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Ethylene Glycol: A Green Solvent for Visible Light-Promoted Aerobic Transition Metal-Free Cascade Sulfonation/Cyclization Reaction

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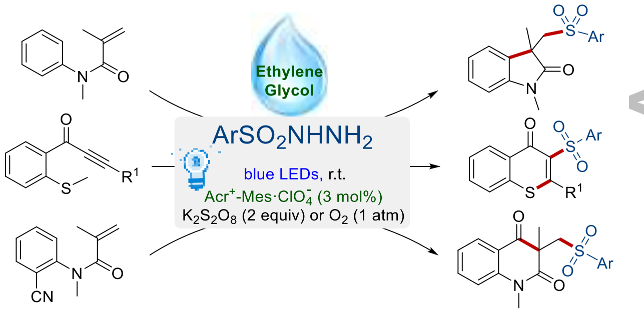
Abstract. With ethylene glycol as a green solvent, a general transition metal-free photocatalytic system using 9-mesityl-10-methylacridinium perchlorate (Acr^+–$Mes{\cdot}ClO_4^-$) as catalyst was developed for the synthesis of sulfone-containing heterocycles including thioflavones, oxindoles, and quinoline-2,4(1*H*,3*H*)-diones through the cascade sulfonation/cyclization reactions under the irradiation of blue light at room temperature.

Keywords: Photocatalysis; Green solvent; Sulfonation; Cyclization; Heterocycles

Visible light-promoted reactions have gained huge attention in the past decade, which are generally conducted under mild reaction conditions and provide high efficiency and selectivity.[1] Therefore, a large number of photocatalytic systems have been developed for the construction of valuable products.[2] In most of the reported photocatalytic systems, conventional volatile organic solvents are often applied as the reaction medium, which would produce large amount of wastes after the reactions.[3] From the standpoint of sustainable chemistry, the exploration of non-volatile and nontoxic green solvents for photocatalytic reactions is highly desirable.[4]

Sulfone-containing compounds play significant roles in the field of agrochemicals, pharmaceuticals and material science. Consequently, enormous efforts have been devoted to the construction of sulfone-containing scaffolds in the past decades.[5] Among the reported procedures, sulfonyl radical triggered cascade sulfonation/cyclization reaction is one of the most effective strategies to construct the valuable heterocyclic scaffolds and introduce the sulfonyl group simultaneously.[6] For example, the copper-catalyzed sulfonation/cyclization reaction for the synthesis of 3-sulfonated indenones from sulfonyl hydrazides was independently reported by Jiang's group[7] and our group[8]. Among those reports, typical reaction conditions still require transition metal catalysts/additives in volatile organic solvents under elevated temperature.[9] Therefore, the development of a transition metal-free photocatalytic approach for the cascade sulfonation/cyclization reactions in a green solvent under room temperature is highly attractive.

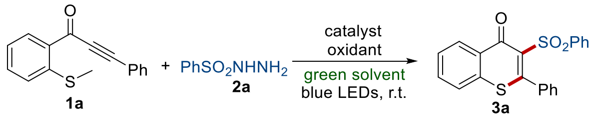
Ethylene glycol (EG) is an abundant resource in chemical industry, which can be produced from renewable biomass.[10] Moreover, EG is also an odourless, non-volatile, low toxic solvent, which has enormous applications in various industrial processes.[11] With our continuing interest in green chemistry and tandem reactions,[12] we herein disclosed that EG could be an excellent green solvent for photocatalytic cascade sulfonation/cyclization reactions using 9-mesityl-10-methylacridinium perchlorate (Acr^+–$Mes{\cdot}ClO_4^-$) as a transition metal-free photocatalyst in the presence of $K_2S_2O_8$ or molecular oxygen as oxidant (Scheme 1). Through this versatile catalytic system, various sulfone-containing heterocycles including thioflavones, oxindoles, and quinoline-2,4(1*H*,3*H*)-diones, were successfully constructed under mild conditions.



