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# Palladium catalyzed annulation of benzylamines and arynes via C–H activation to construct 5,6-dihydrophenanthridine derivatives

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ABSTRACT

An efficient and versatile strategy employing palladium catalyst to synthesize 5,6-dihydrophenanthridine derivatives by annulation of benzylamines and arynes through C–H activation has been reported. This is promising one pot methodology which includes the use of Kobayashi's aryne precursor to construct plethora of 5,6-dihydrophenanthridine derivatives in moderate to good yield.



## 1. Introduction

The scientific community has witnessed the growing number of reports for the synthesis of phenanthridine and their analogue due to their promising biological activities and pharmaceutical applications [1]. Among them 5,6-dihydrophenanthridine skeleton have been emanated as potent alkaloid which inhibits acetylcholinesterase [2] and acts as a bradykinin B1 receptor antagonists [3].

However, being efficient scaffold methods leading to access them directly in one step are much less abundant. Some of the synthetic routes that have been documented to construct 5,6-dihydrophenanthridine skeleton are palladium-catalyzed domino *N*-benzylation/intramolecular direct arylation [4], palladium-catalyzed enantioselective C–H arylation [5], palladium-catalyzed domino Suzuki–Miyaura/Aza-Michael Reactions [6], Pictet–Spengler reaction mediated by propylphosphonic anhydride (T3P) [7], modified Pictet–Spengler reaction of biphenyl-2-amines and aromatic aldehydes [8], sequential cyclization-reduction reaction of *N*-acylcarbamates [9], *retro*-carbopalladation of chiral *o*-bromobenzylamines [10], intramolecular C–C coupling of 2,6-disubstituted-1-bromoaryls [11], ruthenium catalyzed intramolecular C–H amination [12], enantioselective hydrogenation of phenanthridine derivatives employing ruthenium catalyst [13] (Fig. 1). Therefore, the search for alternative methods offering clean and shortest route to construct these frameworks is of foremost interest. In these context transition metal-catalyzed annulation of arynes encompassing C–H activation as a key step has emerged as powerful and versatile tool to synthesize numerous ring systems in one pot under mild condition [14].

Over the years, aryne chemistry has received significant attention due to its wide range of application in organic synthesis [15]. The remarkable success in this field is due to the development of arynes under mild condition from ortho-(trimethylsilyl)aryltriflates employing fluoride source by Kobayashi and co-workers [16]. To the best of our knowledge till date only one report had been documented to access 5,6-dihydrophenanthridine skeleton employing Kobayashi's aryne precursor [17] (Scheme 1). Moreover, synthetic protocols involving these precursors and transition metal catalyst includes cycloaddition [18], insertion into sigma bond [19], C–H activation [20], annulations [21] etc. Among these strategies, the ease of forming C–C and C-heteroatom bond can be achieved by palladium mediated C–H activation methodology which is otherwise difficult to generate by conventional methods [22].

Looking at the advantage of this strategy and our continuing

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0040-4020/

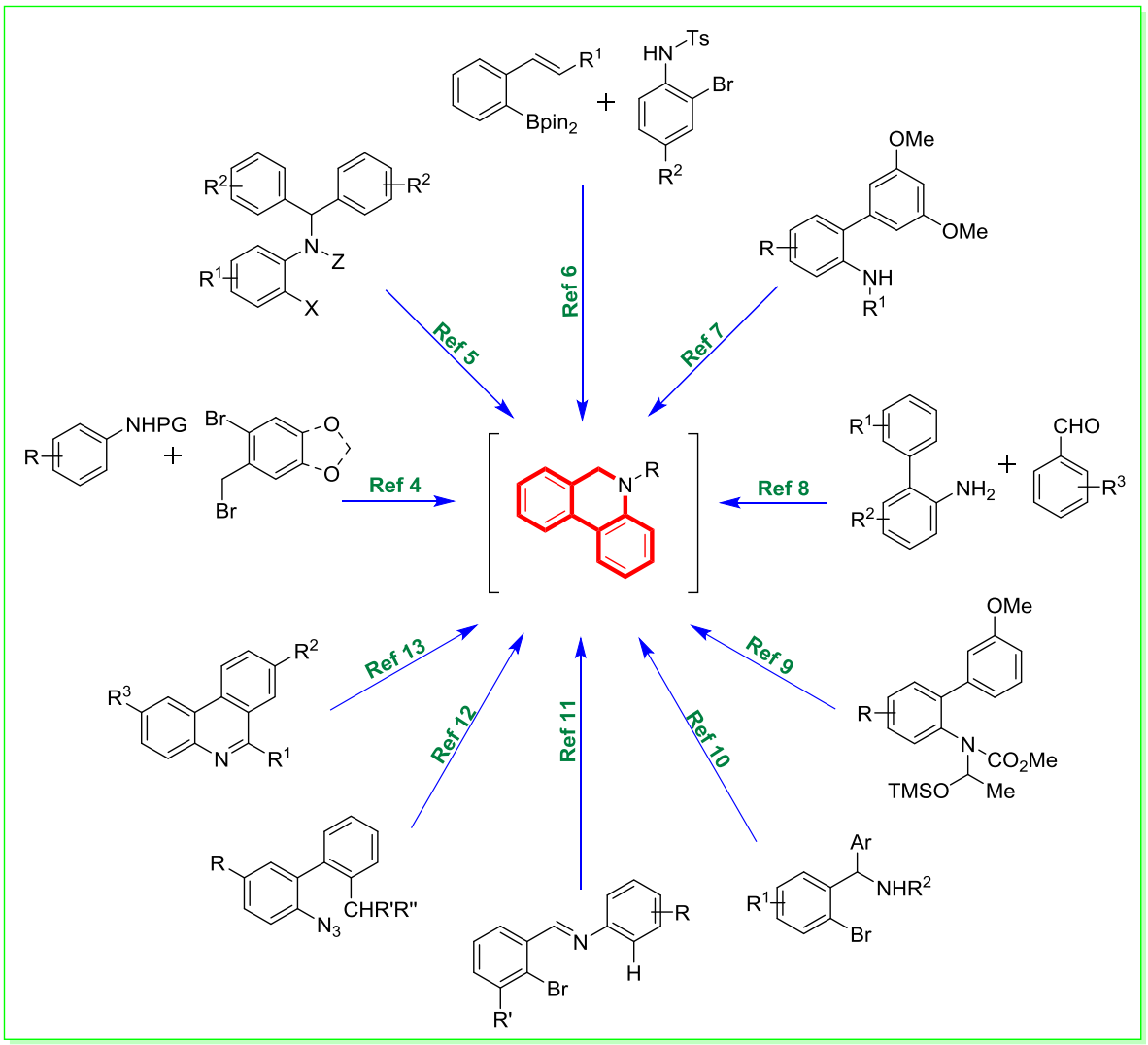
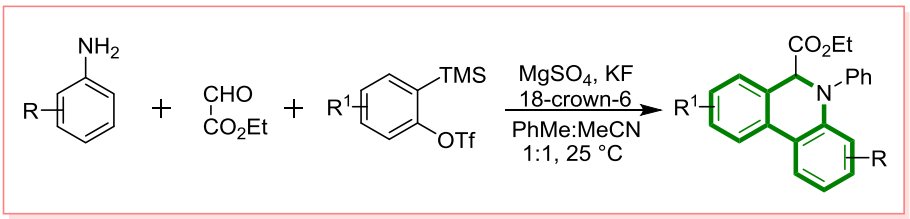



