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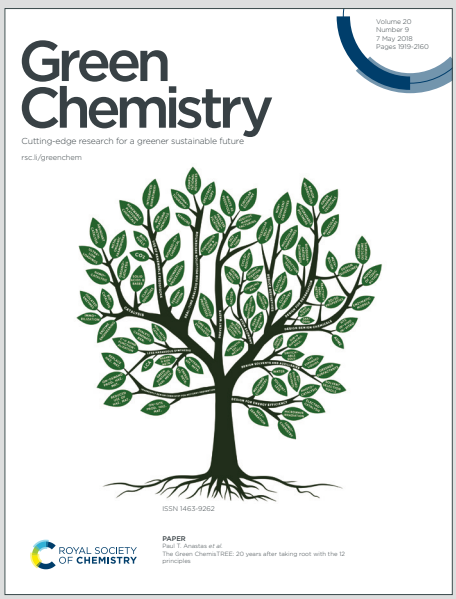

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Metal-free, visible-light-promoted oxidative radical cyclization of N-biarylglycine esters: one-pot construction of phenanthridine-6-carboxylates in water

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Abstract

A metal-free, visible-light (blue LED: hν = 425±15 nm) photoredox-catalyzed intramolecular cyclization reaction of N-biarylglycine esters to phenanthridine-6-carboxylates in water under open air atmosphere at ambient condition has been developed. A plausible mechanism is proposed for the reaction. Using catalytic amount (5 mol%) of rose bengal and a blue LED, the N-biarylglycine esters have been transformed into radical intermediates, which then underwent intramolecular cyclization reaction followed by dehydrogenation in one-pot to give desired products in up to 93% yield. This convention is pertinent for the gram-scale synthesis, eco-friendly and atom economy as compared to reported methods for the synthesis of phenanthridines. Moreover, to the best of our knowledge, no instance has hitherto been accounted for on the visible-light photocatalyzed transformation of inexpensive and biocompatible *N*-biarylglycine esters to phenanthridines.

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Introduction

Phenanthridine[1] and its derivatives are important structural motifs that are widespread in many naturally occurring alkaloids, pharmaceuticals, agrochemicals and fluorescence staining agents.[2] In pharmaceuticals, phenanthridines are integral to a large number of synthetic drug substances that exhibit antitumor, antiviral, antifungal, antibacterial, antiseptic, cytotoxic and DNA intercalation properties.[3] Besides, the phenanthridines are also used in functional materials as hole and electron transporting materials.[4] Several synthetic strategies have been accounted for their preparations.[1-4,5] Among, in the course of the most recent decade, the profoundly used methodology is the visible-light-induced photoredox catalysis including i) a tandem radical addition-cyclization reaction of 2-isocyanobiphenyls[6] and 2-(1-azidovinyl)-1,1'-biaryls[7] with diverse radical precursors (Scheme 1, a and b) and ii) the N-O bond homolysis cyclization reactions of oxime ethers[8] and oxime esters[9] (Scheme 1, c and d). Despite the energy efficient, mild and best usage, these strategies remain associated with specific hindrances, for example, selection of toxic and explosive reagents, solvents and metal catalysts. As a consequence, the development of a practical and environmentally benign synthetic protocol to get access to phenanthridine derivatives is profoundly attractive and proceeding with enthusiasm for the fields of organic, material and pharmaceutical chemistry.

N-biarylglycine esters[10] are biocompatible, can be stored for longer periods of time under ambient conditions, wide variety of derivatives are commercially available and were extensively applied for the synthesis of structurally diverse and biologically active functional amines.[10,11] However, to the best of our knowledge, no occasion has up to this point been accounted for on the visible-light photocatalyzed synthesis of phenanthridines using *N*-biarylglycine esters as a sole precursor.

