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Intramolecular dehydrogenative coupling of biaryl tertiary amines promoted with *t*-BuOK/DMF: A convenient synthesis of 6-aryl-5,6-dihydrophenanthridines

Ting Zhang, Lu Qian, Zhen-yu Chen, Yong Zou, Xue-jing Zhang,* and Ming Yan*

Institute of Drug Synthesis and Pharmaceutical Process, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China
Email: zhangxj33@mail.sysu.edu.cn

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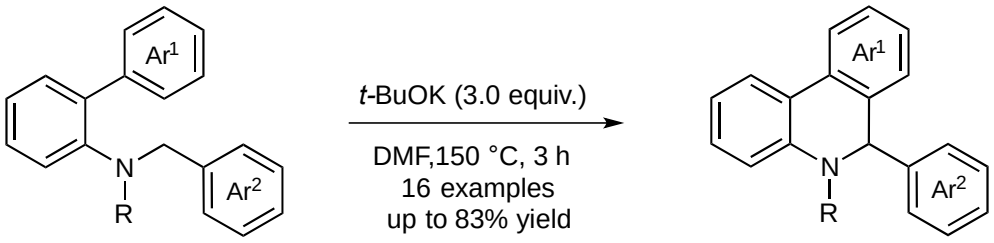
Abstract

A number of 6-aryl-5,6-dihydrophenanthridines were prepared in good yields via an intramolecular dehydrogenative coupling of biaryl tertiary amines promoted by *t*-BuOK/DMF. A reaction mechanism involving α-aminoalkyl radical intermediates is suggested.

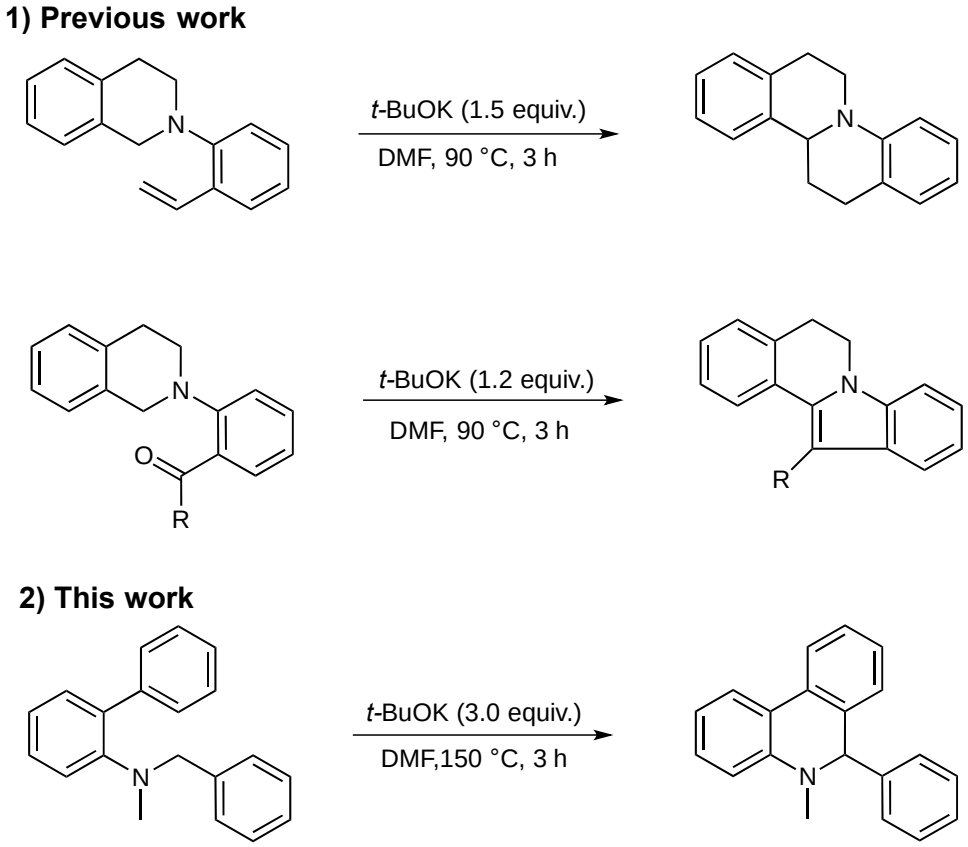


Keywords: Tertiary amine, α-aminoalkyl radical, cross-dehydrogenative coupling, dihydrophenanthridine

