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A mild and efficient method for the synthesis of 8,9-dihydro-11-aryl-7H-cyclopenta $[b][4,7]$ phenanthrolin-10 $(11 H)$-one derivatives via three-component reaction of aromatic aldehyde, quinolin-6-amine and cyclopentane-1,3-dione is described catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$. The features of this procedure are mild reaction conditions, good to high yields, and operational simplicity.
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## INTRODUCTION

Over the past few years, $\mathrm{Yb}(\mathrm{OTf})_{3}$ has emerged as a powerful catalyst for various organic transformations to afford the products in good to excellent yields. Owing to several advantages such as inexpensive, nontoxic, ecofriendly nature, $\mathrm{Yb}(\mathrm{OTf})_{3}$ has been used as a catalyst in the investigation of different organic reactions [1].

Phenanthrolines are important core structures found in a variety of biologically important molecules [2]. It is reported that metallic complexes possess a wide range of biological activities, which confer applications as anticancer [3], antiinflammatory [4], antitumor [5], antimicrobial [6], and antibacterial agents [7]. Therefore, much attention is devoted to the synthesis of these active frameworks in recent years [8].

To the best of our knowledge, there is no report concerning the synthesis of cyclopenta $[b][4,7]$ phenanthrolin$10(11 H)$-one derivatives. Such variations may contribute to the bioactivity differences and enrich the phenanthroline library for biomedical screening. As a continuation of our research devoted to the development of new methods for the preparation of heterocycles catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$ [9], herein, we would like to synthesize of 8,9 -dihydro-11-aryl-7H-cyclopenta[b][4,7] phenanthrolin-10(11H)-one by a reaction of aromatic aldehyde, quinolin-6-amine, and cyclopentane-1,3-dione catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$.

## RESULTS AND DISCUSSION

Treatment of aromatic aldehyde, quinolin-6-amine, and cyclopentane-1,3-dione in reflux THF in the presence
of $1 \mathrm{~mol} \% \mathrm{Yb}(\mathrm{OTf})_{3}$, afforded the corresponding 8,9-dihydro-11-aryl-7 H -cyclopenta $[b][4,7]$ phenanthrolin-10 $(11 H)$-one derivatives 4 in good to high yields (Scheme 1).

Using the conversion of 2-fulorobenzaldehyde 1a, quinolin-6-amine and cyclopentane-1,3-dione as a model, several parameters were explored as shown in Table 1. The yield of $\mathbf{4 a}$ was moderate at reflux in the absence of $\mathrm{Yb}(\mathrm{OTf})_{3}(62 \%$, Table 1, entry 1) and much greater in the presence of various quantities of the catalyst, reaching a maximum of $87 \%$ yield with $1 \mathrm{~mol} \% \mathrm{Yb}$ $(\mathrm{OTf})_{3}$ (Table 1, entries 2-11). The yield of 4a was also dependent on temperature (entries 2,5 , and 6 ), proceeding smoothly at reflux. Different solvents were also tested and THF appeared to be the best medium for this transformation (entry 2 vs . 13-14).

This process can tolerate both electron-donating (alkyl and alkoxy) and electron-withdrawing (halogen) substituents on the aromatic aldehydes (Table 2). In all cases, the reactions proceeded efficiently in THF at reflux to afford the corresponding 7 H -cyclopenta[b] [4,7]phenanthrolin- $10(11 H)$-one 4a-l in high yields. All the compounds were characterized by ${ }^{1} \mathrm{H}$ NMR, IR, and HRMS.

The formation of $\mathbf{4}$ is likely to proceed via initial condensation of aldehyde $\mathbf{1}$ with cyclopentane-1,3-dione 2 to afford 2-benzylidenecyclopentane-1,3-dione 5, which further undergoes Michael addition with quinolin-6-amine 3 to furnish 6. Intramolecular nucleophilic reaction of its isomer 7 could afford the compound 8 , which could eliminate one molecule of $\mathrm{H}_{2} \mathrm{O}$ to afford title product 4 (Scheme 2). The role of the catalyst $\mathrm{Yb}(\mathrm{OTf})_{3}$ is activating the carbonyl groups in intermediate products 5 and 7.

