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Preparation of Substituted Phenanthridines from the Coupling of Aryldiazonium Salts with Nitriles: A Metal Free Approach

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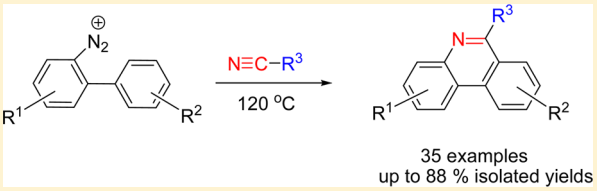
Supporting Information

ABSTRACT: A transition metal free approach for the synthesis of substituted phenanthridines from the coupling reaction of aryldiazonium tetrafluoroborates with nitriles has been developed. This operationally simple protocol proceeds through a substitution of aryldiazonium with nitriles followed by an intramolecular arylation to provide the corresponding phenanthridines in moderate to excellent yields.



Phenanthridines are an important class of *N*-heteroaryl compounds with a wide range of applications in material[1] and medicinal chemistry,[2] Substituted phenanthridines are versatile scaffolds and building blocks in pharmaceuticals with potential therapeutic utility.[3] Drugs with this ubiquitous framework possess broad spectrum of biological activities ranging from antibacterial,[4] antituberculosis,[5a] to antitumoral activity.[5b,c] Because of these applications, synthesis of substituted phenanthridine motif has spurred vigorous research for the development of new methodologies.

The Pictet−Hubert reaction is a classical method leading to phenanthridine, which involved the zinc chloride promoted dehydration of *N*-acyl-2-biphenylamine followed by cyclization at elevated temperatures (>200 °C).[6a] Later, the dehydration agent in this reaction was replaced by phosphorus oxychloride.[6b] However, these reactions require harsh conditions to facilitate the cyclization. In recent years, quite a number of approaches have developed including transition metal catalyzed approaches,[7] radical promoted cyclization,[8] addition of a nitrile to 2-fluoro-2′-lithiobiphenyl,[9a,b] cycloaddition,[9c−f] insertion[9g−k] and hypervalent iodine promoted cyclization.[10] Some approaches from *ortho*-functionalized biaryls to phenanthridines were summarized in Figure 1.[11] Despite the demonstrated advantages, there are limitations to exclude the transition metal catalysts and complicated prefunctionalized sites. Thus, appealing alternatives with easily accessible precursors are in demand rather than pursuing a sequence of strict conditions.

Aryl diazonium salts have been served as reactive aryl halide surrogates in Pd-catalyzed cross coupling reactions for C−C bond formation.[12] The inherent electrophilicity of dizonium salts comes from N_2 being an excellent leaving group and offers a pathway to introduce various groups into an aromatic ring to yield a wide range of compounds. In addition, the interest in using aryl diazonium salts lies in their ease of preparation and large choice of functional groups. In this context, Barba and coworkers have made a research to synthesis of anilides from aryldiazonium salts and nitriles under microwave irradiation.[13] Encouraged by this report, we sought to make a subtle approach for pheananthridine core by modification of this protocol. Herein, we report an efficient strategy for the synthesis of substituted phenanthridines from a reaction of 2-aryldiazonium tetrafluoroborates with a variety of nitriles under a transition metal catalyst-free condition.

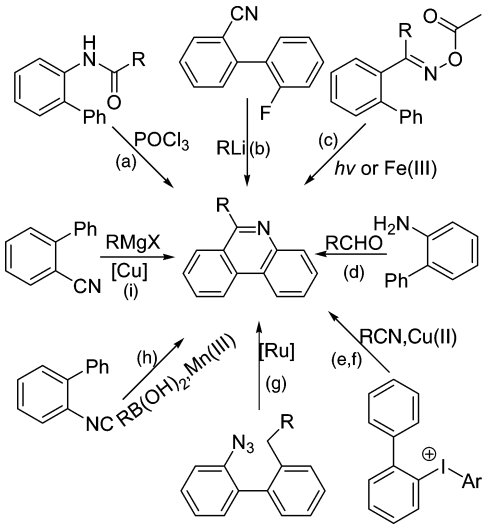


Figure 1. Synthetic approaches leading to phenanthridines from *ortho* functionalized biaryls. (a) Reference 6a. (b−i) References 11a−11i, respectively.

First, the reaction of phenyldiazonium salt **1** with acetonitrile was carried out to find the optimum reaction conditions (Table 1). With 20 mol % of Cu(I)Br as the catalyst at refluxing temperature in the air, the reaction proceeded to yield 6-methyl phenanthridine **3a** and the amide derivative **2** as a separable mixture (eq 1). Similar results were obtained under metal or acid-catalyzed conditions (Table 1 entries 1, 3, 4). Carrying out the reaction in various solvents provided poor results (entries 2, 5, 6). Performing the reaction at elevated temperature both

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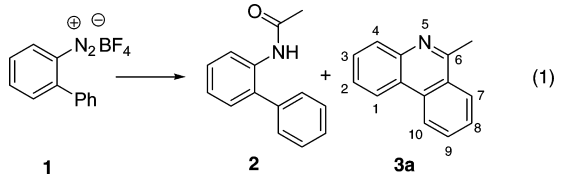
Table 1. Reaction Optimization[a]

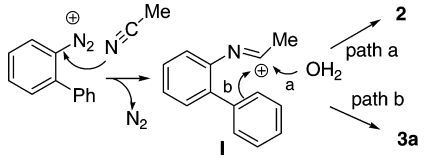
entry	additive	temp (°C)	time (h)	conv. (%)	2/3a[b]
1	CuBr	80	12	100	1:1
2	$Cu(OTf)_2$/DCE[c]	85	12		–
3	$Sc(OTf)_3$	80	12	100	1:1
4	CF_3COOH	80	12	100	1:2
5	THF (solvent)[c]	67	12		–
6	toluene (solvent)[c]	110	15		–
7[d]	–	170	8	100	1:1
8[d]	–	135	1	100	1:1
9[e]	–	120	3	100	88:0[f]
10[g]	–	120	3	65	65:0

[a]Reaction conditions: **1a** (0.3 mmol) and additive in acetonitrile (0.3 mL) in open air. [b]Determined by NMR. [c]Solvent used (0.3 mL); DCE = 1,2-dichloroethane. [d]Microwave irradiation in air. [e]In a sealed tube under anhydrous conditions. [f]Isolated yield. [g]In a sealed tube under anhydrous conditions but with 0.1 mL CH_3CN.



under conventional and microwave heating resulted the mixture of the products without appreciable increment in the formation of **3a** (entries 7–8). Presumably, the formation of **2** comes from hydrolysis of the resulting carbocation **I** via the nucleophilic substitution of nitrile toward diazonium salt (Scheme 1, path a). Thus, we investigated the reaction under

Scheme 1. Reaction Pathway for 2 and 3a

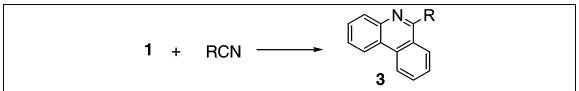


anhydrous conditions in a seal reaction vessel. To our delight, the reaction proceeded efficiently to afford the desired pheanthridine in 88% isolated yield as a sole product (Table 1, entry 9). Apparently, under the anhydrous condition, the direct electrophilic aromatic substitution took place on the adjacent ring to give the product (Scheme 1, path b). Although this is resemble to the classical Pictet–Hubert reaction, the reaction conditions developed in this work appeared to be much milder.