Introduction

Recently, the construction of carbon-carbon bonds via cross-dehydrogenative coupling (CDC) from two simple C–H bonds has made great progress.[1-10] This strategy, introduced by Li and other researchers, is demonstrated to be a superior alternative to classic coupling procedures using prefunctionalized starting materials. CDC reactions are generally achieved in the presence of transition-metal catalysts and sacrificial oxidants or H-acceptors. In recent years, transition-metal-free CDC reactions have also been developed.[11-16] In 2015, Wu and co-workers developed a *t*-BuOLi-promoted CDC reaction of quinolone *N*-oxides and 1,3-azoles without external oxidants.[17] A *t*-BuOK/DMSO mediated intermolecular CDC reaction of nitroarenes and indoles in an open flask was also reported.[18] These transformations usually proceed via oxidative SET (single electron transfer) C–H activation and the subsequent generation of radical intermediates.

Recently, our group has developed a series of *t*-BuOK/DMF promoted coupling reactions of tertiary amines, amides and diphenylmethanes with alkenes, alkynes and ketones.[19-25] The formation of α-amino alkyl radicals or diphenylmethyl radicals initiated by *t*-BuOK/DMF was proposed. We speculated that α-amino alkyl radicals would also react with arenes which could provide a new entry to the preparation of polycyclic heterocyclic compounds, such as 5,6-dihydrophenanthridine derivatives. Dihydrophenanthridine derivatives are present in the skeleton of a wide number of biologically active compounds, natural products and materials,[26-29] however, only a few synthetic methods for this class of compounds have been reported.[30-35] Furthermore, the reported methods generally suffer from limited functional group tolerance and undesired in situ oxidation. Herein, we report an intramolecular dehydrogenative coupling of biaryl tertiary amines promoted by *t*-BuOK/DMF. The reaction provides a new synthetic approach to 6-aryl-5,6-dihydrophenanthridines (Scheme 1).

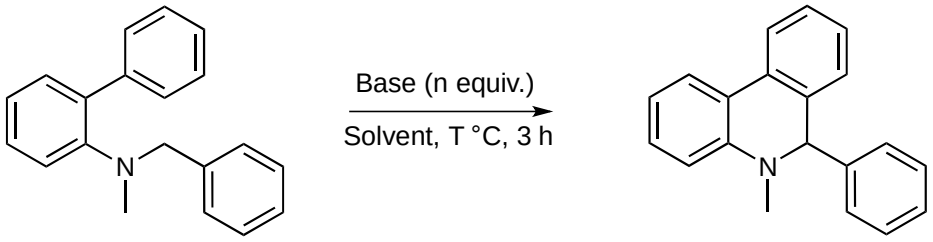


Scheme 1. *t*-BuOK /DMF promoted carbon–carbon bond formations.

Results and Discussion

Initially, we examined the reaction of **1a** in DMF with 3.0 equiv. of *t*-BuOK at 120 °C. To our delight, **2a** was obtained in a moderate yield. Furthermore, a number of bases and reaction solvents were examined and the results are summarized in Table 1. *t*-BuONa, *t*-BuOLi, and K_2CO_3 were tested, however, no **2a** was obtained (Table 1, entries 2-4). The reaction in DMSO was also applicable, but a lower yield was observed (Table 1, entry 5). THF was found to be incompatible with the reaction and no product **2a** was obtained. The effect of *t*-BuOK loading was also examined and the best yield was obtained with 3.0 equiv. of *t*-BuOK (Table 1, entries 7-8). The reaction was tested at 90, 150 and 180 °C respectively. The reaction at 150 °C gave the best result (Table 1, entries 9-11).

