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Graphical Abstract

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[a] *Department of Chemical Science & Technology, Kunming University, Kunming 650214, China*
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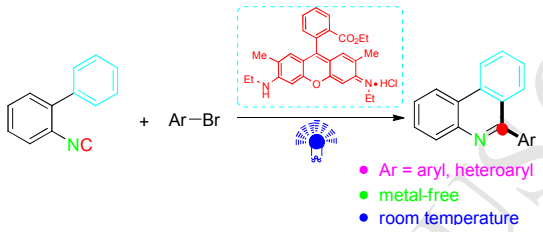

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ABSTRACT

A visible-light-catalyzed synthesis of 6-aryl substituted phenanthridines from aryl bromides and 2-isocyanobiphenyls at room temperature has been discovered. This metal-free cross-coupling reaction offers rapid and sustainable access to a series of structurally complex and diverse phenanthridines. The usage of inexpensive Rhodamine 6G as the catalyst with easy operation makes this protocol very practical.

1. Introduction

Nitrogen heterocycles are among the most important structural classes of chemical substances, which are particularly widespread prevalence in natural products, biologically active structures and medicinally relevant compounds.[1] Phenanthridines represent an important class of nitrogen-containing heterocycles, which are the basic constituents of numerous natural products, biologically active alkaloids, functional materials and pharmaceuticals.[2] Given the fact that the construction of 6-substituted phenanthridines is a successful strategy to improve its performance, many C6-diversified phenanthridines, especially 6-aryl substituted derivatives featuring good biological activities have been documented over the last several years.[3] Consequently, the development of synthetic methods used for the preparation of 6-aryl substituted phenanthridines has received a lot of attention.[4] Among the numerous methods that have been developed, isonitrile insertion has emerged as a powerful strategy for their preparation.[5] In this field, aryl radicals easily add to the carbon atom of isonitrile to form animidoyl radical intermediate, which is able to undergo subsequent cyclization to eventually afford 6-aryl substituted phenanthridines. In this context, numerous aryl radical precursors have been reported, such as boronic acids,[4g] hydrazines[4e] and aryl sulfonyl chlorides.[4f] Though, it is still necessary to develop more aryl radical precursors to realize isonitrile insertion via a radical process used for synthesis of 6-aryl substituted phenanthridines.

Visible-light is non-polluting, infinitely available and easy to handle. Since the milestone made by Macmillan and Yoon in 2008, the use of visible light as a driving force for chemical reactions has attracted a lot of scientific and technological interest.[6] Photoredox catalysis employing visible light has recently emerged as a valuable platform for the design of unique one-electron-transfer pathways that allow the invention of valuable new chemical reactions.[7] However, most of the previously reported studies are based on the use of transition metal (usually ruthenium and iridium) polypyridyl complexes. Although there are many advantages related to the use of ruthenium and iridium polypyridyl complexes in visible-light photocatalysis, their exorbitant price and related environmental pollution limited their further application in industrial processes. Organic dyes, which are inexpensive and easily available, have been used as a viable alternative in photoredox catalysis.[8] Rhodamine 6G (Rh-6G) is a widely applied organic dye. Rh-6G is converted to the corresponding excited radical anion [Rh-6G$^{\bullet-}$]* upon irradiation with blue light (455 nm) in the presence of DIPEA (*N*,*N*-diisopropylethylamine) under a nitrogen atmosphere and has a reduction potential of ca. −2.4 V vs SCE, which is sufficient to activate an aryl halide.[9] The initial aryl halide radical anion may cleave into a halide anion and an aryl radical, which can further react with different coupling partners, such as arenes,[9] heteroarenes,[10] alkenes,[9] alkynes[11] and trialkyl

