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Annulation of Benzamides with Arynes Using Palladium with Photoredox Dual Catalysis

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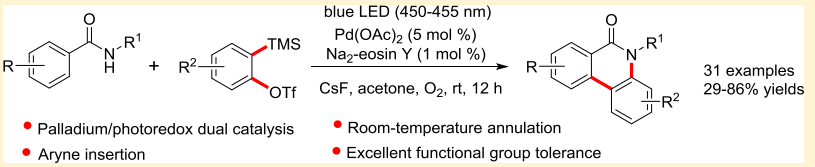
Supporting Information



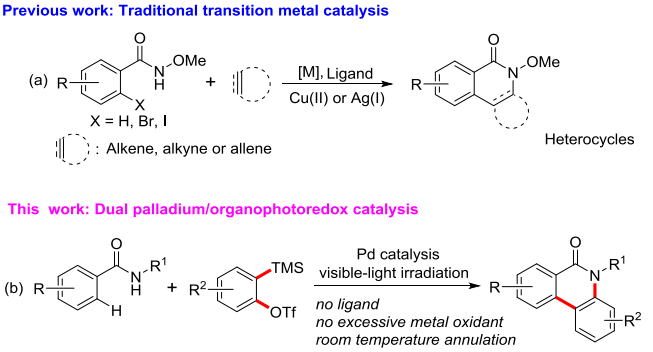
ABSTRACT: Efficient annulation of benzamides with arynes using palladium and photoredox dual catalysis under an oxygen atmosphere is disclosed, which circumvents the use of external toxic metal oxidant and proceeds readily via aryne insertion at room temperature to construct the phenanthridinone backbone.

INTRODUCTION

Over the past years, visible light-mediated photoredox catalysis has garnered considerable attention in the construction of complex organic molecules that are not achievable through the conventional transition-metal catalysis.[1] Particularly, a strategy of photoredox with transition-metal dual catalysis, also termed metallaphotoredox catalysis pioneered by MacMillan, extremely drives the rapid advancement of photochemistry in the field of organic synthesis.[2] In fact, some elegant works using this dual catalysis strategy have demonstrated the high efficiency and significant advantages in enabling catalytic access to unconventional C−C and C−heteroatom bond formation.[3] Hitherto, several representative combinations of transition-metal catalyst, such as Pd,[3b,c] Cu,[4a] and some others[2d,4b,c] with the photoredox catalyst have been well established in this area.[4] Despite advances, the merger of photoredox and Pd catalysis as a highly versatile platform is still in its infancy, which can be further employed to establish mild and environmentally benign synthetic methodologies for more challenging organic transformations.

Recently, aryne chemistry has been gaining the renaissance in the construction of heterocycles and complex organic molecules, largely due to their inherent strain that made themselves highly reactive.[5] Indeed, the unique properties of arynes have witnessed the powerful ability to manipulate a variety of chemical bonds.[6] Particularly, noteworthy is that the mild generation of arynes using Kobayashi's protocol[7] has made it relatively easy to discover more reaction modes.[6] In particular, Larock,[8] Biju,[9] Greaney,[10] Li,[11] and others[12] subsequently reported elegant results with respect to benzyne insertion, enabling the difunctionalization of benzene under mild conditions.[6−12] Among such transformations, annulation of arynes seemed to be significantly valuable in organic synthesis for their diverse reaction modes. For selected examples, Larock and co-workers in 2012 realized Pd-catalyzed annulation of *ortho*-halobenzamides with arynes, affording N-substituted phenanthridinones in good yields (Scheme 1a).[8b]

Scheme 1. Strategies for the Construction of Phenanthridinones



Very recently, Xu's group and Jeganmohan's group almost simultaneously reported the direct cyclization of benzamides with arynes using the amide-directed C−H activation strategy.[12b,c] However, a stoichiometric amount of copper salt or persulfate salt is required for regeneration of the Pd(II) catalyst, which is extremely detrimental in practical organic synthesis. Inspired by the recent strategy of palladium metallaphotoredox catalysis, we envisioned that molecular O_2 theoretically may take the place of the toxic metal salts under the visible-light irradiation to enable Pd-catalyzed annulation. Additionally, the majority of the reactions involving arynes

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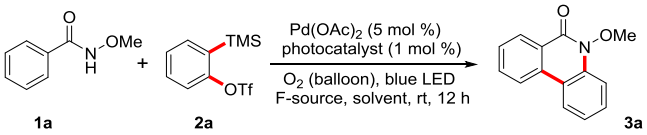
often require heating or critical conditions, which are actually not the ideal methodologies in synthetic chemistry.[13] Therefore, the development of mild and eco-friendly benzyne chemistry proceeding at room temperature would be highly desirable. Herein, we will report the application of dual palladium and photoredox catalysis strategy in room-temperature annulation of benzamides with arynes under an oxygen atmosphere (Scheme 1b).

RESULTS AND DISCUSSION

We then started the work by optimizing the annulation reaction conditions with *N*-methoxybenzamide (**1a**) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) selected as model substrates (Table 1). Based on our recent work on

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

Entry	photocatalyst	F-source	solvent	yield (%)[b]
1	Na_2-eosin Y	CsF	CH_3CN	12
2	Na_2-eosin Y	TBAF	CH_3CN	trace
3	Na_2-eosin Y	KF	CH_3CN	11
4	Na_2-eosin Y	CsF	PhMe	8
5	Na_2-eosin Y	CsF	THF	0
6	Na_2-eosin Y	CsF	DCM	26
7	Na_2-eosin Y	CsF	DCE	40
8	*Na_2-eosin Y*	*CsF*	*acetone*	*80*
9	Na_2-eosin Y	CsF	DMF	trace
10	Na_2-eosin Y	CsF	DMSO	0
11	$Ru(bpy)_3Cl_2$	CsF	acetone	0
12	rose bengal	CsF	acetone	21
13	methylene blue	CsF	acetone	15
14	acid red 94	CsF	acetone	9
15		CsF	acetone	0
16	Na_2-eosin Y		acetone	0
17	Na_2-eosin Y	CsF	acetone	0,[c] 0[d]
18	Na_2-eosin Y	CsF	acetone	73[e]

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), $Pd(OAc)_2$ (5 mol %), photocatalyst (1 mol %), F-source (2.2 equiv), and solvent (1.0 mL), irradiated with blue light-emitting diode (LED) (450−455 nm) at room temperature under an O_2 atmosphere for 12 h. [b]Isolated yield. [c]N_2. [d]80 °C in dark for 12 h. [e]Air.