**Fig. 1.** Various synthetic route to construct 5,6-dihydrophenanthridine skeleton.




**Scheme 1.** Synthesis of Dihydrophenanthridines by Yun He and Co-workers.

interest in C–H activation [23] herein we report a new method to synthesize 5,6-dihydrophenanthridine derivatives by the annulation of readily available benzylamines and arynes employing palladium catalyst.

## 2. Results and discussion

Our investigation on 5,6-dihydrophenanthridine begins by reacting *N*-methyl-1-phenylmethanamine (**1a**) and o-(trimethylsilyl)phenyl triflate (**2a**) as aryne precursor and fluoride source under Pd(II) catalyst in the presence of $Cu(OAc)_2$ as oxidant (Table 1). It was observed that employing catalyst $Pd(TFA)_2$ or $PdCl_2$ with KF/18-crown-6 as fluoride source under $Cu(OAc)_2$ in $CH_3CN$ at 120 °C for 24 h gave the desired product in low yield along with the generation of byproduct (Table 1, entries 1–2). A slight increase in yield of **3a** was obtained when fluoride source was changed to CsF (Table 1, entries 3–4). In view of catalyst $[Ru(p\text{-cymene})Cl_2]_2$ was also tested but no improvement in yield was observed (Table 1, entry 5). To our delight, when $Pd(OAc)_2$ was used as a catalyst the resultant transformation was achieved in highest yield and

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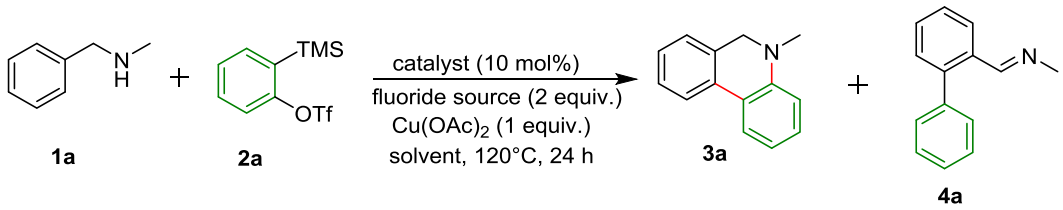
**Table 1**
Optimization of the reaction conditions.[a]




| Entry | Catalyst | Fluoride source | Solvent | Yield[b] | |
|---|---|---|---|---|---|
| | | | | 3a (%) | 4a(%) |
| 1 | $Pd(TFA)_2$ | KF/18-crown-6 | $CH_3CN$ | 13 | 19 |
| 2 | $PdCl_2$ | KF/18-crown-6 | $CH_3CN$ | 11 | 24 |
| 3 | $Pd(TFA)_2$ | CsF | $CH_3CN$ | 23 | 32 |
| 4 | $PdCl_2$ | CsF | $CH_3CN$ | 34 | 11 |
| 5 | $[Ru(p\text{-cymene})Cl_2]_2$ | CsF | $CH_3CN$ | 9 | 0 |
| **6** | **$Pd(OAc)_2$** | **CsF** | **$CH_3CN$** | **86** | 6 |
| 7 | $Pd(OAc)_2$ | CsF | DMSO | 43 | 16 |
| 8 | $Pd(OAc)_2$ | CsF | DMF | 47 | 30 |
| 9 | $Pd(OAc)_2$ | CsF | toluene | 65 | 23 |
| 10 | $Pd(OAc)_2$ | CsF | 1,1-dioxane | 51 | 15 |
| 11 | $Pd(OAc)_2$ | KF/18-crown-6 | $CH_3CN$ | 59 | 9 |
| 12 | $Pd(OAc)_2$ | TBAT | $CH_3CN$ | 31 | 37 |
| 13 | – | CsF | $CH_3CN$ | 0 | 0 |
| 14[c] | $Pd(OAc)_2$ | CsF | $CH_3CN$ | 44 | 13 |
| 15[d] | $Pd(OAc)_2$ | CsF | $CH_3CN$ | 33 | 28 |
| 16[e] | $Pd(OAc)_2$ | CsF | $CH_3CN$ | 57 | 17 |

[a] Reaction conditions: **1a** (0.30 mmol, 1 equiv.), **2a** (0.60 mmol, 2 equiv.), Pd(II) catalyst (10 mol%), CsF (0.90 mmol, 3 equiv.), $Cu(OAc)_2$ (0.30 mmol, 1 equiv.) in 3.0 mL of solvent for 24 h at 120 °C.
[b] Isolated yield.
[c] Oxidant is $Cu(TFA)_2$.
[d] Oxidant is $CuCl_2$..
[e] Reaction carried out at room temperature.

formation of byproduct was least (Table 1, entry 6). Next, replacing $CH_3CN$ with different solvent systems could not improve the yield of **3a** (Table 1, entries 7–10). Further evaluation of several fluoride source with catalyst $Pd(OAc)_2$ showed no increase in the yield of the desied product (Table 1, entries 11–12). Moreover, no product was formed when reaction was performed without Pd catalyst (Table 1, entry 13). When oxidant $Cu(OAc)_2$ was replaced by $Cu(TFA)_2$ or $CuCl_2$ or carrying out the reaction at room temperature couldn't make any difference (Table 1, entries 14–16).