Scheme 1. The reaction of $\mathbf{1 , 2}$, and $\mathbf{3}$ catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$.


Table 1
Synthesis of $\mathbf{4 a}$ at different reaction conditions. ${ }^{\text {a }}$

| Entry | $T\left({ }^{\circ} \mathrm{C}\right)$ | Solvent | Cat. $(\mathrm{mol} \%)$ | Yield $^{\mathrm{b}}(\%)$ |
| :--- | :---: | :---: | :---: | :---: |
| 1 | Reflux | THF | 0 | 62 |
| 2 | Reflux | THF | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | 87 |
| 3 | Reflux | THF | $\mathrm{Yb}(\mathrm{OTf})_{3}(5)$ | 86 |
| 4 | Reflux | THF | $\mathrm{Yb}(\mathrm{OTf})_{3}(10)$ | 87 |
| 5 | r.t | THF | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | Trace |
| 6 | 50 | THF | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | 73 |
| 7 | Reflux | THF | $\mathrm{AgOTf}(1)$ | 83 |
| 8 | Reflux | THF | $\mathrm{Cu}(\mathrm{OTf})_{2}(1)$ | 80 |
| 9 | Reflux | THF | $\mathrm{Zn}(\mathrm{OTf})_{2}(1)$ | 78 |
| 10 | Reflux | THF | $\mathrm{Y}(\mathrm{OTf})_{3}(1)$ | 85 |
| 11 | Reflux | THF | $\mathrm{Fe}(\mathrm{OTf})_{2}(1)$ | 79 |
| 12 | Reflux | $\mathrm{CH} \mathrm{H}_{3} \mathrm{CN}$ | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | 85 |
| 13 | Reflux | Benzene | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | 84 |
| 14 | 80 | DMF | $\mathrm{Yb}(\mathrm{OTf})_{3}(1)$ | 80 |

${ }^{\text {a }}$ Reaction condition: 10 mL solvent, 2-fluorobenzaldehyde ( 0.248 g , 2.0 mmol ), quinolin- 6 -amine ( $0.288 \mathrm{~g}, 2.0 \mathrm{mmol}$ ), cyclopentane-1,3dione ( $0.196 \mathrm{~g}, 2.0 \mathrm{mmol}$ ).
${ }^{\mathrm{b}}$ Isolated yields.

Table 2
Synthetic results of $\mathbf{4}$ in THF catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}{ }^{\text {a }}{ }^{\text {a }}$

| Entry | Ar | Products | Time <br> (h) | Isolated Yields <br> $(\%)$ |
| :--- | :---: | :---: | :---: | :---: |
| 1 | $2-\mathrm{FC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 a}$ | 12 | 87 |
| 2 | $2-\mathrm{ClC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 b}$ | 12 | 88 |
| 3 | $4-\mathrm{ClC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 c}$ | 14 | 92 |
| 4 | $3-\mathrm{BrC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 d}$ | 14 | 82 |
| 5 | $4-\mathrm{BrC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 e}$ | 16 | 86 |
| 6 | $4-\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4}$ | $\mathbf{4 f}$ | 16 | 90 |
| 7 | $3-\mathrm{CH}_{3} \mathrm{OC}_{6} \mathrm{H}_{4}$ | $\mathbf{4 g}$ | 16 | 92 |
| 8 | $3,4-\mathrm{Cl}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ | $\mathbf{4 h}$ | 10 | 86 |
| 9 | $3,4-\left(\mathrm{CH}_{3}\right)$ | $\mathbf{4 i}$ | 16 | 83 |
| 10 | $2 \mathrm{C}_{6} \mathrm{H}_{3}$ |  | $4,4-$ | $\mathbf{4 j}$ |
|  | 3,46 | 86 |  |  |
| 11 | $\mathrm{OCH}_{2} \mathrm{OC}_{6} \mathrm{H}_{3}$ |  | 16 |  |
| 12 | $2,3-\mathrm{Cl}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ | $\mathbf{4 k}$ | 12 | 90 |

${ }^{\mathrm{a}}$ Reagents and conditions: $\mathbf{1}(2.0 \mathrm{mmol}), \mathbf{2}(0.288 \mathrm{~g}, 2.0 \mathrm{mmol}), \mathbf{3}$ $(0.196 \mathrm{~g}, 2.0 \mathrm{mmol})$, THF $(10 \mathrm{~mL}) . \mathrm{Yb}(\mathrm{OTf})_{3}(0.012 \mathrm{~g}, 0.02 \mathrm{mmol})$.