Under the optimized reaction conditions, the generality and the limitations of this protocol were examined with varieties of nitriles including aliphatic, aryl, heteroaryl, and benzyl nitriles. The results are summarized in Table 2. As illustrated, all the reactions proceeded cleanly and provided the corresponding 6-substituted phenanthridines in moderate to excellent yields. We are pleased to find that various functionalized nitriles do proceed the reaction even with the bromo-substituted one (Table 2, entry 4).

With the use of the percent yield of the phenanthridines within the first 2 h as a measurement of k_X, a Hammett plot analysis of the formation of 6-aryl substituted products (log k_X/k_H) against σ^+ values gives a line with a slope (ρ^+) of −0.54.

Table 2. Reaction of Diazonium Salt 1 with Various Nitriles[a]



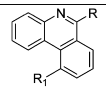
entry	nitrile	Product (yield)[b]
1	CH_3CN	**3a**, R = Me (88%)
2	$CH_3(CH_2)_2CN$	**3b**, R = ^{n}Pr (86%)
3	$(CH_3)_2CHCN$	**3c**, R = ^{i}Pr (76%)
4	$CH_3CH(Br)CN$	**3d**, R = $CH_3CH(Br)$- (73%)
5	$PhCH_2CN$	**3e**, R = $PhCH_2$- (73%)
6	PhCN	**3f**, R = Ph (76%)
7	*p*-MeC_6H_4CN	**3g**, R = *p*-MeC_6H_4- (68%)
8	*p*-BrC_6H_4CN	**3h**, R = *p*-BrC_6H_4- (54%)
9	*o*-BrC_6H_4CN	**3i**, R = *o*-BrC_6H_4- (58%)
10	*m*-$MeOC_6H_4CN$	**3j**, R = *m*-$MeOC_6H_4$- (52%)
11		**3k**, R = 3-thienyl (78%)

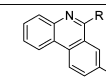
[a]**1** (0.3 mmol) and nitrile (0.3 mL) in a sealed tube at 120 °C for 3 h. [b]Isolated yield after column chromatography.

This observation clearly suggests the involvement of an intermediate with a developing positive charge in the reaction, consistent with the proposed species **I** (Scheme 1).

Having established the reaction conditions, this protocol was then applied to a variety of substituted diazonium salts. Thus, 2-(substituted phenyl)benzenediazonium tetrafluoroborate **4–6** and substituted 2-phenylbenzenediazonium tetrafluoroborate **7** were subjected for this investigation. Table 3 summarizes the

Table 3. Phenanthridines from 2-(Substituted Phenyl)Benzenediazonium Salts 4–6[a,b]





8a, R = Me, R^1 = Me (81%)	**9a**, R = Me, R^1 = MeO (86%)
8b, R = ^{n}Pr, R^1 = Me (78%)	**9b**, R = ^{n}Pr, R^1 = MeO (83%)
8c, R = ^{i}Pr, R^1 = Me (74%)	**9c**, R = ^{i}Pr, R^1 = MeO (74%)
8d, R = Ph, R^1 = Me (71%)	**9d**, R = Ph, R^1 = MeO (77%)
	9e, R = Ph, R^1 = F (43%)
	9f, R = Me, R^1 = F (58%)

[a]Substrate (0.3 mmol) and RCN (0.3 mL) in a sealed tube at 120 °C for 3 h. [b]Isolated yield given in parentheses.

preparation of phenanthridines from **4–6**. Reaction of 2-(*o*-methylphenyl)benzenediazonium tetrafluoroborate **4** with various nitrile yielded 6,10-substituted phenanthridines **8a–8d** in good isolated yields, whereas 2-(*p*-methoxyphenyl)-benzenediazonium tetrafluoroborate **5** gave 6,8-substituted phenanthridines **9a–9d** in good yields. The fluoro-substituted substrate, 2-(*p*-fluorophenyl)benzenediazonium tetrafluoroborate **6**, reacted with benzonitrile and acetonitrile to give 8-fluorophenanthridines **9e** (43%) and **9f** (58%), respectively.

It is noticed that reaction of benzonitrile with 2-(*o*-methoxyphenyl)benzenediazonium tetrafluoroborate **10** did

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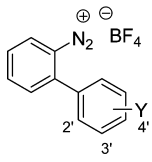
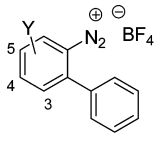


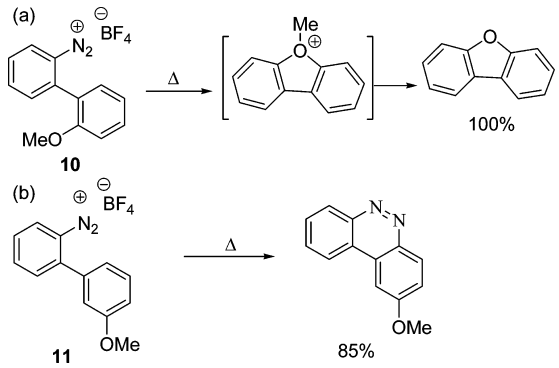
4, Y = 2'-CH_3
5, Y = 4'-CH_3O
6, Y = 4'-F



7a, Y = 4-CF_3
7b, Y = 4-Cl
7c, Y = 4-CH_3
7d, Y = 5-CH_3
7e, Y = 4-

not provide the corresponding phenanthridine, but dibenzofuran was obtained the major product (Scheme 2a).[14] Apparently

Scheme 2



the oxygen atom of the methoxy group acts as a nucleophile to undergo the displacement followed by the elimination of methyl group. For the *meta* analogue **11**, the diazonium coupling reaction took place directly, instead of the nucleophilic attack by the nitrile, to give benzo[*c*]cinnoline in 85% yield, presumably due to the double activation of the substituents (Scheme 2b).[15]

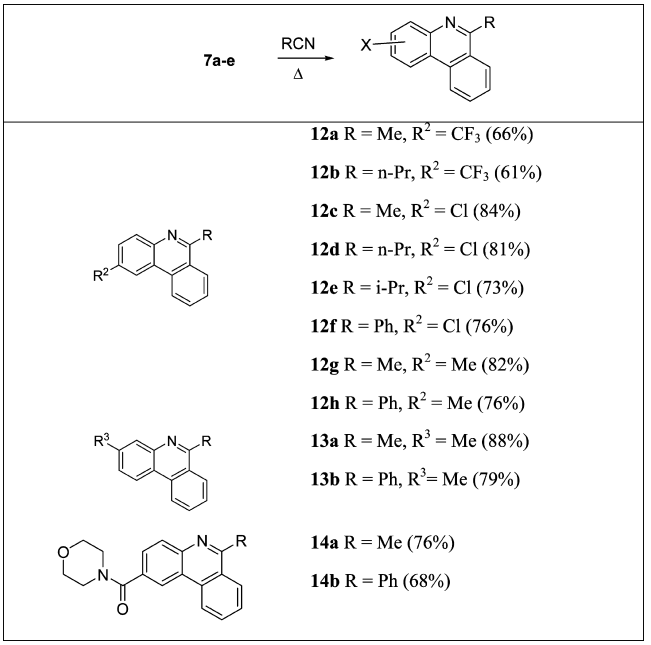
To further diversify the scope of the reaction, we next sought to investigate the substituent effect on the arene ring possessing the diazonium functionality (Table 4). It was found that reaction of 4-CF_3 substituted diazonium salt **7a** provided the desired product in moderate yields (**12a,b**), whereas 4-Cl and 4-Me substituted 2-phenyl benzenediazonium tetrafluoroborates furnished the corresponding phenanthridines in excellent yields (**12c−12h**). Preparation of other regio-isomers **13a,b** and 2-phenanthridinecarboxamides **14a,b** can be also achieved from **7d** and **7e**, respectively.