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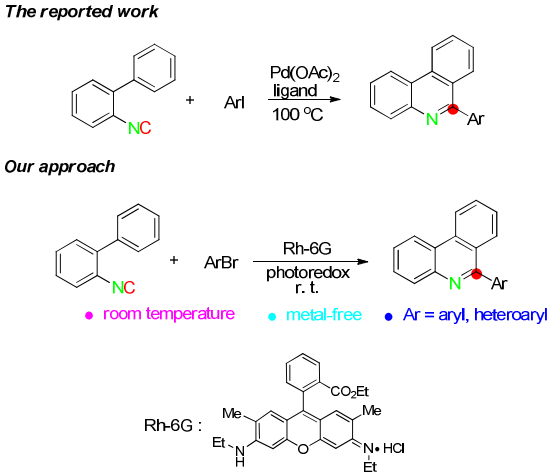
phosphites.[12] We presumed that aryl isonitriles might serve as good coupling partners to trap aryl radicals which can be easily generated from aryl halides. Herein, we disclose our preliminary results on the visible-light-promoted transformation of aryl bromides and 2-isocyanobiphenyls towards the synthesis of 6-aryl substituted phenanthridines.

The significance of the present finding is threefold: 1) Simple and readily available Rh-6G emerges as an efficient catalyst, rather than a transition-metal catalyst, which is often expensive with noble metal, and is intractable to be completely removed from the products, especially in the synthesis of pharmaceutical compounds, 2) visible-light is employed as a safe, renewable and inexpensive source of chemical energy to facilitate the construction of 6-aryl substituted phenanthridines and 3) readily accessible aryl (heteroaryl) bromides are used as starting materials.

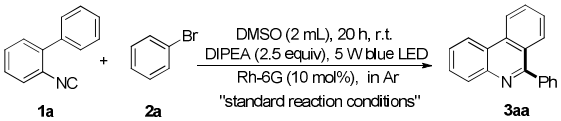


Schem 1 Synthesis of 6-aryl substituted phenanthridines via cyclization of 2-isocyanobiphenyls with aryl halides

2. Results and discussion

First, visible-light photoredox cyclization of 2-isocyanobiphenyl **1a** with bromobenzene **2a** was selected as the model to optimize conditions. Various solvents, photocatalysts, and bases were examined at room temperature. Dimethyl sulfoxide (DMSO) was found to be a good solvent for the photoreaction (Table 1, entries1-4). It was found that DIPEA was superior to other bases (Table 1, entries 1, 5-7). By screening photocatalysts, we found that Rh-6G was the best photocatalyst for this cascade cyclization process (Table 1, entries 1, 8-10). The control experiment showed that the reaction could not proceed in the absence of a photocatalyst and visible light (Table 1, entries 11-12). Gratifyingly, a 1.07 g (6.0 mmol) scale reaction of 2-isocyanobiphenyl **1a** was successfully performed with bromobenzene **2a**, providing the desired product **3aa** in 62% yield (Table 1, entry 13). In these reaction, biphenyls were always formed in 5-15% yields.

Table 1
Optimization of the reaction conditions [a]

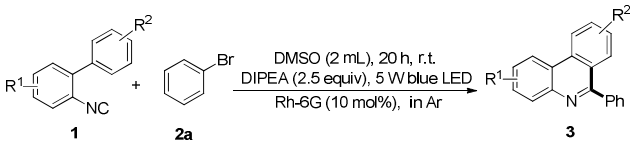


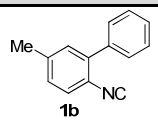
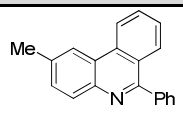
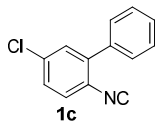
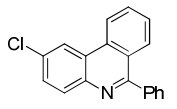
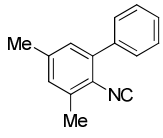
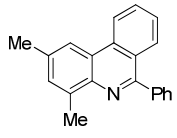
Entry	Variation from the "standard reaction conditions"	Yield [b] (%)
1	none	79
2	MeCN as solvent	57
3	DMF as solvent	32
4	$PhCF_3$ as solvent	trace
5	with triethylamine (2.5 equiv) as base	39
6 [c]	with $NaHCO_3$ (2.5 equiv) as base	6
7	in the absence of DIPEA	none
8	$Ir(ppy)_3$ (10 mol%) as PC	13
9	Eosin Y (10 mol%) as PC	trace
10	Rose Bengal (10 mol%) as PC	trace
11	without PC	0
12	in the absence of visible-light	0
13 [d]	none	62