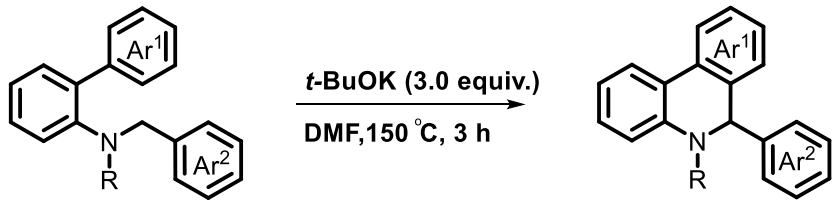
Table 1. Optimization of reaction conditions[a]



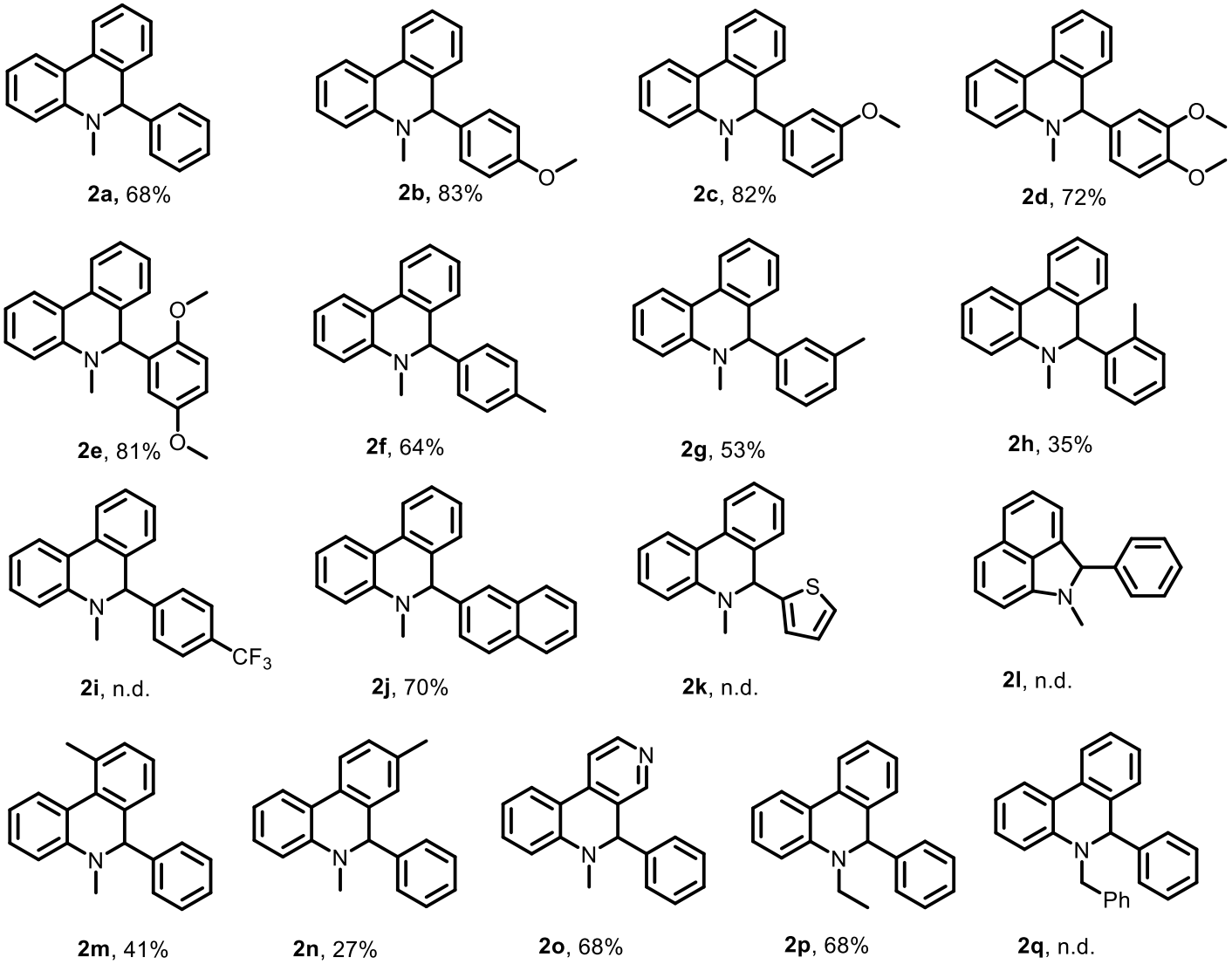
1a **2a**

Entry	Solvent	Base	n (equiv.)	T (°C)	Yield (%)[b]
1	DMF	*t*-BuOK	3	120	50
2	DMF	*t*-BuONa	3	120	n.d.[c]
3	DMF	*t*-BuOLi	3	120	n.d.[c]
4	DMF	K_2CO_3	3	120	n.d.[c]
5	DMSO	*t*-BuOK	3	120	15
6	THF	*t*-BuOK	3	reflux	n.d.[c]
7	DMF	*t*-BuOK	2	120	34
8	DMF	*t*-BuOK	4	120	47
9	DMF	*t*-BuOK	3	90	17
10	DMF	*t*-BuOK	3	150	64 (68)
11	DMF	*t*-BuOK	3	180	55

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), base (n equiv.), solvent (2.0 mL), at the indicated temperature for 3 hours under nitrogen atmosphere. [b] Yields were obtained by GC with *n*-dodecane as the internal standard. The value in the parentheses is the isolated yield after column chromatography. [c] Not detected.



