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Visible-Light Photoredox Catalyzed Oxidative/Reductive Cyclization Reaction of *N*-Cyanamide Alkenes for the Synthesis of Sulfonated Quinazolinones

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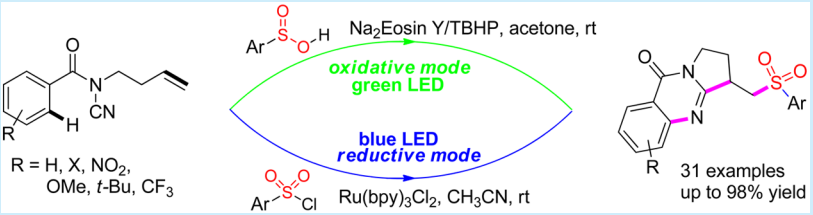
Supporting Information



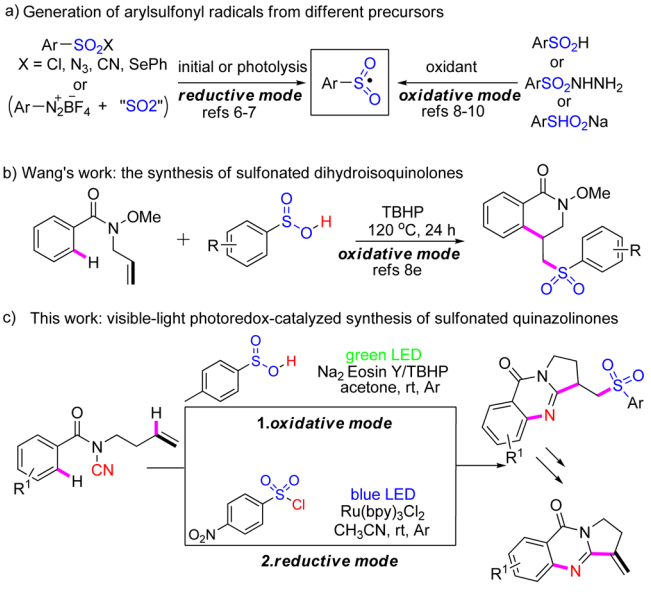
ABSTRACT: An efficient photocatalytic oxidative/reductive cyclization reaction of *N*-cyanamide alkenes with arylsulfinic acids or arylsulfonyl chlorides, which proceeds through C−S, C−C, and C−N bond formations, is reported. This photocatalytic reaction was carried out under mild conditions, which provides a new strategy for the synthesis of sulfonated quinazolinones. Furthermore, a one-pot procedure to achieve terminal alkenes has been explored via elimination of the obtained sulfonated quinazolinones under basic conditions.

Quinazolinone structural units widely exist in many natural products and have been found to process biological activities.[1] In particular, sulfonyl modified quinazolinone derivatives play a critical role in the performance of drugs, such as Idrolone, Hydromox,[1] and Sildenafil citrate.[2] Taking advantages of radical cascade cyclization and difunctionalization of alkenes, several types of privileged *N*-heteroaromatics[3] have been constructed. Thus, sulfonyl radical addition to alkenes[4] triggering a cascade cyclization process would be an efficient strategy to prepare such sulfonated *N*-heteroaromatics.

Arylsulfonyl radicals[5] can be generated from different precursors, which are usually divided into reductive mode and oxidative mode. In the presence of light, radical initiators or catalysts, sulfonyl radicals can be obtained from sulfonyl chloride, sulfonyl azides, sulfonyl cyanides, sulfonyl selenides and others via a reductive mode (Scheme 1a).[6,7] In this mode, the reaction always undergoes a previously established oxidative quenching cycle.[6f] On the other hand, sulfinic acids,[8] sulfinates[9] and sulfonyl hydrazides[10] can be oxidized and provide an alternative access to sulfonyl radicals (Scheme 1a), correspondingly, an reductive quenching cycle[6f] is included in these reactions. However, the preparation of sulfonated *N*-heteroaromatics by means of difunctionalization of unactivated alkenes via sulfonyl radical addition is still seldom used. Just recently, the Wang group reported a related work on the synthesis of dihydroisoquinolones from sulfinic acids via oxidative mode at high temperature (Scheme 1 b).[8e]