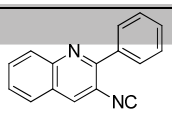
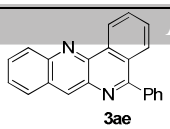
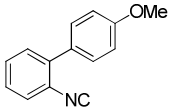
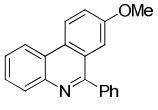
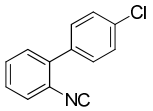
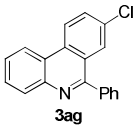
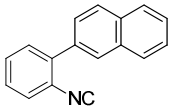
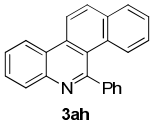
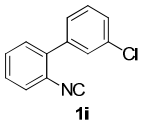
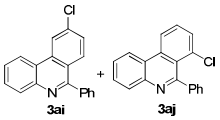
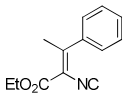
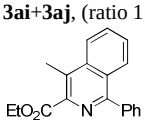
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.35mmol), Rh-6G (10 mol%), solvent (2.0 mL), DIPEA (0.75 mmol), in Ar atmosphere, room temperature, 5 W blue LED light for 20 h. [b] Isolated yield. [c] GC analysis. [d] **1a** (6.0 mmol), **2a** (7.0 mmol), solvent (10 mL), DIPEA (15.0 mmol) for 48h. PC = photocatalyst.

Having optimized the reaction conditions, we examined the scope of the reaction of bromobenzene **2a** with different 2-isocyanobiphenyls **1** to define the scope of this transformation. The isocyanides bearing either an electron-rich or an electron-deficient substituent on the isocyano-bearing phenyl ring was compatible under the standard conditions, leading to the desired product **3ab**-**3ac** in 60% and 68% yields, respectively (Table 2, entries 1-2). Notably, the poly-substituted isocyanide **1d** gave the desired product **3ad** with a good yield (Table 2, entry 3). Interestingly, the introduction of heterocycles into this system made this methodology more useful for the preparation of pharmaceuticals and materials (Table 2, entry 4). Subsequently, a series of functional groups on the non-isocyano bearing aromatic ring were also evaluated, and good results were obtained. For example, Cl and MeO groups provided the desired products with good yields (Table 2, entries 5-6). It was found that the reactions of 2-(2-isocyanophenyl)naphthalene **1h** with bromobenzene **2a** proceeded well and gave the desired product **3ah** in 58% yield. In addition, when employing 2-isocyanobiphenyl derivative **1i** as the substrate, the reaction afforded the two regioisomers **3ia** and **3ja** in the ratio of 1 : 1.7 (Table 2, entry 8). Apart from 2-isocyanobiphenyls, ethyl 2-isocyano-3-phenylbut-2-enoate **1k** smoothly reacted with **2a** and gave the corresponding product **3ak** in 77% yield (Table 2, entry 9).

Table 2
Scope of 2-isocyanobiphenyls **1** [a]



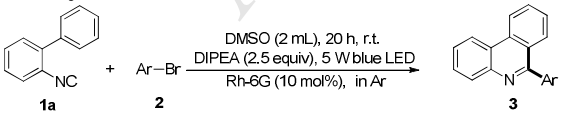
Entry	Substrates **1**	Products **3**	Yield [b] (%)
1	 **1b**	 **3ab**	60
2	 **1c**	 **3ac**	68
3	 **1d**	 **3ad**	71

4	 **1e**	 **3ae**	64
5	 **1f**	 **3af**	67
6	 **1g**	 **3ag**	51
7	 **1h**	 **3ah**	58
8	 **1i**	 **3ai**+**3aj**, (ratio 1:1.7)	63
9	 **1k**	 **3ak**	77

