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Oxidative organophotoredox catalysis: a regioselective synthesis of 2-nitro substituted imidazopyridines and 3-substituted indoles, initiated by visible light†

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We have established a mild, metal-free, one pot, visible light-catalyzed procedure for a highly regioselective synthesis of 2-nitro-3-arylimidazo [1,2-*a*] pyridines *via* nitroalkene and 2-aminopyridine under an open atmosphere involving a photoredox catalyst, Eosin Y, which is an inexpensive organic dye that has been employed as a photo sensitizer in the conversion. This protocol serves as an example of green chemistry, due to the fact that molecular oxygen and visible light have been utilized effectively for the transformation. The procedure involves intramolecular C–N heterocyclization, followed by aerobic oxidation and C–C bond formation at room temperature. This green protocol has also been successfully extended to the regioselective synthesis of 3-substituted indoles *via* indole and nitroalkene by a free radical pathway.

Introduction

A desperate demand for highly eco-efficient and feasible synthetic protocols can be regarded as the impetus for several novel discoveries, since it provokes innovative reimagining of published approaches, which can in turn lead to the genesis of new chemistry.[1] Currently, visible light photoredox catalysts (VLPC) have emerged as new aids for heterocyclic synthesis[2] due to the fact that visible light is an eco-friendly and unending resource that is easy to handle and its use promotes an elevation of green standards for chemical transformations.[3] The research company of Stephenson *et al.*, MacMillan *et al.* and Yoon *et al.* described the use of photo catalysts in effectively promoting chemical transformations *via* reductive or oxidative quenching.[4] The visible light photoredox catalyst is particularly attractive because it can activate atmospheric oxygen, a green and natural oxidizing agent.[5] In contrast, transition metal catalysts suffer from many drawbacks, like adverse inherent malignancy, high cost and low durability.[6] On the other hand, some organic dyes are eco-efficient, easily handled and find vast applications in visible light-catalyzed reactions.[7]

Nitroalkenes are key intermediates in the synthesis of various products, for example pharmacologically active compounds,[8] fungicides[9] and insecticides.[10] This wide utility is due to the electron-deficiency of nitroalkenes and the easy conversion of the nitro part into different functional groups.[11] Our interest in the synthesis of nitroalkenes was drawn by their important role in medicinal chemistry and synthetic chemistry.[12] We have put our best efforts to propose two highly regioselective synthetic routes; one leading to the formation of 2-nitroimidazopyridines *via* nitroalkenes and 2-aminopyridine and the other producing 3-substituted indoles *via* indoles and nitroalkenes. Several bioactive compounds, natural products and biomolecules having fused heterocycles form an important key structural unit in agrochemical and pharmaceutical molecules.[13] Among them, imidazopyridine, an elite class of nonbenzodiazepine,[14] is one of the crucial nuclei having broad applications in material science and bioscience.[15] Both 2-arylimidazopyridine and 3-arylimidazopyridine moieties exhibit activities like being antimicrobial, antiviral, fungicidal, *etc.*[16] In particular, 3-arylimidazopyridines exhibit many biological activities, some of which are given in Fig. 1.[17] Nitroalkenes, being highly electron deficient, act as strong Michael acceptors in addition reactions with nucleophiles.[18] For example, derivatives of 3-substituted indoles, which serve as valuable ingredients for the construction of bioactive compounds, can be synthesized by the conjugate addition of indoles (good Michael donors) to nitroalkenes (good Michael acceptors). Several bioactive natural products, agrochemicals and drugs can be synthesized *via* the alkylated indoles.[19] For example, Panobinostat[20a]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6nj02365g