## CONCLUSION

In conclusion, we found a mild and efficient method for the synthesis of 11 -aryl- 7 H -cyclopenta $[b][4,7]$ phenanthrolin-

Scheme 2. Reaction mechanism of $\mathbf{1 , 2}$, and $\mathbf{3}$ catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$.



3
6

$10(11 \mathrm{H})$-one derivatives via three-component reaction of aromatic aldehyde, quinolin-6-amine, and cyclopentane-1,3dione catalyzed by $\mathrm{Yb}(\mathrm{OTf})_{3}$. The features of this procedure are mild reaction conditions, good to high yields, and operational simplicity.

## EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr pellet. ${ }^{1} \mathrm{H}$ NMR spectra was obtained from a solution in DMSO- $d_{6}$ with $\mathrm{Me}_{4} \mathrm{Si}$ as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyzer.

General procedure for the synthesis of $\mathbf{7 H}$-cyclopenta [b][4,7]phenanthrolin- $\mathbf{1 0}(\mathbf{1 1 H})$-one derivatives 4 . A dry $50-\mathrm{mL}$-flask was charged with aromatic aldehyde ( 2.0 mmol ), quinolin-6-amine ( $2.0 \mathrm{mmol}, 0.288 \mathrm{~g}$ ), and cyclopentane-1,3dione ( $2.0 \mathrm{mmol}, 0.196 \mathrm{~g}$ ), THF $(10 \mathrm{~mL})$ and $\mathrm{Yb}(\mathrm{OTf})_{3}(0.02$ $\mathrm{mmol}, 0.012 \mathrm{~g}$ ). The reaction mixture was stirred at reflux for $12-16 \mathrm{~h}$, after completion of the reaction as indicated by TLC, another portion of THF was added to the mixture until all the yellow solid was dissolved. The desired products 4 were obtained as yellow powder by filtration, when the mixture was cooled to room temperature.

11-(2-Fluorophenyl)-8,9-dihydro-7H-cyclopenta[b][4,7]phe-nanthrolin-10(11H)-one 4a. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400 \mathrm{MHz}$ ): $\delta_{\mathrm{H}}$ 2.21-2.32 (m, 2H, CH $)_{2}$, 2.67-2.76 (m, 2H, CH2), $5.81(\mathrm{~s}, 1 \mathrm{H}$, CH), $6.90-7.19(\mathrm{~m}, 4 \mathrm{H}, ~ \mathrm{ArH}), 7.41(\mathrm{~s}, 1 \mathrm{H}, ~ A r H), 7.50$ (d, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.90(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.18$ (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $8.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 10.50(\mathrm{~s}, 1 \mathrm{H}$, NH). IR (KBr): v $3242,3173,3092,3040,2923,1668,1624$, $1609,1576,1530,1487,1416,1399,1342,1272,1241,1219$, 831, 756, $699 \mathrm{~cm}^{-1}$. HRMS (ESI, $\mathrm{m} / \mathrm{z}$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{FN}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right)$331.1247, found 331.1232.

11-(2-Chlorophenyl)-8,9-dihydro-7H-cyclopenta $[b][4,7]$ phenanthrolin-10(11H)-one 4b. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ MHz ): $\delta_{\mathrm{H}}$ 2.19-2.31 (m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.67-2.72 (m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $5.93(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 7.06-7.12(\mathrm{~m}, 3 \mathrm{H}, \mathrm{ArH}), 7.31(\mathrm{~d}, J=7.6$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.39\left(\mathrm{dd}, J=8.4 \mathrm{~Hz}, J^{\prime}=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right)$, $7.50(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.91(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}$,

ArH), 8.16 (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \operatorname{ArH}$ ), 8.64 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{ArH}$ ), 10.50 (s, 1H, NH). IR (KBr): v 3245, 3180, 3098, 3040, 2971, 2921, 1682, 1629, 1577, 1530, 1468, 1416, 1394, 1273, 1218, 1051, 1034, 834, 746, $699 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd. for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{ClN}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right) 347.0951$, found 347.0953 .