Thus, development of a mild and efficient method for construction of sulfonated *N*-heteroaromatics via difunctionalization of unactivated alkenes becomes very urgent. Notably, the Cui group developed a transition metal-catalyzed cyclization reaction of *N*-cyanamide alkenes for the synthesis of phosphor-

Scheme 1. Acquisition Modes of Sulfonyl Radicals and Difunctionalization of Alkenes To Afford Sulfonated *N*-Heteroaromatics



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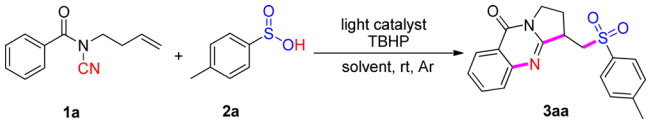
us[2c] and trifluoromethyl[2d] quinazolinone at high temperature. Herein, we report the first example of a visible-light photoredox catalyzed[11] approach to construct sulfonated quinazolinones by a radical cascade C−X (X = S, C, N) bond formation process at room temperature (Scheme 1c). Sulfonyl chlorides and sulfinic acids were used as arylsulfonyl sources for this reaction, which proceeded through a reductive transformation ($Ru(bpy)_3Cl_2$/blue light) and an oxidative transformation (Na_2-Eosin Y/TBHP/green light), respectively. Furthermore, the stepwise and one-pot elimination procedures of the corresponding sulfonated quinazolinones to achieve terminal alkenes by C−S bond cleavage have also been developed, which makes this new strategy more attractive and useful.

Initially, the reaction between *N*-(but-3-en-1-yl)-*N*-cyanobenzamide **1a** and 4-methylbenzenesulfinic acid **2a** was conducted in water at room temperature with the use of TBHP as oxidant in the presence of dye sensitizer photocatalysts[12] (entries 1−5, Table 1). The results indicated Na_2-Eosin Y was the best choice,

Table 1. Optimization of Reaction Conditions[a]



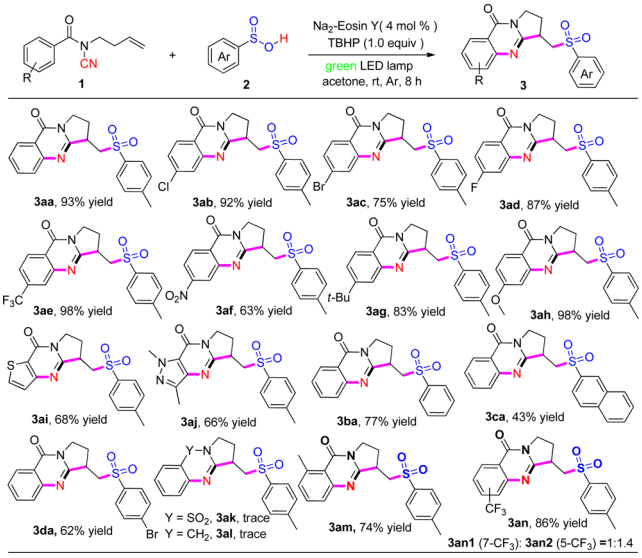
entry	catalyst	light	solvent (mL)	yield (%)[b]
1	rhodamine B	white LED	H_2O (0.5)	0
2	Eosin Y	white LED	H_2O (0.5)	0
3	fluororescein	white LED	H_2O (0.5)	0
4	rose bengal	white LED	H_2O (0.5)	0
5	Na_2-Eosin Y	white LED	H_2O (0.5)	67
6	Na_2-Eosin Y	white LED	H_2O (1.0)	73
7	Na_2-Eosin Y	white LED	H_2O (1.0)	47[c]
8	Na_2-Eosin Y	white LED	H_2O (1.0)	trace[d]
9[e]	Na_2-Eosin Y	white LED	H_2O (1.0)	64
10	Na_2-Eosin Y	blue LED	H_2O (1.0)	59
11	Na_2-Eosin Y	green LED	H_2O (1.0)	76
12	Na_2-Eosin Y	fluorescent	H_2O (1.0)	69
13[f]	Na_2-Eosin Y	none	H_2O (1.0)	0
14	Na_2-Eosin Y	green LED	DCE (1.0)	71
15	Na_2-Eosin Y	green LED	acetone (1.0)	93
16	Na_2-Eosin Y	green LED	CH_3CN (1.0)	91
17	Na_2-Eosin Y	green LED	EtOAc (1.0)	78
18	Na_2-Eosin Y	green LED	EtOH (1.0)	25