aryne insertion,[14] the model reaction was preferentially performed using acetonitrile as the solvent and CsF as a base, mainly because of which facilitates the formation of the benzyne intermediate at room temperature. This annulation could proceed by using 5 mol % $Pd(OAc)_2$ and 1 mol % Na_2-eosin Y as a photocatalyst with blue LED (1.5 W) irradiation under an oxygen atmosphere for 12 h, affording the desired product **3a** in 12% yield (entry 1). Instead of CsF, both tetra-n-butylammonium fluoride (TBAF) and potassium fluoride (KF) did not effectively promote this annulation under the similar reaction conditions (entries 2 and 3). Then, the solvent effect was explored under the above conditions. It was found that PhMe resulted in the formation of **3a** in 8% yield (entry 4). Annulation did not proceed in tetrahydrofuran (THF), and no **3a** was detected (entry 5). The use of dichloromethane (DCM) and 1,2-dichloroethane (DCE) can accelerate the process and improve the yield of **3a** (entries 6 and 7). To our delight, acetone was found to be the best reaction medium for annulation of **1a** with **2a**, leading to 80% yield of **3a** (entry 8). However, annulation did not work when using polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (entries 9 and 10). Furthermore, some common photocatalysts, including $Ru(bpy)_3Cl_2$, rose bengal, methylene blue, and acid red 94, were evaluated in this model annulation, and no improved results were observed (entries 11−14). In the absence of Na_2-eosin Y or CsF, no desired product **3a** was isolated (entries 15 and 16). Annulation did not proceed under a nitrogen atmosphere, showing that the molecular oxygen plays a crucial role in the catalytic recycle. Similarly, the reaction did not occur when carried out at 80 °C in dark for 12 h, indicating that blue LED is irreplaceable for the excitation of ground-stated photocatalyst Na_2-eosin Y (entry 17). Finally, the screening of the light source showed that blue LED (450−455 nm) is most effective in this annulation (Table S1 of Supporting Information). Finally, it is found that annulation also can proceed under air to give the **3a** in slightly decreased yield (entry 18).

Then, the annulation reactions of several substituted *N*-methoxylbenzamides with benzyne were examined under the optimal conditions, and the results are listed in Table 2. It is found that parasubstituted substrates with incorporation of electron-donating substituents, such as Me, Et, *t*-Bu, MeO, and EtO, reacted efficiently with **2a** to produce the desired products (**3b−f**) in good yields. Inversely, annulation of benzyne with aryl amides having electron-withdrawing substituents including CO_2Me, CF_3, NO_2, and CN proceeded smoothly to give **3g−j** in decreasing yields. Moreover, introducing halogens such as F and Cl into the phenyl ring slightly retarded the annulation process (**3k** and **l**). Installation of Me, MeO, and Cl at the meta-position were also allowed to react with **2a**, affording the products **3m−o** in 65−81% yields. We found that weak steric hindrance existed in this Pd-catalyzed annulation when ortho-substituted aryl amides were investigated (**3b** vs **3m**, **3o** vs **3q**). Particularly, reactions with some other amides possessing π-conjugated groups gave the target products in moderate to good yields (**3r−t**). In case of arylamides with bis-substitution, slightly reduced product yields were observed, affording 72% of **3u** and 75% of **3v**, respectively. Replacing Me with MeO on nitrogen of amide retarded this cyclization process, and longer reaction time (36 h) was required for 66% of product **3w**. Additionally, the reaction of benzamide with benzyne still delivers the product **3x** in 29% yield. Unfortunately, *N*-phenyl amide did not work under the standard reaction conditions.

Next, we focused on exploring the scope of aryne precursors **2** under the optimized reaction conditions, and the results are listed in Table 3. As we expected, the employment of asymmetric arynes for annulation provided the products **4a**/**4a′** (3.6:1) and **4b**/**4b′** (1.6:1) in satisfactory yields, albeit with low regioselectivity. Interestingly, it is found that introducing Cl into aryne led to the selective formation of **4c** as the final product, indicating the significant halogen effect. The reaction of asymmetric arynes possessing electron-donating alkyl or 1,3-dioxole at both 3- and 4-positions with **1a** proceeded efficiently to form the corresponding annulation products in acceptable yields (**4d−f**). Particularly, we found that one asymmetric aryne generated from **1a** with 2-(trimethylsilyl)naphthalen-1-yl trifluoromethansulfeo-nate reacted to generate **4g** as a sole product in 62% yield.

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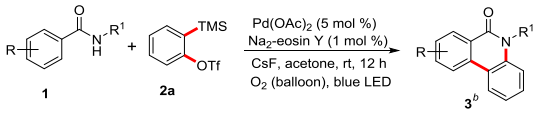
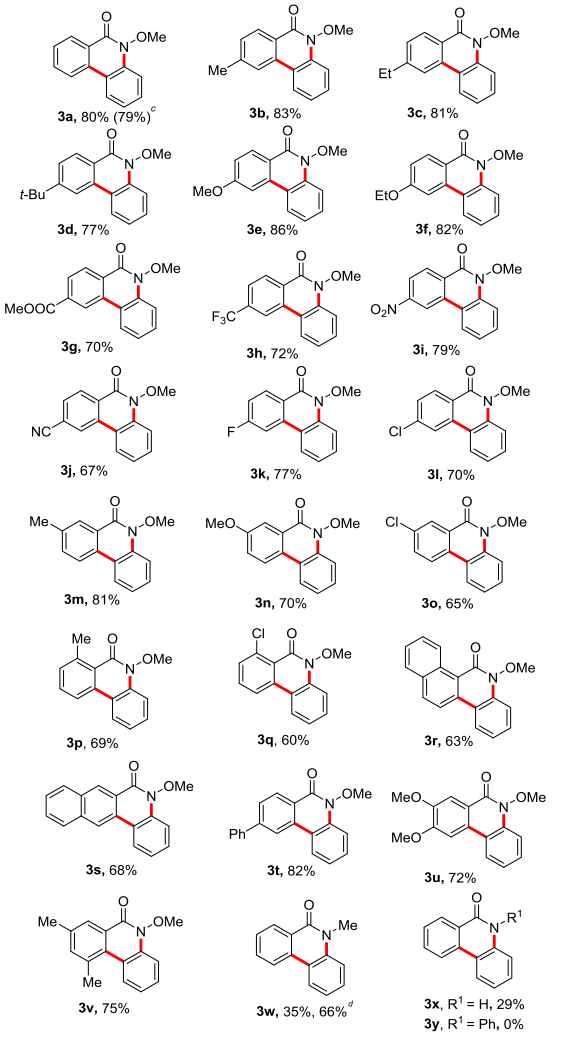
Table 2. Scope of Substituted Benzamides[a]

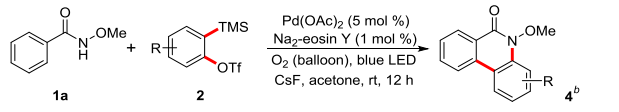


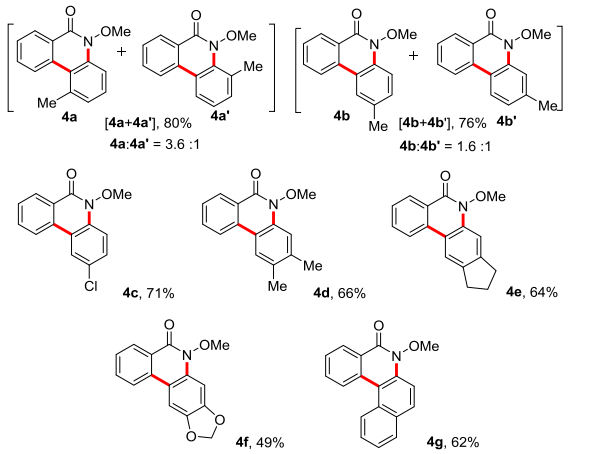


[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.22 mmol), $Pd(OAc)_2$ (5 mol %), Na_2-eosin Y (1 mol %), CsF (2.2 equiv) in acetone (1.0 mL) irradiated with blue LED (450−455 nm) at room temperature under an O_2 atmosphere for 12 h. [b]Isolated yield. [c]1 mmol scale. [d]36 h.