In continuation of our studies on the visible-light-induced photoredox catalysis,[12] we demonstrate herein a novel, efficient and eco-friendly protocol for the preparations of phenanthridine-6-carboxylates from *N*-biarylglycine esters in the presence of 5 mol% of rose bengal as a photocatalyst, water as a solvent, molecular oxygen as an oxidant and blue LED (hν = 425±15 nm) as irradiation sources at ambient conditions, cf. Scheme 1. A plausible mechanism is proposed for the reaction. The N-biarylglycine esters have been transformed into radical intermediates, which at that point experienced intramolecular cyclization reaction followed by

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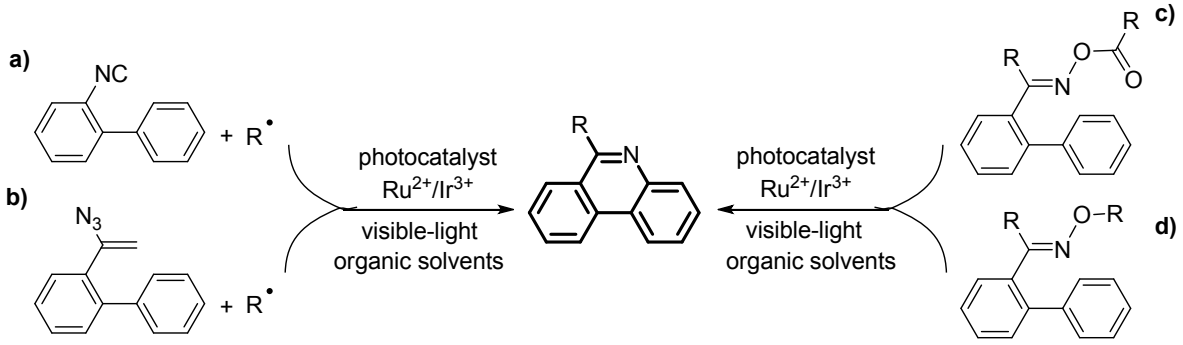
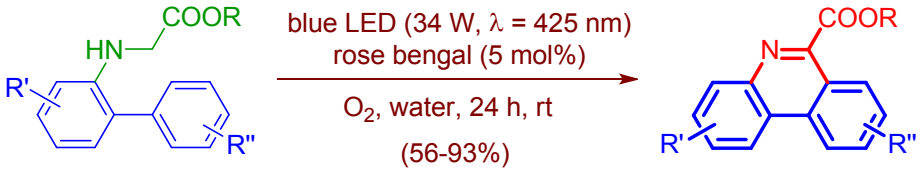
dehydrogenation in one-pot to give desired products in good to excellent yields. It is worth nothing that in addition to the use of organic photocatalyst, i.e., rose bengal, this convention exploits oxygen and water as clean, abundant, and sustainable chemical reagents/solvents.



Scheme 1. Well-known and largely investigated methods for the synthesis of phenanthridines under visible-light photocatalysis.[6-9]



Scheme 2. A metal-free, visible-light photoredox-catalyzed intramolecular cyclization reaction of N-biarylglycine esters to phenanthridine-6-carboxylates in water at ambient condition reported in this work.

Results and Discussion

An environmentally friendly and commercially available methyl 2-([1,1'-biphenyl]-2-ylamino)acetate (**1a**) and $[Ru(bpy)_3]^{2+}$, respectively, were picked as model substrate and photocatalyst to optimize the reaction conditions. When acetonitrile solution containing **1a** and a catalytic amount of $[Ru(bpy)_3]^{2+}$ (3.0 mol%) was irradiated by blue LEDs (34 W, hν = 425±15 nm) in an open vessel under ambient conditions for 36 h, and the desired methyl phenanthridine-6-carboxylate (**2a**) was obtained in 47% yield, cf. Table 1 and Entry 1. The product **2a** was characterized by mass and NMR analysis, cf. Electronic Supporting Information (ESI). A few different photocatalysts including $Ir(ppy)_3$, rose bengal, methylene blue, fluorescein, eosin Y and rhodamine were then examined, and rose bengal was observed to be the best for this reaction (Table 1 and Entry 3). Thus, rose bengal was chosen as the photocatalyst for the reaction. Next,-