1a-q **2a-q**



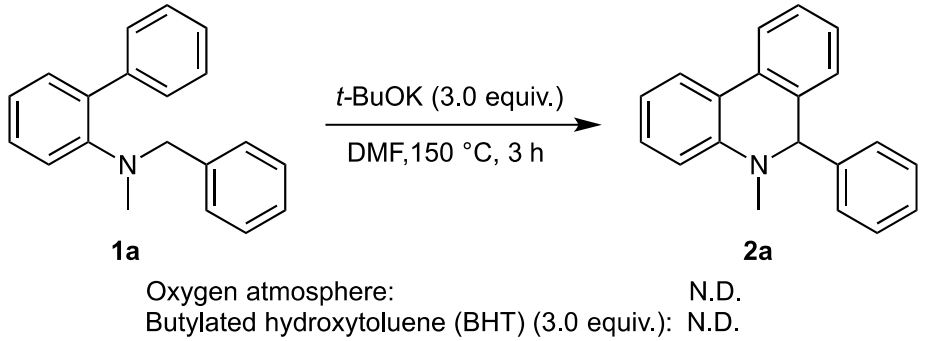
Scheme 2. Intramolecular cyclization of biaryl tertiary amines **1a-1q** promoted by *t*-BuOK/DMF.
Reaction conditions: **1a-1q** (0.2 mmol), *t*-BuOK (0.6 mmol), DMF (2.0 mL), nitrogen atmosphere, 150 °C, 3 h. Isolated yields.

With the optimal reaction conditions in hand, the reaction was extended to a variety of biaryl tertiary amines, and the results are summarized in Scheme 2. Substrates with electron-donating groups such as methoxyl and methyl groups on the aryl amine motif were well tolerated. Substrates with single and double methoxyl substitutions gave the products **2b**–**2e** in good yields. The substrates with a methyl substitution gave the products **2f**–**2h** in lower yields. Radical delocalization between the methyl group and amino alkyl group accounts for the poor yield of products. The *ortho*-methyl substituted substrate **1h** gave a poor yield which

implies that this transformation is sensitive to steric hindrance. Substitution with an electron-withdrawing CF_3 group showed a detrimental effect. Although complete consumption of **1i** was observed, no expected product **2i** could be isolated. A substrate with a naphthyl group was also examined and the product **2j** was obtained in a moderate yield. The 2-thienyl substituted substrate **1k** was found to be unreactive.