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), light catalyst (4 mol %), TBHP (0.2 mmol), solvent and stirring for 8 h under an argon atmosphere. [b]Isolated yield. [c]Air atmosphere. [d]Under O_2. [e]TBHP (0.3 mmol). [f]In the dark.

and afforded the corresponding sulfonated quinazolinone **3aa** in 67% yield (entry 5). This positive result encouraged us to carry out the further optimization of reaction conditions. Increasing the amount of H_2O led to a slightly higher yield of **3aa** (73% yield, entry 6). The reaction performed in air atmosphere also worked, however, with a less efficient outcome (47% yield, entry 7). No expected product was obtained when the reaction was conducted under O_2 atmosphere (entry 8). Increasing the amount of oxidant (TBHP) to 3 equiv resulted in no improvement at all (64% yield, entry 9). Subsequently, we investigated the effect of different light sources, including blue LEDs, green LEDs and fluorescent lamps (entries 10−12). Green LEDs might be considered as the best choice with a 76% yield of **3aa**. As expected, the reaction did not occur without the irradiation of light (entry 13). Finally, the media for this reaction was examined by changing water to organic solvents (entries 14−18). Acetone was the best solvent, and afforded the highest yield (93% yield, entry 15).

With the optimized conditions in hand, the substrate scope study for this reaction was performed by using various of *N*-cyanamide alkenes **1** and arylsulfinic acids **2** (Scheme 2).

Scheme 2. Substrate Study with Variation of *N*-Cyanamidealkenes 1 and Arylsulfinic Acids 2[a,b]



[a]Reaction condition: **1** (0.1 mmol), sulfinic acid **2** (0.2 mmol), Na_2-Eosin Y (4 mol %), TBHP (0.2 mmol), in acetone (1 mL) under argon atmosphere in the presence of 5 W green LED for 12 h. [b]Isolated yields.

Gratifyingly, both electron-withdrawing (**1b−1f**) and electron-donating (**1g−1h**, **1m**) aromatic substituents were well tolerated in the reaction with up to 98% yields (**3ae−3ah**, **3am**). In the case of a substrate with a strong electron-withdrawing substituent (nitro group), the reaction resulted in a moderate yield (**3af**, 63% yield). The heteroaryl-substituted alkenes (thienyl **1i** and pyrazolyl **1j**) were also suitable substrates and allowed the formation of product **3ai** (68% yield) and **3aj** (66% yield), respectively. Subsequently, we examined the feasibility of this sulfonylation reaction with respect to arylsulfinic acids **2**. Benzenesulfinic acid (**2b**), naphthalene-2-sulfinic acid (**2c**) and 4-bromobenzenesulfinic acid (**2d**) were applied to the reaction, which also worked, affording the targeted products **3ba−3da** in 43−77% yields. We tried the unactivated alkenes derived from benzenesulfonamide and benzylamine (**1k** and **1l**) as substrates for this reaction, but the desired products were not observed. Finally, a substrate with *m*-CF_3 substituted benzamide was used for this reaction, which gave two regioisomers in 86% yield with the ratio of 1:1.4.