With the successful establishment of optimized reaction condition for palladium mediated annulation strategy to construct **3a**, the substrate scope of this transformation was explored by testing wide range of benzylamines (**1a** − **1i**) with aryne precursor **2a**. It was noted that all the combinations which were tested gave the desired product irrespective of electron donating or electron withdrawing group at $R^1$ which revealed the existence of high functional group tolerance (Table 2, entries **3a-3i**). The reaction of electron donating substituent at substrate **1** generated the products with good to high yields (Table 2, entries **3a-3f**), whereas with electron withdrawing substituents the yields were lowered (Table 2, entries **3g-3h**). In addition, it was also observed that alkoxy-substituted benzylic amine **1i** underwent the desired transformation smoothly resulting into the formation of product in 71% (Table 2, entry **3i**).

Furthermore, the scope of other arynes **2b**, **2c** and **2d** was also investigated with benzylamine **1a**, **1b**, **1c and 1g** under optimized reaction condition. Electron rich aryne precursors 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2b)** and 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2c)** gave 5,6-dihydrophenanthridines in good yields on treatment with **1a**, **1b** and **1c** (Table 2, entries **3j-3o**), however, the yields of desired cyclic product was decreased with **1g** due to the presence of electron withdrawing group on it (Table 2, entries **3p-3q**). Moreover, the reaction of 6-(trimethylsilyl)-2,3-dihydro-1H-inden-5-yl trifluoromethanesulfonate (**2d**) with **1a**, **1b**, **1c** and **1g** provided the desired product in good to moderate yields (Table 2, entries **3r-3u**).

On the basis of the above results and literature reports [24], a possible reaction mechanism is proposed in Fig. 2. Initially **1a** would react with $Pd(OAc)_2$ to form Pd–N adduct $\mathbf{Z_1}$ followed by C–H bond activation which generated five-membered palladacycle $\mathbf{Z_2}$. Seven membered-palladacycle $Z_3$ is formed by coordinative insertion of aryne into Pd–C bond of $\mathbf{Z_3}$. Finally, $Z_3$ would undergo reductive elimination to give desired product **3** leaving behind Pd(0) catalyst which was reoxidized to Pd(II) by $Cu(OAc)_2$.. However, in accordance with the proposed catalytic cycle it is noteworthy that intermediate $\mathbf{Z_3}$ can undergo a $\beta$-hydride elimination reaction to afford byproduct **4a** and regenerate the Pd(0) catalyst.

## 3. Conclusion

In summary, we have developed a prominent and efficient strategy to synthesize 5,6-dihydrophenanthridines by annulation of benzylamines with aryne through C–H activation in the presence of palladium(II) catalyst in one pot. The proposed synthetic methodology proved to be an effective one as it overshadows the long synthetic route to access this framework. In addition, the desired compounds were synthesized in good to excellent yields with high functional group tolerance. Moreover, efforts to construct biologically active cyclic scaffolds through C–H activation are underway in our laboratory.

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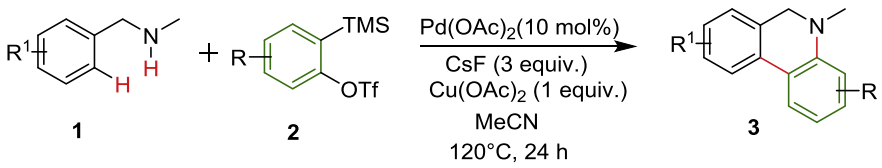
**Table 2**
Substrate scope.



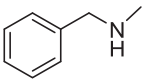
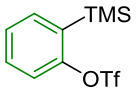
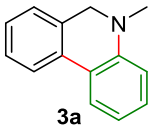
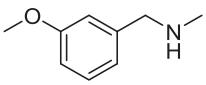
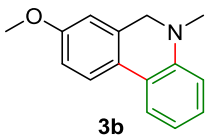
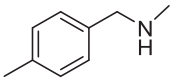
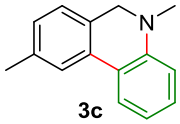
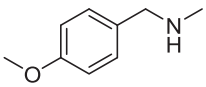
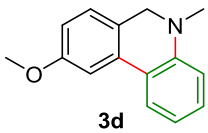
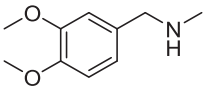
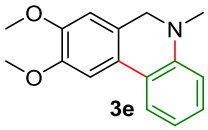
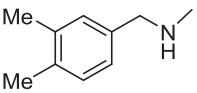
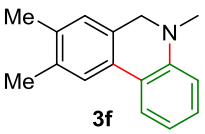
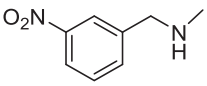
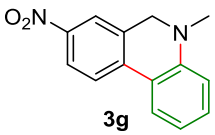
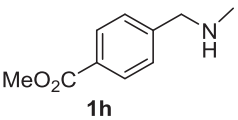
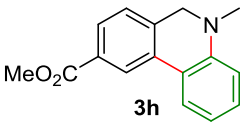

| Entry | 1 | 2 | 3 | Yield |
|---|---|---|---|---|
| 1 |  **1a** $R^1$= H |  **2a** R= H |  **3a** | 86% |
| 2 |  **1b** $R^1$= 3-$OCH_3$ | **2a** |  **3b** | 88% |
| 3 |  **1c** $R^1$= 4-$CH_3$ | **2a** |  **3c** | 81% |
| 4 |  **1d** $R^1$= 4-$OCH_3$ | **2a** |  **3d** | 87% |
| 5 |  **1e** $R^1$= 3,4-$OCH_3$ | **2a** |  **3e** | 90% |
| 6 |  **1f** $R^1$= 3,4-$CH_3$ | **2a** |  **3f** | 84% |
| 7 |  **1g** $R^1$= 3-$NO_2$ | **2a** |  **3g** | 58% |
| 8 |  **1h** $R^1$= 4-$CO_2Me$ | **2a** |  **3h** | 60% |