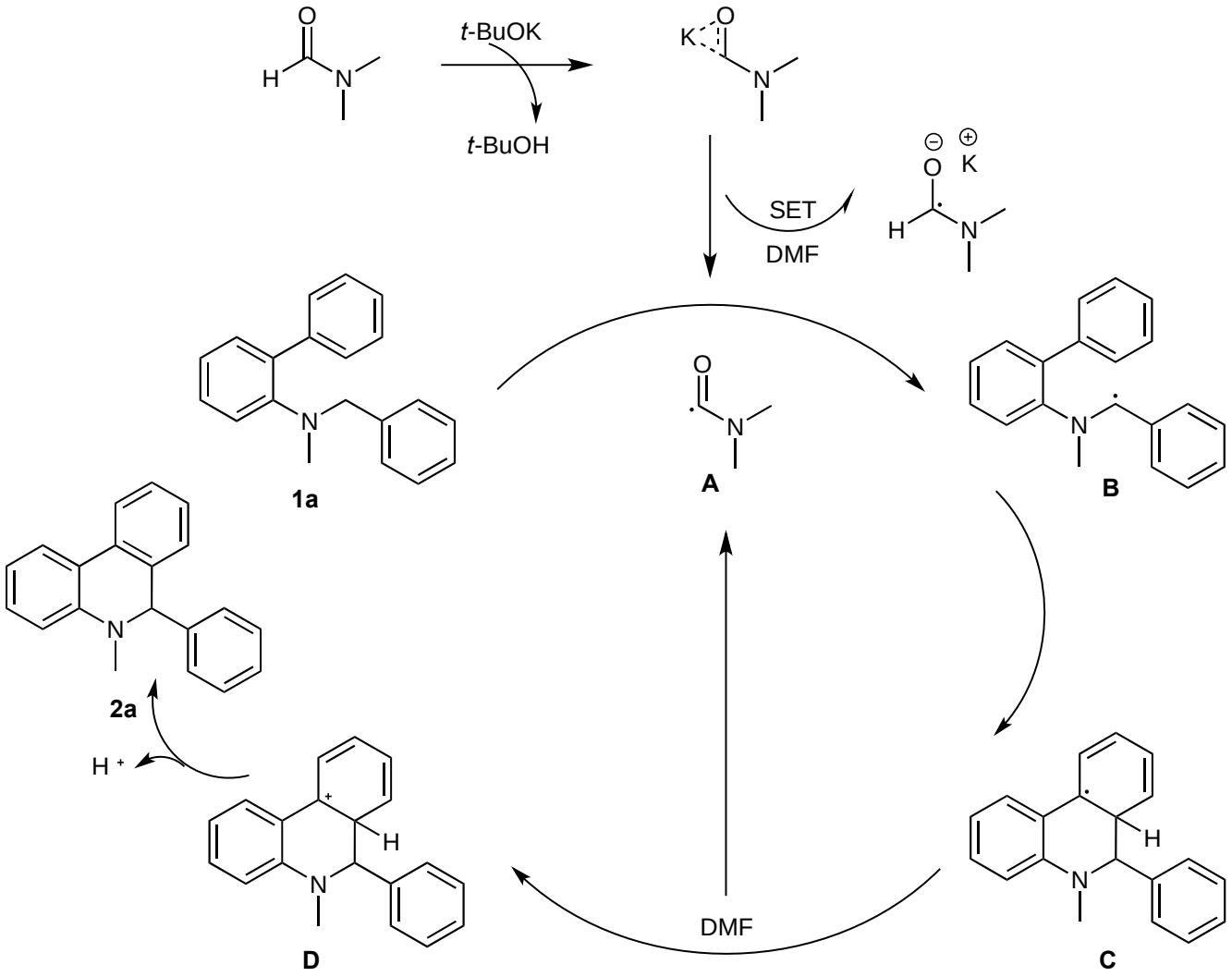
The effect of the substitutions on the biaryl motif was also examined. The replacement of biaryl group with a naphthyl group (**1l**) led to the loss of the reactivity. The substrates with a methyl substitution gave the products **2m–2n** in poor yields. However, the substrate with a pyridyl group (**1o**) gave a 68% yield. When the methyl group on the nitrogen was changed to ethyl, the product **2p** was obtained in a 68% yield. However, the benzyl replacement (**1q**) proved to inhibit the reaction.

To have a better understanding of the mechanism, radical trapping experiments were performed (Scheme 3). The reaction was totally inhibited in the presence of oxygen and butylated hydroxytoluene (BHT). The results implicate a radical reaction pathway.



Scheme 3. Radical trapping experiments.

Based on our previous studies and the present results, a tentative reaction mechanism is proposed (Scheme 3). DMF is deprotonated by *t*-BuOK to give the carbamoyl radical **A**. After a single-electron transfer (SET) step, the *α*-amino alkyl radical **B** is generated. **B** then undergoes an intramolecular radical addition to the phenyl ring. The resulting aryl radical **C** transfers an electron to DMF and is subsequently deprotonated by *t*-BuOK to give **2a.**



Scheme 4. Proposed reaction mechanism.

Conclusions

In summary, we have developed an intramolecular dehydrogenative coupling of biaryl tertiary amines promoted by *t*-BuOK/DMF. A number of 6-aryl-5,6-dihydrophenanthridines were prepared in good yields. A radical reaction pathway is proposed. The finding provides a new synthetic approach to dihydrophenanthridine derivatives.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26). Chemical shifts of carbon are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0) unless otherwise stated. Peaks are labeled as singlet (s), broad singlet (br), doublet (d), triplet (t), double doublet (dd), multiplet (m). Melting points were measured on a WRS-2A melting

point apparatus and are uncorrected. GC spectra were taken on an Agilent-6890A instrument. All products were further characterized by HRMS (high resolution mass spectra). The *t*-BuOK was purchased from Alfa Aesar chemical company and used without further purification. THF, DMF were dried and redistilled according to standard methods. DMSO was dried over 4Å molecular sieves.