Arylsulfinic acids can be prepared from arylsulfonyl chlorides in a conventional method,[13] so we considered that using arylsulfonyl chlorides as sulfonylation reagents for the sulfonylation reaction may be another new strategy (Scheme 3). Fortunately, we found that arylsulfonyl chlorides could be used as sulfonyl precursors in this cyclization system after many condition optimizations (for details, see Supporting Information). In this Ru^{II}/Ru^{III} catalytic process, up to 90% chemical yields were obtained at room temperature in the presence of blue

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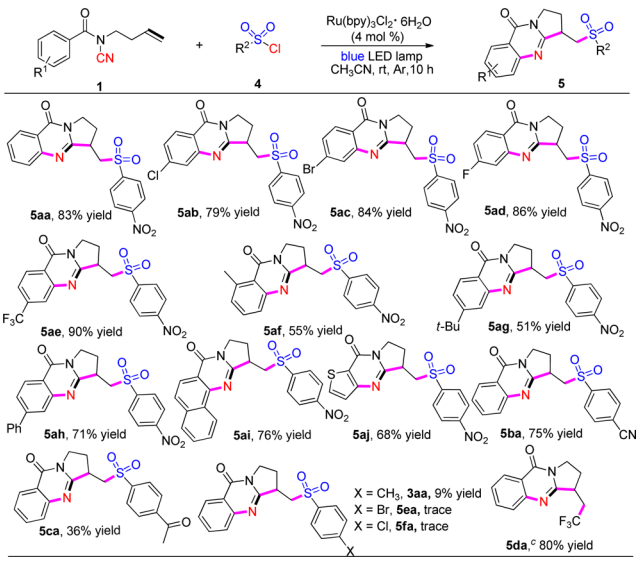
Scheme 3. Substrate Study with Variation of *N*-Cyanamidealkenes 1 and Sulfonyl Chlorides 4[a,b]

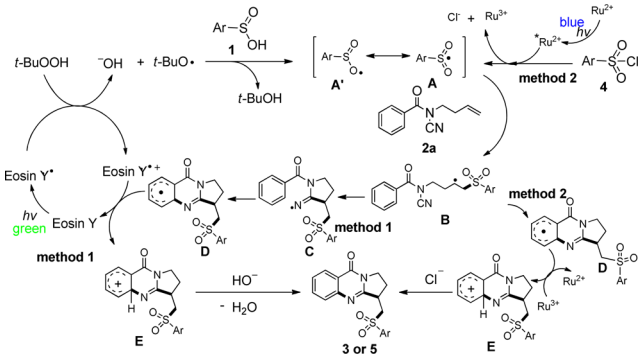


[a]Reaction condition: **1** (0.1 mmol), sulfonyl chloride **4** (0.15 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (4 mol %), in acetonitrile (1 mL) under argon atmosphere in the presence of 30 W blue LED for 10 h. [b]Isolated yields. [c]CF_3SO_2Cl (0.25 mmol).

LEDs. The substituents, including halo (**1b**, **1c** and **1d**), alkyl (**1e**, **1f** and **1g**) and phenyl (**1h**) groups, were well tolerated in this cascade cyclization reaction. Compared with *tert*-butyl (**1g**) and phenyl (**1h**) substituted *N*-cyanamidealkenes, the substrates bearing electron-withdrawing groups (**1b**−**1e**) afforded the corresponding products with higher yields (79−90%, **5ab**−**5ae**). To achieve more structurally interesting derivatives, naphthyl- and thienyl-substituted alkenes (**1i** and **1j**) were tried in the current system. Fortunately, they reacted smoothly with sulfonyl chlorides, giving the desired product in moderate yields (68−76%). In addition, the scope of sulfonyl chlorides was also examined. Arylsulfonyl chlorides with electron-withdrawing groups (cyano **4b** and acetyl **4c**) worked well, affording the corresponding products **5ba** and **5ca** in 75% and 36% yield, respectively. However, arylsulfonyl chlorides with methyl or halo groups provided none of the corresponding products (**3aa**, **5ea** and **5fa**). To further explore the potential of this methodology, trifluoromethanesulfonyl chloride[13] was used under the standard reaction conditions, and the desired product (**5da**) was isolated in good yield (80%).