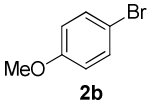
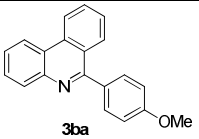
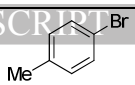
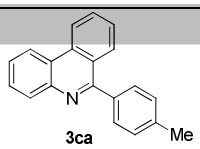
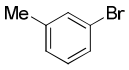
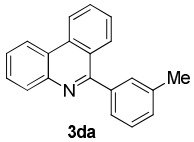
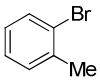
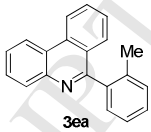
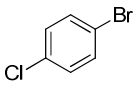
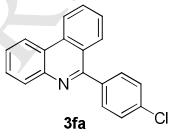
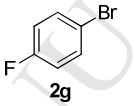
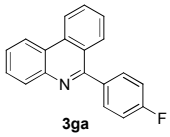
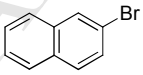
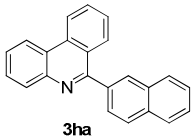
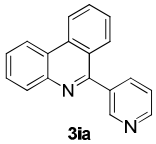
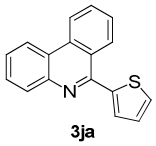
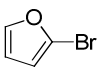
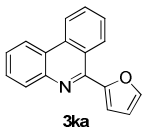
[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.35mmol), Rh-6G (10 mol%), DMSO (2.0 mL), DIPEA (0.75 mmol), in Ar atmosphere, room temperature, 5 W blue LED light for 20 h. [b] Isolated yields.

The substrate scope was further investigated by reacting 2-isocyanobiphenyl **1a** with different aryl bromides **2**. It is noted that the broad availability of substituted aryl bromides **2** rendered us access to various substituted 6-aryl substituted phenanthridines. Notably, aryl bromides with electron-rich substituents (like Me and MeO) on the aromatic rings could proceed smoothly. The substituents at the *ortho*-, *meta*-, or *para*-position have no distinct influence on the reaction. For example, substrates **2c**-**2e** with a Me group were transformed into products **3ca**, **3da** and **3ea** in 49%, 56% and 52% yields, respectively (Table 3, entries 2-4). Electron-deficient aryl bromides were demonstrated to be well-tolerated under our standard conditions (Table 3, entries 5-6). In addition, aryl bromide with a naphthyl group also participated in this cyclization, affording the product **3ha** in 73 % yield (Table 3, entry 7). Heteroaromatic molecules bearing heteroaryl-heteroaryl bonds are an important class of building blocks found in a variety of areas. The visible-light-induced cyclization process allowed the synthesis of 6-heteroaryl substituted phenanthridines **3ia**-**3ka** in moderate to good yields (Table 3, entries 8-10).

Table 3
Scope of aryl bromides **2** [a]



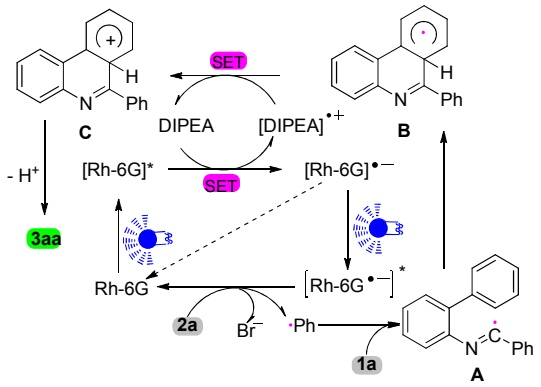
1a + **2** → **3**

Entry	Substrates **2**	Products **3**	Yield [b] (%)
1	 **2b**	 **3ba**	50
2	 **2c**	 **3ca**	49
3	 **2d**	 **3da**	56
4	 **2e**	 **3ea**	52
5	 **2f**	 **3fa**	58
6	 **2g**	 **3ga**	66
7	 **2h**	 **3ha**	73
8	 **2i**	 **3ia**	70
9	 **2j**	 **3ja**	61
10	 **2k**	 **3ka**	54

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.35 mmol), Rh-6G (10 mol%), DMSO (2.0 mL), DIPEA (0.75 mmol), in Ar atmosphere, room temperature, 5 W blue LED light for 20 h. [b] Isolated yields.