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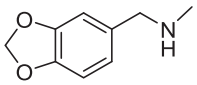
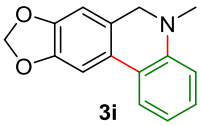
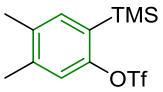
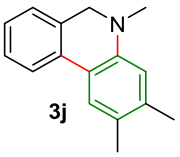
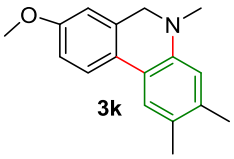
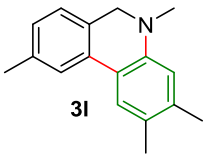
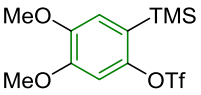
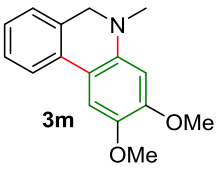
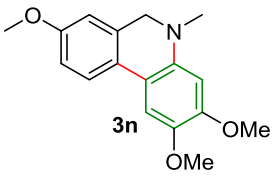
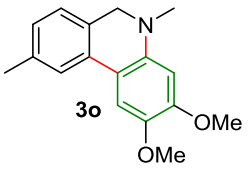
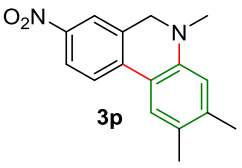
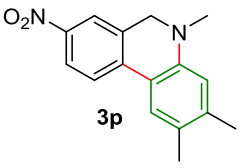
**Table 2** (*continued*)

| Entry | 1 | 2 | 3 | Yield |
|---|---|---|---|---|
| 9 |  **1i** $R^1$= -O-$CH_2$-O- | **2a** |  **3i** | 71% |
| 10 | **1a** |  **2b** R= 4,5-$CH_3$ |  **3j** | 73% |
| 11 | **1b** | **2b** |  **3k** | 80% |
| 12 | **1c** | **2b** |  **3l** | 70% |
| 13 | **1a** |  **2c** R= 4,5-OMe |  **3m** | 78% |
| 14 | **1b** | **2c** |  **3n** | 91% |
| 15 | **1c** | **2c** |  **3o** | 75% |
| 16 | **1g** | **2b** |  **3p** | 61% |
| 17 | **1g** | **2c** |  **3p** | 66% |

(*continued on next page*)

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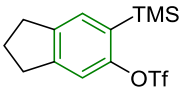
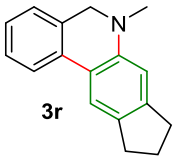
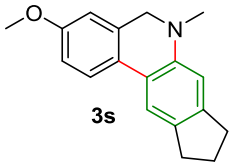
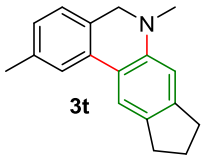
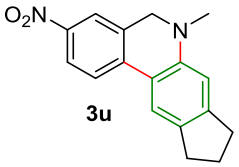
**Table 2** (*continued*)

| Entry | 1 | 2 | 3 | Yield |
|---|---|---|---|---|
| 18 | **1a** |  **2d** R= 4,5--$(CH_2)_3$- |  **3r** | 62% |
| 19 | **1b** | **2d** |  **3s** | 77% |
| 20 | **1c** | **2d** |  **3t** | 68% |
| 21 | **1g** | **2d** |  **3u** | 63% |

## 4. Experimental section

### 4.1. General information

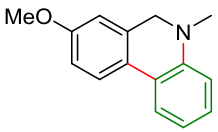
All the reagents and solvents were purchased from Sigma-Aldrich and Merck and were used as recieved without any further purification. The synthesized compounds were characterized by $^1$H NMR, $^{13}$C NMR, and elemental analysis. Melting points were determined in open capillaries on a Veego electronic apparatus VMP-D (Veego Instrument Corporation, Mumbai, India) and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR) using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as internal standard. HRMS spectra were recorded on XEVO G2-XS QTOF spectrophotometer. $^1$H NMR and $^{13}$C NMR chemical shifts are reported as parts per million (ppm) downfield from TMS. The splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analysis (C, H, N) were performed using a Heraeus CarloErba 1180 CHN analyzer (Hanau, Germany).

### 4.2. General procedure to prepare 5,6-dihydrophenanthridines (3) from benzylamines (1) employing palladium catalyst

A mixture of $Pd(OAc)_2$ (6.7 mg, 0.030 mmol, 10 mmol%), $Cu(OAc)_2$ (54.45 mg, 0.30 mmol, 1 equiv.), **1a** (32.1 mg, 0.30 mmol, 1 equiv.), CsF (136.7 mg, 0.90 mmol, 3 equiv.) was dissolved in a solvent of acetonitrile (3 mL) followed by addition of **2a** (179 mg, 0.60 mmol, 2 equiv.). The reaction mixture was stirred at 120 °C for 24 h and progress of the reaction was monitored continuously by TLC with ethyl acetate: hexane eluent system. Upon completion of reaction the mixture was cooled to room temperature, poured into brine, and extracted with EtOAc. The combined extracts were dried over $MgSO_4$ and filtered through pad of Celite eluting with ethyl acetate. The filtrate was concentrated under reduced pressure and was purified by column chromatography (EtOAc/hexane) on silica gel to afford the 5,6-dihydrophenanthridine **3a**. Compound **1i** was synthesized in accordance with reported literature [25].

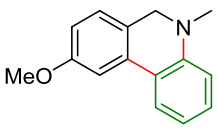
Characterization data of compounds 3a, 3c, and 3e were found exactly similar as reported in the literature (References of above compounds are mentioned in Supplementary data).

