

Visible-Light-Mediated Three-Component Cascade Sulfonylative Annulation

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ABSTRACT: Visible-light-promoted cascade radical cyclization for the synthesis of sulfonylated benzimidazo/indolo[2,1-*a*]iso-quinolin-6(*SH*)-ones has been reported. The reaction provides transition-metal-free and expeditious access to sulfonylated polyaromatics. The use of sodium metabisulfite as a SO₂ surrogate and the rapid generation of molecular complexity using a three-component photochemical protocol are the salient features of this reaction manifold.



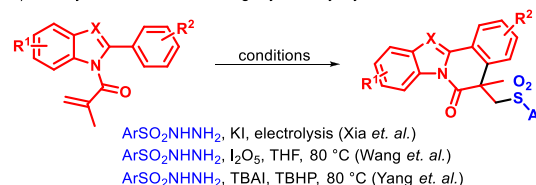
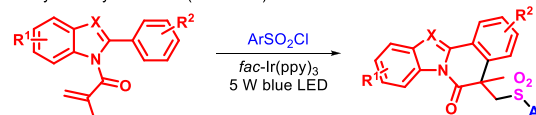
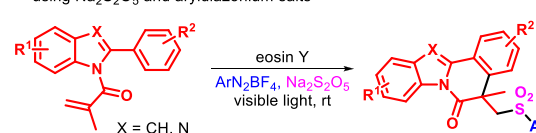
INTRODUCTION

Sulfonylated molecules are ubiquitous in a large selection of pharmaceuticals, agrochemicals, and synthetic intermediates.^{1–4} Traditional routes for sulfonylation rely on sulfonic acids and their salts,^{5–10} sulfonylhydrazides,^{11–13} tosyl chloride,^{14–17} or the oxidation of sulfides and sulfoxides.¹⁸ Typically, sulfonylation processes require harsh oxidizing conditions, high temperatures, and/or equivalent amounts of additives, leading to issues of scalability and limited substrate scope. DABSO is an interesting SO₂ surrogate^{19–21} but is expensive and tedious to synthesize.²² In this context, sodium metabisulfite offers an alternative method to incorporate SO₂, as it is readily available and inexpensive.²³ We envisioned that sulfonyl radical formation from the incorporation of SO₂ into photochemically generated aryl radicals would provide an alternate method toward sulfonylated derivatives.^{24–30} Due to their lower redox potential (0 V vs SCE), diazonium salts are very useful aryl surrogates.^{20,31}

Multicomponent cascade reactions involving radical intermediates have emerged as efficient and ecofriendly^{32–35} pathways for the synthesis of substituted benzimidazo/indolo[2,1-*a*]iso-quinolin-6(*SH*)-ones. Yu and coworkers have reported a silver-catalyzed decarboxylative radical cyclization³⁶ and perfluoroalkylation.³⁷ Subba Reddy *et al.* have reported an interesting acylation/cyclization methodology.³⁸ Sun *et al.* have developed the synthesis of THF-incorporated benzimidazo/indolo[2,1-*a*]iso-quinolin-6(*SH*)-ones.³⁹ Recently, a visible-light-promoted tri- and difluoroalkylation/cyclization cascade was reported by Guo and coworkers.⁴⁰ The Adiyala group has demonstrated a deaminative alkylation/cyclization continuous flow.⁴¹ Xu and coworkers have reported a ketone-catalyzed photochemical synthesis of imidazoisoquinolinone derivatives.⁴² An electrochemical radical cyclization was developed by the Lei group employing Mn catalysis.⁴³ In the context of sulfonylative cyclizations, Wang *et al.*,⁴⁴ Xia *et al.*,⁴⁵ and Yang *et al.*⁴⁶ have employed sulfonylhydrazides as a SO₂ surrogate (Scheme 1a),

Scheme 1. (a–c) Synthetic Strategies for Benzimidazo/indolo[2,1-*a*]iso-quinolin-6(*SH*)-ones

a) Sulfonylative annulations using aryl sulfonyl hydrazides

b) [Ir]-catalyzed photochemical sulfonylative annulation using aryl sulfonyl chlorides (Gao *et al.*)c) This work: Eosin Y catalyzed photochemical sulfonylative annulation using Na₂S₂O₅ and aryldiazonium salts

and Li and coworkers demonstrated sulfonylation as well as carbamoylation under transition-metal-free conditions.⁴⁷ Gao and coworkers demonstrated visible-light-mediated sulfonylation using sulfonyl chlorides (Scheme 1b).¹⁴ Sodium metabisulfite has also been explored as a SO₂ surrogate.^{48–50} Xie and coworkers recently incorporated SO₂ (using K₂S₂O₅)

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into *N*-propargylindoles toward the assembly of 9*H*-pyrrolo[1,2-*a*]indoles.³¹ He and coworkers reported a four-component tandem reaction using Na₂S₂O₅ as a SO₂ precursor for the synthesis of sulfonylated quinoxalin-2(1*H*)-ones.⁴⁹ We envisioned a visible-light-promoted three-component sulfonylative annulation toward sulfonylated benzimidazo/indolo[2,1-*a*]isoquinolin-6(5*H*)-ones involving acrylamides, aryl diazonium salts, and Na₂S₂O₅ (Scheme 1c).