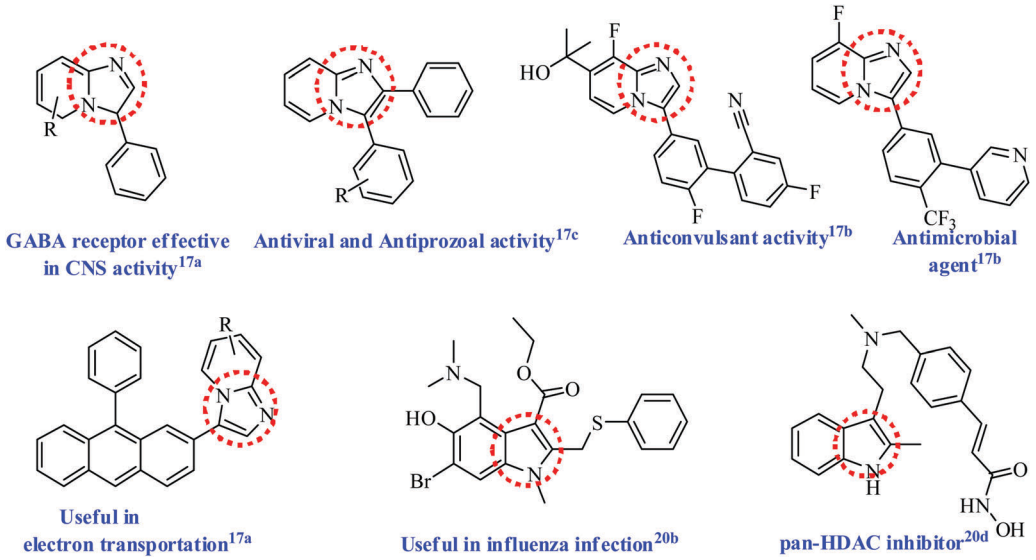
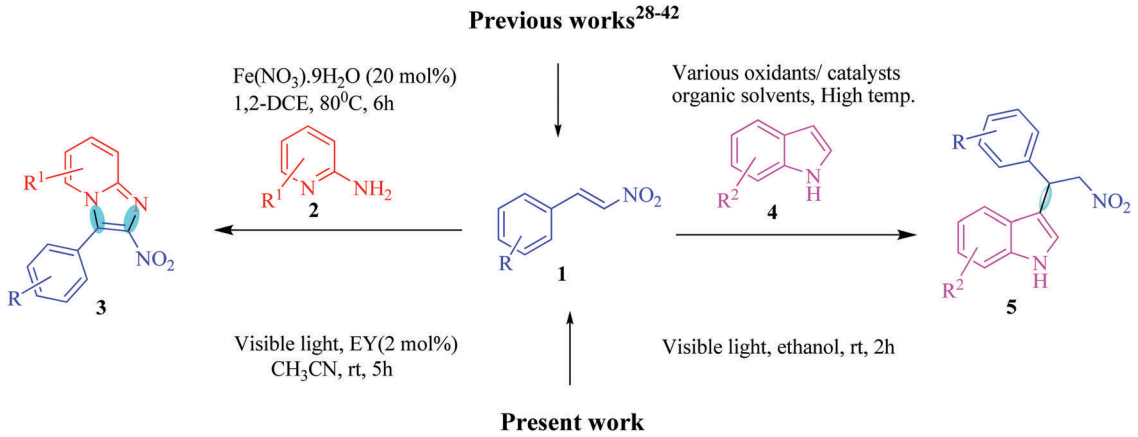
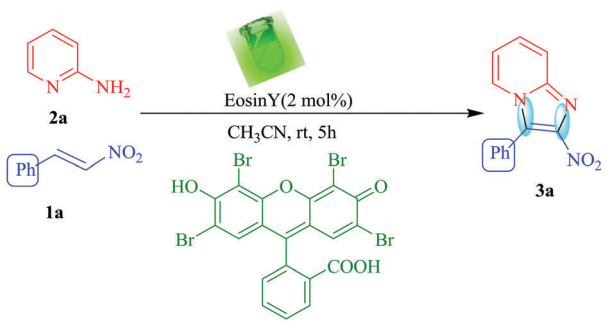


Fig. 1 Some biologically active heterocycles containing 3-aryl substituted imidazopyridines and 3-substituted indoles.