Although Pd-catalyzed cyclization of benzoamides with arynes has been established under traditional conditions, a reasonable reaction pathway in which employing stoichiometric copper salt to regenerate the palladium catalyst was also provided. When it comes to palladium metallaphotoredox catalysis in this annulation, the reaction seemed to proceed via a distinct pathway. To figure out the issue, a series of control experiments were carried out to investigate this catalytic system (Scheme 2). A mixture of [D_5]-**1a**/**1a** (1:1) was used to react with **2a** under optimized conditions, resulting into the formation of **3a** in 22% yield. Then, the ^{1}H NMR analysis determined the kinetic isotope effect (KIE) value (k_H/k_D = 5.9, Scheme 2a), indicating that the insertion of Pd(II) into the C−H bond may be the rate-determining step in the catalytic cycle (Scheme 3). The annulation reaction was specially performed under an oxygen atmosphere (balloon) in the absence of the

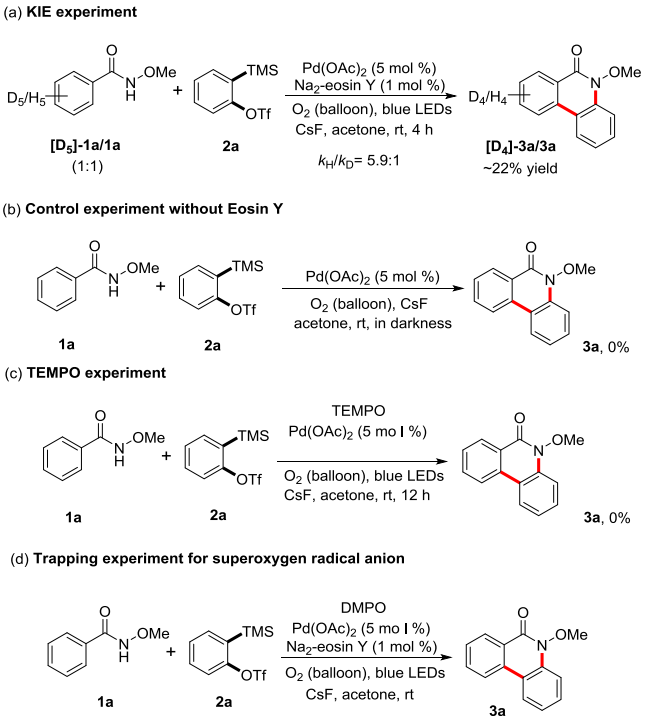
Table 3. Scope of Aryne Precursors





[a]Reaction conditions: **1a** (0.20 mmol), **2** (0.22 mmol), $Pd(OAc)_2$ (5 mol %), Na_2-eosin Y (1 mol %), and CsF (2.2 equiv) in acetone (1 mL) irradiated with blue LED (450−455 nm) at room temperature under an O_2 atmosphere for 12 h. [b]Isolated yield.

Scheme 2. Mechanistic Studies



eosin Y (Scheme 2b), but no product **3a** was observed, excluding the possibility that O_2 acts as an oxidant. Additionally, employing stoichiometric 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, a common radical scavenger) as an additive in the reaction system did not produce **3a**, demonstrating that a highly reactive radical species may be involved in the photoredox catalysis (Scheme 2c). Following that, the electron spin resonance (ESR) experiment with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the radical trapping

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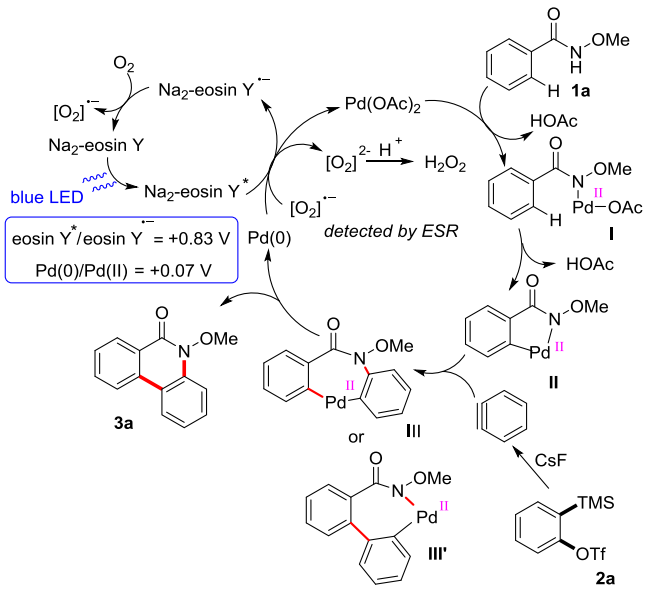
Scheme 3. Proposed Reaction Mechanism



reagent successfully detected the trapping adducts (Scheme 2d), confirming the presence of the superoxygen radical anion (Figure 1) and which is crucial for the regeneration of the Pd(II) catalyst (Scheme 3).

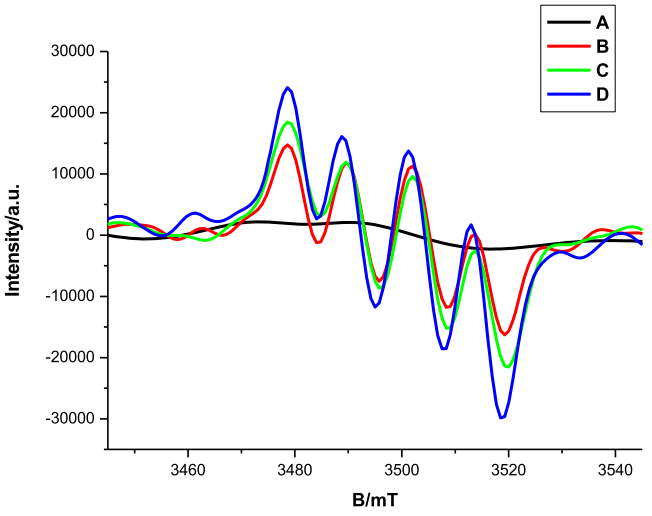


Figure 1. All the ESR spectra were measured in a solution of DMPO (2.0×10^{-2} M), Na_2-eosin Y (1 mol %) in oxygen-saturated acetone. (A) Without blue LED irradiation; (B) with blue LED irradiation for 5 s; (C) with blue LED irradiation for 10 s; (D) with blue LED irradiation for 15 s.