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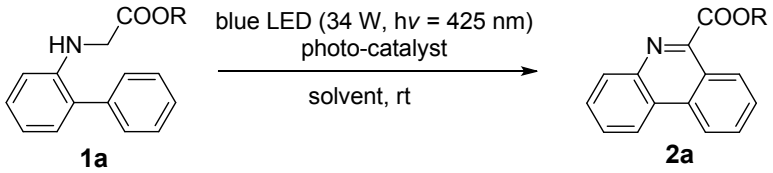
Table 1. Selected results of screening the optimal conditions for the photocatalytic synthesis of phenanthridine-6-carboxylates from N-biarylglycine esters[a]



Entry	Catalyst (mol%)[b]	Solvent[c]	Time (h)	Yield (%)
1	$[Ru(bpy)_3]^{2+}$ (3)	CH_3CN	36	47
2	$Ir(ppy)_3$ (3)	CH_3CN	36	22
3	rose bengal (3)	CH_3CN	36	84
4	methylene blue (3)	CH_3CN	36	13
5	fluorescein (3)	CH_3CN	36	21
6	rhodamine (3)	CH_3CN	36	29
7	eosin Y (3)	CH_3CN	36	16
8	rose bengal (5)	CH_3CN	24	89
9	rose bengal (10)	CH_3CN	22	91
10	Nil	CH_3CN	36	NR[d]
11	rose bengal (5)	hexane	24	<10
12	rose bengal (5)	DMSO	24	43
13	rose bengal (5)	CH_3OH	24	33
14	rose bengal (5)	DMF	24	40
15	rose bengal (5)	water	24	93
16	rose bengal (5)	water-CH_3CN	24	95
17	rose bengal (5)	water	24	18[e]
18	rose bengal (5)	water	24	<5%[f]
19	rose bengal (5)	water	6	39
20	rose bengal (5)	water	12	68
21	rose bengal (5)	water	18	83
22	rose bengal (5)	water	21	89
23	rose bengal (5)	water	30	94

[a] Unless stated otherwise all reactions were performed in a vial equipped with 2-([1,1'-biphenyl]-2-ylamino)acetate (**1a**, 0.3 mmol) and 5.0 mol% of photocatalyst in solvent were irradiated using 34 W blue LEDs under an open air atmosphere at room temperature for 24-36 h. [b] Commercially available high purity catalyst were purchased and utilized as such. [c] Solvents were purified before use. [d] Standard conditions without catalyst. [e] Reaction performed under N_2 atmosphere. [f] Reaction was carried in dark. N.R. no reaction.

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the impact of amount of rose bengal on the product yield was likewise explored. An increase in the catalyst amount from 3.0 mol% to 5.0-10.0 mol%, the reaction time was clearly abbreviated with 89-91% yield of **2a** (Table 1 and Entries 8-9). In any case, no product was seen without a photocatalyst (Table 1 and Entry 10). Afterwards, the influence of solvents on the formation of **2a** was explored (Table 1 and Entries 11-16). The examination uncovered that acetonitrile, water and their combinations were the most effective medium to promote the reaction with 93-95% yield (Table 1 and Entries 15-16). Water was picked as a solvent for this transformation (Scheme 2). Later, we explored the influence of atmosphere on the reaction. Switching the reaction atmosphere from open air/O_2 (balloon) to N_2, inferior yields of **2a** were obtained (Table 1 and Entry 17). Finally, the control experiments proposed that photocatalyst, light, and oxygen were essential for this reaction to proceed (Table 1 and Entries 10, 17-18). Thus, the optimized conditions for the synthesis of phenanthridine-6-carboxylates from N-biarylglycine esters were 5.0 mol% of rose bengal, blue LED lights, water and molecular oxygen at ambient condition for about 24 h. Under the optimized reaction conditions, we also performed a model reaction at different time intervals (6 h, 12 h, 18 h, 21 h and 30 h) to check the reaction progress. As expected, product yield is directly proportional to the reaction time (Table 1 and Entries 19-21) until 24 h.