On the basis of these observations and previous studies,[9-12] a plausible mechanism was proposed as shown in Scheme 2. Under the visible-light irradiation, Rh-6G was converted to the excited [Rh-6G]*. A single electron transfer between [Rh-6G]* and DIPEA afforded a radical anion/radical cation pair: [Rh-6G$^{\bullet-}$] and [DIPEA$^{\bullet+}$]. Continuous irradiation of the radical anion [Rh-6G$^{\bullet-}$] with blue light triggers a single electron transfer from the excited [Rh-6G$^{\bullet-}$]* to bromobenzene **2a** producing the transient [Ph-Br$^{\bullet-}$] radical anion and regenerating Rh-6G completing the

catalytic cycle. Thereafter, [Ph-Br$^{\bullet-}$] radical anion undergoes fragmentation to release a phenyl radical (Ph•), which reacts with 2-isocyanobiphenyl **1a** to form the imidoyl radical **A**. Subsequently, the intermediate **A** cyclizes to generate the cyclohexadienyl radical **B**. Oxidation of radical **B** affords species **C**. Then the desired phenanthridine **3aa** is delivered after deprotonation.



Scheme 2 Plausible mechanism for synthesis of **3aa**

3. Conclusion

In conclusion, we have developed a novel metal-free approach to 6-aryl substituted phenanthridines that involves the functionalization of C(sp^2)-Br and C(sp^2)-H bonds. The mild reaction conditions are compatible with many functional groups and the scope of 2-isocyanobiphenyls and aryl bromides is broad providing various 6-aryl substituted phenanthridines with good yields. Simple and commercially available Rh-6G is employed as the photoredox catalysts. All of these features as well as its metal-free conditions make this method highly efficient and practical. Further investigations of the mechanism of the reaction and its application are ongoing in our laboratory.

4. Experimental section

4.1 General materials and methods

Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. Substrates **1** were prepared according the literature methods.[4g] ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (*J*) were measured in Hz. GC-MS analyses were performed on a SHIMADZU QP2010. High Resolution mass spectrometer (HRMS) spectra were recorded on a Bruker micrOTOF-Q II analyzer. 200-300 mesh silica gel was used for column chromatography.

4.2 General procedure for synthesis of 6-aryl (heteroaryl) substituted phenanthridines 3

To a Schlenk tube were added 2-isocyanobiphenyls **1** (0.3 mmol), aryl bromides **2** (0.35 mmol), DMSO (2.0 mL), Rh-6G (0.03 mmol), DIPEA (0.75 mmol), Then the tube was charged with argon, and was stirred at room temperature with the irradiation of a 5 W blue LED for about 20-24 h. After the reaction was finished, the reaction mixture was diluted in 40 mL ethyl acetate, washed with a saturated solution of brine (8 mL), a solution of 1 mol/L HCl (10 mL), a saturated solution of brine (8 mL), saturated $NaHCO_3$ (10 mL), a saturated solution of brine (8 mL), dried (Na_2SO_4) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the substituted phenanthridines **3**.

6-Phenylphenanthridine (3aa).[5b] Yield: 79%, 60.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.70 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.30-8.27 (m, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.89-7.84 (m, 1H), 7.81-7.68 (m, 4H), 7.64-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.1, 143.7, 139.8, 133.3, 130.5, 130.4, 129.6, 128.9, 128.7, 128.6, 128.3, 127.0, 126.7, 125.0, 123.2, 122.0, 121.6; LRMS (EI 70 ev) *m/z* (%): 255 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{19}H_{14}N$ (M+H)$^+$ 256.1126, found 256.1123.

2-Methyl-6-phenylphenanthridine (3ab).[4e] Yield: 60%, 48.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.66 (d, *J* = 8.0 Hz, 1H), 8.34 (s, 1H), 8.11, (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.70-7.67 (m, 2H), 7.53-7.44 (m, 5H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 160.7, 142.1, 139.6, 136.4, 133.1, 130.5, 130.1, 129.8, 129.5, 128.7, 128.4, 128.3, 126.8, 125.2, 123.2, 122.1, 121.2, 21.6; LRMS (EI 70 ev) *m/z* (%): 269 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ (M+H)$^+$ 270.1283, found 270.1285.

2-Chloro-6-phenylphenanthridine (3ac).[4f] Yield: 68%, 59.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.63 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 3.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.90-7.87 (m, 1H), 7.71-7.61 (m, 4H), 7.57-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.2, 142.0, 139.3, 133.1, 132.4, 131.7, 131.2, 129.8, 129.4, 129.1, 129.0, 128.6, 127.9, 125.3, 124.8, 122.4, 122.0; LRMS (EI 70 ev) *m/z* (%): 289 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ (M+H)$^+$ 290.0737, found 290.0742.