General procedure for intramolecular dehydrogenative coupling. To a dried 10 mL reaction tube was added **1a** (54.3 mg, 0.2 mmol), *t*-BuOK (67.4 mg, 0.6 mmol) and DMF (2 mL). The mixture was stirred at 150 °C for 3 h under nitrogen atmosphere. Water (20.0 mL) was then added and the mixture was extracted with CH_2Cl_2 (15 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was obtained which was purification by column chromatography to give the product **2a** (36.9 mg, 68%) as a colorless oil.

5-Methyl-6-phenyl-5,6-dihydrophenanthridine (2a).[36] Colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54 (d, *J* 7.9 Hz, 1H), 7.48 (dd, *J* 7.7, 1.3 Hz, 1H), 6.99–6.94 (m, 1H), 6.90–6.77 (m, 8H), 6.49–6.39 (m, 1H), 6.29 (d, *J* 8.1 Hz, 1H), 5.20 (s, 1H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.9, 146.8, 140.7, 135.3, 134.8, 133.6, 132.8, 132.6, 132.6, 132.2, 131.6, 128.29, 127.5, 126.5, 122.6, 117.4, 71.0, 41.9. HRMS (ESI) calculated for $C_{20}H_{18}N$ $(M+H)^+$: 272.1434, found: 272.1433.

6-(4-Methoxyphenyl)-5-methyl-5,6-dihydrophenanthridine (2b).[36] White solid, M.p. (153.4–156.6 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* 7.5 Hz, 1H), 7.76 (dd, *J* 7.7, 1.4 Hz, 1H), 7.28 (td, *J* 7.7, 1.4 Hz, 1H), 7.22–7.15 (m, 2H), 7.06–7.02 (m, 3H), 6.83 (td, *J* 7.5, 1.0 Hz, 1H), 6.71–6.67 (m, 2H), 6.59 (d, *J* 8.1 Hz, 1H), 5.31 (s, 1H), 3.69 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 144.8, 136.0, 133.9, 130.6, 129.4, 128.0, 127.5, 127.3, 127.0, 123.1, 122.5, 122.0, 117.7, 113.8, 112.5, 67.2, 55.1, 37.0. HRMS (ESI) calculated for $C_{21}H_{20}NO$ $(M+H)^+$: 302.1539, found: 302.1554.

6-(3-Methoxyphenyl)-5-methyl-5,6-dihydrophenanthridine (2c).[36] White solid, M.p. (133.4–146.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* 7.5 Hz, 1H), 7.75 (dd, *J* 7.7, 1.4 Hz, 1H), 7.30–7.25 (m, 1H), 7.22–7.14 (m, 2H), 7.10–7.05 (m, 2H), 6.82 (td, *J* 7.5, 1.1 Hz, 1H), 6.73 (dd, *J* 7.7, 1.1 Hz, 1H), 6.71–6.66 (m, 2H), 6.61 (d, *J* 8.2 Hz, 1H), 5.32 (s, 1H), 3.60 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 145.0, 143.2, 135.6, 130.65, 129.5, 127.7, 127.3, 127.0, 123.2, 122.5, 122.0, 119.1, 117.8, 112.8, 112.5, 112.4, 67.9, 55.0, 37.2. HRMS (ESI) calculated for $C_{21}H_{20}NO$ $(M+H)^+$: 302.1539, found: 302.1550.

6-(3,4-Dimethoxyphenyl)-5-methyl-5,6-dihydrophenanthridine (2d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* 7.9 Hz, 1H), 7.76 (dd, *J* 7.7, 1.5 Hz, 1H), 7.29 (td, *J* 7.7, 1.4 Hz, 1H), 7.23–7.20 (m, 1H), 7.19–7.16 (m, 1H), 7.09–7.06 (m, 1H), 6.83 (td, *J* 7.5, 1.1 Hz, 1H), 6.71 (dd, *J* 8.2, 1.9 Hz, 1H), 6.69–6.66 (m, 1H), 6.63 (d, *J* 1.6 Hz, 1H), 6.61 (d, *J* 0.6 Hz, 1H), 5.27 (s, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 148.6, 145.1, 136.2, 134.3, 130.6, 129.5, 127.6, 127.3, 126.9, 123.1, 122.5, 122.3, 119.0, 117.8, 112.6, 111.0, 109.9, 67.6, 55.8, 55.6, 37.1. HRMS (ESI) calculated for $C_{22}H_{22}NO_2$ $(M+H)^+$: 332.1645, found: 332.1643.