Other substituted phenanthridines can be prepared as well. Typically, preparation of a 2,6,8-trisubstitued phenanthridine was achieved as illustrated in Scheme 3. Suzuki-coupling of 2-bromo-*p*-toluidine with *p*-methoxyphenyl-boronic acid gave the desired biarylamine **15**. Diazotization of **15** yielded the diazonium salt **16**, which was heated in acetonitrile to give **17** in 86% yield.

Finally, we studied the cyclization with 1-naphthalenylbenzenediazonium tetrafluoroborate **18**. Surprisingly, using **18**, acetonitrile, and the conditions optimized in Table 1 afforded a mixture of fluoranthene **19** and 6-methylbenzo[*k*]-phenanthridine **20** in a ratio of 71%:11% (Scheme 4), indicating that the electrophilic aromatic substitution took place majorly at α'-position of the naphthylenyl ring.

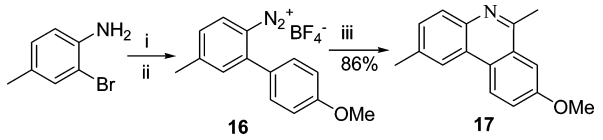
In summary, a thermal-cyclization to construct phenanthridines from 2-phenylbenzenediazonium salt and nitriles under

Table 4. Phenanthridines from Substituted 2-Phenylbenzene-Diazonium Salts 7[a,b]



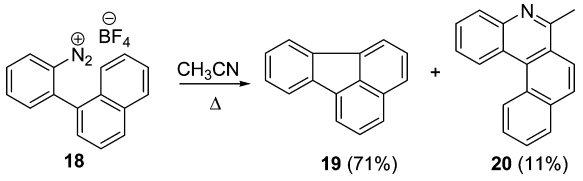
[a]Substrate (0.3 mmol) and RCN (0.3 mL) in a sealed tube at 120 °C for 3 h. [b]Isolated yield given in parentheses.

Scheme 3. Preparation of Trisubstituted Phenanthridine 17[a]



[a](i) *p*-$MeOC_6H_4B(OH)_2$, $PdCl_2(PPh_3)_2$; (ii) $NaNO_2$, HBF_4; (iii) CH_3CN, Δ.

Scheme 4. Reaction of 1-Naphthalenylbenzenediazonium Tetrafluoroborate



anhydrous conditions was developed. The scope of the method was examined using a variety of nitriles and 2-phenylbenzenediazonium tetrafluoroborate. It is noteworthy that the purification of solid products can be accomplished by a simple filtration. This strategy allows convenient and easy access to a wide range of functionality. Compared to the Pictet-Hubert reaction, experimental simplicity, mild reaction conditions and easy access to various substituents in the molecules are delivered by this methodology. Further studies on the development of this methodology to construct complicated molecules are ongoing in this laboratory.

EXPERIMENTAL SECTION

General Information. ^1H and ^{13}C NMR were recorded in a 400 MH_Z spectrometer in $CDCl_3$ and CD_3CN referenced to TMS. All the nitriles were dried over activated 4 Å molecular sieves, and solid

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nitriles were purchased and used without any further drying. Other chemicals were used as purchased. Flash chromatography was performed using silica gel 230−400 mesh. In cases of known compounds, their ^{1}H and ^{13}C NMR values were compared with the literature values. 2-Aminobiaryls were synthesized by Suzuki−Miyaura coupling of arylboronic acids and 2-bromo anilines. Unless otherwise noted, all the reactions were performed without any special precautions.

General Procedure for Preparing 2-Aminobiaryls. All the 2-aminobiaryls were synthesized by following the reported methods. Spectral data of the compounds are in agreement with those reported in the literature. A typical procedure for preparing 2-(*o*-tolyl)-aniline is shown below.[16]

2-Bromoaniline (2.90 mmol, 1 equiv), 2-methylphenylboronic acid (3.78 mmol, 1.3 equiv), $PdCl_2(PPh_3)_2$ (0.29 mmol, 0.1 equiv), and potassium carbonate (8.72 mmol, 3 equiv) were suspended in DMF (15 mL) and water (3 mL) in a 50 mL Schlenk bottle. The flask was equipped with a reflux condenser and heated to 80 °C for 24 h under nitrogen atmosphere. Upon completion, reaction mixture was cooled to room temperature and diluted with ethyl acetate (50 mL). After passing through a short Celite pad, the filtrate was washed with saturated aqueous sodium bicarbonate (2 × 20 mL) and brine (20 mL). Combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, 2−10% EA-hexane) to give 2(2-methylphenyl)-aniline in (430 mg, 2.34 mmol, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−7.21 (m, 5H), 6.92 (d, J = 7.2 Hz, 1H), 6.71 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.34 (bs, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.5, 136.9, 130.2, 130.04, 130.02, 128.3, 127.6, 127.4, 126.1, 118.2, 115.0, 19.6.

4′-Methoxy-5-methyl-[1,1′-biphenyl]-2-amine (15).[16b] 2-Bromo-4-methylaniline (1.88 mmol, 1 equiv), 4-methoxyphenylboronic acid (2.44 mmol, 1.3 equiv), $PdCl_2(PPh_3)_2$ (0.18 mmol, 0.1 equiv), and potassium carbonate (5.64 mmol, 3 equiv) were suspended in DMF (10 mL) and water (2 mL) in a 50 mL Schlenk bottle. The flask was equipped with a reflux condenser and heated to 80 °C for 24 h under nitrogen atmosphere. Upon completion, reaction mixture was cooled to room temperature and diluted with ethyl acetate (30 mL). After passing through a short Celite pad, the filtrate was washed with saturated aqueous sodium bicarbonate (2 × 15 mL) and brine (15 mL). Combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, 2−10% EA-hexane) to give 4′-methoxy-5-methyl-[1,1′-biphenyl]-2-amine (280 mg, 1.31 mmol, 71% yield) as a viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 6.94−6.99 (m, 4H), 6.68 (d, J = 7.6 Hz, 1H), 3.84 (s, 3H), 3.52 (bs, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 140.9, 131.8, 130.9, 130.1, 128.6, 127.8, 127.4, 115.7, 114.1, 55.2, 20.3; HRMS (ESI) m/z = 214.1232 calcd. for $C_{14}H_{16}NO$ $(M + H)^+$, found 214.1236.