#### 4.2.1. 8-Methoxy-5-methyl-5,6-dihydrophenanthridine (3b)



Yield: 88%. white solid; mp: 136–137 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, $J$ = 8.1 Hz, 1H), 7.22 (td, $J$ = 7.4, 1.6 Hz, 1H), 7.15 (dd, $J$ = 7.1, 2.2 Hz, 1H), 6.96 (dd, $J$ = 5.9, 2.2 Hz, 1H), 6.89 (d, $J$ = 7.8 Hz, 1H), 6.73 (td, $J$ = 7.8, 1.2 Hz, 1H), 6.68 (dd, $J$ = 6.7, 1.4 Hz, 1H), 4.67 (s, 2H), 3.82 (s, 3H), 2.84 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.83, 142.72, 133.27, 129.16, 126.64, 126.03, 125.05, 124.54, 118.75, 113.33, 113.18, 111.28, 56.05, 50.90, 39.93. Anal. Calcd. For $C_{15}H_{15}NO$: C: 79.97; H: 6.71; N: 6.22; O: 7.10. Found: C: 79.95; H: 6.70; N: 6.23; O: 7.08. HRMS-ESI ($m/z$) calcd. for $C_{15}H_{15}NO$ $[M + H]^+$ 226.1228, found 226.1241.

#### 4.2.2. 9-Methoxy-5-methyl-5,6-dihydrophenanthridine (3d)



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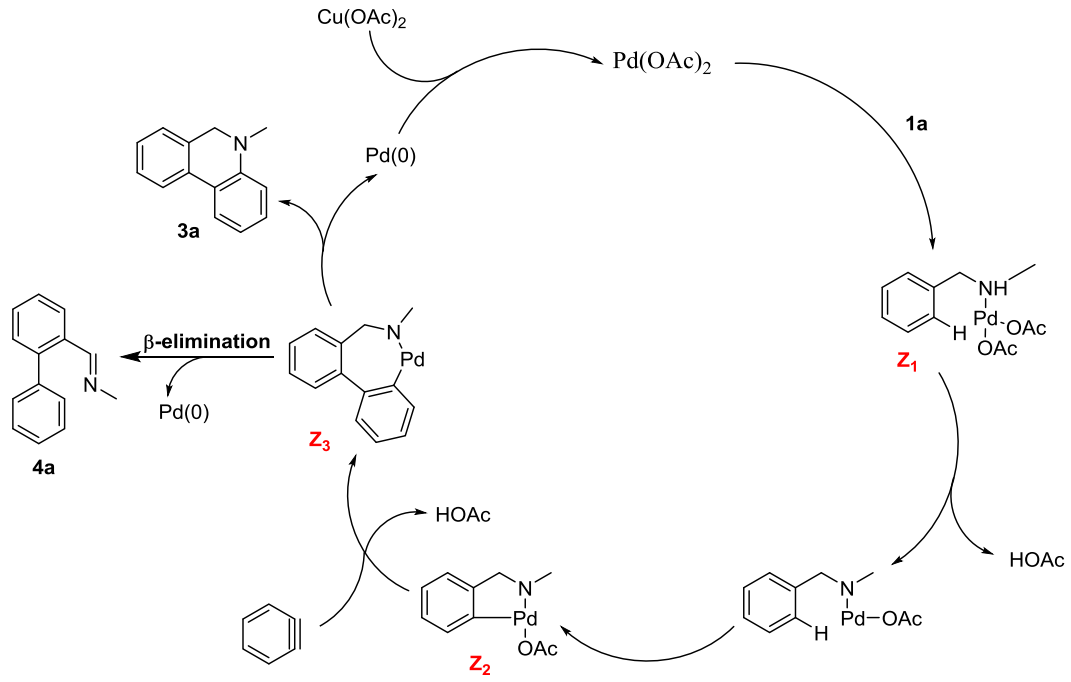
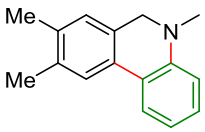



**Fig. 2.** Plausible mechanism.

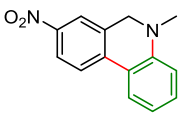
Yield: 87%. white solid; mp: 155–156 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, $J$ = 7.2, 2.4 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 1H), 7.17 (d, $J$ = 8.0 Hz, 1H), 7.13 (td, $J$ = 7.6, 1.4 Hz, 1H), 6.91 (dd, $J$ = 5.9, 2.2 Hz, 1H), 6.75 (td, $J$ = 7.8, 1.2 Hz, 1H), 6.73 (dd, $J$ = 6.8, 1.6 Hz, 1H), 4.65 (s, 2H), 3.83 (s, 3H), 2.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.28, 142.78, 130.46, 129.45, 128.81, 126.09, 124.74, 123.82, 118.43, 113.69, 113.18, 109.48, 56.06, 51.65, 39.93. Anal. Calcd. For $C_{15}H_{15}NO$: C: 79.97; H: 6.71; N: 6.22; O: 7.10. Found: C: C: 79.96; H: 6.69; N: 6.20; O: 7.11. HRMS-ESI ($m/z$) calcd. for $C_{15}H_{15}NO$ [M + H]$^+$ 226.1228, found 226.1234.

*4.2.3. 5,8,9-Trimethyl-5,6-dihydrophenanthridine (3f)*



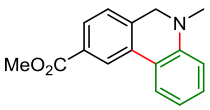

Yield: 84%. white solid; mp: 143–144 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.41 (s, 1H), 7.38 (dd, $J$ = 7.9, 1.8 Hz, 1H), 7.11 (td, $J$ = 7.5, 2.6 Hz, 1H), 7.07 (s, 1H), 6.76 (td, $J$ = 7.8, 2.6 Hz, 1H), 6.72 (dd, $J$ = 6.5, 2.1 Hz, 1H), 4.66 (s, 2H), 2.85 (s, 3H), 2.34 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.77, 138.06, 132.90, 132.47, 131.40, 129.44, 128.47, 127.53, 126.08, 124.75, 118.43, 113.146, 50.90, 39.91, 20.36. Anal. Calcd. For $C_{16}H_{17}N$: C: 86.05; H: 7.67; N: 6.28. Found: C: 86.06; H: 7.66; N: 6.25. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{17}N$ [M + H]$^+$ 224.1487, found 224.1481.