6-(2,5-Dimethoxyphenyl)-5-methyl-5,6-dihydrophenanthridine (2e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* 7.8 Hz, 1H), 7.74 (dd, *J* 7.7, 1.4 Hz, 1H), 7.19 (m, 4H), 6.83–6.80 (m, 1H), 6.78 (s, 1H), 6.73–6.64 (m, 1H), 6.62 (m, 1H), 6.57 (d, *J* 3.1 Hz, 1H), 6.05 (s, 1H), 3.86 (s, 3H), 3.40 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 149.7, 145.5, 136.2, 131.5, 130.8, 129.4, 127.4, 127.2, 126.8, 123.1, 122.4, 122.0, 117.5, 113.4, 113.4, 112.1, 111.9, 58.9, 56.2, 55.2, 36.8. HRMS (ESI) calculated for $C_{22}H_{22}NO_2$ $(M+H)^+$: 332.1645, found: 332.1639.

5-Methyl-6-*p*-tolyl-5,6-dihydrophenanthridine (2f).[36] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (t, *J* 6.5 Hz, 1H), 7.75 (dd, *J* 7.7, 1.4 Hz, 1H), 7.29–7.25 (m, 1H), 7.23–7.18 (m, 1H), 7.18–7.14 (m, 1H), 7.07–7.04 (m, 1H), 7.02 (dd, *J* 6.6, 4.8 Hz, 2H), 6.96 (d, *J* 8.1 Hz, 2H), 6.84–6.80 (m, 1H), 6.59 (d, *J* 8.0 Hz, 1H), 5.32 (s, 1H), 2.87 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 138.6, 137.2, 135.9, 130.7, 129.4, 129.2, 128.3,

127.5, 127.3, 127.0, 126.7, 123.1, 122.5, 117.6, 112.4, 67.6, 37.1, 21.0. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1590, found: 286.1603.

5-Methyl-6-*m*-tolyl-5,6-dihydrophenanthridine (2g). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.83–7.72 (m, 2H), 7.27 (d, *J* 7.3 Hz, 1H), 7.19 (m, 2H), 7.04 (m, 2H), 6.98–6.89 (m, 3H), 6.83 (dd, *J* 11.8, 7.7 Hz, 1H), 6.63–6.57 (m, 1H), 5.32 (s, 1H), 2.87 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.0, 141.6, 138.0, 135.8, 130.6, 129.5, 128.5, 128.4, 127.6, 127.5, 127.3, 127.1, 123.9, 123.2, 122.5, 121.9, 117.6, 112.4, 67.9, 37.2, 21.6. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1590, found: 286.1585.

5-Methyl-6-*o*-tolyl-5,6-dihydrophenanthridine (2h). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.81 (d, *J* 7.5 Hz, 1H), 7.76 (dd, *J* 7.7, 1.4 Hz, 1H), 7.23–7.20 (m, 1H), 7.20–7.16 (m, 1H), 7.16–7.11 (m, 2H), 7.11–7.06 (m, 2H), 7.00 (dd, *J* 7.2, 6.0 Hz, 1H), 6.81 (dd, *J* 10.7, 4.3 Hz, 2H), 6.62 (d, *J* 7.9 Hz, 1H), 5.82 (s, 1H), 2.73 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.6, 141.0, 136.1, 134.7, 130.9, 130.8, 129.5, 128.8, 127.5, 127.4, 127.2, 126.8, 126.6, 123.1, 122.1, 121.4, 117.5, 112.1, 63.5, 36.3, 20.1. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1590, found: 286.1580.