General Procedure for Preparing Biaryldiazonium Tetrafluoroborates.[17] Corresponding aniline (10 mmol) was dissolved in a mixture of water (4 mL) and 50% aqueous hydrofluoroboric acid (19.3 mmol, 1.92 equiv). The mixture was cooled to 0 °C and a solution of $NaNO_2$ (10 mmol in 1.5 mL of water) was added slowly. The resulting reaction mixture was stirred at 0 °C for 30 min and the precipitate was collected by filtration. The solid product was dissolved in minimum acetone and reprecipitated using diethyl ether to yield aryldiazonium tetrafluoroborate, which was dried under a vacuum.

2-Biphenyldiazonium tetrafluoroborate (1).[17b] 633 mg, 80%, pale green solid: ^{1}H NMR (400 MHz, CD_3CN) δ; 8.60 (d, J = 8.4 Hz, 1H), 8.31 (t, J = 7.6 Hz, 1H), 7.91−7.97 (m, 2H), 7.68−7.69 (m, 5H); ^{13}C NMR (100 MHz, CD_3CN) δ 147.7, 143.1, 134.5, 133.7, 132.4, 131.7, 131.0, 131.0, 129.7, 114.1; HRMS (ESI) calcd. for $C_{12}H_9$ $(M - BF_4 - N_2)^+$ m/z = 153.0705, found 153.0669.

2′-Methyl-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (4).[17a] 654 mg, 85%, off-white solid: ^{1}H NMR (400 MHz, CD_3CN) δ 8.61 (bs, 1H), 8.29 (t, J = 7.6 Hz, 1H), 7.95 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.42−7.57 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 147.0, 142.6, 137.8, 134.5, 134.2, 132.8, 132.6, 132.2, 131.8, 130.2, 127.9, 115.7, 20.0.

4′-Methoxy-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (5).[17a] 601 mg, 80%, yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.55 (d, J = 8.4 Hz, 1H), 8.25 (t, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 163.2, 147.2, 142.8, 134.3, 133.3, 131.4, 131.0, 125.8, 116.4, 113.4, 56.4; HRMS (ESI) calcd. for $C_{13}H_{11}N_2O$ $(M - BF_4)^+$ m/z = 211.0871, found 211.0873.

4′-Fluoro-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (6). 450 mg, 69%, yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.61 (d, J = 8.0 Hz, 1H), 8.29 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.90−7.92 (m, 1H), 7.71−7.74 (m, 2H), 7.41 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 165.3 (d, J = 249 Hz), 145.9, 143.0, 134.5, 133.7, 132.3 (d, J = 10.0 Hz), 131.7, 130.1 (d, J = 10.0 Hz), 118.0 (d, J = 22.0 Hz), 114.3; HRMS (ESI) calcd. for $C_{12}H_8F$ $(M - BF_4 - N_2)^+$ m/z = 171.0610, found 171.0609.

2′-Methoxy-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (10). 448 mg, 83%, yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.56 (d, J = 7.6 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.89 (t, J = 7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.25 (t, J = 7.6 Hz, 2H), 3.92 (s, 3H); HRMS (ESI) calcd. for $C_{13}H_{11}N_2O$ $(M - BF_4)^+$ m/z = 211.0871, found 211.0873. Pure ^{13}C NMR could not be obtained due to the simultaneous formation of dibenzofuran.

3′-Methoxy-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (11). 474 mg, 80%, yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (d, J = 8.3 Hz, 1H), 8.27 (m, 1H), 9.50 (m, 2H), 7.57 (m, 1H), 7.22 (m, 3H). Pure ^{13}C NMR could not be obtained due to the simultaneous formation of 2-methoxybenzo[*c*]cinnoline.

5-Trifluoromethyl-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (7a). 454 mg, 71%, pale yellow solid: ^{1}H NMR (400 MHz, CD_3CN) δ 8.82 (d, J = 8.8 Hz, 1H), 8.27 (s, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.70−7.76 (m, 5H); ^{13}C NMR (100 MHz, CD_3CN) δ 147.9, 141.3 (q, J = 136.8 Hz), 135.6, 132.9, 132.7, 131.1, 130.8, 129.9, 128.3, 124.5, 121.8; HRMS (ESI) calcd. for $C_{13}H_8F_3N_2$ $(M - BF_4)^+$ m/z = 249.0640, found 249.0638.

5-Chloro-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (7b). 511 mg, 76%, off-white powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (d, J = 8.8 Hz, 1H), 8.0 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.68 (bs, 5H); ^{13}C NMR (100 MHz, CD_3CN) δ 150.0, 148.4, 135.8, 133.9, 132.8, 132.7, 132.0, 131.0, 129.7, 112.4; HRMS (ESI) calcd. for $C_{12}H_8Cl$ $(M - BF_4 - N_2)^+$ m/z = 187.0314, found 187.0301.

5-Methyl-(1,1′-biphenyl)-2-diazonium tetrafluoroborate (7c).[17a] 422 mg, 55%, pale yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.48 (d, J = 8.6 Hz, 1H), 7.79 (s, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.66 (bs, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 157.3, 146.9, 134.4, 134.3, 133.8, 132.5, 132.2, 130.9, 129.6, 109.9, 23.2 HRMS (ESI) calcd. for $C_{13}H_{11}$ $(M - BF_4 - N_2)^+$ m/z = 167.0861, found 167.0857

4-Methyl-[1,1′-biphenyl]-2-diazonium tetrafluoroborate (7d). 498 mg, 86%, pale yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.37 (s, 1H), 8.11−8.14 (m, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.66 (bs, 5H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 144.6, 144.2, 143.2, 133.7, 133.6, 133.3, 132.2, 131.0, 129.7, 113.6, 21.0; HRMS (ESI) calcd. for $C_{13}H_{11}$ $(M - BF_4 - N_2)^+$ m/z = 167.0861, found 167.0848.

[1,1′-Biphenyl]-3-yl)(morpholino)methanone-6-diazonium tetrafluoroborate (7e). 430 mg, 81%, pale yellow powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.65 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 1.2 Hz, 1H), 7.85 (dd, J = 8.4, 1.2 Hz, 1H), 7.66−7.71 (m, 5H), 3.70 (d, J = 2.4 Hz, 4H), 3.58 (d, J = 4.4 Hz, 2H), 3.32 (d, J = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 166.5, 149.6, 147.8, 135.2, 133.3, 132.6, 131.5, 131.0, 129.8, 129.7, 114.5, 67.0, 66.9, 48.4, 43.1; HRMS (ESI) calcd. for $C_{17}H_{16}N_3O_2$ $(M - BF_4)^+$ m/z = 294.1243, found 294.1232.

4′-Methoxy-5-methyl-[1,1′-biphenyl]-2-diazonium tetrafluoroborate (16). 270 mg, 66%, orange solid: ^{1}H NMR (400 MHz, CD_3CN) δ 8.42 (d, J = 8.8 Hz, 1H), 7.75 (s, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 163.1, 157.1,

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147.1, 134.2, 133.9, 131.9, 131.3, 125.9, 116.4, 109.3, 56.4, 23.2; HRMS (ESI) calcd. for $C_{14}H_{13}N_2O$ $(M - BF_4)^+$ m/z = 225.1022, found 225.1039.