2,4-Dimethyl-6-phenylphenanthridine (3ad).[4f] Yield: 71%, 60.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.67 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.13 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.79-7.75 (m, 3H), 7.56-7.46 (m, 4H), 7.41 (s, 1H); 2.81 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 158.6, 140.7, 140.0, 137.2, 136.1, 133.5, 131.2, 130.0, 129.9, 128.4, 128.3, 128.2, 126.5, 124.7, 123.4, 122.2, 119.1, 22.3, 18.4; LRMS (EI 70 ev) *m/z* (%): 283 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{21}H_{18}N$ (M+H)$^+$ 284.1439, found 284.1437.

5-Phenyldibenzo[*b,h*][1,5]naphthyridine (3ae).[4f] Yield: 64%, 58.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 9.49 (d, *J* = 7.6 Hz, 1H), 8.98 (s, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.12 (dd, *J* = 3.2 Hz, *J* = 2.0 Hz, 2H), 7.99-7.96 (m, 1H), 7.87-7.74 (m, 4H), 7.64-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 163.1, 148.2, 143.0, 139.4, 136.5, 136.1, 134.2, 131.4, 130.3, 129.8, 129.7, 129.7, 129.3, 128.8, 128.7, 128.6, 128.5, 127.4, 126.5, 124.6; LRMS (EI 70 ev) *m/z* (%): 306 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{22}H_{15}N_2$ (M+H)$^+$ 307.1235, found 307.1229.

8-Methoxy-6-phenylphenanthridine (3af).[4e] Yield: 67%, 57.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.59 (d, *J* = 8.4 Hz, 1H), 8.51-8.47 (m, 1H), 8.17 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.74-7.67 (m, 2H), 7.63-7.58 (m, 2H), 7.55-7.48 (m, 3H), 7.44-7.40 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.7, 158.3, 143.1, 139.2, 130.3, 130.0, 129.3, 128.4, 128.0, 127.8, 127.1, 124.1, 121.5, 121.1, 116.1, 114.5, 110.0, 56.1; LRMS (EI 70 ev) *m/z* (%): 285 (M$^+$, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ (M+H)$^+$ 286.1232, found 286.1231.

8-Chloro-6-phenylphenanthridine (3ag).[4e] Yield: 51%, 44.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.61 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.79-7.74 (m, 2H), 7.70-7.63 (m, 3H), 7.58-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.3, 143.1, 139.2, 133.0, 131.6, 131.2, 130.2, 129.5, 129.2, 128.9, 128.4, 127.7, 127.0,

126.1, 124.3, 123.0, 121.8; LRMS (EI 70 ev) *m/z* (%): 289 (M^+, 90); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0744.

5-Phenylbenzo[*i*]phenanthridine (3ah).[4f] Yield: 58%, 53.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67-8.63 (m, 2H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.80-7.76 (m, 2H), 7.72-7.69 (m, 1H), 7.62-7.59 (m, 2H), 7.51-7.46 (m, 4H), 7.23-7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 144.2, 143.6, 134.4, 133.2, 132.6, 130.4, 129.7, 129.3, 129.1, 129.0, 128.6, 128.5, 128.2, 127.0, 126.5, 126.1, 123.7, 122.4, 121.5, 120.2; LRMS (EI 70 ev) *m/z* (%): 305 (M^+, 100); HRMS m/z (ESI) calcd for $C_{23}H_{16}N$ $(M+H)^+$ 306.1283, found 306.1279

9-Chloro-6-phenylphenanthridine (3ai).[4f] Yield: 23%, 20.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.70-7.67 (m, 3H), 7.55-7.50 (m, 4H); ^{13}C NMR (100 MHz, CDCl3) δ: 160.6, 144.0, 139.4, 137.1, 134.5, 130.6, 130.1, 129.4, 129.0, 128.8, 128.4, 127.6, 127.2, 123.5, 122.7, 122.0, 121.8; LRMS (EI 70 ev) m/z (%): 289 (M^+, 100); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0739.