Based on the above experimental results and relating reports,[3b,c,12b,c,15a] a possible reaction mechanism is proposed in Scheme 3. Initially, Pd(II) coordinated with nitrogen of **1a** to form **I**, followed by the ortho C−H insertion (activation), afforded the five-membered palladacycle species **II**.[15a] Then, benzyne was in situ generated from **2a** using CsF as a base and which underwent coordinative insertion into **II**, delivering the intermediate **III** or **III′**. The key reductive elimination of **III** or **III′** released the product **3a** and Pd(0). In addition, upon irradiation under blue LED, ground-stated eosin Y was easily excited to its excited-state Na_2-eosin Y* (Na_2-eosin Y*/Na_2-eosin $Y^{\bullet-}$ = +0.83 V),[16] which was theoretically quenched by Pd(0) to give eosin $Y^{\bullet-}$ as well as the regeneration of Pd(II) for the catalytic cycle. Furthermore, the interaction of molecular oxygen with Na_2-eosin $Y^{\bullet-}$ yielded superoxygen anion radical species, which is detected by ESR experiment (Figure 1).[15a] In addition, the formation of H_2O_2 was also examined by a starch potassium iodide test paper, and the paper changed to blue. However, the possibility of the superoxygen anion radical acts as an oxidant to enable the same oxidation of Pd(0) into Pd(II) should not be ruled out.[3b]

CONCLUSIONS

In conclusion, we have established mild annulation of benzamides with arynes under air using dual palladium and organophotoredox catalysis, providing a useful tool to construct the phenanthridinone derivatives in an efficient manner. Mechanistic studies indicate the crucial role of O_2 in this dual catalytic system. The further applications of palladium and organophotoredox catalysis are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Information. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 and 100 MHz, respectively) and 600 MHz Bruker FT-NMR spectrometer (600 and 150 MHz, respectively). All chemical shifts are given as the δ value (ppm) with reference to tetramethylsilane as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; and q, quartet. The coupling constants, J, are reported in hertz. High-resolution mass spectroscopy data of the products were collected on Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Fisher Scientific LTQ FTICR-MS instrument. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}). Melting points were determined in an open capillary tube using a WRS-1B digital melting point apparatus.

The starting materials, benzamide derivatives and 2-(trimethylsilyl)phenyl trifluoromethanesulfonates, were prepared according to the reported methods.[7,17] All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate (3:1 to 5:1).

Typical Procedure for Annulation of Benzamides with Arynes. Under an air atmosphere, a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with *N*-methoxybenzamide (**1a**, 30.2 mg, 0.20 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), Na_2-esoin Y (1.4 mg, 1 mol %), CsF (66.9 mg, 0.44 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 65.7 mg, 0.22 mmol), and freshly distilled acetone (1.0 mL). Then, the resulted solution was placed in a distance of ∼1.5 cm from 1.5 W blue LED (450−455 nm) at room temperature for 12 h. The reaction process was detected by thin-layer chromatography (TLC). After the reaction, the crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1 to 5:1), affording the desired product **3a** as a white solid (36.0 mg, 80% yield).

Typical Procedure for the Synthesis of 3a in the 1 mmol Scale. Under an air atmosphere, a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with *N*-methoxybenzamide (**1a**, 151.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.2 mg, 5 mol %), Na_2-esoin Y (6.9 mg, 1 mol %), CsF (334.2 mg, 2.2 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 327.8 mg, 1.1 mmol), and freshly distilled acetone (1.0 mL). Then, the resulted solution was placed in a distance of ∼1.5 cm from 1.5 W blue LED (450−455 nm) at room temperature for 12 h. The reaction process was detected by TLC. After the reaction, the crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl

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acetate = 3:1 to 5:1), affording the desired product **3a** as a white solid (177.8 mg, 79% yield).

*5-Methoxyphenanthridin-6(5H)-one (**3a**).*[18] It is obtained as a white solid; 36.0 mg, 80% yield; mp 107−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 8.0 Hz, 1H), 8.27 (dd, J_1 = 8.0 Hz, J_2 = 3.2 Hz, 2H), 7.78 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.59 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 4.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.2, 135.8, 132.9, 132.6, 129.9, 128.5, 128.0, 126.3, 123.2, 121.9, 118.5, 112.6, 62.7.

*5-Methoxy-9-methylphenanthridin-6(5H)-one (**3b**).*[18] It is obtained as a white solid; 39.7 mg, 83% yield; mp 152−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 7.66 (dd, J_1 = 8.4 Hz, J_2 = 0.9 Hz, 1H), 7.57 (td, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 4.13 (s, 3H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.3, 143.2, 135.9, 132.9, 129.8, 129.5, 128.5, 124.0, 123.1, 123.0, 121.9, 118.5, 112.6, 62.7, 22.1.

*9-Ethyl-5-methoxyphenanthridin-6(5H)-one (**3c**).* It is obtained as a white solid; 41.0 mg, 81% yield; mp 158−160 °C. IR (KBr): 3071, 2968, 2934, 1672, 1617, 1509, 1308, 1127, 1023, 955, 827, 739. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.66 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.57 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.4 Hz, 1H), 4.13 (s, 3H), 2.86 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.3, 149.3, 135.9, 133.0, 129.7, 128.6, 128.3, 124.2, 123.1, 122.9, 120.8, 118.6, 112.55, 62.6, 29.4, 15.4. HRMS (ESI): ([M + H]$^+$) calcd for $[C_{16}H_{15}NO_2]^+$, 254.1176; found, 254.1174.

*9-(tert-Butyl)-5-methoxyphenanthridin-6(5H)-one (**3d**).*[18] It is obtained as a white solid; 43.3 mg, 77% yield; mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.27 (d, J = 1.6 Hz, 1H), 7.69−7.66 (m, 2H), 7.58 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 4.13 (s, 3H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.1, 135.9, 132.6, 129.7, 128.3, 126.1, 124.0, 123.0, 122.9, 118.9, 118.0, 112.6, 62.6, 35.5, 31.2.

*5,9-Dimethoxyphenanthridin-6(5H)-one (**3e**).*[18] It is obtained as a white solid; 43.9 mg, 86% yield; mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.57 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.15 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 4.13 (s, 3H), 3.98 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.1, 157.1, 136.2, 134.9, 130.6, 130.0, 123.2, 122.9, 119.8, 118.2, 115.8, 112.6, 104.9, 62.7, 55.6.

*9-Ethoxy-5-methoxyphenanthridin-6(5H)-one (**3f**).* It is obtained as a white solid; 44.1 mg, 82% yield; mp 142−144 °C. IR (KBr): 3037, 2934, 2890, 1657, 1608, 1446, 1249, 1205, 1175, 1018, 955, 758. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.56 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.30 (t, J = 6.8 Hz, 1H), 7.12 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 4.20 (q, J = 6.8 Hz, 1H), 4.12 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.5, 157.1, 136.1, 134.8, 130.5, 129.9, 123.1, 122.8, 119.6, 118.2, 116.1, 112.5, 105.4, 63.8, 62.6, 14.7. HRMS (ESI): ([M + H]$^+$) calcd for $[C_{16}H_{16}NO_3]^+$, 270.1125; found, 270.1123.

*Methyl 5-Methoxy-6-oxo-5,6-dihydrophenanthridine-9-carboxylate (**3g**).*[18] It is obtained as a white solid; 39.6 mg, 70% yield; mp 163−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.19 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 4.16 (s, 3H), 4.02 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.3, 156.6, 136.0, 133.6, 133.0, 130.5, 129.2, 128.9, 128.1, 123.9, 123.5, 118.1, 112.7, 62.8, 52.6.

*5-Methoxy-9-(trifluoromethyl)phenanthridin-6(5H)-one (**3h**).*[18] It is obtained as a white solid; 42.2 mg, 72% yield; mp 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 8.4 Hz, 1H), 8.51 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.70 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.64 (td, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 7.39 (t, J = 8.4 Hz, 1H), 4.16 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.2, 136.2, 134.2 (q, J = 32.0 Hz), 133.3, 130.9, 129.6, 128.7, 124.1 (q, J = 3.4 Hz), 123.7 (q, J = 270.0 Hz), 123.6, 123.3, 119.3 (q, J = 4.0 Hz), 117.6, 112.8, 62.8.