2-(1-Naphthalenyl)-benzenediazonium tetrafluoroborate (18). 430 mg, 86%, orange powder: ^{1}H NMR (400 MHz, CD_3CN) δ 8.68 (d, J = 7.5 Hz, 1H), 8.37 (t, J = 7.8 Hz, 1H), 8.20 (dd, J = 5.8, 3.2 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.04 (t, J = 7.5 Hz, 2H), 7.61−7.75 (m, 5H); HRMS (ESI) calcd. for $C_{16}H_{11}$ $(M - BF_4 - N_2)^+$ m/z = 203.0855, found 203.0787. Pure ^{13}C NMR could not be obtained due to the simultaneous formation of fluoroanthene.

General Procedure for the Preparation of Phenanthridines. In a dry 10 mL glass sealed tube, aryldiazonium salt (0.3 mmol) was suspended in 0.3 mL of appropriate anhydrous nitrile. The tube was sealed with a Teflon screw cap and stirred in a preheated oil bath (120 °C) for 3 h. After cooling to room temperature, solvents were removed under reduced pressure and purified by silica gel column chromatography (SiO_2, DCM/MeOH, 99:1) to get the desired compounds.

6-Methylphenanthridine (3a).[11f] 49 mg, 88%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.2 Hz, 1H), 8.51 (dd, J = 8.0, 1.0 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 8.10 (dd, J = 8.2, 0.8 Hz, 1H), 7.82 (td, J = 7.6, 1.2 Hz, 1H), 7.65−7.71 (m, 2H), 7.60 (td, J = 7.6, 1.2 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.5, 132.5, 130.5, 129.2, 128.6, 127.3, 126.5, 126.3, 125.8, 123.7, 122.3, 121.9, 23.3; HRMS (ESI) calcd. for $C_{14}H_{12}N$ $(M + H)^+$ m/z = 194.0970, found 194.0976.

6-Propylphenanthridine (3b).[7a] 57 mg, 86%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.2 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.80 (td, J = 5.9, 1.3 Hz, 1H), 7.64−7.71 (m, 2H), 7.59 (td, J = 5.9, 1.3 Hz, 1H), 3.31−3.35 (m, 2H), 1.95 (sex, J = 7.6 Hz, 2H), 1.11 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 143.7, 132.9, 130.2, 129.5, 128.5, 127.1, 126.3, 126.2, 125.2, 123.6, 122.4, 121.8, 38.3, 22.8, 14.4; HRMS (ESI) calcd. for $C_{16}H_{16}N$ $(M + H)^+$ m/z = 222.1282, found 222.1285.

6-Isopropylphenanthridine (3c).[11g] 51 mg, 76%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.2 Hz, 1H), 8.46 (d, J = 8.2 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.3 Hz, 1H), 7.59−7.64 (m, 2H), 7.50−7.54 (m, 1H), 3.92 (sept, J = 6.7 Hz, 1H), 1.44 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 143.8, 133.0, 129.9, 129.9, 128.4, 127.0, 126.1, 125.6, 124.7, 123.4, 122.5, 121.8, 31.5, 21.9; HRMS (ESI) calcd. for $C_{16}H_{16}N$ $(M + H)^+$ m/z = 222.1282, found 222.1289.

6-(1-Bromoethyl)phenanthridine (3d). 51 mg, 73%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.2 Hz, 1H), 8.53 (dd, J = 8.1, 1.4 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H), 8.18 (dd, J = 8.1, 1.2 Hz, 1H), 7.83 (ddd, J = 15.3, 7.6, 1.2 Hz, 1H), 7.70 (m, 2H), 7.65 (ddd, J = 15.0, 7.6, 1.4 Hz, 1H), 6.00 (q, J = 6.7 Hz, 1H), 2.37 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 143.2, 133.4, 130.5 (2C), 128.7, 127.4, 127.2, 125.6, 124.1, 123.7, 122.6, 121.9, 44.8, 22.9; HRMS (ESI) calcd. for $C_{15}H_{13}BrN$ $(M + H)^+$ m/z = 286.0231, found 286.0237.

6-Benzylphenanthridine (3e).[18a] 64 mg, 73%, pale yellow solid: mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 8.2, 0.6 Hz, 1H), 8.53 (dd, J = 8.0, 0.7 Hz, 1H), 8.18 (ddd, J = 8.9, 5.2, 1.2 Hz, 2 H), 7.71−7.74 (m, 2H), 7.63 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 7.55 (m, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.21−7.24 (m, 2H), 7.15 (t, J = 7.3 Hz, 1H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 143.7, 139.1, 133.2, 130.3, 129.8, 128.6, 128.5, 128.4, 127.2, 127.0, 126.6, 126.3, 125.3, 123.9, 122.4, 121.9, 43.0; HRMS (ESI) calcd. for $C_{20}H_{16}N$ $(M + H)^+$ m/z = 270.1283, found 270.1280.

6-Phenylphenanthridine (3f).[8i] 58 mg, 76%, white solid: mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.3 Hz, 1H), 8.60 (dd, J = 8.1, 1.3 Hz, 1H), 8.24 (dd, J = 8.1, 1.0 Hz, 1H), 8.09 (dd, J = 8.3, 0.6 Hz, 1H), 7.83 (td, J = 8.3, 1.3 Hz, 1H), 7.71−7.76 (m, 3H), 7.67 (td, J = 8.3, 1.3 Hz, 1H), 7.49−7.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 143.7, 139.7, 133.4, 130.5, 130.3, 129.7, 128.9, 128.8, 128.7, 128.4, 127.1, 126.9, 125.2, 123.7, 122.1, 121.9; HRMS (ESI) calcd. for $C_{19}H_{14}N$ $(M + H)^+$ m/z = 256.1126, found 256.1124.

6-(*p*-Tolyl)phenanthridine (3g).[11h] 57 mg, 68%, white solid: mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.2 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.70−7.60 (m, 4H), 7.37 (d, J = 7.8 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 143.7, 138.5, 136.8, 133.4, 130.4, 130.2, 129.6, 129.0, 128.9, 128.7, 127.0, 126.7, 125.3, 123.6, 122.1, 121.8, 21.3.); HRMS (ESI) calcd. for $C_{20}H_{16}N$ $(M + H)^+$ m/z = 270.1283, found 270.1275.

6-(4-Bromophenyl)phenanthridine (3h).[11i] 48 mg, 54%, white solid: mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 8.3 Hz, 1H), 8.60 (dd, J = 8.2, 1.2 Hz, 1H), 8.20 (dd, J = 8.2, 1.2 Hz, 1H), 8.01−8.05 (m, 1H), 7.85 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.75 (ddd, J = 8.3, 7.0, 1.5 Hz, 1H), 7.66−7.70 (m, 3H), 7.59−7.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 143.7, 138.6, 133.5, 131.6, 131.4, 130.7, 130.3, 128.9, 128.4, 127.2, 127.1, 124.9, 123.7, 123.1, 122.3, 121.9; HRMS (ESI) calcd. for $C_{19}H_{13}BrN$ $(M + H)^+$ m/z = 334.0231, found 334.0228.

