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Visible-Light-Photocatalyzed Synthesis of Phenanthridinones and Quinolinones via Direct Oxidative C−H Amidation

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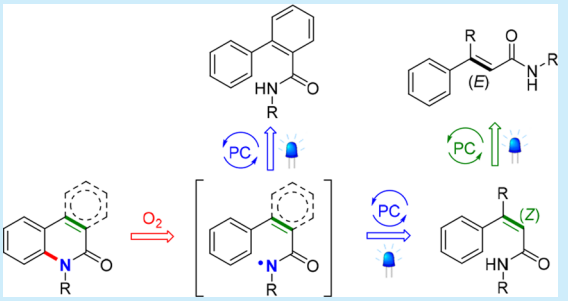
Supporting Information

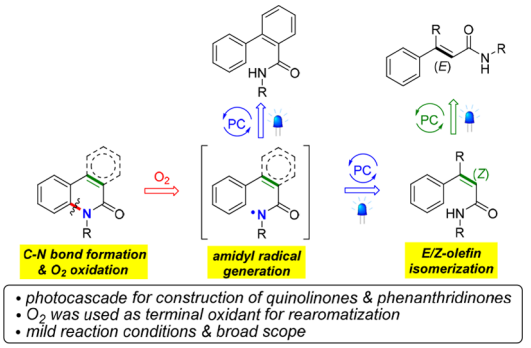
ABSTRACT: A straightforward synthetic strategy to construct biologically relevant phenanthridinones and quinolinones was developed via visible-light-promoted direct oxidative C−H amidation. In this photocatalytic system, amidyl radicals can be generated by homolysis of the N−H bond of simple amide precursors via single-electron transfer under blue LED illumination, which leads to oxidative intramolecular C−H amidation. Moreover, an efficient synthetic strategy using a photocascade enabled facile assembly of quinolinone structures through a catalytic sequence involving triplet energy (E_T) transfer-based E/Z olefin isomerization and subsequent photocatalytic generation of amidyl radical intermediates.



Quinolinone and phenanthridinone motifs are important structural constituents of numerous naturally occurring compounds[1] and privileged scaffolds in medicinal chemistry that display a variety of valuable optical properties and biological activities.[2] Accordingly, a number of synthetic strategies have been investigated to construct these skeletons, most of which rely on intramolecular lactam ring formation as the key step. However, these classical approaches require installation of amino groups to the aryl rings of the precursors. To complement the existing methodology, a versatile and flexible retrosynthetic disconnection to construct quinolinone[3] and phenanthridinone[4] scaffolds under mild reaction conditions without requiring prefunctionalization is highly desirable; this inspired us to explore a visible-light photocatalyzed direct C−N bond formation route.

Recently, visible-light-induced[5] direct conversion of an N−H bond into the corresponding nitrogen-centered radical via homolytic bond activation by photocatalysis has proven to be a valuable approach for direct C−N bond formation without requiring prefunctionalization of the amide.[6−8] With this foundation, we envisioned that a novel synthetic route to construct phenanthridinone scaffolds could be developed using intramolecular C−N bond formation with amidyl radicals generated by visible-light-driven photocatalysis. Furthermore, we were intrigued by the possibility of a new retrosynthetic disconnection of the quinolinone moiety from merging a catalytic sequence involving a triplet energy (E_T) transfer-based E/Z olefin isomerization[9] and subsequent photocatalytic generation of an amidyl radical intermediate, which leads to oxidative intramolecular C−H amidation to furnish a new C−N bond (Scheme 1). Our system is based on the understanding that both the E/Z olefin isomerization and generation of an amidyl radical could proceed by the action of the a single photocatalyst,