11-(4-Chlorophenyl)-8,9-dihydro-7H-cyclopenta[b][4,7] phenanthrolin-10(11H)-one $4 \mathrm{c} .{ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.27-2.34\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.67-2.74\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $5.70(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 7.18-7.24(\mathrm{~m}, 4 \mathrm{H}, \mathrm{ArH}), 7.36(\mathrm{dd}, J=8.4$ $\left.\mathrm{Hz}, J^{\prime}=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 7.55(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $7.95(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.18(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $8.68\left(\mathrm{dd}, J=4.4 \mathrm{~Hz}, J^{\prime}=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 10.45(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$. IR (KBr): v 3273, 3179, 3095, 3052, 2969, 2931, 1668, 1625, 1578, 1517, 1489, 1466, 1388, 1338, 1272, 1242, 1218, 1087, 1013, 957, 832, 790, 768, $689 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{15} \mathrm{ClN}_{2} \mathrm{ONa}\left(\mathrm{M}+\mathrm{Na}^{+}\right) 369.0771$, found 369.0790 .

11-(3-Bromophenyl)-8,9-dihydro-7H-cyclopenta $[b][4,7]$ phenanthrolin- $10(\mathbf{1 1 H})$-one $4 \mathrm{~d} .{ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}}$ 2.25-2.35 (m, 2H, CH2), 2.64-2.77 (m, 2H, CH $\mathrm{CH}_{2}$ ), 5.71 (s, 1H, CH), 7.11 (d, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), 7.24 (d, $J=6.4 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}), 7.36-7.40(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.55(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $7.95(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.20(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 8.68 (d, $J=3.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 10.51 (s, 1H, NH). IR (KBr): v 3281, 3199, 3117, 3067, 3032, 2918, 1672, 1627, 1607, 1520, 1466, 1392, 1323, 1272, 1214, 1174, 1162, 1116, 1073, 1011, 839, 801, 787, 753, $685 \mathrm{~cm}^{-1}$. HRMS (ESI, m/z): Calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{BrN}_{2} \mathrm{O}$ $\left(\mathrm{M}+\mathrm{H}^{+}\right) 391.0446$, found 391.0448 .

11-(4-Bromophenyl)-8,9-dihydro-7H-cyclopenta $[b][4,7]$ phenanthrolin- $10(11 H)$-one $4 \mathrm{e} .{ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.27-2.34\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.67-2.73\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, 5.69 (s, 1H, CH), 7.12-7.16 (m, 2H, ArH), 7.37-7.38 (m, 3H, ArH), 7.55 (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.95(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{ArH}), 8.18(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.68(\mathrm{dd}, J=4.0 \mathrm{~Hz}$, $\left.J^{\prime}=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 10.48(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}) . \mathrm{IR}(\mathrm{KBr}): \mathrm{v} 3172$, 3092, 3049, 2968, 2929, 2856, 1667, 1624, 1575, 1518, 1465, $1415,1387,1336,1271,1217,1181,1157,1111,1069,1010$, 956, 832, 788, 767, 729, $687 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{BrN}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right) 391.0446$, found 391.0443 .