6-(2-Bromophenyl)phenanthridine (3i).[18b] 63 mg, 58%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 8.3 Hz, 1H), 8.63 (dd, J = 8.0, 1.1 Hz, 1H), 8.24 (dd, J = 8.0, 1.1 Hz, 1H), 7.84 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.65−7.78 (m, 4H), 7.58 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.46−7.51 (m, 2H), 7.37 (ddd, J = 9.2, 6.3, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 143.6, 140.5, 132.9, 132.8, 131.0, 130.7, 130.4, 130.0, 128.8, 128.4, 127.5, 127.3, 127.2, 125.2, 124.0, 122.8, 122.1, 122.0; HRMS (ESI) calcd. for $C_{19}H_{13}BrN$ $(M + H)^+$ m/z = 334.0231, found 334.0229.

6-(3-Methoxyphenyl)phenanthridine (3j). 44 mg, 52%, white solid: mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.2 Hz, 1H), 8.59 (d, J = 8.1 Hz, 1H), 8.24 (dd, J = 8.1, 1.2 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.83 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.74 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.64−7.69 (m, 1H), 7.59 (t, J = 8.1 Hz, 1H), 7.45 (t, J = 8.2 Hz, 1H), 7.27 (d, J = 7.4 Hz, 2H), 7.04−7.07 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 159.6, 143.7, 141.0, 133.4, 130.5, 130.3, 129.4, 128.9, 128.8, 127.1, 126.9, 125.2, 123.7, 122.2, 122.1, 121.9, 114.9, 114.7, 55.4.); HRMS (ESI) calcd. for $C_{20}H_{16}NO$ $(M + H)^+$ m/z = 286.1232, found 286.1221.

6-(Thiophen-3-yl)phenanthridine (3k). 66 mg, 78%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.2 Hz,1H), 8.57 (dd, J = 8.2, 0.7 Hz, 1H), 8.27 (dd, J = 8.2, 0.7 Hz, 1H), 8.19−8.21 (m, 1H), 7.81−7.85 (m, 1H), 7.71−7.77 (m, 2H), 7.61−7.67 (m, 2H), 7.55−7.57 (m, 1H), 7.49 (ddd, J = 5.0, 2.9, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 143.8, 140.8, 133.4, 130.5, 130.2, 129.2, 128.8, 128.4, 127.2, 126.8, 126.3, 125.7, 125.4, 123.6, 122.2, 121.9; HRMS (ESI) calcd. for $C_{17}H_{12}NS$ $(M + H)^+$ m/z = 262.0690, found 262.0682.

6,10-Dimethylphenanthridine (8a).[19] 53 mg, 81%, white solid: mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.4 Hz, 1H), 8.12 (dd, J = 7.2, 5.2 Hz, 2H), 7.58−7.59 (m, 2H), 7.61−7.70 (m, 2H), 3.10 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.7, 135.4, 134.7, 132.0, 129.5, 127.8, 127.3, 126.6, 126.5, 125.4, 125.2, 125.0, 26.8, 24.1; HRMS (ESI) calcd. for $C_{15}H_{14}N$ $(M + H)^+$ m/z = 208.1126, found 208.1125.

10-Methyl-6-propylphenanthridine (8b). 52 mg, 78%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.4 Hz, 1H), 8.15−8.18 (m, 2H), 7.64−7.71 (m, 2H), 7.55−7.59 (m, 2H), 3.32−3.36 (m, 2H), 3.10 (s, 3H), 1.89−1.99 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 144.7, 135.6, 134.5, 132.5, 129.7, 127.8, 126.7, 126.6, 126.5, 125.4, 125.0, 124.8, 38.9, 26.9, 22.9, 14.4; HRMS (ESI) calcd. for $C_{17}H_{18}N$ $(M + H)^+$ m/z = 236.1439, found 236.1438.

6-Isopropyl-10-methylphenanthridine (8c). 51 mg, 74%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 6.5 Hz, 1H), 7.63−7.70 (m, 2H), 7.54−7.59 (m, 2H), 3.98 (sept, J = 6.7 Hz, 1H), 3.11 (s, 3H), 1.50 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 144.9, 135.7, 134.2, 132.6, 130.1, 127.6, 127.6, 126.4, 126.2, 125.2, 124.8, 124.1, 31.8, 27.0, 22.0; HRMS (ESI) calcd. for $C_{17}H_{18}N$ $(M + H)^+$ m/z = 236.1439, found 236.1441.

10-Methyl-6-phenylphenanthridine (8d).[7d] 54 mg, 71%, white solid: mp 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J =

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8.4 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.72−7.76 (m, 1H), 7.63−7.68 (m, 4H), 7.46−7.55 (m, 4H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 144.8, 140.4, 135.2, 134.8, 132.8, 130.5, 129.6, 128.5, 128.3, 128.0, 127.7, 126.8, 126.5, 126.4, 126.0, 125.1, 26.8; HRMS (ESI) calcd. for $C_{20}H_{16}N$ $(M + H)^+$ m/z = 270.1283, found 270.1287.

8-Methoxy-6-methylphenanthridine (9a).[20a] 54 mg, 66%, pale yellow solid: mp 109−111 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (d, J = 9.0 Hz, 1H), 8.45 (dd, J = 7.7, 1.1 Hz, 1H), 7.93 (dd, J = 7.7, 1.1 Hz, 1H), 7.58−7.67 (m, 2H), 7.47 (td, J = 9.0, 2.5 Hz, 2H), 3.95 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 160.0, 159.4, 142.0, 128.9, 128.7, 127.8, 127.7, 127.6, 125.2, 124.7, 122.9, 122.7, 108.1, 56.4, 23.2; HRMS (ESI) calcd. for $C_{15}H_{14}NO$ $(M + H)^+$ m/z = 224.1075, found 224.1080.

8-Methoxy-6-propylphenanthridine (9b). 57 mg, 83%, pale yellow solid: mp 75−76 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (d, J = 9.0 Hz, 1H), 8.52 (dd, J = 7.9, 1.1 Hz, 1H), 7.96−7.98 (m, 1H) 7.57−7.66 (m, 3H), 7.48 (dd, J = 9.0, 2.6 Hz, 1H), 3.97 (s, 3H), 3.28 (t, J = 7.6 Hz, 2H), 1.92−1.95 (m, 2H), 1.09 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 162.2, 159.9, 143.9, 130.3, 128.5, 127.8, 127.6, 127.4, 125.3, 124.6, 122.8, 121.5, 107.7, 56.4, 38.5, 22.6, 14.6; HRMS (ESI) calcd. for $C_{17}H_{18}NO$ $(M + H)^+$ m/z = 252.1388, found 252.1396.