Scheme 1. Transition metal-free photocatalytic cascade sulfonation/cyclization reaction in ethylene glycol

For the initial investigation, methylthiolated alkynone **1a** and benzenesulfonyl hydrazide ($PhSO_2NHNH_2$) **2a** were employed as the reactants for the model reaction using water as solvent in open air (Table 1). Considering the solubility of organic photocatalysts in water, the slat Acr$^+$–Mes·ClO$_4^-$ was firstly applied as photocatalyst for the screening of various oxidants including *tert*-butyl hydroperoxide (TBHP), benzoyl peroxide (BPO), H_2O_2, di-*tert*-butyl peroxide (DTBP), and $K_2S_2O_8$ (entries 1-5). Gratifyingly, the desired product sulfonated thioflavone **3a** were observed in all cases, suggesting the photocatalyst and oxidants were compatible in water. Among them, $K_2S_2O_8$ showed the highest activity, delivering **3a** in 37% yield (entry 5). When the reaction was conducted under N_2 atmosphere, the yield of **3a** was slightly increased (entry 6). Then various organic photocatalysts were surveyed in the presence of $K_2S_2O_8$ under N_2 atmosphere. For instance, when eosin Y, 4CzIPN, uranine, rhodamine B, methylene blue, and rose bengal were employed, only poor yields of **3a** were observed (entries 7-12). These results indicate that Acr$^+$–Mes·ClO$_4^-$ is a unique photocatalyst for the cascade sulfonation/cyclization reaction in water. To further improve the yield, several green solvents like dimethyl carbonate (DMC), polyethylene glycol (PEG$_{600}$), and ethylene glycol (EG) were evaluated under N_2 atmosphere (entries 13-15). To our surprise, 82% yield of **3a** were given when the reaction was performed in EG (entry 15). Further optimization revealed that the yield of **3a** was almost retained when the reaction was catalyzed by 3 mol% of Acr$^+$–Mes·ClO$_4^-$ in the presence of **2a** (2 equiv) and $K_2S_2O_8$ (2 equiv) (entry 16). Importantly, when the reaction was carried out under O_2 balloon, the product **3a** could be isolated in 65% yield (entry 17), which was improved to 84% by increasing the reaction time from 12 h to 24 h (entry 18). These results suggested the molecular oxygen was a green oxidant in this transformation. Moreover, the control experiments without either Acr$^+$–Mes·ClO$_4^-$ or visible light did not give any product (entries 19 and 20), demonstrating the photocatalyst and light irradiation play significant roles in this process. Therefore, the optimal

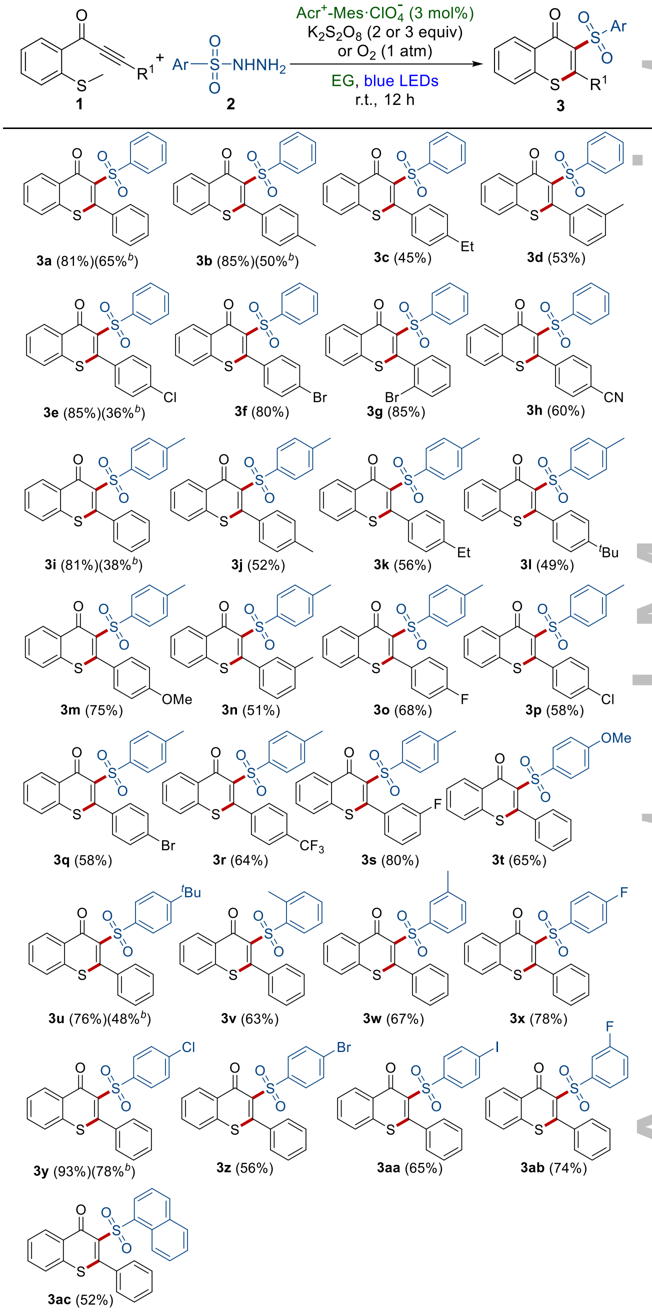
Table 1. Optimization of reaction conditions[a]