7-Chloro-6-phenylphenanthridine (3aj).[4f] Yield: 40%, 34.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, *J* = 8.0 Hz, 1H), 8.58 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.07 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.82-7.78 (m, 1H), 7.70-7.64 (m, 4H), 7.59-7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 143.6, 139.0, 136.1, 133.7, 131.4, 130.2, 129.9, 129.1, 128.6, 128.3, 127.4, 127.1, 125.6, 123.4, 122.5, 122.0; LRMS (EI 70 ev) m/z (%): 289 (M^+, 90); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0740.

Ethyl 4-methyl-1-phenylisoquinoline-3-carboxylate (3ak).[4c] Yield: 77%, 67.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.81-7.67 (m, 1H), 7.70-7.67 (m, 2H), 7.60-7.57 (m, 1H), 7.53-7.46 (m, 3H), 4.52 (q, *J* = 7.2 Hz, 2H), 2.83 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.9, 158.8, 142.0, 139.1, 136.6, 130.4, 130.1, 128.6, 128.3, 128.1, 127.8, 126.9, 124.3, 61.4, 14.3, 14.2; LRMS (EI 70 ev) *m/z* (%): 291 (M^+, 100); HRMS m/z (ESI) calcd for $C_{19}H_{18}NO_2$ $(M+H)^+$ 292.1338, found 292.1336.

6-(4-Methoxyphenyl)phenanthridine (3ba).[4e] Yield: 50%, 42.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 7.2 Hz, 1H), 8.27-8.22 (m, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.85-7.80 (m, 1H), 7.75-7.56 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 160.0, 143.1, 133.4, 132.2, 131.0, 130.4, 130.1, 129.0, 128.6, 127.1, 126.6, 125.4, 123.3, 122.1, 121.8, 113.6, 55.2; LRMS (EI 70 ev) *m/z* (%): 285 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M+H)^+$ 286.1232, found 286.1226.

6-(*p*-Tolyl)phenanthridine (3ca).[4e] Yield: 49%, 39.6 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, *J* = 8.4 Hz, 1H), 8.59-8.57 (m, 1H), 8.23 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 8.12 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1H), 7.82-7.80 (m, 1H), 7.76-7.59 (m, 5H), 7.39-7.35 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 143.4, 138.1, 136.5, 133.0, 130.4, 130.1, 129.6, 129.1, 129.0, 128.9, 128.8, 127.2, 126.5, 123.4, 122.1, 121.6, 21.4; LRMS (EI 70 ev) *m/z* (%): 269 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1287.

6-(*m*-Tolyl)phenanthridine (3da).[4e] Yield: 56%, 45.2 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.21 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.86-7.82 (m, 1H), 7.77-7.73 (m, 1H), 7.70-7.65 (m, 1H), 7.62-7.58 (m, 1H), 7.55 (s, 1H), 7.49-7.41 (m, 2H), 7.31 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1, 143.3, 139.5, 138.1, 133.3, 130.6, 130.1, 129.9, 129.3, 129.0, 128.7, 128.1, 127.1, 126.8, 126.4, 125.3, 123.6, 121.9, 121.7, 21.7; LRMS (EI 70 ev) *m/z* (%): 269 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1277.

6-(*o*-Tolyl)phenanthridine (3ea).[4e] Yield: 52%, 42.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, *J* = 8.0 Hz, 1H), 8.63 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.85-7.81 (m, 1H), 7.77-7.72 (m, 1H), 7.69-7.64 (m, 2H), 7.60-7.55 (m, 1H), 7.41-7.34 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3, 143.7, 138.9, 136.6, 133.1, 130.8, 130.2, 129.8, 129.2, 128.7, 128.3, 128.0, 127.2, 127.1, 126.3, 125.5, 123.8, 122.3, 122.0, 21.1; LRMS (EI 70 ev) *m/z* (%): 269 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{16}N$ $(M+H)^+$ 270.1283, found 270.1281.

6-(4-Chlorophenyl)phenanthridine (3fa).[5b] Yield: 58%, 50.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.88-7.81 (m, 1H), 7.75-7.68 (m, 4H), 7.62 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 143.6, 138.1, 135.2, 133.4, 131.1, 130.5, 130.1, 129.2, 128.4, 128.0, 127.3, 126.6, 125.1, 123.4, 122.2, 122.0; LRMS (EI 70 ev) *m/z* (%): 289 (M^+, 100); HRMS m/z (ESI) calcd for $C_{19}H_{13}ClN$ $(M+H)^+$ 290.0737, found 290.0740.

