (d, \(J = 7.6\) Hz, 2H) ppm.

![Image of 3-Methoxybiphenyl (9c)](OMe)

2-Methoxybiphenyl (9d)
Following the general procedure, the mixture was stirred at heated at 100 °C for 24 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as colorless oil (30.5 mg, 83% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 3.82\) (s, 3H), 6.99-7.06 (m, 2H), 7.34 (m, 3H), 7.42 (t, \(J = 7.6\) Hz, 2H), 7.54 (d, \(J = 7.6\) Hz, 2H) ppm.

![Image of 2-Methoxybiphenyl (9d)](O)

\(n\)-Butyl cinnamate (10a)
A mixture of a iodobenzene (168.0 ul, 1.5 mmol), \(n\)-butylacrylate (427.5 ul, 3.0 mmol), 2.0\times10^{-4} mmol/mL Pd(OAc)\(_2\) (0.05 mL, 1.0\times10^{-5} mmol), 1.0\times10^{-4} mmol/mL 2,3,8,9-Tetraphenyl-1,10-phenanthroline (0.1 mL, 1.0\times10^{-5} mmol) and K\(_2\)CO\(_3\) (414.5...
mg, 3.0 mmol) in DMF (2.0 mL) were allowed to react in a sealed tube at 130 °C for 10 h. Purification via silica gel column chromatography (Petroleum ether/EtOAc = 20/1, v/v) afforded the desired product as colorless liquid. (302.9 mg, 99% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.97 (t, $J = 7.4$ Hz, 3H), 1.40-1.47 (m, 2H), 1.66-1.73 (m, 2H), 4.21 (t, $J = 6.6$ Hz, 2H), 6.45 (d, $J = 16.0$ Hz, 1H), 7.38 (m, 3H), 7.53 (m, 2H), 7.69 (d, $J = 16.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.9, 19.3, 30.9, 64.6, 118.4, 128.2, 129.0, 130.3, 134.6, 144.7, 167.2 ppm.

XII. References


XIII. Copies of NMR spectra
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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