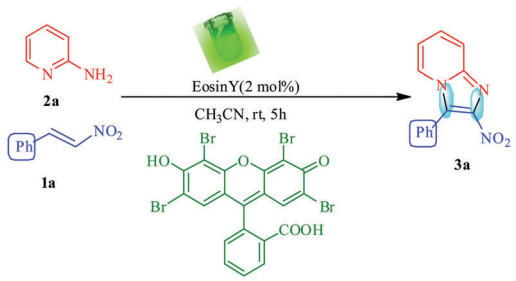
Scheme 1 Visible light catalyzed synthesis of 3-aryl substituted imidazopyridine and 3-substituted indoles.

(LBH-589), a hydroxamic acid,[20b] is useful in a large number of anti-cancerous drugs and Umifenovir (Arbidol)[20c] is used in antiviral drugs (Fig. 1).[20] There is a variety of synthetic protocols reported for the construction of both 3-aryl substituted imidazopyridines and 3-substituted indoles. While some routes mentioned in literature for the synthesis of 3-substituted imidazopyridines are catalysed by transition metals, there are others that are transition metal free methods. For instance, palladium-catalyzed direct arylation,[21] reaction between aryl chloride and imidazoles catalyzed by palladium complexes, both with phosphines/NHC[22] and without phosphines,[23] from alkynyliodonium salts,[24] oxime esters with pyridine,[25] catalytic C–H arylation using magnetically recyclable Pd–Fe_3O_4 with aryl bromide,[26] regioselective arylation with aryl tosylates and mesylates in the presence of palladium-phosphine complexes[27] and Fridael Craft alkylation *via* nitrostyrene and 2-aminopyridine catalysed by $Fe(NO_3)_3{\cdot}9H_2O$.[28] Similarly, several synthetic methods have been reported for 3-substituted indoles involving boric acid,[29] metal halide hydrates,[30] *t*-butyl ammonium hydrogen sulfate,[31] graphite oxide,[32] ultrasound assisted methods,[33] Bronsted acid,[34] palladium(II) surfactant combined catalysts,[35] silanediol,[36] *N*-bromosuccinimide,[37] hydrogen bond donor catalyst Feist's acid,[38] Montmorillonite K10,[39] catalyst free,[40] solvent free methods,[41a] HY zeolite under solvent free condition[41b] and Baker yeast catalyzed methods.[42] Recently, various visible light-catalyzed reactions



Scheme 2 Visible light synthesis of 3-arylimidazopyridine.

Table 1 Screening and control experiments[a]

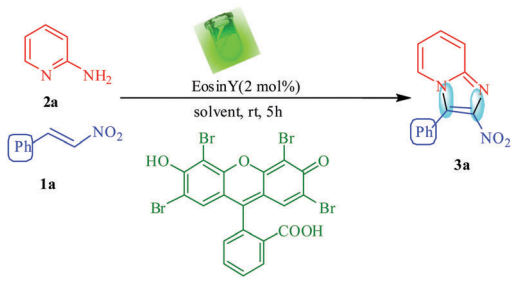


Entry	Visible light	Eosin Y	Air	Time (h)	Yield[b] (%)
1	+	+	+	5	78
2	+	–	+	8	Trace
3	–	+	+	10	Trace[c]
4	+	+	–	7	Trace
5	+	+	+	9	68[d]
6	+	+	+	8	56[e]
7	+	+	N_2	10	Trace
8	+	+	+	12	n.d.[f]

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), CH_3CN (5 ml), green LEDs (2.5 W, λ = 535 nm) irradiation under an open atmosphere at r.t. [b] Isolated yield of product. [c] Reaction performed in dark. [d] Reaction performed in daylight. [e] Reaction performed under compact florescent light. [f] Reaction was quenched with TEMPO (2.0 equiv.).

of indoles have been reported, like aerobic thiocyanation using nano photocatalyst,[43] C–H arylation *via* diazonium salt, α-arylation of α-amino carbonyl compounds[44] and C-3 formylation reactions.[45] There is a big concern regarding the reactions of nitrostyrenes and 2-aminopyridines about the selectivity in formation of 3-arylimidazopyridine and 2-arylimidazopyridine. Despite the fact that a huge number of methods[46] have been reported for the synthesis of 2-arylimidazopyridines, there are only a very few reported methods for the synthesis of 3-arylimidazopyridine scaffolds.