8,9-Dihydro-11-p-tolyl-7H-cyclopenta[b][4,7]phenanthrolin$\mathbf{1 0 ( 1 1 H )}$-one 4f. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400 \mathrm{MHz}$ ): $\delta_{\mathrm{H}} 2.14$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), 2.21-2.33 (m, 2H, CH 2 ), 2.68-2.70 (m, 2H, $\mathrm{CH}_{2}$ ), $5.61(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 6.95(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 7.06$ $(\mathrm{d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 7.34\left(\mathrm{dd}, J=8.4 \mathrm{~Hz}, J^{\prime}=4.4 \mathrm{~Hz}\right.$, $1 \mathrm{H}, \mathrm{ArH}), 7.54(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.92(\mathrm{~d}, J=9.2 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}$ ), 8.20 (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 8.66 (dd, $J=8.0 \mathrm{~Hz}$, $\left.J^{\prime}=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 10.40(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$. IR (KBr): v 3178 , 3093, 3044, 3017, 2929, 2854, 1669, 1625, 1586, 1516, 1466, 1416, 1387, 1272, 1219, 1111, 1012, 957, 828, 790, 776, $690 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right)$ 327.1497, found 327.1495 .

8,9-Dihydro-11-(3-methoxyphenyl)-7H-cyclopenta[b][4,7] phenanthrolin-10(11H)-one 4g. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.34-2.35\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.63-2.73(\mathrm{~m}, 2 \mathrm{H}$, $\mathrm{CH}_{2}$ ), 3.64 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{O}$ ), 5.63 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{CH}$ ), 6.61-6.66 (m, $2 \mathrm{H}, \mathrm{ArH}$ ), $6.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.04-7.07(\mathrm{~m}, 1 \mathrm{H}, \mathrm{ArH}), 7.37$ (dd, $J=8.4 \mathrm{~Hz}, J^{\prime}=4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.55(\mathrm{~d}, J=8.8$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.93(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.22(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 8.67 (d, $J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 10.46 (s, 1H, NH). IR (KBr): v 3238, 3170, 3091, 3028, 2930, 2835, 1668, 1627, 1606, 1528, 1487, 1465, 1438, 1394, 1311, 1259, 1217, 1143, 1046, 1013, 831, $689 \mathrm{~cm}^{-1}$. HRMS (ESI,
$m / z$ ): Calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Na}\left(\mathrm{M}+\mathrm{Na}^{+}\right)$365.1266, found 365.1259 .

11-(3,4-Dichlorophenyl)-8,9-dihydro-7H-cyclopenta[b][4,7] phenanthrolin- $10(11 H)$-one $\mathbf{4 h} .{ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.29-2.34\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.67-2.73\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $5.76(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}), 7.03\left(\mathrm{dd}, J=8.4 \mathrm{~Hz}, J^{\prime}=2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right)$, $7.37-7.42(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.54(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.56$ (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.97(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.21(\mathrm{~d}$, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.69\left(\mathrm{dd}, J=4.0 \mathrm{~Hz}, J^{\prime}=1.6 \mathrm{~Hz}\right.$, $1 \mathrm{H}, \mathrm{ArH}$ ), 10.53 (s, 1H, NH). IR (KBr): v 3177, 3083, 3053, 3020, 2962, 2927, 1668, 1624, 1590, 1511, 1465, 1415, 1388, $1342,1273,1241,1218,1187,1132,1029,1014,993,956,883$, 832, 791, 728, $691 \mathrm{~cm}^{-1}$. HRMS (ESI, m/z): Calcd for $\mathrm{C}_{21} \mathrm{H}_{15} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right) 381.0561$, found 381.0574 .

8,9-Dihydro-11-(3,4-dimethylphenyl)-7H-cyclopenta[b][4,7] phenanthrolin- $10(11 H)$-one 4 i. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.04\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}\right), 2.21-2.33\left(\mathrm{~m}, 2 \mathrm{H}, \quad \mathrm{CH}_{2}\right)$, 2.61-2.72 (m, 2H, CH 2 ), $5.55(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 6.83-6.75(\mathrm{~m}, 3 \mathrm{H}$, ArH), 7.35 (dd, $\left.J=8.0 \mathrm{~Hz}, J^{\prime}=4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 7.52$ (d, $J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 7.91 (d, $J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 8.20 $(\mathrm{d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 10.39(\mathrm{~s}, 1 \mathrm{H}$, NH). IR (KBr): v 3237, 3166, 3087, 3034, 2921, 2856, 1665, 1625, 1607, 1576, 1467, 1415, 1396, 1272, 1242, 1215, 1150, $1125,1112,1061,1041,1012,990,957,828,803,781,760$, $719,700 \mathrm{~cm}^{-1}$. HRMS (ESI, m/z): Calcd for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{ONa}$ $\left(\mathrm{M}+\mathrm{Na}^{+}\right) 363.1473$, found 363.1484 .