Entry	Catalyst (5 mol%)	Oxidant (equiv)	Solvent	Yield (%)
1	Acr$^+$–Mes·ClO$_4^-$	TBHP (2)	H_2O	25
2	Acr$^+$–Mes·ClO$_4^-$	BPO (2)	H_2O	34
3	Acr$^+$–Mes·ClO$_4^-$	H_2O_2 (2)	H_2O	25
4	Acr$^+$–Mes·ClO$_4^-$	DTBP (2)	H_2O	29
5	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	H_2O	37
6[b]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	H_2O	42
7[b]	Eosin Y	$K_2S_2O_8$ (2)	H_2O	15
8[b]	4CzIPN	$K_2S_2O_8$ (2)	H_2O	trace
9[b]	Uranine	$K_2S_2O_8$ (2)	H_2O	trace
10[b]	Rhodamine B	$K_2S_2O_8$ (2)	H_2O	trace
11[b]	Methylene blue	$K_2S_2O_8$ (2)	H_2O	trace
12[b]	Rose bengal	$K_2S_2O_8$ (2)	H_2O	N.R.
13[b]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	DMC	8
14[b]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	PEG$_{600}$	26
15[b]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	EG	82
16[b,c]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	EG	81
17[d]	Acr$^+$–Mes·ClO$_4^-$	O_2 balloon	EG	65
18[d,e]	Acr$^+$–Mes·ClO$_4^-$	O_2 balloon	EG	84
19[b]	—	$K_2S_2O_8$ (2)	EG	N.R.
20[b,f]	Acr$^+$–Mes·ClO$_4^-$	$K_2S_2O_8$ (2)	EG	N.R.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (3 equiv), catalyst (5 mol%), oxidant (2 equiv), solvent (2 mL), room temperature, blue LEDs, 12 h, in air. Isolated yields were given based on **1a**. [b] Reaction under N_2 atmosphere. [c] **2a** (2 equiv), 3 mol% of catalyst were used. [d] 3 mol% of catalyst were used. [e] 24 h. [f] Without light.

Table 2. Substrate scope of the cascade sulfonation/cyclization reaction[a]

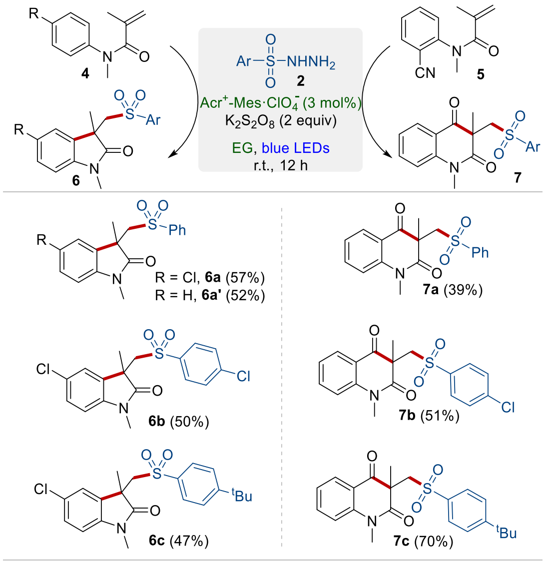


[a] Reaction *conditions A*: **1** (0.2 mmol), **2** (2 equiv), Acr$^+$–Mes·ClO$_4^-$ (3 mol%), $K_2S_2O_8$ (2 equiv), EG (2 mL), blue LEDs, 12 h, under nitrogen. Isolated yields were given based on **1**. [b] Reaction *conditions B*: **1** (0.2 mmol), **2** (3 equiv), Acr$^+$–Mes·ClO$_4^-$ (3 mol%), EG (2 mL), blue LEDs, 12 h, under oxygen balloon. Isolated yields were given based on **1**.