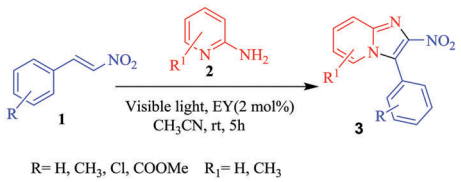
Table 2 Optimization of solvent and catalyst amount[a]



Entry[a]	Eosin Y (mol%)	Solvent	Time (h)	Yield[b] (%)
1	**2**	**CH_3CN**	**5.0**	**78**
2	2	THF	7.30	60
3	2	Toluene	7.30	31
4	2	DMF	6.30	39
5	2	DMSO	5.45	45
6	2	EtOAc	5.30	71
7	3	CH_3CN	5.0	78
8	1	CH_3CN	6.30	48

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), solvent (5 ml), green LEDs (2.5 W, λ = 535 nm) irradiation under an open atmosphere at r.t. [b] Isolated yield of product.

Table 3 Substrate scope[a]



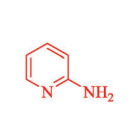
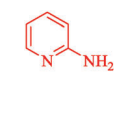
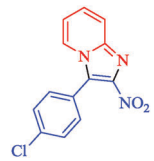
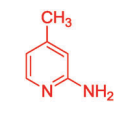
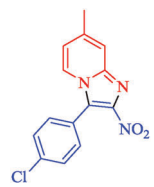
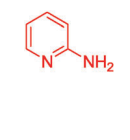
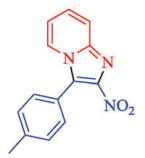
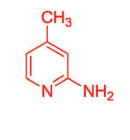
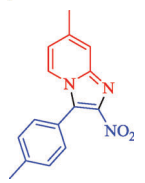
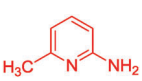
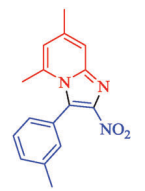
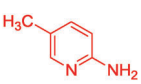
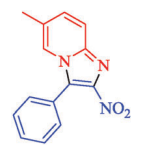
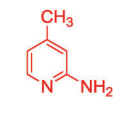
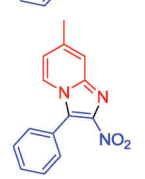
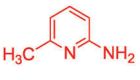
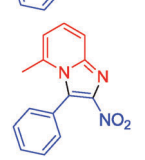
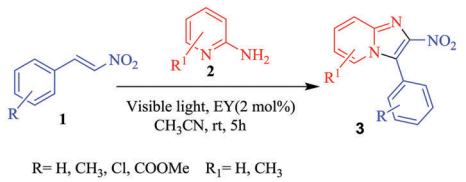
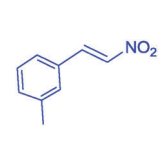
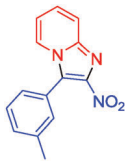
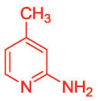
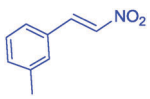
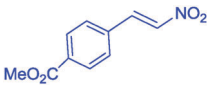
Entry	Nitroalkene (**1**)	2-Aminopyridine (**2**)	Product (**3**)	Yield[b] (%)
1				78
2				75
3				69
4				75
5				67
6				76
7				74
8				79
9				73

Table 3 (*continued*)



R= H, CH_3, Cl, COOMe R_1= H, CH_3

Entry	Nitroalkene (**1**)	2-Aminopyridine (**2**)	Product (**3**)	Yield[b] (%)
10				73
11				75
12				76

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), CH_3CN (5 ml), green LEDs (2.5 W, λ = 535 nm) irradiation under an open atmosphere at r.t. for 5 h. [b] Isolated yield of product.