*4.2.4. 5-Methyl-8-nitro-5,6-dihydrophenanthridine (3g)*



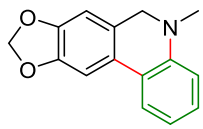

Yield: 58%. yellow solid; mp: 116–117 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 8.21 (dd, $J$ = 6.1, 2.2 Hz, 1H), 8.13 (d, $J$ = 8.1 Hz, 1H), 7.72 (d, $J$ = 7.9 Hz, 1H), 7.25 (td, $J$ = 7.4, 1.6 Hz, 1H), 7.18 (dd, $J$ = 7.1, 2.2 Hz, 1H), 6.74 (td, $J$ = 7.8, 1.2 Hz, 1H), 6.69 (dd, $J$ = 6.7, 1.4 Hz, 1H), 4.68 (s, 2H), 2.86 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.47, 142.72, 135.96, 133.33, 130.61, 129.14, 126.04, 124.95, 124.52, 123.88, 118.73, 113.34, 50.91, 39.92. Anal. Calcd. For $C_{14}H_{12}N_2O_2$: C: 69.99; H: 5.03; N: 11.66; O: 13.32. Found: C: 69.98; H: 5.01; N: 11.63; O: 13.33. HRMS-ESI ($m/z$) calcd. for $C_{14}H_{12}N_2O_2$ [M + H]$^+$ 241.0919, found 241.0922.

*4.2.5. Methyl 5-methyl-5,6-dihydrophenanthridine-9-carboxylate (3h)*




Yield: 60%. white solid; mp: 187–188 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, $J$ = 8.2 Hz, 1H), 7.95 (dd, $J$ = 6.1, 1.6 Hz, 1H), 7.50 (d, $J$ = 7.8 Hz, 1H), 7.43 (dd, $J$ = 7.2, 2.4 Hz, 1H), 7.15 (td, $J$ = 7.6, 1.4 Hz, 1H), 6.76 (td, $J$ = 7.8, 2.6 Hz, 1H), 6.74 (dd, $J$ = 6.8, 1.6 Hz, 1H), 4.66 (s, 2H), 3.96 (s, 3H), 2.86 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.70, 142.77, 135.68, 129.90, 129.45, 129.18, 127.47, 127.12, 126.08, 124.73, 124.41, 118.43, 113.16, 52.09, 51.66, 39.92. Anal. Calcd. For $C_{16}H_{15}NO_2$: C: 75.87; H: 5.97; N: 5.53; O: 12.63. Found: C: 75.88; H: 5.94; N: 5.55; O: 12.61. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{15}NO_2$ [M + H]$^+$ 254.1146, found 254.1161.

*4.2.6. 5-Methyl-5,6-dihydro-[1,3]dioxolo[4,5-j]phenanthridine (3i)*

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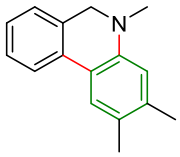
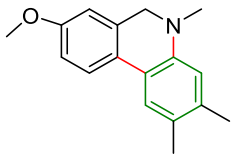
Yield: 71%. white solid; mp: 130–131 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.34 (dd, $J$ = 6.8, 2.1 Hz, 1H), 7.25 (s, 1H), 7.10 (td, $J$ = 7.5, 2.6 Hz, 1H), 7.01 (s, 1H), 6.75 (td, $J$ = 7.8, 2.5 Hz, 1H), 6.71 (dd, $J$ = 6.8, 2.4 Hz, 1H), 5.91 (s, 2H), 4.68 (s, 2H), 2.86 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.37, 147.98, 142.79, 129.47, 127.16, 126.04, 124.73, 121.93, 118.45, 113.15, 109.93, 107.16, 102.11, 50.90, 39.90. Anal. Calcd. For $C_{15}H_{13}NO_2$: C: 75.30; H: 5.48; N: 5.85; O: 13.37. Found: C: 75.32; H: 5.44; N: 5.82; O: 13.38. HRMS-ESI ($m/z$) calcd. for $C_{15}H_{13}NO_2$ $[M + H]^+$ 240.1030, found 240.1024.

*4.2.7. 2,3,5-Trimethyl-5,6-dihydrophenanthridine (3j)*



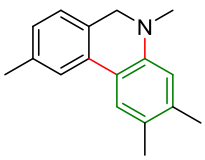
Yield: 73%. white solid; mp: 152–154 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.66 (d, $J$ = 7.8 Hz, 1H), 7.30–7.35 (m, 3H), 7.14 (s, 1H), 6.46 (s, 1H), 4.68 (s, 2H), 2.85 (s, 3H), 2.37 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.62, 135.46, 132.70, 130.73, 129.80, 128.79, 127.77, 127.56, 127.20, 124.95, 119.35, 110.56, 51.64, 39.91, 20.38. Anal. Calcd. For $C_{16}H_{17}N$: C: 86.05; H: 7.67; N: 6.28. Found: C: 86.04; H: 7.69; N: 6.24. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{17}N$ $[M + H]^+$ 224.1487, found 224.1496.

*4.2.8. 8-Methoxy-2,3,5-trimethyl-5,6-dihydrophenanthridine (3k)*



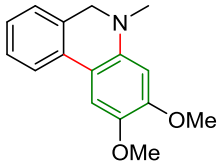
Yield: 80%. white solid; mp: 170–171 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.60 (d, $J$ = 7.6 Hz, 1H), 7.07 (s, 1H), 6.94 (dd, $J$ = 6.4, 2.2 Hz, 1H), 6.86 (d, $J$ = 7.8 Hz, 1H), 6.45 (s, 1H), 4.68 (s, 2H), 3.82 (s, 3H), 2.85 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.21, 147.62, 135.47, 133.60, 129.81, 127.18, 127.11, 124.73, 119.34, 113.42, 111.41, 110.56, 56.05, 50.91, 39.92, 20.36. Anal. Calcd. For $C_{17}H_{19}NO$: C: 80.60; H: 7.56; N: 5.53; O: 6.31. Found: C: 80.58; H: 7.57; N: 5.51; O: 6.30. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{19}NO$ $[M + H]^+$ 254.1568, found 254.1576.