*5-Methoxy-9-nitrophenanthridin-6(5H)-one (**3i**).*[18] It is obtained as a white solid; 42.7 mg, 79% yield; mp 210−212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.74 (d, J = 8.8 Hz, 1H), 8.39−8.33 (m, 2H), 7.76−7.68 (m, 2H), 7.46 (td, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 4.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.9, 150.5, 136.4, 134.2, 131.6, 130.6, 130.3, 124.0, 123.7, 121.7, 117.8, 117.4, 113.1, 62.9.

*5-Methoxy-6-oxo-5,6-dihydrophenanthridine-9-carbonitrile (**3j**).* It is obtained as a white solid; 33.5 mg, 67% yield; mp 150−152 °C. IR (KBr): 3440, 2920, 1652, 1608, 1559, 1327, 1112, 946, 886, 748. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.67 (d, J = 8.4 Hz, 1H), 8.59 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.82 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 7.73 (dd, J_1 = 8.4 Hz, J_2 = 1.0 Hz, 1H), 7.71−7.66 (m, 1H), 7.43 (t, J = 8.4 Hz, 1H), 4.16 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.0, 136.3, 133.6, 131.4, 129.9, 129.7, 129.0, 126.8, 123.9, 123.4, 118.0, 116.9, 116.4, 113.0, 62.9. HRMS (ESI): ([M + H]$^+$) calcd for $[C_{15}H_{11}N_2O_2]^+$, 251.0815; found, 251.0813.

*9-Fluoro-5-methoxyphenanthridin-6(5H)-one (**3k**).*[19] It is obtained as a pale yellow solid; 37.4 mg, 77% yield; mp 157−159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59−8.55 (m, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.88 (dd, J_1 = 10.0 Hz, J_2 = 1.2 Hz, 1H), 7.68 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.62 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.36 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.33−7.27 (m, 1H), 4.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.7 (d, J = 251.3 Hz), 156.6, 136.3, 135.6 (d, J = 9.0 Hz), 131.7 (d, J = 9.7 Hz), 130.7, 123.4, 123.2, 122.8, 117.7 (d, J = 3.1 Hz), 116.3 (d, J = 22.0 Hz), 112.8, 107.9 (d, J = 24.0 Hz), 62.8.

*9-Chloro-5-methoxyphenanthridin-6(5H)-one (**3l**).*[18] It is obtained as a white solid; 36.3 mg, 70% yield; mp 170−172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.62 (td, J_1 = 7.8 Hz, J_2 = 0.8 Hz, 1H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 4.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 139.4, 136.2, 134.4, 130.7, 130.3, 128.4, 124.7, 123.4, 123.3, 121.9, 117.4, 112.8, 62.8.

*5-Methoxy-8-methylphenanthridin-6(5H)-one (**3m**).*[18] It is obtained as a white solid; 38.7 mg, 81% yield; mp 107−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.66 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.61−7.53 (m, 2H), 7.33 (t, J = 8.4 Hz, 1H), 4.13 (s, 3H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.3, 138.3, 135.4, 133.9, 130.5, 129.4, 128.2, 126.2, 123.1, 122.9, 121.9, 118.7, 112.5, 62.6, 21.3.

*5,8-Dimethoxyphenanthridin-6(5H)-one (**3n**).*[12c] It is obtained as a white solid; 35.7 mg, 70% yield; mp 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20−8.17 (m, 2H), 7.97 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.54 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.38−7.32 (m, 2H), 4.15 (s, 3H), 3.97 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.6, 157.1, 134.7, 128.8, 127.7, 126.5, 123.7, 123.2, 122.6, 122.5, 118.6, 112.5, 108.9, 62.7, 55.7.

*8-Chloro-5-methoxyphenanthridin-6(5H)-one (**3o**).*[12b] It is obtained as a white solid; 33.7 mg, 65% yield; mp 152−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 7.71 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 4.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.2, 135.7, 134.3, 132.9, 131.4, 130.3, 128.0, 127.6, 123.6, 123.4, 123.2, 117.8, 112.8, 62.8.

*5-Methoxy-7-methylphenanthridin-6(5H)-one (**3p**).*[18] It is obtained as a white solid; 33.0 mg, 69% yield; mp 197−199 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.60−7.48 (m, 3H), 7.31 (d, J = 7.2 Hz, 1H), 7.26 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 4.09 (s, 3H), 2.97 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.0, 142.7, 135.8, 134.3, 131.6, 131.5, 129.7, 124.4, 123.4, 122.7, 120.0, 118.3, 112.0, 62.3, 24.0.

*7-Chloro-5-methoxyphenanthridin-6(5H)-one (**3q**).*[12c] It is obtained as a white solid; 31.1 mg, 60% yield; mp 135−137 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (t, J = 8.4 Hz, 2H), 7.61−7.56 (m,

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4H), 7.30 (t, J = 8.4 Hz, 1H), 4.12 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 155.6, 136.3, 135.9, 132.0, 131.6, 130.6, 123.6, 123.1, 122.6, 120.9, 117.3, 112.3, 62.5.

6-Methoxybenzo[i]phenanthridin-5(6H)-one (**3r**). It is obtained as a white solid; 34.7 mg, 63% yield; mp 167−169 °C. IR (KBr): 3055, 2919, 1650, 1605, 1475, 1443, 1298, 1237, 1186, 1152, 952, 824, 739. ^1H NMR (400 MHz, $CDCl_3$): δ 10.27 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.81−7.72 (m, 2H), 7.68−7.62 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 4.2 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.1, 136.1, 134.1, 134.0, 132.9, 132.3, 130.3, 128.7, 128.2, 127.8, 126.9, 123.9, 122.9, 120.3, 119.3, 118.0, 112.2, 62.7. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{18}H_{14}NO_2]^+$, 276.1019; found, 276.1022.

5-Methoxybenzo[j]phenanthridin-6(5H)-one (**3s**). It is obtained as a white solid; 37.4 mg, 68% yield; mp 148−150 °C. IR (KBr): 3045, 2943, 1672, 1626, 1602, 1469, 1347, 1322, 1225, 1151, 1033, 956, 881, 755. ^1H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.70 (s, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.68−7.62 (m, 2H), 7.58 (t, J = 7.8 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 4.17 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.7, 135.7, 135.1, 132.1, 129.8, 129.7, 129.2, 129.0, 128.5, 128.1, 126.8, 124.2, 123.3, 123.3, 121.1, 118.9, 112.8, 62.7. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{18}H_{14}NO_2]^+$, 276.1019; found, 276.1012.

5-Methoxy-9-phenylphenanthridin-6(5H)-one (**3t**).[19] It is obtained as a pale yellow solid; 49.4 mg, 82% yield; mp 149−151 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.0 Hz, 1H), 8.44 (s, 1H), 8.35 (d, J = 8.0 Hz, 1H), 7.82 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.73−7.67 (m, 3H), 7.60 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 4.16 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.2, 145.5, 140.2, 136.1, 133.3, 130.1, 129.1, 129.0, 128.3, 127.5, 127.2, 125.1, 123.2, 123.2, 120.4, 118.6, 112.7, 62.7.

5,8,9-Trimethoxyphenanthridin-6(5H)-one (**3u**).[19] It is obtained as a white solid; 41.1 mg, 72% yield; mp 195−197 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.57 (s, 1H), 7.54 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 4.13 (s, 3H), 4.09 (s, 3H), 4.04 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.8, 153.3, 149.8, 135.2, 128.9, 127.6, 122.9, 122.5, 120.2, 118.3, 112.6, 108.6, 102.8, 62.7, 56.2, 56.1.