Therefore, we have focused our efforts on development of a protocol that can control the selectivity of groups on imidazopyridine *via* reaction between 2-aminopyridine and nitroalkene. In continuation of our previous work[47] for the development of green, metal free, facile and safe protocols, herein, we have proposed a visible light-catalyzed synthesis of 2-nitroimidazopyridines. In addition, we have extended our protocol by the effective synthesis of 3-substituted indoles *via* nitroalkenes (Scheme 1).

Result and discussion

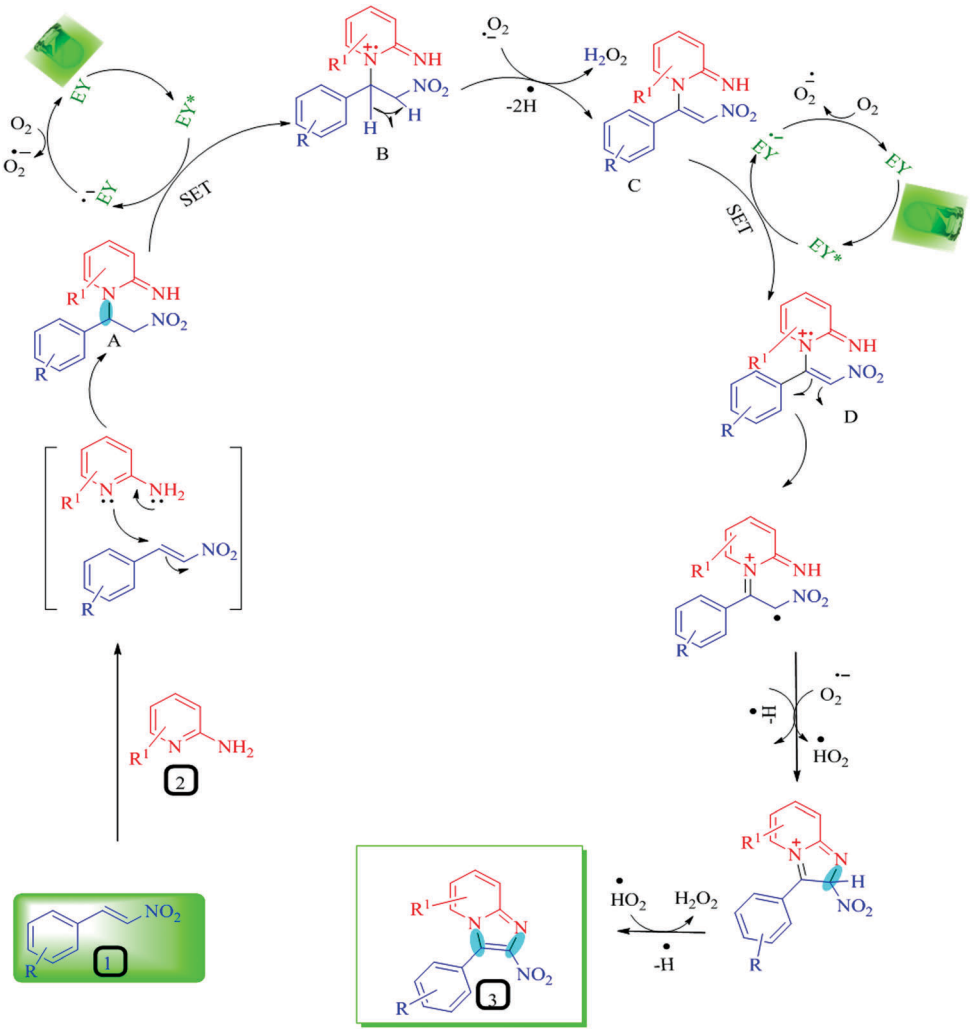
For our initial approach, nitrostyrene (**1a**) and 2-aminopyridine (**2a**) were taken as model substrates; they were irradiated together under green LEDs at room temperature in acetonitrile solution and in the presence of 2 mol% Eosin Y under open atmosphere. Interestingly, the reaction did not give the expected 2-arylimidazopyridine as the major product. Instead, 3-arylimidazopyridine **(3a)** was obtained in 78% yield (Scheme 2).