conditions for this photocatalytic reaction were established as follow: **1a** (0.2 mmol), **2a** (2 equiv or 3 equiv), Acr^+–Mes·ClO_4^- (3 mol%) as catalyst, $K_2S_2O_8$ (2 equiv) (*conditions A*) or O_2 (1 atm) (*conditions B*) as oxidant, ethylene glycol (2 mL) as solvent, at room temperature under the irradiation of blue light (λ_{max} = 460 nm).

With the optimal conditions in hand, we then investigated the scope and generality of this photocatalytic system for the cascade sulfonation/cyclization reaction to synthesize diverse sulfonated thioflavones **3** from the corresponding methylthiolated alkynones **1** and arylsulfonyl hydrazides **2**. As shown in Table 2, the methylthiolated alkynones containing electron-donating groups (*e.g.*, 4-Me, 4-Et, 3-Me) and the electron-withdrawing groups (*e.g.*, 4-Cl, 4-Br, 2-Br, 4-CN) reacted well with benzenesulfonyl hydrazide **2a** under *conditions A*, affording the corresponding sulfonated thioflavone products **3b-3h** in moderate to good yields (45-85%). For the reaction with *p*-toluenesulfonyl hydrazide under *conditions A*, various electron-donating groups and electron-withdrawing groups on the phenyl ring of methylthiolated alkynones could also be tolerated, giving the corresponding products **3i-3s** in 49-81% yields. Moreover, the substituted arylsulfonyl hydrazides were also studies under *conditions A*, which showed excellent compatibilities with a broad range of functional groups (*e.g.*, 4-OMe, 4-^{t}Bu, 2-Me, 3-Me, 4-F, 4-Cl, 4-Br, 4-I, 3-F, and 1-naphthyl), providing the corresponding products **3t-3ac** in good to excellent yields. These results demonstrated that the electronic effects were not obvious under *conditions A*. Additionally, typical substrates were also applied under *conditions B*. In the cases of **3b**, **3e**, **3i**, **3u** and **3y**, moderate to good yields were also obtained, albeit lower than that of *conditions A*.

Given that the photocatalytic system tolerates the wide scope of functional groups for the synthesis of sulfonated thioflavones, we then extend this sustainable catalytic system to the synthesis of different sulfonated heterocycles under *conditions A* (Scheme 2). To our delight, the substrates *N*-aryl-*N*-methylmethacrylamide **4** and *N*-(2-cyanophenyl)-*N*-methylmethacrylamide **5** were applicable under the standard conditions giving the corresponding sulfonated oxindoles **6** and sulfonated quinoline-2,4(1*H*,3*H*)-diones **7** in moderate to good yields (39-70%). The arylsulfonyl hydrazides **2** bearing an electron-donating group (i.e., 4-Cl) and an electron-withdrawing group (i.e., 4-^{t}Bu) were also well tolerated.



Reactions were conducted under conditions A.

Scheme 2. Synthesis of sulfonated oxindoles and sulfonated quinoline-2,4(1*H*,3*H*)-diones

To get a deeper insight into this photocatalyzed cascade sulfonation/cyclization reaction, the Stern-Volmer fluorescence quenching experiments were conducted by mixing the photocatalyst Acr^+–Mes·ClO_4^- with the substrates **1a** and **2a**, respectively. As shown in Figure 1, the luminescence quenching effect was observed when **1a** was added to the solution of photocatalyst. Additionally, the linear relationship between I_0/I and the concentration of **1a** confirmed that **1a** was an effective quencher of the excited state of Acr^+–Mes·ClO_4^- (see the Supporting Information).