On the basis of the above experiments and relevant reports,[2c,3l,4a,8e,14] a possible mechanism is proposed in Scheme 4. Initially, Eosin Y is irradiated by green LED light to generate the excited-state Eosin Y*. TBHP gets an electron from Eosin Y*, generating *tert*-butyloxy radical and OH^-. Then the hydrogen atom of arylsulfinic acid **1** is trapped by *tert*-butyloxy radical to produce a new oxygen-centered radical **A′**. The arylsulfonyl radical **A** and **A′** are resonance structures. Then the sulfonyl radical **A** adds to the C=C bond of alkene **2a**, affording the radical intermediate **B**. After reacting with the cyano group, **B** is transformed to the nitrogen-centered radical **C**. Subsequently, the key intermediate **D** forms by means of intramolecular cyclization. Then a cation radical Eosin Y^{*+} oxidizes the intermediate **D** to produce cationic intermediate **E** through a SET route as well as releasing the photocatalyst Eosin Y.[15] Finally, the expected product **3** forms after a deprontonation

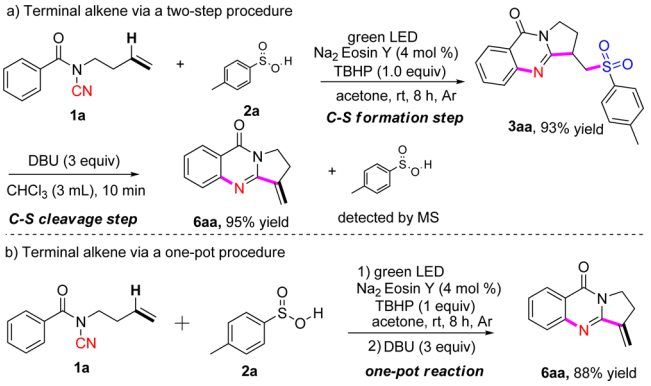
Scheme 4. Proposed Mechanism



process under the condition of base OH^-. Similar to method 1, method 2 undergoes a Ru^{II}/Ru^{III} catalytic cyclic under blue light, via a series of similar radical intermediate **B**, **C**, **D** and **E**. Finally, the intermediate **E** leads to the formation of target product **5** under the aid of Cl^-.

The synthetic value of this cascade reaction was further demonstrated by the following related elimination reaction of obtained sulfonated quinazolinones (Scheme 5). First, we

Scheme 5. Elimination of Sulfonated Quinazolinone



prepared terminal olefins in an excellent yield via a two-step reaction (Scheme 5a). In the second step, sulfonated quinazolinone **3aa** was subjected to DBU for 5 min, and the olefin **6aa** was obtained in 95% yield. Also, 4-methylbenzenesulfinic acid **2a** formed in the reaction, which is determined by LC−MS (see Supporting Information). Then, a one-pot procedure was tried to provide terminal olefins **6aa**, without isolation of the sulfonated quinazolinone **3aa** (Scheme 5b). We were pleased that an excellent chemical yield of **6aa** was obtained from this one-pot reaction. It should be mentioned that terminal olefins are very important synthetic building blocks, and their preparation is usually difficult by the previously reported methods.[16]

In summary, we have developed a novel, photocatalytic difunctionalization of unactivated alkenes for the preparation of sulfonated quinazolinones. This strategy features mild conditions, readily available sulfonylation reagents, and broad substrate suitability for accessing complex *N*-heterocycles. This reaction is the first example of the cyclization reaction on *N*-cyanamide alkenes under visible-light photoredox catalysis conditions. Furthermore, a one-pot procedure to achieve significant terminal alkenes starting with *N*-cyanamide alkenes

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has also been tried, which makes this photocatalytic system more attractive and useful.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02163.

Experimental procedures, full spectroscopic data for compounds **3**, **5** and **6aa**, copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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