This remarkable regioselectivity mediated by visible light and Eosin Y inspired us to carry out a batch of control experiments to increase the yield of the 3-substituted product and decrease the overall reaction time. It was observed that in the absence of any one of the above mentioned reaction conditions, a very small amount of product was formed (Table 1, entries 2, 3 and 4). The use of either a compact fluorescent lamp or daylight in place of LEDs was found to be less effective (Table 1, entries 5 and 6). Green LED light was therefore essential to effective catalysis of the reaction by Eosin Y. Only a trace amount of product was obtained under nitrogen atmosphere, thereby indicating that the presence of oxygen is also essential for the reaction to be efficient (Table 1, entry 7). Continuous experimentation led to the conclusion that all of the initial reaction parameters, *i.e.*, visible light, photocatalyst and air, are necessary for successful synthesis of the desired product. It is also noteworthy that when 2.0 equiv. of TEMPO, a well known radical scavenger, was added under the ideal reaction conditions the desired product scaffold was not formed (Table 1, entry 8), clearly indicating that the reaction involved a radical mechanistic pathway.[48]

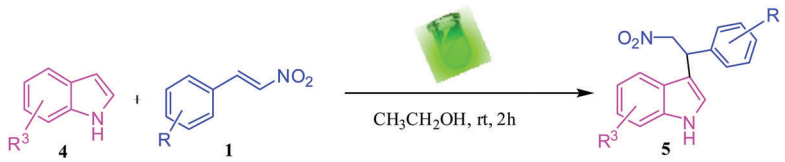
Our next endeavour was to optimize the solvent and the amount of catalyst. It was observed that acetonitrile was the best among the tested solvents, providing the maximum yield (Table 2, entry 1). The optimum loading of catalyst for the reaction was 2 mol% (Table 2, entry 7). On decreasing the catalyst loading from 2 mol% to 1 mol%, the yield was significantly decreased (Table 2, entry 8). However, an increase in catalyst loading did not result in an increase in yield.

Next, we established the scope and functional group affinity under the optimized reaction conditions. A broad range of substituted 2-aminopyridines and nitrostyrenes were studied to observe the electronic effects of the substrates. Nitrostyrenes having electron-donating and electron-withdrawing functional groups did not affect the course of reaction and the desired products were obtained in good yields. However, aliphatic nitrostyrenes did not result in the target molecule.[28] Furthermore, we observed that 2-aminopyridines with methyl substitution in different positions reacted smoothly with nitrostyrene and gave good yields. Thus, the substituent position of 2-aminopyridine had negligible effect on the chemical yield of the desired product (Table 3).

On the basis of our observation and literature survey[28,44,47] the plausible mechanism of the reaction is presented in Scheme 4. In the first step, the endocyclic nitrogen of 2-aminopyridine (**2**) undergoes Michael addition with nitrostyrene (**1**) to give Michael adduct **A**. Organophotoredox catalyst Eosin Y (EY) is excited to its singlet state (^{1}EY*) on absorption of visible light. The singlet state further converts into its more stable triplet state (^{3}EY*) *via* intersystem crossing and then undergoes single electron transfer (SET) forming radical cation (**B**). The *in situ* formation of superoxide radical anion $(O_2)^{\bullet-}$ and its combination with two hydrogens of **B** results in the formation of intermediate **C**, along with the removal of H_2O_2. Furthermore, another equivalent of Eosin Y undergoes SET and gives radical cation **D**. This radical cation **D** undergoes intramolecular cyclization, followed by oxidation, which leads to formation of the desired product **3** by removal of H_2O_2. Formation of hydrogen peroxide was confirmed using KI/starch indicator.[49] It was further proven experimentally that the reaction was not quenched in the presence of DABCO (2 mol%), which indicated that the triplet



Scheme 3 Plausible photocatalytic pathway for synthesis of 3-aryl substituted imidazopyridine.



Scheme 4 Photocatalytic approach for synthesis of 3-substituted indole.