5-Methyl-6-(naphthalen-2-yl)-5,6-dihydrophenanthridine (2j). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.84 (d, *J* 7.8 Hz, 1H), 7.79 (dd, *J* 7.7, 1.4 Hz, 1H), 7.75–7.71 (m, 1H), 7.71–7.68 (m, 1H), 7.63–7.58 (m, 2H), 7.39 (m, 2H), 7.31–7.26 (m, 1H), 7.24–7.19 (m, 2H), 7.17–7.13 (m, 1H), 7.08 (dd, *J* 7.6, 1.1 Hz, 1H), 6.85 (td, *J* 7.6, 1.0 Hz, 1H), 6.61 (d, *J* 8.0 Hz, 1H), 5.52 (s, 1H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.0, 139.3, 135.5, 133.2, 133.0, 130.8, 129.6, 128.6, 128.1, 127.7, 127.6, 127.3, 126.1, 125.8, 125.2, 125.2, 123.2, 122.5, 121.82, 117.8, 112.4, 68.1, 37.1. HRMS (ESI) calculated for $C_{24}H_{20}N$ $(M+H)^+$: 322.1590, found: 322.1592.

5,10-Dimethyl-6-phenyl-5,6-dihydrophenanthridine (2m). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.81 (d, *J* 7.9 Hz, 1H), 7.77 (d, *J* 7.7 Hz, 1H), 7.24–7.13 (m, 4H), 7.12–7.07 (m, 2H), 7.00 (t, *J* 7.2 Hz, 1H), 6.83 (t, *J* 7.6 Hz, 2H), 6.62 (d, *J* 8.2 Hz, 1H), 5.82 (s, 1H), 2.74 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.6, 141.0, 136.1, 134.7, 131.8, 130.9, 129.5, 128.7, 127.5, 127.5, 127.2, 126.8, 126.6, 123.1, 122.2, 121.4, 117.5, 112.1, 63.4, 36.3, 20.2. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1590, found: 286.1580.

5,8-Dimethyl-6-phenyl-5,6-dihydrophenanthridine (2n). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.75–7.68 (m, 2H), 7.20–7.14 (m, 4H), 7.13–7.08 (m, 3H), 6.88 (s, 1H), 6.82 (td, *J* 7.5, 1.0 Hz, 1H), 6.57 (d, *J* 8.0 Hz, 1H), 5.30 (s, 1H), 2.86 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 144.6, 141.7, 137.1, 135.6, 129.0, 128.6, 128.5, 128.0, 127.6, 127.6, 126.8, 122.8, 122.5, 122.1, 117.6, 112.3, 68.0, 37.1, 21.2. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1590, found: 286.1583.

6-Methyl-5-phenyl-5,6-dihydrobenzo[c][2,7]naphthyridine (2o). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (d, *J* 5.4 Hz, 1H), 8.32 (s, 1H), 7.75 (dd, *J* 7.8, 1.3 Hz, 1H), 7.58 (d, *J* 5.3 Hz, 1H), 7.33–7.28 (m, 1H), 7.19 (dd, *J* 6.3, 3.6 Hz, 3H), 7.14 (dd, *J* 6.6, 3.1 Hz, 2H), 6.84 (dd, *J* 10.9, 4.1 Hz, 1H), 6.65 (d, *J* 8.2 Hz, 1H), 5.45 (s, 1H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.6, 148.4, 146.0, 141.2, 137.9, 131.9, 130.1, 128.8, 128.0, 126.4, 124.1, 118.8, 117.7, 116.0, 112.6, 65.1, 37.2. HRMS (ESI) calculated for $C_{19}H_{17}N_2$ $(M+H)^+$: 273.1386, found: 273.1364.

5-Ethyl-6-phenyl-5,6-dihydrophenanthridine (2p). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.81–7.71 (m, 2H), 7.27–7.23 (m, 1H), 7.21–7.17 (m, 3H), 7.14 (m, 3H), 7.10–7.01 (m, 2H), 6.79 (m, 1H), 6.72 (d, *J* 8.2 Hz, 1H), 5.49 (s, 1H), 3.47 (m, 1H), 3.25 (m, 1H), 1.17 (t, *J* 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 144.2, 143.6, 135.7, 130.6, 129.4, 128.5, 127.5, 127.4, 127.1, 127.0, 126.6, 123.5, 122.5, 121.7, 117.2, 112.4, 65.5, 44.1, 12.6. HRMS (ESI) calculated for $C_{21}H_{20}N$ $(M+H)^+$: 286.1517 286.1590, found: 286.1611.

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