To explore the substrate scope of this methodology (Scheme 2), the optimized reaction conditions (Table 1) were applied to a series of *N*-biarylglycine esters. First, we studied the effect of the substituents in the aromatic ring with glycine ester group and the outcomes are summarized in Table 2. Notice that the reaction was slightly affected by the electronic effects of substituents in the aromatic ring with glycine ester group. The substrates bearing electron-donating groups (CH_3 and OCH_3) provided expected phenanthridine-6-carboxylates (**2b**, **2c**, **2d** and **2e**) in higher yields than those bearing electron-deficient groups (F, Cl, NO_2, and $COOCH_3$): probably due to the lower oxidation potentials of latter precursors.[13] Afterwards, the effects of substituents at the 4-position of the aromatic ring without the glycine ester group were examined. Obviously, both electron-rich and electron-deficient substrates underwent cyclization readily producing the desired products **2j-2p** in moderate to good yields (Table 2). Therefore, different ester groups (ethyl, n-propyl and C_6H_5) were explored, and corresponding products **2q**, **2r** and **2s** were obtained in good yield (Table 2). Interestingly, no desired products were detected for the

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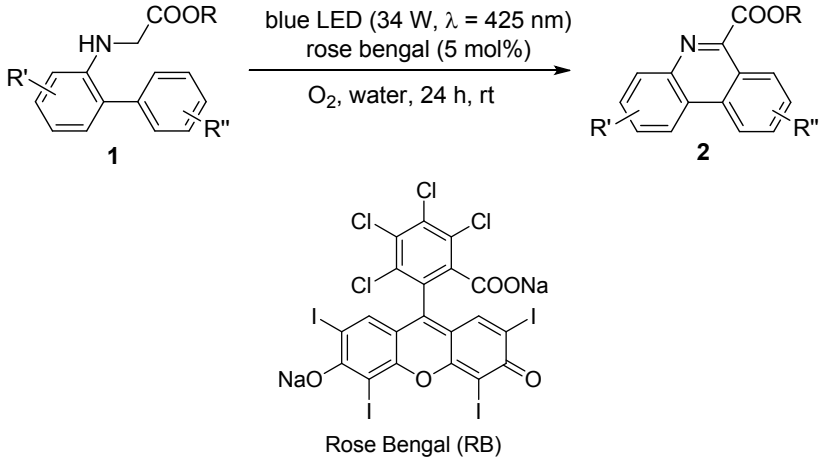
reactions with **1t** and **1u** as substrates, most likely due to poor stabilization of radical intermediates as well as over oxidation.[6,10] In this way, a wide range of electronically and structurally diverse *N*-biarylglycine esters can proficiently be transformed to phenanthridines with moderate to good yields, cf. Table 2. Notably, various functional groups such as methoxy, chloro, fluoro, trifluoromethyl, and nitro groups were tolerated well under the present experimental conditions, which will be suitable for potential further functionalization.[1-3]

Table 2. Substrate scope for the transformation of biarylglycine esters into phenanthridine-6-carboxylates[a]



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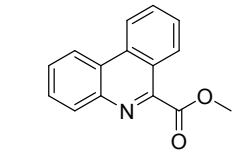
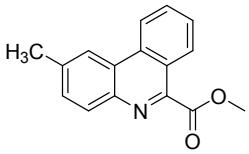
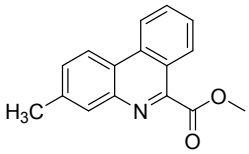
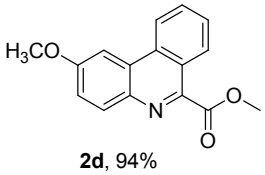
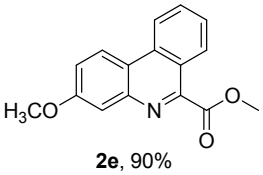
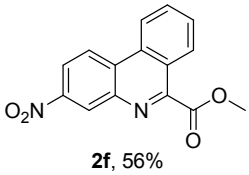