*4.2.9. 2,3,5,9-Tetramethyl-5,6-dihydrophenanthridine (3l)*



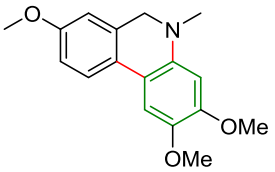
Yield: 70%. white solid; mp: 181–182 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.44 (d, $J$ = 8.3 Hz, 1H), 7.31 (d, $J$ = 8.3 Hz, 1H), 7.15 (dd, $J$ = 6.7, 1.6 Hz, 1H), 7.11 (s, 1H), 6.46 (s, 1H), 4.66 (s, 2H), 2.85 (s, 3H), 2.35–2.37 (s, 6H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.68, 137.19, 135.95, 129.68, 129.06, 128.27, 127.89, 127.53, 127.11, 126.30, 118.82, 110.81, 51.67, 39.92, 21.20, 20.37. Anal. Calcd. For $C_{17}H_{19}N$: C: 86.03; H: 8.07; N: 5.90. Found: C: 86.01; H: 8.08; N: 5.89. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{19}N$ $[M + H]^+$ 238.1609, found 238.1627.

*4.2.10. 2,3-Dimethoxy-5-methyl-5,6-dihydrophenanthridine (3 m)*



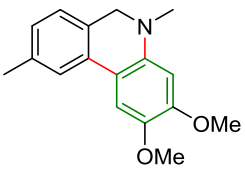
Yield: 78%. white solid; mp: 126–127 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.62 (d, $J$ = 7.6 Hz, 1H), 7.31–7.35 (m, 3H), 7.12 (s, 1H), 6.47 (s, 1H), 4.67 (s, 2H), 2.84 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.06, 147.08, 143.53, 142.99, 132.69, 130.71, 128.78, 127.77, 127.54, 124.95, 116.20, 112.14, 107.25, 56.79, 51.67, 39.92. Anal. Calcd. For $C_{16}H_{17}NO_2$: C: 75.81; H: 7.11; N: 5.20; O: 11.88. Found: C: 75.80; H: 7.14; N: 5.18; O: 11.86. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{17}NO_2$ $[M + H]^+$ 256.1392, found 256.1378.

*4.2.11. 2,3,8-Trimethoxy-5-methyl-5,6-dihydrophenanthridine (3n)*



Yield: 91%. white solid; mp: 138–139 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.61 (d, $J$ = 7.9 Hz, 1H), 6.95 (dd, $J$ = 8.0, 2.8 Hz, 1H), 6.85 (d, $J$ = 8.2 Hz, 1H), 6.83 (s, 1H), 6.18 (s, 1H), 4.71 (s, 2H), 3.81 (s, 9H), 2.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.21, 150.06, 143.52, 142.97, 133.63, 127.11, 124.73, 116.21, 113.42, 112.12, 111.41, 107.23, 56.78, 56.03, 50.90, 39.92. Anal. Calcd. For $C_{17}H_{19}NO_3$: C: 71.56; H: 6.71; N: 4.91; O: 16.82. Found: C: 71.54; H: 6.72; N: 4.89; O: 16.81. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{19}NO_3$ $[M + H]^+$ 286.1433, found 286.1439.

*4.2.12. 2,3-Dimethoxy-5,9-dimethyl-5,6-dihydrophenanthridine (3°)*



Yield: 75%. white solid; mp: 140–141 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, $J$ = 7.2 Hz, 1H), 7.16 (d, $J$ = 5.6 Hz, 1H), 7.14 (s, 1H), 6.54 (s, 1H), 6.13 (s, 1H), 4.67 (s, 2H), 3.83-3.82 (s, 6H), 2.83 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.64, 143.33, 143.02, 137.19, 129.66, 128.27, 127.91, 127.12, 126.30, 115.60, 112.18, 107.01, 56.78, 51.67, 39.92, 21.20. Anal. Calcd. For $C_{17}H_{19}NO_2$: C: 75.81; H: 7.11; N: 5.20; O: 11.88. Found: C: 75.80; H: 7.12; N: 5.17; O: 11.84. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{19}NO_2$ $[M + H]^+$ 270.1488, found 270.1502.

*4.2.13. 2,3,5-Trimethyl-8-nitro-5,6-dihydrophenanthridine (3p)*

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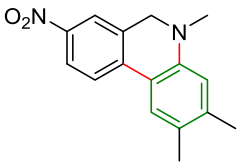
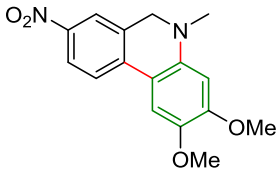


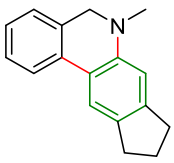
Yield: 61%. yellow solid; mp: 150–151 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 8.21 (dd, $J$ = 8.6, 2.4 Hz, 1H), 8.10 (d, $J$ = 4.2 Hz, 1H), 7.91 (d, $J$ = 6.8 Hz, 1H), 7.20 (s, 1H), 6.48 (s, 1H), 4.70 (s, 2H), 2.86 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.62, 147.08, 135.88, 135.45, 133.86, 130.48, 129.81, 127.18, 124.73, 124.39, 119.35, 110.55, 50.90, 39.91, 20.37. Anal. Calcd. For $C_{16}H_{16}N_2O_2$: C: 71.62; H: 6.01; N: 10.44; O: 11.93. Found: C: 71.64; H: 6.02; N: 10.41; O: 11.91. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{16}N_2O_2$ [M + H]$^+$ 269.1245, found 269.1257.