6-Isopropyl-8-methoxyphenanthridine (9c). 54 mg, 74%, pale yellow solid: mp 92−94 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.64 (d, J = 9.0 Hz, 1H), 8.54 (dd, J = 8.0, 1.5 Hz, 1H), 7.98−8.00 (m, 1H), 7.71 (d, J = 2.6 Hz, 1H), 7.58−7.67 (m, 2H), 7.50 (dd, J = 9.0, 2.6 Hz, 1H), 3.96 (s, 3H), 3.97−4.06 (m, 1H), 1.45 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ 166.2, 160.0, 143.8, 130.4, 128.5, 128.0, 127.4, 127.0, 125.5, 125.5, 122.8, 121.4, 107.4, 56.4, 32.1, 22.2; HRMS (ESI) calcd. for $C_{17}H_{18}NO$ $(M + H)^+$ m/z = 252.1388, found 252.1380.

8-Methoxy-6-phenylphenanthridine (9d).[20b] 65 mg, 77%, pale yellow solid: mp 127−129 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.68 (d, J = 9.0 Hz, 1H), 8.59−8.61 (m, 1H), 8.06−8.08 (m, 1H), 7.65−7.74 (m, 4H), 7.55−7.61 (m, 3H), 7.51 (dd, J = 9.0, 2.7 Hz, 1H), 7.44 (d, J = 2.7 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 161.1, 159.7, 144.0, 141.0, 130.9, 130.5, 129.7, 129.3, 128.9, 128.5, 128.1, 127.4, 125.3, 124.7, 122.9, 122.0, 109.6, 56.1; HRMS (ESI) calcd. for $C_{20}H_{16}NO$ $(M + H)^+$ m/z = 286.1232, found 286.1230.

8-Fluoro-6-phenylphenanthridine (9e).[11i] 32 mg, 43%, pale yellow solid: mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 9.2 Hz, 1H), 8.54 (dd, J = 8.0, 0.8 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.66−7.76 (m, 5H), 7.50−7.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 247 Hz), 160.38, 143.4, 139.2, 130.4, 130.1, 129.5, 128.9, 128.7, 128.6, 127.3, 126.5 (d, J = 8.0 Hz), 124.7 (d, J = 8.4 Hz), 123.3, 121.7, 119.7 (d, J = 23 Hz), 113.2 (d, J = 22 Hz); HRMS (ESI) calcd. for $C_{19}H_{13}FN$ $(M + H)^+$ m/z = 274.1032, found 274.1040.

8-Fluoro-6-methylphenanthridine (9f).[20c] 34 mg, 58%, pale yellow solid: mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 9.0, 5.3 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.78 (dd, J = 9.6, 2.6 Hz, 1H), 7.67 (td, J = 8.2, 1.2 Hz, 1H), 7.52−7.61 (m, 2H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 158.0 (d, J = 222.7 Hz), 143.3, 129.4, 129.2, 128.5, 127.0 (d, J = 7.4 Hz), 126.7, 124.8 (d, J = 33.2 Hz), 123.2, 121.6, 119.4 (d, J = 29.6 Hz), 111.1 (d, J = 21.2 Hz), 23.3; HRMS (ESI) calcd. for $C_{14}H_{11}FN$ $(M + H)^+$ m/z = 212.0876, found 212.0881.

6-Methyl-2-(trifluoromethyl)phenanthridine (12a).[11d] 44 mg, 66%, white solid: mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.61 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.86−7.90 (m, 2H), 7.74 (td, J = 8.2, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 145.0, 132.1, 131.1, 130.1, 128.2, 126.7, 126.1, 125.7, 124.6, 123.4, 123.0, 122.3, 119.8 (d, J = 3.9 Hz), 22.3; HRMS (ESI) calcd. for $C_{15}H_{11}F_3N$ $(M + H)^+$ m/z = 262.0844, found 262.0849.

6-Propyl-2-(trifluoromethyl)phenanthridine (12b). 45 mg, 61%, white solid: mp 59−60 °C; ^{1}H NMR (400 MHz, CDCl3) δ 8.71 (s, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.77−7.83 (m, 2H), 7.66 (td, J = 8.2, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 145.1, 132.1, 130.9, 130.3, 128.1, 126.5, 125.7, 125.5, 124.5, 123.2, 123.0, 122.4, 119.7 (d, J = 3.9 Hz), 38.2, 22.6, 14.3; HRMS (ESI) calcd. for $C_{17}H_{15}F_3N$ $(M + H)^+$ m/z = 290.1157, found 290.1160.

2-Chloro-6-methylphenanthridine (12c).[21] 54 mg, 84%, white solid: mp 120−121 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.61 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 2.2 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.87 (td, J = 8.2, 1.0 Hz, 1H), 7.76 (td, J = 8.2, 1.0 Hz, 1H), 7.65 (td, J = 8.7, 2.2 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 159.4, 142.0, 131.4, 131.1, 130.8, 130.7, 128.6, 128.1, 126.6, 125.7, 124.7, 122.4, 121.7, 22.5; HRMS (ESI) calcd. for $C_{14}H_{11}ClN$ $(M + H)^+$ m/z = 228.0580, found 228.0589.

2-Chloro-6-propylphenanthridine (12d). 60 mg, 81%, white solid: mp 97−98 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.64 (d, J = 8.2 Hz, 1H), 8.59 (d, J = 2.1 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.87 (t, J = 8.2 Hz, 1H), 7.76 (t, J = 8.2 Hz, 1H), 7.65 (dd, J = 8.6, 2.2 Hz, 1H), 3.29 (t, J = 7.6 Hz, 2H), 1.88−1.95 (m, 2H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 163.9, 143.6, 132.9, 132.9, 132.4, 132.1, 130.1, 129.6, 127.8, 126.7, 126.1, 124.1, 123.3, 38.8, 23.2, 14.9; HRMS (ESI) calcd. for $C_{16}H_{15}ClN$ $(M + H)^+$ m/z = 256.0893, found 256.0893.

2-Chloro-6-isopropylphenanthridine (12e). 53 mg, 73%, white solid: mp 128−130 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.69 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 2.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.89 (td, J = 8.4, 1.2 Hz, 1H), 7.79 (td, J = 8.4, 1.2 Hz, 1H), 7.68 (dd, J = 8.8, 2.4 Hz, 1H), 4.04 (sept, J = 6.8 Hz, 1H), 1.44 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ 167.6, 143.2, 132.8, 132.6, 132.2, 131.7, 129.8, 129.3, 126.9, 125.7, 125.6, 123.9, 122.9, 32.1, 22.3; HRMS (ESI) calcd. for $C_{16}H_{15}ClN$ $(M + H)^+$ m/z = 256.0888, found 256.0897.

2-Chloro-6-phenylphenanthridine (12f).[8e] 62 mg, 76%, white solid: mp 143−145 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.73 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 8.0, 3.2 Hz, 1H), 7.92 (t, J = 8.0 Hz, 2H), 7.69−7.74 (m, 4H), 7.57−7.61 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 162.4, 143.3, 140.6, 133.4, 133.3, 132.7, 132.0, 130.7, 130.2, 129.8, 129.6, 129.3, 129.2, 126.2, 125.8, 123.7, 123.0; HRMS (ESI) calcd. for $C_{19}H_{13}ClN$ $(M + H)^+$ m/z = 290.0737, found 290.0735.