2a, 93%

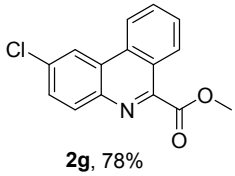

2b, 92%

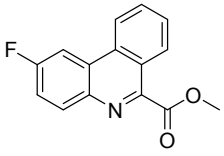

2c, 88%

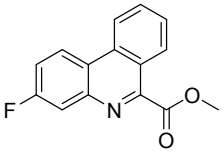

2d, 94%

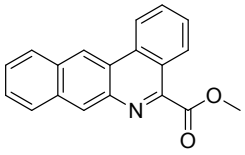

2e, 90%

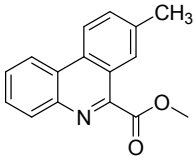

2f, 56%

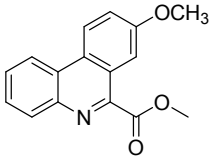

2g, 78%

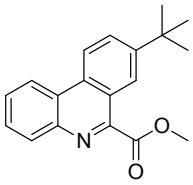

2h, 69%

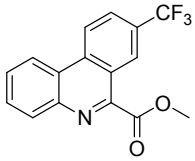

2i, 77%

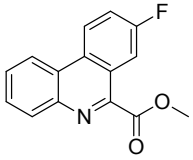

2j, 91%

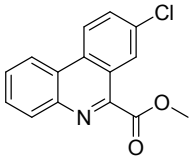

2k, 88%

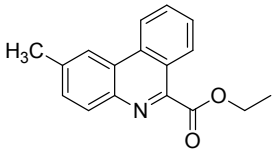

2l, 90%

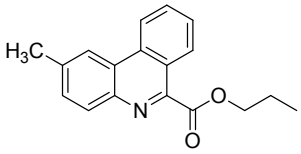

2m, 92%

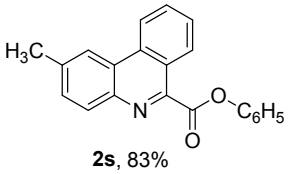

2n, 89%

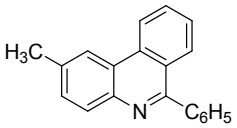

2o, 84%

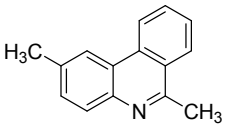

2p, 87%


2q, 92%


2r, 93%


2s, 83%


2t, < 5%


2u, trace

[a] Unless stated otherwise all reactions were performed in crimp vials equipped with **1** (0.3 mmol) and rose bengal (5.0 mol%) in water (3-5 mL) was irradiated using a 34 W blue LEDs under an open air/O_2 atmosphere at room temperature for 24 h.

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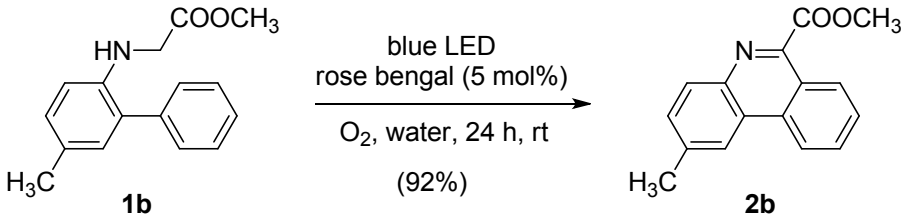
To further illustrate the preparative utility of this methodology, a scale-up synthesis of **2b** was conducted (Scheme 3). A gram-scale reaction of **1b** (10.0 mmol, Scheme 3) was done under the optimized reaction conditions (Table 1), and product **2b** was obtained in 92% isolated yield, which demonstrated the efficacy of this protocol.



Scheme 3. A scale-up synthesis of **2b** from **1b** using optimized reaction conditions.

Based on the control experiments and our experience with visible light photocatalysis,[12] a conceivable mechanism for the formation of phenanthridine-6-carboxylates from *N*-biarylglycine esters is proposed in Scheme 4. Upon irradiation by blue LEDs, rose bengal (RB) got excited, i.e., RB* [E_{red}(RB*/RB$^{\bullet-}$) = +0.99 V vs SCE].[14] RB* is single electron reduced by glycine ester **1a** [E_{ox}(1a/1a$^{\bullet+}$) = +0.86 V vs SCE][13] to form RB$^{\bullet-}$ and amine radical cation of **1a** (**1-I**, Scheme 4). Afterward, RB$^{\bullet-}$ is single electron oxidized by molecular oxygen and leading to the ground state RB and superoxide anion radical ($O_2^{\bullet-}$). A deprotonation reaction between **1-I** and $O_2^{\bullet-}$ was afforded biarylglycine ester radical **1-II** and hydroperoxyl radical HOO$^{\bullet}$. At that point, radical **1-II** experienced intramolecular C–H aromatic coupling to form a new radical intermediate 1-I**II**. Hydrogen radical transfer between 1-I**II** and HOO• gives methyl-5,6-dihydrophenanthridine-6-carboxylate (**1-IV**) and H_2O_2 (Scheme 4). A second photoredox catalytic cycle between excited-state rose bengal and **1-IV**, and subsequent loss of proton (H^+) and H• loss managed the desired product **2a**, cf. Scheme 4.