*4.2.14. 2,3-Dimethoxy-5-methyl-8-nitro-5,6-dihydrophenanthridine (3q)*



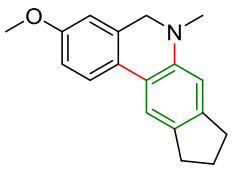
Yield: 66%. yellow solid; mp: 163–164 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 8.20 (dd, $J$ = 8.5, 2.9 Hz, 1H), 8.08 (d, $J$ = 5.6 Hz, 1H), 7.90 (d, $J$ = 6.8 Hz, 1H), 6.91 (s, 1H), 6.24 (s, 1H), 4.68 (s, 2H), 3.81 (s, 6H), 2.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.04, 147.09, 143.52, 142.98, 135.87, 133.86, 130.49, 124.75, 124.38, 116.20, 112.13, 107.25, 56.80, 50.91, 39.92. Anal. Calcd. For $C_{16}H_{16}N_2O_4$: C: 63.99; H: 5.37; N: 9.33; O: 21.31. Found: C: 63.98; H: 5.38; N: 9.31; O: 21.28. HRMS-ESI ($m/z$) calcd. for $C_{16}H_{16}N_2O_4$ [M + H]$^+$ 301.1178, found 301.1188.

*4.2.15. 6-Methyl-6,8,9,10-tetrahydro-5H-cyclopenta[b] phenanthridine (3r)*



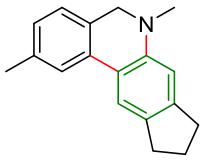
Yield: 62%. white solid; mp: 161–162 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.62 (d, $J$ = 7.4 Hz, 1H), 7.36 (m, 1H), 7.35 (d, $J$ = 8.5 Hz, 1H), 7.31–7.34 (m, 2H), 6.70 (s, 1H), 4.66 (s, 2H), 3.00 (t, $J$ = 7.8 Hz, 2H), 2.90 (t, $J$ = 7.4 Hz, 2H), 2.83 (s, 3H), 2.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.38, 143.15, 139.10, 132.66, 130.74, 128.79, 127.78, 127.56, 124.93, 123.48, 117.71, 106.08, 51.67, 39.90, 33.84, 26.92. Anal. Calcd. For $C_{17}H_{17}N$: C: 86.77; H: 7.28; N: 5.95. Found: C: 86.79; H: 7.29; N: 5.87. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{17}N$ [M + H]$^+$ 236.1423, found 236.1431.

*4.2.16. 3-Methoxy-6-methyl-6,8,9,10-tetrahydro-5H-cyclopenta[b] phenanthridine (3s)*



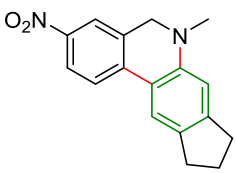
Yield: 77%. white solid; mp: 121–122 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.60 (d, $J$ = 7.6 Hz, 1H), 7.32 (s, 1H), 6.94 (dd, $J$ = 8.3, 1.8 Hz, 1H), 6.85 (d, $J$ = 7.9 Hz, 1H), 6.69 (s, 1H), 4.67 (s, 2H), 3.80 (s, 3H), 2.99 (t, $J$ = 7.6 Hz, 2H) 2.89 (t, $J$ = 7.2 Hz, 2H), 2.84 (s, 3H), 2.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.21, 143.38, 143.15, 139.11, 133.63, 127.10, 124.73, 123.48, 117.71, 113.44, 111.42, 106.07, 56.03, 50.91, 39.91, 33.84, 26.91. Anal. Calcd. For $C_{18}H_{19}NO$: C: 81.47; H: 7.22; N: 5.28; O: 6.03. Found: C: 81.46; H: 7.21; N: 5.30; O: 6.01. HRMS-ESI ($m/z$) calcd. for $C_{18}H_{19}NO$ [M + H]$^+$ 266.1575, found 266.1582.

*4.2.17. 2,6-Dimethyl-6,8,9,10-tetrahydro-5H-cyclopenta[b] phenanthridine (3t)*



Yield: 68%. white solid; mp: 110–111 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 7.42 (d, $J$ = 8.4 Hz, 1H), 7.35 (s, 1H), 7.30 (s, 1H), 7.17 (dd, $J$ = 6.8, 1.6 Hz, 1H), 6.70 (s, 1H), 4.66 (s, 2H), 3.00 (t, $J$ = 7.8 Hz, 2H), 2.88 (t, $J$ = 7.2 Hz, 2H), 2.85 (s, 3H), 2.36 (s, 3H), 2.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.55, 143.42, 139.57, 137.17, 129.68, 129.29, 128.25, 127.91, 127.12, 123.31, 116.68, 105.94, 51.68, 39.92, 33.84, 26.92, 21.21. Anal. Calcd. For $C_{18}H_{19}N$: C: 86.70; H: 7.68; N: 5.62. Found: C: 86.69; H: 7.67; N: 5.60. HRMS-ESI ($m/z$) calcd. for $C_{18}H_{19}N$ [M + H]$^+$ 250.1669, found 250.1656.

*4.2.18. 6-Methyl-3-nitro-6,8,9,10-tetrahydro-5H-cyclopenta[b] phenanthridine (3u)*



Yield: 63%. yellow solid; mp: 118–119 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ, 8.21 (dd, $J$ = 8.8, 2.8 Hz, 1H), 8.09 (d, $J$ = 4.9 Hz, 1H), 7.91 (d, $J$ = 6.8 Hz, 1H), 7.40 (s, 1H), 6.71 (s, 1H), 4.70 (s, 2H), 3.01 (t, $J$ = 7.9 Hz, 2H), 2.92 (t, $J$ = 7.7 Hz, 2H), 2.85 (s, 3H), 2.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.08, 143.39, 143.14, 139.10, 135.87, 133.86, 130.48, 124.74, 124.38, 123.50, 117.71, 106.08, 50.90, 39.91, 33.84, 26.91. Anal. Calcd. For $C_{17}H_{16}N_2O_2$: C: 72.84; H: 5.76; N: 9.99; O: 11.41. Found: C: 72.82; H: 5.77; N: 9.97; O: 11.40. HRMS-ESI ($m/z$) calcd. for $C_{17}H_{16}N_2O_2$ [M + H]$^+$ 281.1254, found 281.1272.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.05.011.

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