Scheme 1. Design of a Visible-Light Photocatalyzed Synthesis of Phenanthridinones and Quinolinones



which would set the stage for intramolecular radical cyclization. To achieve these diverse reactions, the photocatalyst should meet two critical criteria. First, the photocatalyst needs to possess a higher triplet state energy (E_T) level than that of the excited state of the (E)-olefin substrate to enable the isomerization process, and ideally the E_T level would be lower than that of the (Z)-isomer.[9b] Second, the photocatalyst must have a high redox potential for homolytic activation of the strong N−H bonds[10] in simple amide precursors. In the latter process, an oxidative proton-coupled electron transfer (PCET) protocol[8] can be a powerful approach to efficiently activate the N−H bonds of amides. Herein, we report a visible-light photocatalyzed cascade strategy to construct valuable phenanthridinone and quinolinone scaffolds via a sequential (E/Z-isomerization)/amidyl radical

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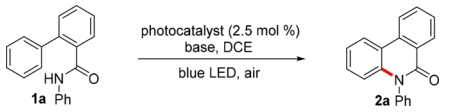
generation/C−N bond formation/O_2-mediated oxidation process.

To prove the viability of the proposed reactions, the feasibility of the photocatalytic C−H amidation of amide **1a** was investigated in a model system. The addition of a suitable acid or base could promote direct homolytic bond activations by activating chemical bonds or modulating redox potentials.[11] After extensive screening of potential catalytic systems, illuminating the reaction mixture with a blue LED in the presence of 2.5 mol % of Ir complex provided significant amounts of the corresponding phenanthridinone product **2a** under basic conditions, which confirmed that the overall process was operating effectively (Table 1). Various light sources were

Table 1. Optimization of the Reaction Conditions[a]



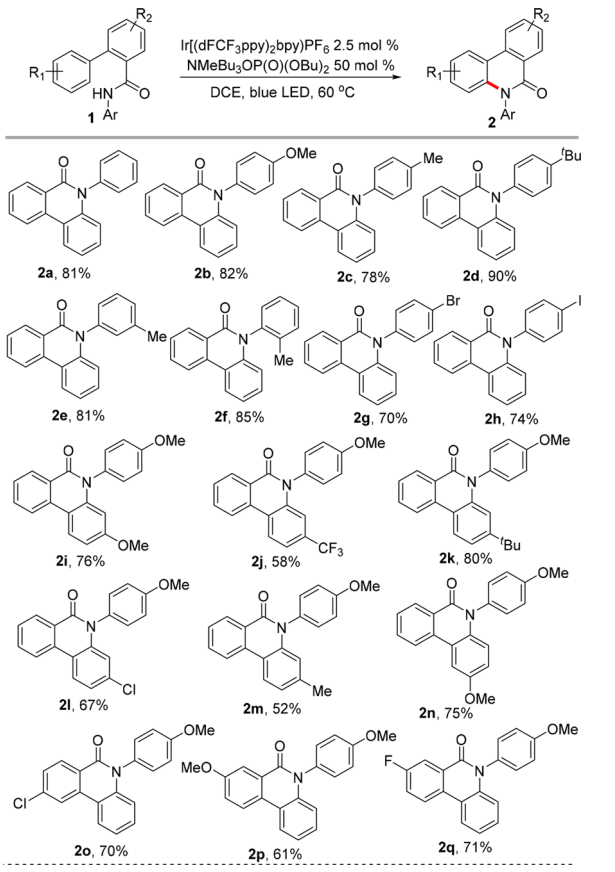
entry	photocat (2.5 mol %)	additive (0.5 equiv)	temp (°C)	yield[b] (%)
1	$Ru(bpy)_3(PF_6)_2$	$NMeBu_3OP(O)(OBu)_2$	25	
2	$Ir(ppy)_3$	$NMeBu_3OP(O)(OBu)_2$	25	
3	Eosin Y	$NMeBu_3OP(O)(OBu)_2$	25	
4	[Ir]	$NMeBu_3OP(O)(OBu)_2$	25	58
5	[Ir]	$NMeBu_3OP(O)(OBu)_2$	40	66
6	[Ir]	$NMeBu_3OP(O)(OBu)_2$	60	85
7	[Ir]	K_3PO_4	60	77
8	[Ir]	$NaHCO_3$	60	45
9	[Ir]		60	39
10	[Ir]	TFA	60	35
11		$NMeBu_3OP(O)(OBu)_2$	60	
12[c]	[Ir]	$NMeBu_3OP(O)(OBu)_2$	60	
13[d]	[Ir]	$NMeBu_3OP(O)(OBu)_2$	60	
14[e]	[Ir]	$NMeBu_3OP(O)(OBu)_2$	60	trace