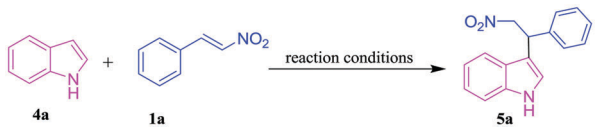
oxygen is utilized in the reaction mechanism.[50] Presence of triplet oxygen is a characteristic feature of a radical reaction (Scheme 3).

We further augmented the scope of our protocol by carrying out Friedel Craft alkylation of the nitroalkene derivatives with indole. We irradiated nitrostyrene (**1**, 1 mmol) and indole (**4**, 1 mmol) in ethanol with visible light, and a regioselective Michael type addition took place, resulting in 3-substituted indole **5** in excellent yield (Scheme 4).

We performed several experiments to ensure the best reaction conditions (Table 4). It was observed that ethanol was the best solvent for our protocol (Table 4, entry 5). We also observed that only a very trace amount of product was formed in the absence of light (Table 4, entries 9 and 10), which again indicates that light is essential for our protocol. A very trace amount of product was obtained in the presence of TEMPO, showing that the reaction undergoes radical pathways (Table 4, entry 11).

Inspired by these results, we explored the generality of our protocol with respect to various substituted derivatives of indoles and nitroalkenes (Table 5). Several products were obtained with substituents at the 3-position of the

Table 4 Optimization of reaction conditions[a]

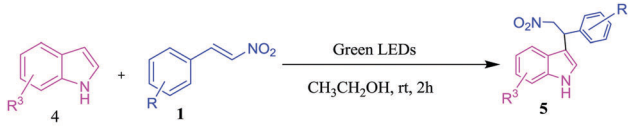


4a 1a 5a

Entry	Reaction conditions	Yield[b] (%)
1	DMF	Trace
2	DMSO	45
3	CH_3CN	60
4	THF	Trace
5	EtOH	75
6	MeOH	70
7	**LEDs, EtOH**	**85**
8	CFL, EtOH	80
9[c]	EtOH	Trace
10[d]	EtOH	72
11[e]	LEDs, EtOH	Trace

[a] Reaction conditions: **4a** (1.0 mmol), **1a** (1 mmol), solvent (5 ml), green LEDs (2.5 W, λ = 535 nm) irradiation under an open atmosphere at r.t. for 2 h. [b] Isolated yield of product. [c] Reaction performed in dark. [d] Reaction performed in daylight. [e] Reaction was quenched with TEMPO (2.0 equiv.).

Table 5 Substrate Scope[a]



4 1 5

R= R_3= H, CH_3, OCH_3, Cl

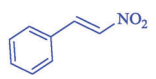
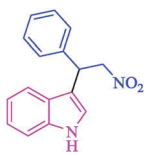
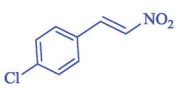
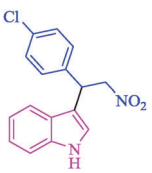
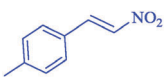
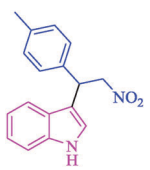
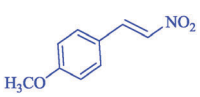
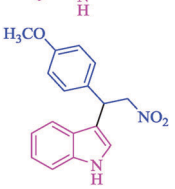
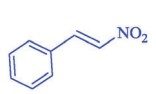
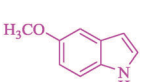
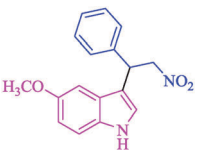
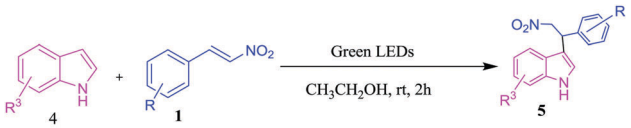
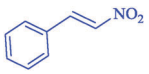
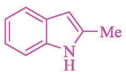
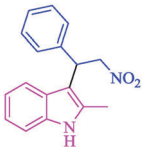
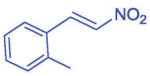
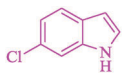
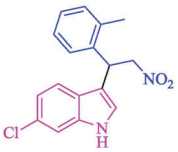
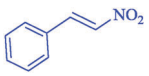
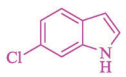
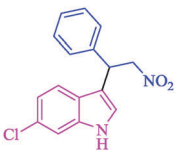
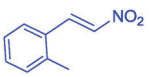
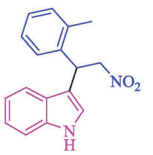
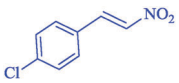
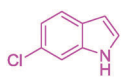
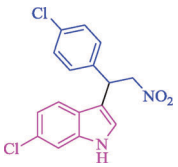
Entry	Nitroalkene (**1**)	Indole (**4**)	Product (**5**)	Yield[b] (%)
1				85
2				82
3				80
4				78
5				82