RESULTS AND DISCUSSION

For the initial studies, we chose the benzimidazole derivative **1a** as the model substrate, and the results are outlined in Table 1. In the preliminary reaction in a dichloroethane (DCE)

Table 1. Optimization Studies^a



entry	photocatalyst (mol %)	solvent	yield
1	Eosin Y (2)	DCE	67
2 ^b	Eosin Y (2)	DCE	48
3 ^c	Eosin Y (2)	DCE	42
4	Eosin Y (2)	DMF	41
5	Eosin Y (2)	MeCN	46
6	Eosin Y (2)	MeOH	35
7	Eosin Y (2)	THF	21
8	Eosin Y (2)	acetone	trace
9	Eosin Y (2)	DCM	64
10	rose bengal (2)	DCE	54
11	4CzIPN (2)	DCE	trace
12	Eosin Y (5)	DCE	81
13		DCE	28
14 ^d	Eosin Y	DCE	trace
15 ^e		DCE	NR

^aThe reaction was performed with 0.18 mmol of **1a**, phenyldiazonium salt **2a** in the presence of the photocatalyst (mol %), and Na₂S₂O₅ (equiv) dissolved in 2 mL of a solvent and irradiated with blue LED strips. ^b2 equiv of Na₂S₂O₅ was employed. ^c4 equiv of Na₂S₂O₅ was employed. ^dReaction vial wrapped by Al foil (in the dark). ^eReaction performed in the absence of light and a photocatalyst.

solvent, 67% yield of the product **3a** was obtained when 1.5 equiv of the phenyl diazonium salt was used (Table 1, entry 1). On increasing and decreasing the amount of Na₂S₂O₅ (to 2 and 4 equiv, respectively), diminished yields were observed (Table 1, entries 2 and 3). No improvement in the yield was observed when we evaluated solvents such as DMF, MeCN, and MeOH, which provided the product in 41, 46, and 35% yields, respectively (Table 1, entries 4–6). Employing acetone as the solvent did not lead to any measurable product formation. When the reaction was performed in dichloromethane (DCM), 64% yield of **3a** was obtained (Table 1, entry 9). We selected DCE as the solvent for further optimization. Evaluation of other photocatalysts (rose bengal, 4CzIPN, rhodamine B, and rhodamine 6G) also failed to enhance the yield. On increasing the amount of Eosin Y from 2 to 5 mol %, we obtained 81% yield of **3a** (Table 1, entry 12). We discovered that very slow product formation occurred in the absence of the photocatalyst (28% yield in 24 h; Table 1, entry 13). The reaction did not yield any product when performed in

the dark in the presence of the photocatalyst. Further, no product was obtained when the reaction was performed in the absence of both the photocatalyst and light (Table 1, entry 15).

After establishing the optimized reaction conditions, we evaluated the generality of this reaction. As depicted in Figure 1, a variety of phenyldiazonium salts underwent the trans-

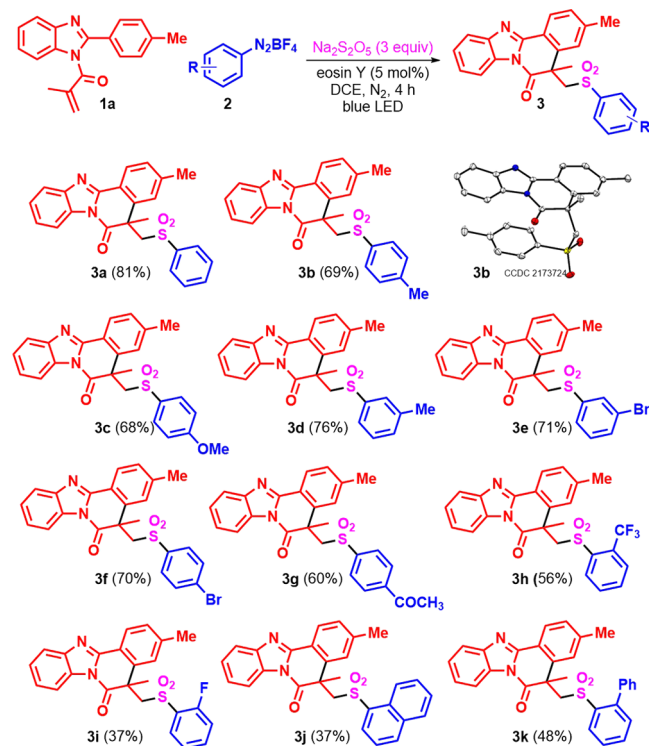


Figure 1. Reaction scope: evaluation of diazonium salts.

formation smoothly. Diazonium precursors featuring electron-donating substituents *p*-methyl (**3b**) and *p*-methoxy (**3c**) provided the products in 69 and 68% yields, respectively. In the case of *m*-methyl (**3d**), we have obtained a 76% yield of the product. *Meta*- and *para*-bromo diazonium salts furnished the corresponding products **3e** and **3f** in good yields (71 and 70% yields, respectively). Certain electron-withdrawing substituents performed well such as the *para*-acylated diazonium salt, which afforded the product **3g** in a 60% yield. *Ortho*-substituted diazonium precursors generally afforded diminished yields, and this effect appears to be independent of the electronic disposition of the substituent. *Ortho*-CF₃- and *o*-F-substituted products **3h** and **3i** were obtained in 56 and 37% yields, respectively. The naphthyl derivative- and the 2-Ph-substituted products **3j** and **3k** were obtained in 37 and 48% yields, respectively.