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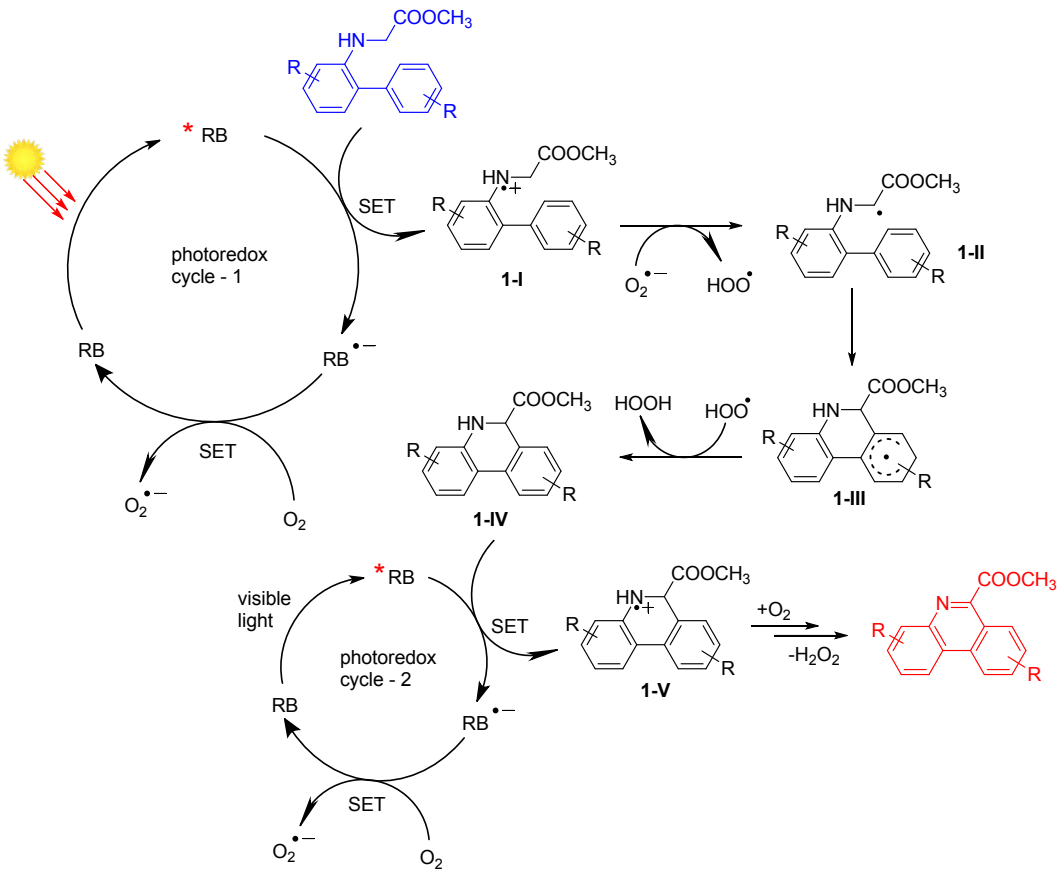
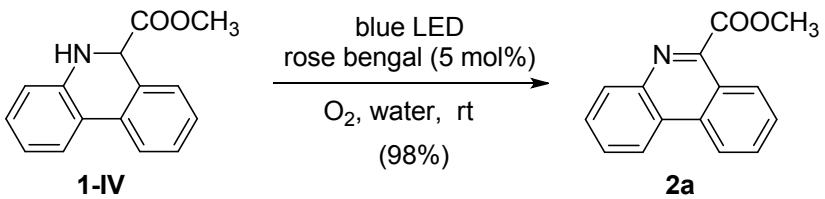


Scheme 4. A plausible mechanism for the formation of phenanthridine-6-carboxylates from *N*-biarylglycine esters under visible-light photocatalysis. SET, single electron transfer. RB, rose bengal.