[a]Reactions were performed using **1a** (0.1 mmol, 1.0 equiv), photocatalyst (2.5 mol %), base (0.5 equiv), and 1,2-dichloroethane (3.0 mL) upon irradiation with blue LEDs for 20 h under air balloon. [b]Yield was determined by 1H NMR. [c]N_2 purged. [d]The reaction was conducted in the dark. [e]TEMPO (1 equiv) was used as additive. [Ir]: $[Ir(dFCF_3ppy)_2bpy]PF_6$. DCE = 1,2-dichloroethane.

screened, and the use of a blue LED resulted in an improved yield. Among the solvents screened for this reaction, 1,2-DCE was most efficient, and the desired product was obtained in 85% yield at 60 °C (entry 5). Control experiments confirmed that the visible light and the photocatalyst were required for the amidation process (entries 11 and 13) and molecular oxygen can be used as the terminal oxidant (entry 12). Complete suppression of the reaction in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (entry 14) supports a radical mechanism being operative. Intriguingly, the reactions run in the absence of a base resulted in significant conversion of the amide starting material (39%, entry 9). Moreover, in the presence of TFA, the product was obtained in 35% yield (entry 10). To gain mechanistic insight, we designed a series of competitive luminescence quenching experiments, and solutions containing **1a** and a constant amount of tetrabutyl ammonium dibutyl phosphate resulted in a large decrease in the emission intensity in concentration-dependent luminescence quenching (see the Supporting Information for details). Remarkably, we observed that *N*-phenylbenzamide **1a** in the absence of an external base could affect the emission intensity of the excited state iridium photocatalyst at 60 °C, albeit with a much lower efficiency. We next investigated the possible role of the in situ generated hydroperoxy anion (see the SI and Figure 1 for details), but no additional quenching was observed in experiments containing the hydroperoxy anion. These Stern−Volmer studies suggest that the excited-state iridium complex is capable of directly activating the N−H bond of the *N*-phenylbenzamide moiety, and it is at least partly responsible for the generation of the nitrogen radical in the reactions.

As illustrated in Scheme 2, the optimal conditions were then applied to a wide range of substrates to demonstrate the utility

Scheme 2. Substrate Scope of Photocatalytic Synthetic Route to Phenanthridinone[a]



[a]Reactions were performed using **1** (0.1 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2bpy]PF_6$ (2.5 mol %), $NMeBu_3OP(O)(OBu)_2$ (0.5 equiv) and 1,2-dichloroethane (3.0 mL) upon irradiation with blue LEDs for 20−24 h at 60 °C under air balloon. Yields of isolated product.

and generality of this method. With this catalytic method, phenanthridinone derivatives bearing a wide variety of substituents could easily be synthesized in good yields. Notably, halides such as fluoro, chloro, bromo, and iodo substituents were tolerated under the reaction conditions. The corresponding desired products were provided, which enable further functionalization at these positions (**2g**, **2h**, **2o**, and **2q**). Considering the facile deprotection of *p*-methoxyphenyl (PMP) group under mild conditions, we subsequently assessed the applicability of our method with respect to substrates bearing PMP groups on the amide nitrogen, which worked well in the optimized system and provided the desired products. Substrates containing methoxy, *tert*-butyl, chloro, or trifluoromethyl substituents at the *para*

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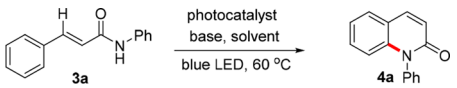
position (**2i**-**2m**) were well tolerated and provided the corresponding products under the standard conditions. Use of *meta*-substituted substrate resulted in C−N bond formation, exclusively at the more sterically accessible C−H bond of the aryl ring to afford only one regioisomer of **2n**.