5-Methoxy-8,10-dimethylphenanthridin-6(5H)-one (**3v**). It is obtained as a white solid; 38.0 mg, 75% yield; mp 197−199 °C. IR (KBr): 3074, 2929, 1662, 1607, 1334, 1250, 1162, 1054, 965, 762. ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.4 Hz, 1H), 8.35 (s, 1H), 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.32 (t, J = 7.8 Hz, 1H), 4.12 (s, 3H), 2.93 (s, 3H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.5, 138.4, 137.3, 135.6, 134.8, 129.8, 128.6, 127.5, 126.9, 122.4, 120.2, 112.3, 62.5, 25.9, 20.9. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{16}H_{16}NO_2]^+$, 254.1176; found, 254.1179.

5-Methylphenanthridin-6(5H)-one (**3w**).[12c] It is obtained as a white solid; 28.8 mg, 66% yield; mp 104−106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 8.0 Hz, 1H), 8.28 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 7.8 (t, J = 8.0 Hz, 1H), 7.61−7.54 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.5, 137.8, 133.4, 132.3, 129.4, 128.7, 127.8, 125.4, 123.1, 122.3, 121.5, 119.1, 114.9, 29.8.

Phenanthridin-6(5H)-one (**3x**).[15a] It is obtained as a white solid; 11.6 g, 29% yield; mp 101−103 °C. ^1H NMR (600 MHz, DMSO-d_6): δ 10.85 (br, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.49 (dd, J_1 = 7.9 Hz, J_2 = 0.8 Hz, 1H), 7.02 (t, J = 8.4 Hz, 1H), 6.81 (t, J = 8.0 Hz, 1H), 6.65 (t, J = 8.3 Hz, 1H), 6.54 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 6.43 (t, J = 8.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6): δ 161.3, 137.0, 134.7, 133.3, 130.0, 128.4, 127.9, 126.1, 123.7, 123.1, 122.8, 118.0, 116.6. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{13}H_{10}NO]^+$, 196.0757; found, 196.0756.

5-Methoxy-1-methylphenanthridin-6(5H)-one (**4a**) *and 5-Methoxy-4-methylphenanthridin-6(5H)-one* (**4a′**).[20] It is obtained as a white solid; 38.3 mg, 80% yield; mp 159−161 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 8.0 Hz, 0.27H), 8.50 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.4 Hz, 0.28H), 8.20 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.77−7.67 (m, 1.3H), 7.63−7.58 (m, 0.35H), 7.54 (t, J = 8.0 Hz, 1.3H), 7.42 (t, J = 8.0 Hz, 0.29H), 7.31 (d, J = 7.2 Hz, 1H), 7.22−7.12 (m, 1.3H), 4.10 (s, 0.8H), 3.96 (s, 3H), 2.90 (s, 0.8H), 2.76 (s, 3.0H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 156.9, 136.3, 134.9, 134.4, 134.1, 133.3, 132.5, 131.6, 128.7, 128.5, 128.2, 127.9, 127.8, 127.1, 126.5, 125.9, 124.2, 124.1, 123.1, 122.1, 121.4, 119.7, 110.8, 62.8, 62.4, 26.2, 23.2.

5-Methoxy-2-methylphenanthridin-6(5H)-one (**4b**) *and 5-Methoxy-3-methylphenanthridin-6(5H)-one* (**4b′**).[12b] It is obtained as a white solid; 36.4 mg, 76% yield; mp 136−138 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.57−8.52 (m, 1.6H), 8.27 (d, J = 8.0 Hz, 0.68H), 8.23 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.06 (s, 0.6H), 7.79−7.73 (m, 1.7H), 7.60−7.55 (m, 2H), 7.48 (s, 1H), 7.40 (d, J = 8.4 Hz, 0.6H), 7.17 (d, J = 8.0 Hz, 1H), 4.14 (s, 3H), 4.13 (s, 1.8H), 2.53 (s, 3H), 2.50 (s, 1.8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.4, 157.0, 140.5, 137.6, 135.8, 133.7, 133.0, 132.6, 132.5, 132.4, 132.2, 130.9, 128.5, 128.4, 128.3, 127.8, 127.5, 124.3, 123.2, 123.0, 121.8, 121.6, 118.4, 116.1, 112.6, 112.5, 62.6, 62.5, 21.8, 21.0.

2-Chloro-5-methoxyphenanthridin-6(5H)-one (**4c**).[19] It is obtained as a white solid; 36.8 mg, 71% yield; mp 142−144 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.55 (dd, J_1 = 6.6 Hz, J_2 = 0.8 Hz, 1H), 8.21−8.19 (m, 2H), 7.81−7.78 (m, 1H), 7.64 (t, J = 8.1 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.53 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1H), 4.13 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 156.9, 134.4, 132.8, 131.8, 129.9, 128.9, 128.7, 128.6, 126.6, 123.0, 122.0, 119.8, 114.1, 62.8.

5-Methoxy-2,3-dimethylphenanthridin-6(5H)-one (**4d**).[19] It is obtained as a white solid; 33.4 mg, 66% yield; mp 152−154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 7.95 (s, 1H), 7.72 (t, J = 8.4 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.41 (s, 1H), 4.13 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.2, 139.4, 133.9, 133.0, 132.3, 131.7, 128.4, 127.3, 126.0, 123.7, 121.6, 116.3, 113.2, 62.6, 20.3, 19.5.

6-Methoxy-6,8,9,10-tetrahydro-5H-cyclopenta[b]phenanthridin-5-one (**4e**). It is obtained as a white solid; 33.9 mg, 64% yield; mp 161−163 °C. IR (KBr): 2954, 2896, 2831, 2361, 1642, 1422, 1316, 1173, 1033, 979, 777. ^1H NMR (600 MHz, $CDCl_3$): δ 8.53 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.09 (s, 1H), 7.75−7.72 (m, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.53 (s, 1H), 4.13 (s, 3H), 3.08−3.03 (m, 4H), 2.20−2.16 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 157.2, 147.3, 139.6, 134.7, 133.3, 132.4, 128.4, 127.3, 125.8, 121.7, 118.4, 117.0, 108.3, 62.5, 33.3, 32.4, 25.7. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{17}H_{16}NO_2]^+$, 266.1176; found, 266.1174.

6-Methoxy-[1,3]dioxolo[4,5-b]phenanthridin-5(6H)-one (**4f**).[12b] It is obtained as a white solid; 25.4 mg, 49% yield; mp 202−204 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.53 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.75−7.73 (m, 1H), 7.64 (s, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.19 (s, 1H), 6.10 (s, 2H), 4.13 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 157.1, 150.0, 144.7, 133.0, 132.5, 132.2, 128.6, 127.0, 125.3, 121.5, 112.4, 102.0, 101.9, 94.0, 62.7.

6-Methoxybenzo[a]phenanthridin-5(6H)-one (**4g**).[19] It is obtained as a white solid; 34.1 mg, 62% yield; mp 137−139 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.84 (d, J = 8.6 Hz, 1H), 8.76 (d, J = 8.4 Hz, 1H), 8.69 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.84 (t, J = 8.4 Hz, 1H), 7.69−7.63 (m, 2H), 7.56 (t, J = 7.0 Hz, 1H), 4.20 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 157.3, 134.8, 133.4, 131.9, 131.1, 130.9, 129.9, 129.0, 128.5, 127.6, 127.3, 127.1, 127.0, 125.8, 125.0, 112.8, 112.5, 63.2.