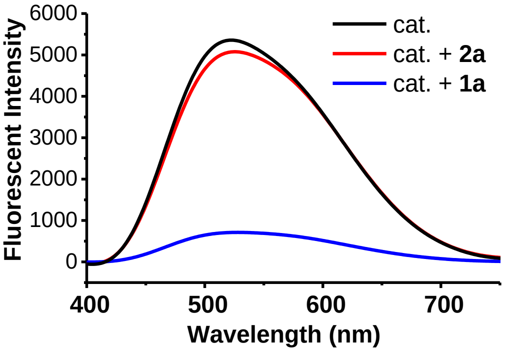
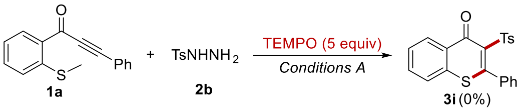


Figure 1. Fluorescence quenching experiments

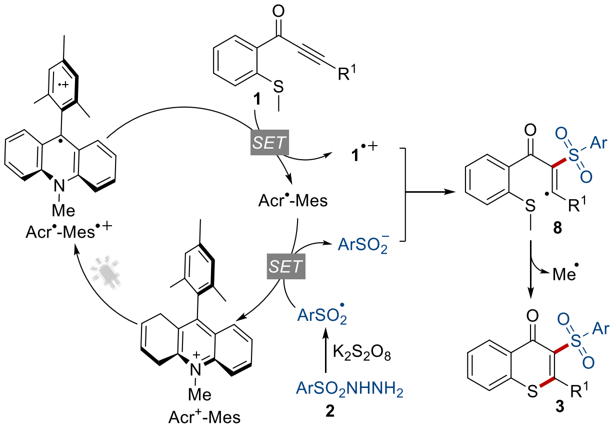
Moreover, when the radical scavenger 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) was added to the reaction of **1a** and **2b** under the standard *conditions A*, no desired product **3i** was generated, indicating that this photocatalytic reaction might involve a radical pathway (Scheme 3).



Scheme 3. Control experiment

Based on the above results and previous reports,[13] a plausible mechanism was proposed. As described in Scheme 4, the long-lived electron-transfer (ET) state ($Acr^•$–$Mes^{•+}$) was firstly generated from the ground state Acr^+–Mes under the irradiation of visible light.[14] Due to the high oxidizing ability of ET state ($Acr^•$–$Mes^{•+}$), the substrate **1** was oxidized to the corresponding radical cation $\mathbf{1}^{•+}$, furnishing the radical $Acr^•$–Mes. On the other hand, the arylsulfonyl radical ($ArSO_2^•$) was produced from the arylsulfonyl hydrazide **2** in the presence of $K_2S_2O_8$.[15] Then the radical $ArSO_2^•$ reacted with $Acr^•$–Mes *via* a single-electron transfer (SET) process to produce the arylsulfinate anion ($ArSO_2^-$) and regenerate the ground state Acr^+–Mes. Subsequently, the combination of $ArSO_2^-$ and $\mathbf{1}^{•+}$ gave the radical intermediate **8**, which was converted into the final product **3** through an intramolecular cyclization by releasing a methyl radical. It is speculated that the employment of polar ethylene glycol as reaction medium might be advantageous to stabilize the ionic intermediates and thus facilitates the cascade sulfonation/cyclization reaction.

Furthermore, the gram scale synthesis was also conducted under the standard *conditions A*. Unfortunately, only 42% yield of the desired product **3a** was obtained (for details see the supporting information). This result is presumably owing to the fast decomposition of arylsulfonyl hydrazide under the photocatalytic conditions.



Scheme 4. The proposed mechanism

In conclusion, we have developed a general and practical photocatalytic system for various cascade sulfonation/cyclization reaction using ethylene glycol as a unique and green medium. With this versatile transition metal-free procedure, sulfone-containing heterocycles including thioflavones, oxindoles, and quinoline-2,4(1*H*,3*H*)-diones, were successfully constructed under the irradiation of blue light at room temperature. It is speculated that the polar ethylene glycol might be critical for the stabilization of ionic intermediates in the reactions. Further studies employ this photocatalytic system for other organic transformations under visible light are being pursued in our laboratory.

Experimental Section

General procedures for the synthesis of 2-sulfonylated thioflavones: In a 25 mL reaction vial with a stirring bar, methylthiolated alkynone **1** (0.2 mmol), arylsulfonyl hydrazide **2** (2 equiv), $K_2S_2O_8$ (2 equiv), and $Acr^+–Mes·ClO_4^-$ (3 mol%) were added. The vial is then evacuated and backfilled three times with N_2, followed by adding ethylene glycol (2 mL). The mixture was stirred at blue LEDs for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was quenched with water (15 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 6/1) to afford the desired product **3**.

Acknowledgements

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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