6-(4-Fluorophenyl)phenanthridine (3ga).[4e] Yield: 66%, 54.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (d, *J* = 8.4 Hz, 1H), 8.71-8.67 (m, 1H), 8.26 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.91-7.86 (m, 1H), 7.82-7.68 (m, 4H), 7.64-7.60 (m, 1H), 7.37-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (d, *J* = 245.7 Hz), 160.1, 143.3, 135.2 (d, *J* = 3.4 Hz), 133.3, 131.4 (d, *J* = 8.2 Hz), 130.6, 130.0, 128.8, 128.5, 127.2, 127.0, 125.4, 123.5, 122.3, 122.0, 116.2 (d, *J* = 22.3 Hz); LRMS (EI 70 ev) *m/z* (%): 273 (M^+, 100); HRMS m/z (ESI) calcd for $C_{19}H_{13}FN$ $(M+H)^+$ 274.1032, found 274.1031.

6-(Naphthalen-3-yl)phenanthridine (3ha).[4b] Yield: 73%, 66.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.97-7.94 (m, 2H), 7.87-7.84 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 6.2 Hz, 1H), 7.63-7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.1, 143.8, 137.2, 133.5, 133.3, 133.2, 130.7, 130.4, 129.2, 128.9, 128.8, 128.4, 128.0, 127.7, 127.3, 127.1, 126.9, 126.6, 126.4, 125.3, 123.7, 122.3, 122.0; LRMS (EI 70 ev) *m/z* (%): 305 (M^+, 100); HRMS m/z (ESI) calcd for $C_{23}H_{16}N$ $(M+H)^+$ 306.1283, found 306.1280.

6-(Pyridin-3-yl)phenanthridine (3ia).[13] Yield: 70%, 53.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (d, *J* = 1.6 Hz, 1H), 8.81 (dd, *J* = 5.6 Hz, *J* = 1.6 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.26 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.13-8.10 (m, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.93-7.90 (m, 1H), 7.82-7.78 (m, 1H), 7.75-7.72 (m, 1H), 7.68-7.64 (m, 1H), 7.55 (dd, *J* = 6.8 Hz, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 150.5, 149.7, 143.6, 137.1, 135.4, 133.3, 130.6, 130.1, 129.0, 127.9, 127.3, 127.1, 124.8, 123.5, 123.2, 122.4, 121.9; LRMS (EI 70 ev) *m/z* (%): 256 (M^+, 100); HRMS m/z (ESI) calcd for $C_{18}H_{13}N_2$ $(M+H)^+$ 257.1079, found 257.1084.

6-(Thiophen-2-yl)phenanthridine (3ja).[13] Yield: 61%, 47.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (d, *J* = 8.4 Hz, 1H), 8.60-8.55 (m, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.74-7.63 (m, 4H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.25-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.6, 143.4, 142.3, 133.2, 130.7, 130.2, 129.1, 128.8, 128.0, 127.8, 127.4, 127.1, 126.8, 124.7, 123.5, 122.2, 121.8; LRMS (EI 70 ev) *m/z* (%): 261 (M^+,

100); HRMS m/z (ESI) calcd for $C_{17}H_{12}NS$ $(M+H)^+$ 262.0690, found 262.0694.

6-(Furan-2-yl)phenanthridine (3ka).[13] Yield: 54%, 39.7 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, J = 8.0 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.92-7.88 (m, 1H), 7.83-7.72 (m, 3H), 7.63-7.58 (m, 1H), 7.35 (d, J = 4.0 Hz, 1H), 6.71-6.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4,144.5, 141.2, 138.1, 133.8, 131.0, 129.8, 129.1, 128.2, 127.8, 127.2, 124.0, 123.8, 122.3, 122.0, 112.0, 108.4; LRMS (EI 70 ev) *m/z* (%): 245 (M^+, 100); HRMS m/z (ESI) calcd for $C_{17}H_{12}NO$ $(M+H)^+$ 246.0919, found 246.0921.

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Supporting Information Available: Characterization data of **3** including the ^{1}H and ^{13}C NMR data.

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