General Procedure for the Kinetic Isotope Effect Experiment. Under an air atmosphere, a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with **1a** (0.20 mmol), [D_5]-**1a** (0.20 mmol), (**2a**, 0.44 mmol), $Pd(OAc)_2$ (5 mol %), Na_2-eosin Y (1 mol %), and CsF (0.88 mmol), and freshly distilled acetone (2.0 mL) was added to the resulted mixture. Then, the solution was placed in a distance of ∼1.5 cm from 1.5 W blue LED (450−455 nm) at room temperature for 4 h. After this, the

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mixture in the reaction tube was detected by TLC. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 3:1 to 5:1) to give the desired product **3a** in 22% yield, 9.9 mg (the yield of **3a** was calculated based on **1a**). The KIE value of 5.9 was determined by ^{1}H NMR of **3a** and [D_4]-**3a**.

General Procedure for the Control Experiment. Under an air atmosphere, a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with *N*-methoxybenzamide (**1a**, 30.2 mg, 0.20 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), CsF (66.9 mg, 0.44 mmol), and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 65.7 mg, 0.22 mmol), and freshly distilled acetone (1.0 mL) was added to the resultant mixture. Then, the solution was placed in a distance of ∼1.5 cm from 1.5 W blue LED (450−455 nm) at room temperature for 12 h. After this, no **3a** was detected by TLC.

General Procedure for the TEMPO Experiment. Under an air atmosphere, a 10 mL oven-dried quartz photoreactor equipped with a magnetic stirrer bar was charged with *N*-methoxybenzamide (**1a**, 30.2 mg, 0.20 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), Na_2-eosin Y (1.4 mg, 1 mol %), CsF (66.9 mg, 0.44 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**, 65.7 mg, 0.22 mmol), and TEMPO (34.7 mg, 0.22 mmol), and freshly distilled acetone (1.0 mL) was added to the resultant mixture. Then, the solution was placed in a distance of ∼1.5 cm from 1.5 W blue LED (450−455 nm) at room temperature for 12 h. After this, the mixture was detected by TLC, and no **3a** was formed.

General Procedure for the Determination of Superoxide Radical Anions. A superoxide radical anion ($O_2^{\bullet-}$) was assumed to be generated from molecular oxygen by single electron transfer.[3b,c] DMPO was used as a probe to capture active species ($O_2^{\bullet-}$).[21] As shown in Figure 1, the solution of DMPO, eosin Y in acetone solution was performed without irradiation of blue LED, leading to no signal was detected. In contrast, upon irradiation with blue LED, each irradiation was performed for 5 s for three consecutive irradiations, a single radical species $O_2^{\bullet-}$ was trapped with the characteristic signal clearly observed by ESR experiments.

General Procedure for the Synthesis of Benzamides Derivatives. The starting materials (benzamides, **1a**−**w**) were prepared according to the reported method.[17]

*N-Methoxybenzamide (**1a**).*[12b] It is obtained as a white solid; 0.28 g, 95% yield; mp 63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.4, 131.9, 131.9, 128.5, 127.3, 64.0.

*N-Methoxy-4-methylbenzamide (**1b**).*[12b] It is obtained as a white solid; 0.32 g, 97% yield; mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.76 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.2, 162.5, 129.1, 124.0, 113.8, 64.3, 55.4.

*4-Ethyl-N-methoxybenzamide (**1c**).* It is obtained as a white solid; 0.35 g, 96% yield; mp 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.67 (q, J = 7.8 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.7, 129.1, 128.0, 127.2, 64.3, 28.7, 15.2. HRMS (ESI): ([M + H]$^+$) calcd for [$C_{10}H_{14}NO_2$]$^+$, 180.1019; found, 180.1016.

*4-(tert-Butyl)-N-methoxybenzamide (**1d**).*[12b] It is obtained as a white solid; 0.39 g, 95% yield; mp 63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (br, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 128.8, 126.9, 125.5, 64.3, 34.9, 31.0.

*N-Methoxy-4-methoxybenzamide (**1e**).*[12b] It is obtained as a white solid; 0.34 g, 93% yield; mp 79−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.2, 162.4, 129.0, 123.9, 113.7, 64.2, 55.3.

*4-Ethoxy-N-methoxybenzamide (**1f**).* It is obtained as a white solid; 0.38 g, 97% yield; mp 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.75 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.02 (d, J = 7.0 Hz, 2H), 3.79 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.1, 161.8, 129.0, 123.7, 114.1, 64.1, 63.5, 14.5. HRMS (ESI): ([M + H]$^+$) calcd for [$C_{10}H_{14}NO_3$]$^+$, 196.0968; found, 196.0969.

*Methyl 4-(Methoxycarbamoyl)benzoate (**1g**).*[12b] It is obtained as a white solid; 0.39 g, 93% yield; mp 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 3.93 (s, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.2, 165.3, 135.7, 132.9, 129.6, 127.2, 64.2, 52.4.

*N-Methoxy-4-(trifluoromethyl)benzamide (**1h**).*[12b] It is obtained as a white solid; 0.38 g, 87% yield; mp 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.1, 135.0, 133.8 (q, J = 31.7 Hz), 127.7, 125.6 (q, J = 3.0 Hz), 124.8 (q, J = 272.0 Hz), 64.3.

*N-Methoxy-4-nitrobenzamide (**1i**).*[12b] It is obtained as a white solid; 0.36 g, 91% yield; mp 176−179 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 6.39 (d, J = 8.6 Hz, 2H), 6.13 (d, J = 8.3 Hz, 2H), 1.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2SO$): δ 161.4, 148.8, 138.6, 128.4, 123.4, 62.9.

*4-Cyano-N-methoxybenzamide (**1j**).* It is obtained as a white solid; 0.32 g, 91% yield; mp 87−89 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.21 (s, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 136.2, 132.5, 127.8, 118.2, 113.9, 63.2. HRMS (ESI): ([M + H]$^+$) calcd for [$C_9H_9N_2O_2$]$^+$, 177.0659; found, 177.0658.

*4-Fluoro-N-methoxybenzamide (**1k**).*[19] It is obtained as a white solid; 0.32 g, 96% yield; mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.21 (s, 1H), 7.87−7.84 (m, 2H), 7.04 (t, J = 8.6 Hz, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.0 (d, J = 251.0 Hz), 165.2, 129.6 (d, J = 8.9 Hz), 127.7, 115.5 (d, J = 21.8 Hz), 63.8. HRMS (ESI): ([M + H]$^+$) calcd for [$C_8H_9FNO_2$]$^+$, 170.0612; found, 170.0611.

*4-Chloro-N-methoxybenzamide (**1l**).*[12b] It is obtained as a white solid; 0.36 g, 97% yield; mp 74−76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 129.9, 128.8, 128.5, 64.2.

*N-Methoxy-3-methylbenzamide (**1m**).*[12b] It is obtained as a white solid; 0.31 g, 95% yield; mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.60 (s, 1H), 7.58 (t, J = 6.5 Hz, 2H), 7.27−7.22 (m, 2H), 3.78 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.3, 138.2, 132.5, 131.5, 128.2, 127.7, 124.1, 63.9, 21.1.