Recently, photoisomerization of (*E*)-olefins was used to efficiently and selectively synthesize (*Z*)-olefins.[9] We envisaged that the (*Z*)-cinnamamide readily accessed in situ as a result of olefin isomerization could be further utilized for C−N bond formation in the same photocatalytic system. In line with our hypothesis, we began our studies by investigating triplet energy (E_T) transfer-based isomerization. Both geometric isomers (*E*)- and (*Z*)-*N*-phenylcinnamamides were independently subjected to the above Ir photocatalytic conditions in the absence of base. Importantly, we observed that the $E \rightarrow Z$ isomerization of both amides proceeded efficiently under blue LED irradiation, and analysis of the crude mixtures revealed *Z*/*E* ratios of 74:26 (Figure S6 in the SI).

Encouraged by the (*Z*)-selectivity of the isomerization, we next turned our attention to the proposed cascade process for the construction of valuable quinolinone derivatives. After extensive screening, we were delighted to observe that the photocascade involving sequential *E*/*Z*-isomerization, amidyl radical generation, C−N bond formation, and O_2-mediated oxidation proceeded well, thus allowing the synthesis of quinolinone **4a** under optimized conditions (70%) in Table 2. Notably, unlike

Table 2. Optimization of the Reaction Conditions[a]



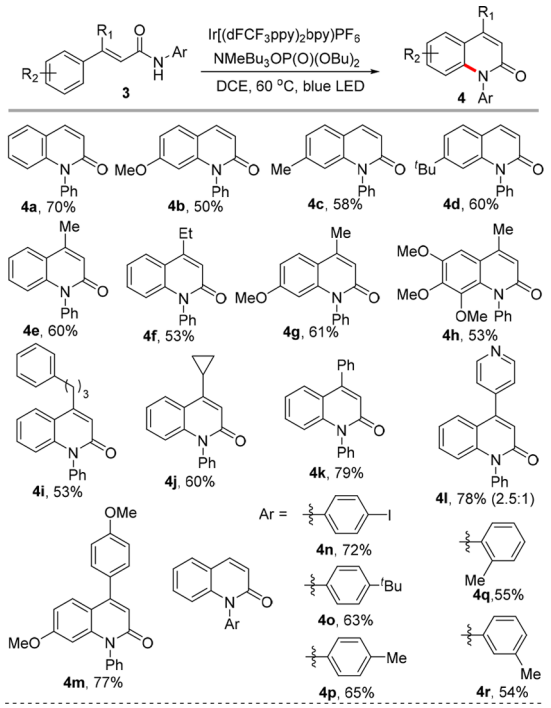
entry	photocat (2.5 mol %)	base (0.5 equiv)	solvent	yield[b] (%)
1	[Ir]		DCE	trace
2	[Ir]	$NMeBu_3OP(O)(OBu)_2$	DCE	70
3	[Ir]	K_3PO_4	DCE	13
4	[Ir]	$NaHCO_3$	DCE	5
5	[Ir]	K_2CO_3	DCE	6
6	[Ir]	$NMeBu_3OP(O)(OBu)_2$	CH_3CN	34
7	[Ir]	$NMeBu_3OP(O)(OBu)_2$	PhCl	37
8	$Ir(dFCF_3ppy)(dtbbpy)PF_6$	$NMeBu_3OP(O)(OBu)_2$	DCE	35
9	$Ru(bpy)_3(PF_6)_2$	$NMeBu_3OP(O)(OBu)_2$	DCE	
10[c]	[Ir]	$NMeBu_3OP(O)(OBu)_2$	DCE	
11		$NMeBu_3OP(O)(OBu)_2$	DCE	

[a]Reactions were carried out using **3a** (0.1 mmol, 1.0 equiv), photocatalyst (2.5 mol %), base (0.5 equiv) and 1,2-dichloroethane (3.0 mL) upon irradiation with blue LEDs for 20 h at 60 °C under air balloon. [b]Yield was determined by ^1H NMR. [c]N_2 purged. [Ir]: $[Ir(dFCF_3ppy)_2bpy]PF_6$.

the reaction conditions for phenanthridinone formation, only a mixture of *E*/*Z*-olefin amide substrates remained and the desired product was not obtained in the absence of an external base (entry 1). This result indicates that a concerted PCET event involving the excited-state Ir photocatalyst and a phosphate base appears to be necessary at the beginning of the reaction to homolytically cleave the N−H bond of the amide substrate for amidyl radical formation.