2,6-Dimethylphenanthridine (12g).[18a] 49 mg, 82%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.2 Hz, 1H), 8.22 (s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.72 (td, J = 8.2, 1.2 Hz, 1H), 7.58 (td, J = 8.2, 1.0 Hz, 1H), 7.44 (dd, J = 8.3, 1.5 Hz, 1H), 2.94 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 141.8, 136.0, 132.3, 130.2, 130.2, 128.9, 127.1, 126.4, 125.9, 123.5, 122.2, 121.5, 23.2, 21.8; HRMS (ESI) calcd. for $C_{15}H_{14}N$ $(M + H)^+$ m/z = 208.1126, found 208.1135.

2-Methyl-6-phenylphenanthridine (12h).[21c]. 61 mg, 76%, white solid: mp 73−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.3 Hz, 1H), 8.37 (s, 1H), 8.13 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.81 (t, J = 7.0 Hz, 1H), 7.70−7.73 (m, 2H), 7.48−7.58 (m, 5H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 142.0, 139.7, 136.8, 133.1, 130.5, 130.3, 129.9, 129.7, 128.8, 128.5, 128.3, 126.9, 125.2, 123.5, 122.1, 121.5, 21.9; HRMS (ESI) calcd. for $C_{20}H_{16}N$ $(M + H)^+$ m/z = 270.1283, found 270.1278.

3,6-Dimethylphenanthridine (13a).[11f] 59 mg, 88%, white solid: mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 8.3, 0.4 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 8.17 (dd, J = 8.3, 0.4 Hz, 1H), 7.88 (s, 1H), 7.77−7.81 (m, 1H), 7.61−7.65 (m, 1H), 7.42 (dd, J = 8.3, 1.4 Hz, 1H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 143.6, 138.7, 132.6, 130.4, 128.8, 128.0, 126.8, 126.5, 125.5, 122.1, 121.7, 121.4, 23.2, 21.5; HRMS (ESI) calcd. for $C_{15}H_{14}N$ $(M + H)^+$ m/z = 208.1126, found 208.1120.

3-Methyl-6-phenylphenanthridine (13b).[7d] 58 mg, 79%, white solid: mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.3 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 8.04 (s, 1H), 7.78−7.82 (m, 1H), 7.69−7.72 (m, 2H), 7.48−7.57 (m, 5H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 143.8, 139.8, 138.9, 133.4, 130.4, 129.8, 129.7, 128.8, 128.6, 128.5, 128.3, 126.6, 124.9, 121.9, 121.7, 121.3, 21.5; HRMS (ESI) calcd. for $C_{20}H_{16}N$ $(M + H)^+$ m/z = 270.1283, found 270.1291.

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(6-Methylphenanthridin-2-yl)(morpholino)methanone (14a). 51 mg, 76%, viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 1.5 Hz, 1H), 8.59 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.83−7.87 (m, 1H), 7.69−7.73 (m, 1H), 7.67 (dd, J = 8.3, 1.5 Hz, 1H), 3.73 (bs, 8H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 160.4, 143.9, 132.9, 132.2, 131.0, 129.3, 127.9, 126.8, 126.7, 126.0, 123.8, 122.3, 121.7, 66.9, 23.3; HRMS (ESI) calcd. for $C_{19}H_{19}N_2O_2$ $(M + H)^+$ m/z = 307.1446, found 307.1447.

(6-Phenylphenanthridin-2-yl)(morpholino)methanone (14b). 52 mg, 68%, white solid: mp 206−208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 1.6 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.80−7.84 (m, 1H), 7.65−7.68 (m, 3H), 7.57−7.61 (m, 1H), 7.45−7.52 (m, 3H), 3.65 (bs, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 162.5, 144.2, 139.3, 133.4, 133.2, 131.0, 130.4, 129.6, 129.1, 128.8, 128.4, 127.7, 127.0, 125.4, 123.7, 122.2, 121.7, 66.9; HRMS (ESI) calcd. for $C_{24}H_{21}N_2O_2$ $(M + H)^+$ m/z = 369.1603, found 369.1593.

8-Methoxy-2,6-dimethylphenanthridine (17).[8c] 59 mg, 86%, pale yellow solid: 124−126 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.53 (d, J = 9.2 Hz, 1H), 8.29 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 2.4 Hz, 1H), 7.42−7.47 (m, 2H), 3.95 (s, 3H), 2.89 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 159.7, 158.0, 142.1, 137.2, 130.1, 129.8, 128.1, 127.2, 125.0, 124.5, 122.3, 121.4, 107.9, 56.3, 23.7, 21.8; HRMS (ESI) calcd. for $C_{16}H_{16}NO$ $(M + H)^+$ m/z = 238.1232, found 238.1237.

Dibenzo[*b*,*d*]furan.[22a] Biaryldiazonium salt **10** (0.23 mmol) was dissolved in 0.5 mL of anhydrous acetonitrile in a 10 mL round bottomed flask and stirred at room temperature for 15 h under nitrogen atmosphere. Removal of solvents under reduced pressure and purification by flash column chromatography (EA/Hexane, 1:0.1) afforded the title compound (39 mg, quantitative) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.6, 0.6 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.44 (dt, J = 8.5, 1.3 Hz, 2H), 7.33 (dt, J = 8.3, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 127.1, 124.2, 122.6, 120.6, 111.6. These data are in agreement with the reported data.

2-Methoxybenzo[*c*]cinnoline.[22c] Biaryldiazonium salt **11** (0.26 mmol) was suspended in 0.26 mL of anhydrous acetonitrile in a sealed tube and heated to 120 °C for 3 h. Purification by flash chromatography (MeOH/DCM, 0.1:10) afforded the title compound (47 mg, 85%) as a viscous oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66−8.68 (m, 1H), 8.62 (d, J = 9.2 Hz, 1H), 8.47−8.50 (m, 1H), 7.83−7.89 (m, 2H), 7.79 (d, J = 2.4 Hz, 1H), 7.47 (dd, J = 8.8, 2.4 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 145.1, 142.0, 133.2, 131.1, 130.7, 129.2, 123.1, 121.4, 120.9, 120.2, 100.5, 55.8; HRMS (ESI) calcd. for $C_{13}H_{11}N_2O$ $(M + H)^+$ m/z = 211.0871, found 211.0867.

Fluoroanthene (19).[22b] 45 mg, 71%, white solid: mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.0 Hz, 2H), 7.91 (dd, 5.5, 3.1 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 8.2, 7.0 Hz, 2H), 7.37 (dd, 5.5, 3.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.9, 132.3, 129.9, 127.9, 127.5, 126.6, 121.4, 120.0. These data are in agreement with the reported data.

6-Methylbenzo[*k*]phenanthridine (20).[19] 6.7 mg, 11%, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12−9.14 (m, 1H), 8.97 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 8.02−8.06 (m, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.71−7.77 (m, 3H), 7.65 (td, J = 8.4, 1.4 Hz, 1H), 3.12 (s, 3H); HRMS (ESI) m/z = 244.1126 calcd. for $C_{18}H_{14}N$ $(M + H)^+$, found 244.1116.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00579.

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Notes

The authors declare no competing financial interest.

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