*N-Methoxy-3-methoxybenzamide (**1n**).*[12c] It is obtained as a white solid; 0.34 g, 93% yield; mp 78−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.56 (s, 1H), 7.33 (t, J = 3.2 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.00 (dd, J_1 = 8.3 Hz, J_2 = 2.2 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.2, 159.7, 133.1, 129.6, 119.3, 118.3, 112.2, 64.1, 55.3.

*3-Chloro-N-methoxybenzamide (**1o**).*[12b] It is obtained as a white solid; 0.36 g, 98% yield; mp 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.4 (s, 1H), 7.78 (s, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.30−7.28 (m, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.1, 134.6, 133.3, 131.9, 129.8, 127.4, 125.3, 64.2.

*N-Methoxy-2-methylbenzamide (**1p**).*[12b] It is obtained as a white solid; 0.28 g, 95% yield; mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 7.33−7.25 (m, 2H), 7.20−7.13 (m, 2H), 3.81 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.9, 136.8, 132.6, 131.0, 130.5, 127.1, 125.6, 64.5, 19.4.

*2-Chloro-N-methoxybenzamide (**1q**).*[12b] It is obtained as a white solid; 0.36 g, 96% yield; mp 75−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (s, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.46−7.29 (m, 3H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.5, 131.9, 131.1, 130.2, 127.1, 64.7.

*N-Methoxy-1-naphthamide (**1r**).*[22] It is obtained as a white solid; 0.37 g, 93% yield; mp 162−163 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (d, J = 7.2 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.67−7.49 (m, 4H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 165.3, 133.1, 131.5, 130.3, 129.9, 128.3, 126.9, 126.3, 125.7, 124.9, 124.8, 63.3.

*N-Methoxy-2-naphthamide (**1s**).*[22] It is obtained as a white solid; 0.36 g, 90% yield; mp 160−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (br, 1H), 8.3 (s, 1H), 7.91−7.88 (m, 3H), 7.80 (d, J = 8.8 Hz,

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1H), 7.61−7.53 (m, 2H), 3.95 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 134.9, 132.5, 128.9, 128.6, 127.9, 127.8, 127.7, 126.9, 123.3, 64.5.

*N-Methoxy-[1,1′-biphenyl]-4-carboxamide (**1t**).*[22] It is obtained as a white solid; 0.44 g, 97% yield; mp 164−166 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 3.95 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.9, 139.7, 128.9, 128.1, 127.6, 127.3, 127.1, 64.7.

*N-Methoxy-3,4-dimethoxybenzamide (**1u**).*[12b] It is obtained as a white solid; 0.38 g, 91% yield; mp 128−130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.40 (s, 1H), 7.33 (d, J = 9.2 Hz, 1H), 6.87 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.90 (d, J = 4.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.1, 124.1, 119.8, 112.8, 110.3, 107.4, 64.5, 56.0.

*N-Methoxy-3,5-dimethylbenzamide (**1v**).* It is obtained as a white solid; 0.34 g, 94% yield; mp 120−122 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 9.40 (br, 1H), 7.39 (s, 2H), 7.16 (s, 1H), 3.88 (s, 3H), 2.35 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8, 138.4, 133.7, 131.7, 124.8, 64.5, 21.2. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{10}H_{14}NO_2]^+$, 180.1019; found, 180.1021.

*N-Methylbenzamide (**1w**).*[12c] It is obtained as a white solid; 0.26 g, 98% yield; mp 57−59 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.2 Hz, 2H), 7.53−7.43 (m, 3H), 6.53 (s, 1H), 3.05 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.4, 134.6, 131.4, 128.5, 126.9, 26.9.

General Procedure for the Synthesis of Aryne Precursor 2. The starting materials (arynes, **2a**−**h**) were prepared according to the reported method.[7,12g]

*2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate (**2a**).*[12b] It is obtained as colorless viscous oil; 0.41 g, 68% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.2 Hz, 1H), 7.51 (t, J = 6.4 Hz, 1H), 7.44−7.37 (m, 2H), 0.44 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 135.3, 132.5, 131.2, 127.5, 120.1, 119.5, 116.7 (d, J = 40 Hz), 0.9.

*3-Methyl-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2b**).* It is obtained as colorless viscous oil; 0.29 g, 46% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.45 (m, 1H), 7.39−7.32 (m, 2H), 2.46 (s, 3H), 0.46 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0, 136.9, 136.1, 134.5, 133.7, 131.4, 127.9, 118.6 (q, J = 317.7 Hz), 17.2, 0.01. HRMS (ESI): ($[M + H]^+$) calcd for $[C_{11}H_{16}F_3O_3SSi]^+$, 313.0536; found, 313.0534.

*5-Methyl-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2c**).*[12b] It is obtained as colorless viscous oil; 0.41 g, 66% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 7.20 (s, 2H), 2.34 (s, 3H), 0.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.1, 137.3, 136.7, 132.2, 131.7, 118.6 (q, J = 317.8 Hz), 20.7, −0.9.

*5-Chloro-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2d**).*[20] It is obtained as colorless viscous oil; 0.38 g, 57% yield. ^1H NMR (600 MHz, $CDCl_3$): δ 7.46 (d, J = 2.6 Hz, 1H), 7.38 (dd, J_1 = 8.8 Hz, J_2 = 2.7 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 0.37 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 153.1, 135.8, 135.3, 133.5, 131.0, 121.0, 118.5 (q, J = 212.2 Hz), −1.0.

*4,5-Dimethyl-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2e**).*[12b] It is obtained as colorless viscous oil; 0.33 g, 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.19 (s, 1H), 2.36 (d, J = 5.2 Hz, 1H), 0.45 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.1, 140.3, 137.0, 136.0, 132.0, 129.0, 119.0 (d, J = 286.8 Hz), 19.9, 19.1, 2.0, 0.6, −0.8.

*6-(Trimethylsilyl)-2,3-dihydro-1H-inden-5-yl Trifluoromethanesulfonate (**2f**).*[12g] It is obtained as colorless viscous oil; 0.41 g, 61% yield. ^1H NMR (600 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.18 (s, 1H), 2.94−2.09 (m, 4H), 2.14−2.09 (m, 2H), 0.35 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 153.9, 148.3, 143.6, 131.3, 129.4, 118.5 (q, J = 318.3 Hz), 115.7, 33.1, 32.1, 25.7, −0.7.

*6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl Trifluoromethanesulfonate (**2g**).*[12b] It is obtained as colorless viscous oil; 0.36 g, 52% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (s, 1H), 6.87 (s, 1H), 6.05 (s, 2H), 0.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.5, 148.7, 146.9, 124.9, 118.5 (q, J = 318 Hz), 113.2, 102.4, −0.7.

*1-(Trimethylsilyl)naphthalen-2-yl Trifluoromethanesulfonate (**2h**).*[23] It is obtained as colorless viscous oil; 0.30 g, 43% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.0 Hz, 1H), 7.90 (t, J = 6.0 Hz, 2H), 7.60−7.52 (m, 2H), 7.40 (d, J = 9.2 Hz, 1H), 0.60 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.4, 137.5, 132.4, 132.3, 129.0, 128.7, 128.3, 126.6, 126.2, 119.1, 2.2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00893.

Mechanistic experiments, characterization of *N*-methoxylbenzamides **1**, arynes **2**, and cyclization products **3** and **4**, and NMR spectra of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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