After successfully achieving the visible light-induced transformation of *N*-phenylcinnamamide **3a** into quinolinone **4a**, we then conducted a series of experiments to investigate the scope of amide substrates. As shown in Scheme 3, we were delighted to

Scheme 3. Substrate Scope of Photocatalytic Synthetic Route to Quinolinone[a]



[a]Reactions were carried out using **3** (0.1 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2bpy]PF_6$ (2.5 mol %), and $NMeBu_3OP(O)(OBu)_2$ (0.5 equiv) in 1,2-dichloroethane (3.0 mL) upon irradiation with blue LEDs for 20−24 h at 60 °C under air balloon. Yields of isolated products.

observe that a variety of substrate patterns were well tolerated in this cascade process and were successfully converted into the corresponding products (**4b**−**d** and **4n**−**r**). Importantly, substrates bearing *β*-substituents from methyl (**4e**, **4g**, and **4h**), ethyl (**4f**), benzene propyl (**4i**), cyclopropyl (**4j**), aryl (**4k** and **4m**), and pyridyl (**4l**) groups reacted well to provide the desired products; this shows the considerable advantages in both simplicity and efficiency of this protocol.

A plausible mechanism for the current transformation is illustrated in Figure 1. Irradiation of Ir^{III} with blue LEDs will generate an excited-state $*Ir^{III}$ species which can play a dual role in the reaction; catalyzing E_T transfer for *E*/*Z* olefin isomerization and serving as a photooxidant to facilitate the direct homolytic bond activations of the N−H bonds of the amides.

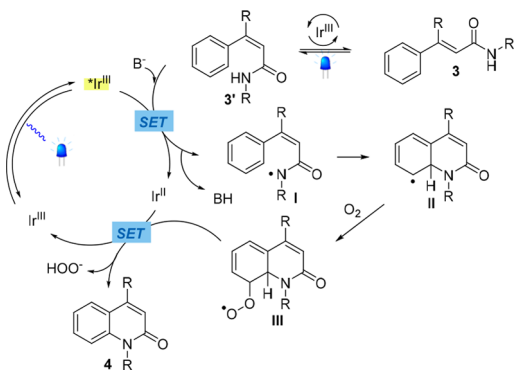


Figure 1. Proposed mechanistic pathway.

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Thus, the (*Z*)-olefin amide **3′** generated in situ from *E*/*Z* isomerization would undergo an additional oxidative C−H amidation event in the second catalytic cycle. The excited-state $*Ir^{III}$ complex would promote homolytic N−H bond activation of (*Z*)-olefin amide **3′** to yield the corresponding *N*-centered radical **I** via a PCET event.[8] The resultant amidyl radical intermediate **I** then engages intramolecular C−N bond formation to give radical **II**. This radical would in turn undergo O_2 addition to form a peroxy radical species **III** that would accept an electron from the reduced Ir photocatalyst to regenerate the catalytically active Ir^{III} complex. Finally, the desired product **4** would be generated after elimination of the hydroperoxy anion. In the process, alternative oxidation pathway could be operative via direct oxidation of radical **II** by O_2, followed by deprotonation to afford the desired product **4**.

In summary, we developed visible-light-induced intramolecular C−N bond formation with amidyl radicals for the direct construction of phenanthridinone motifs using a blue LED as the light source and molecular oxygen as the terminal oxidant. Furthermore, two different photocatalytic events could be successfully linked to enable rapid assembly of quinolinone structures through a sequential E_T transfer-based *E*/*Z* olefin isomerization and subsequent photocatalytic generation of an amidyl radical intermediate. This convenient and versatile photocascade represents a novel synthetic approach for accessing phenanthridinone and quinolinone derivatives, which are prominent structures in synthetic and medicinal chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03600.

Experimental procedure and characterization of new compounds (^1H and ^{13}C NMR spectra) (PDF)

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Notes

The authors declare no competing financial interest.

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