Table 5 (*continued*)



4 1 5

R= R_3= H, CH_3, OCH_3, Cl

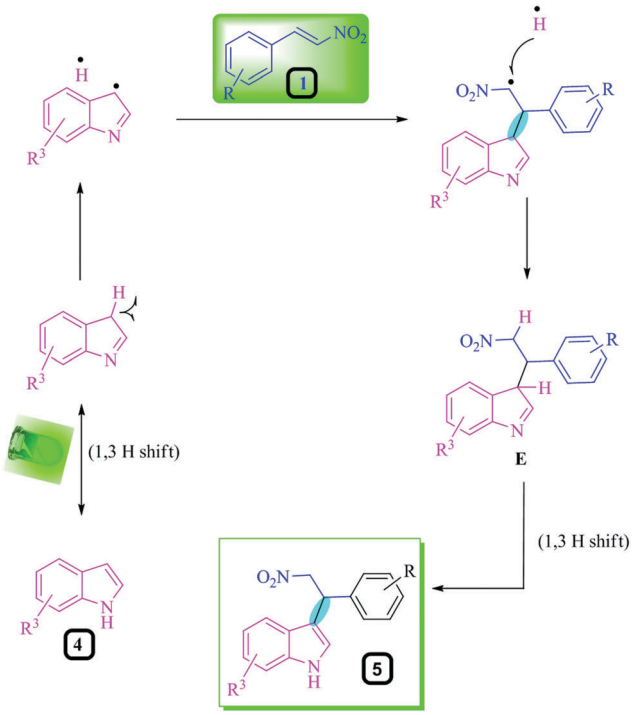
Entry	Nitroalkene (**1**)	Indole (**4**)	Product (**5**)	Yield[b] (%)
6				84
7				81
8				78
9				65
10				48

[a] Reaction conditions: **4** (1.0 mmol), **1** (1 mmol), ethanol (5 ml), green LEDs (2.5 W, λ = 535 nm) irradiation under an open atmosphere at r.t. for 2 h. [b] Isolated yield of product.

indole nucleus, showing that Michael addition took place regioselectively.

Further to our extended protocol, when indole (**4**) reacted with nitroalkene (**1**), it gave Michael type adduct (**E**) through a free radical pathway. This intermediate **E** undergoes a [1, 3] hydrogen shift and gives the desired product **5**. The (Scheme 5).

To conclude, we have developed an eco-friendly, efficient, metal free, visible light-catalyzed, aerobic, oxidative cyclization of 2-aminopyridine with nitroalkene, as well as a Friedel Craft alkylation of indole with nitroalkene for regioselective construction of the 2-nitroimidazopyridine nucleus. Eosin Y was used as a photoredox catalyst and atmospheric oxygen as an oxidant. This protocol tolerates a broad range of functional groups. The proposed method will undoubtedly prove to be a superior choice as compared to the previously reported methods due to its green reagents, feasibility and high efficiency.



Scheme 5 Plausible photocatalytic pathway for synthesis of 3-substituted indoles.

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