11-Methylenedioxophenyl-8,9-dihydro-7H-cyclopenta[b][4,7] phenanthrolin- $\mathbf{1 0}(\mathbf{1 1 H})$-one $\mathbf{4 j} .{ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.28-2.31\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.67-2.71\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $5.60(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}), 5.88\left(\mathrm{~d}, J=11.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.53$ (dd, $\left.J=8.0 \mathrm{~Hz}, J^{\prime}=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 6.67(\mathrm{~d}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}), 6.78(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.38(\mathrm{dd}, J=8.4$ $\mathrm{Hz}, J^{\prime}=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.53(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $7.92(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.24(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, 8.66-8.67 (m, 1H. ArH), 10.45 (s, 1H, NH). IR (KBr): v 3237, 3165, 3086, 3036, 2924, 2853, 1665, 1610, 1536, 1502, 1488, $1467,1397,1363,1254,1216,1180,1036,922,829,810$, $792 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{22} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{O}_{3}\left(\mathrm{M}+\mathrm{H}^{+}\right)$ 357.1239, found 357.1243.

11-(2,3-Dichlorophenyl)-8,9-dihydro-7H-cyclopenta[b][4,7] phenanthrolin- $10(\mathbf{1 1 H})$-one $4 \mathrm{k} .{ }^{\mathrm{i}} \mathrm{H}$ NMR (DMSO- $d_{6}, 400$ $\mathrm{MHz}): \delta_{\mathrm{H}} 2.20-2.34\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.89\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 6.01$ (s, 1H, CH), 7.13-7.17 (m, 2H, ArH), $7.35(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{ArH}), 7.42\left(\mathrm{dd}, J=8.8 \mathrm{~Hz}, J^{\prime}=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 7.53$ (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.92-7.95(\mathrm{~m}, 1 \mathrm{H}, \mathrm{ArH}), 8.06$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, \operatorname{ArH}), 8.67(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, 10.59 (s, 1H, NH). IR (KBr): v 3233, 3165, 3082, 3015, 2928, 2860, 1673, 1625, 1594, 1523, 1464, 1417, 1389, 1270, 1240, 1219, 1174, 1155, 1086, 1042, 1013, 957, 827, 738, 709, 635 $\mathrm{cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{15} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right)$ 381.0561 , found 381.0565 .

11-(2,4-Dichlorophenyl)-8,9-dihydro-7H-cyclopenta[b][4,7] phenanthrolin-10(11H)-one 41. ${ }^{1} \mathrm{H}$ NMR (DMSO- $d_{6}, 400 \mathrm{MHz}$ ): $\delta_{\mathrm{H}} 2.19-2.34\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.73\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 5.92(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})$, $7.14(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.22\left(\mathrm{dd}, J=8.4 \mathrm{~Hz}, J^{\prime}=1.6 \mathrm{~Hz}\right.$, $1 \mathrm{H}, \mathrm{ArH}), 7.41\left(\mathrm{dd}, J=8.4 \mathrm{~Hz}, J^{\prime}=4.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 7.48(\mathrm{~d}$, $J=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.51(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.92$ $(\mathrm{d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, ~ A r H), 8.07(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, 8.66-8.67 (m, 1H, ArH), 10.56 (s, 1H, NH). IR (KBr): v 3238 , $3172,3095,3028,2961,2920,1670,1625,1598,1526$, 1466, 1437, 1390, 1269, 1239, 1221, 1097, 1044, 1013, 957,

845, 827, 769, 690, $645 \mathrm{~cm}^{-1}$. HRMS (ESI, $m / z$ ): Calcd for $\mathrm{C}_{21} \mathrm{H}_{15} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}\left(\mathrm{M}+\mathrm{H}^{+}\right) 381.0561$, found 381.0539 .

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