A proposed reaction mechanism (Scheme 4) was confirmed by conducting an additional experiment as shown in Scheme 5. When methyl 5,6-dihydrophenanthridine-6-carboxylate (1-IV) was irradiated in the presence of rose bengal (5.0 mol%) under the optimized reaction conditions, as expected; a methyl phenanthridine-6-carboxylate (**2a**) was obtained in a quantitative yield, cf. Scheme 5.



Scheme 5. Conversion of a compound **1-IV** into **2a** under optimized reaction conditions at room temperature.

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As mentioned at the beginning, in recent time, synthesis of phenanthridines is to a great extent being led by either tandem radical addition-cyclization of 2-isocyanobiphenyls and 2-(1-azidovinyl)-1,1'-biaryls with diverse radical precursors or the N-O bond homolysis cyclization reactions of oxime ethers and oxime esters. Nevertheless, method reported here is based on the use of *N*-biarylglycine esters as a sole starting material. Moreover, this convention meets a considerable lot of the necessities of green chemistry as: i) the reaction utilizes O_2 from air as the oxidant and water as a solvent; ii) it is atom-economy and iii) organic dye is used as catalyst in the reaction. Thus, we trust that the present protocol may locate a bright future particularly in the pharmaceuticals industries where the necessity for final products to be totally free of traces metals and halogenated solvents.

Conclusion

In summary, we have built up a novel, an atom-economical and ecologically amiable method for the conversion of promptly accessible *N*-biarylglycine esters into the corresponding phenanthridine-6-carboxylates. The transformation proceeds in water employing rose bengal as an organic photoredox catalyst. The desired products are obtained in pure form by simple filtration. Further usage of the strategy to create other heterocyclic compounds is at present under investigation and will be revealed at the appropriate time.

Acknowledgments

The authors are pleased to acknowledge the financial support from the Department of Science & Technology (DST-SERB), New Delhi, India, through start-up research grant for young scientists, vide project no. SB/FT/CS-117/2013. Also, we are indebted to anonymous reviewers for their insightful comments and suggestions.

Supplementary data

Supplementary data (general aspects, experimental characterization data, references and copies of ^{1}H, ^{13}C and ^{19}F NMR spectra) associated with this article can be found, in the online version, at ..

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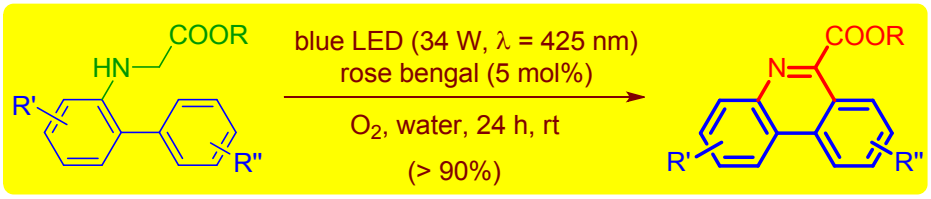

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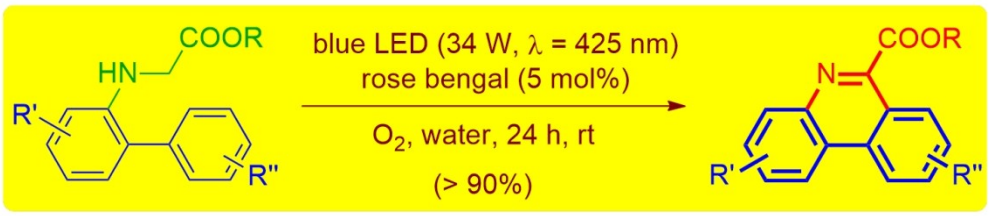

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