In the next stage, we explored various substituted benzimidazoles as outlined in Figure 2. Among the 2-aryl-substituted benzimidazoles, a variety of electronically distinct substitutions were tolerated well on the phenyl ring. The parent derivative **3l** was obtained in a 75% yield. Electron-withdrawing substituents were tolerated well in the *para* position as exemplified by the fluoro- and cyano-substituted products **3m** (68% yield) and **3n** (90% yield). The *m*-OMe derivative afforded a regioisomeric mixture of products in a 76% yield (**3o**). In line with the expected effect of such

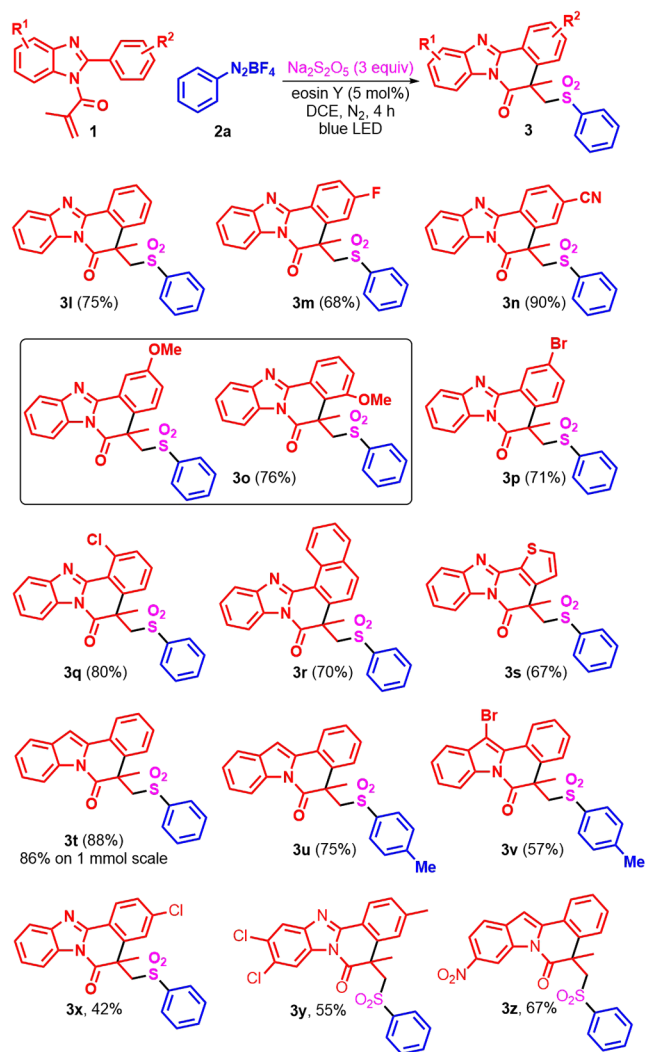


Figure 2. Reaction scope: evaluation of 2-aryl-benzimidazoles and indoles.

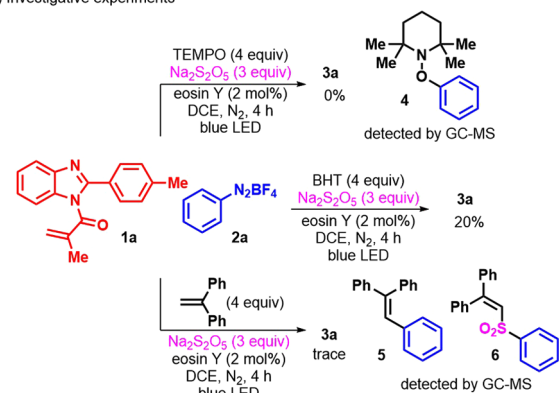
substituents on the regioselectivity, the *m*-Br derivative resulted in a single regioisomer in a 71% yield (**3p**).

The *ortho*-chloro-substituted product (**3q**) was furnished in an 80% yield, while the naphthyl-substituted derivative (**3r**) was obtained in a 70% yield. The 2-thiophene-substituted benzimidazole precursor resulted in the product **3s** in a good yield (67%). The dichloro benzimidazole precursor afforded a 55% yield of the corresponding product **3y**. We also evaluated indolyl methacrylate precursors, which furnished products **3t–v** in up to an 88% yield (Figure 2). The nitro-substituted indolyl precursor afforded a 67% yield of **3z**. We discovered that precursors with a free phenolic –OH group, internal olefins, and acrylate derivatives did not afford the desired product. We also performed the synthesis of **3t** starting with 1 mmol of the precursor and obtained the product in an 86% yield.

We performed some preliminary experiments to obtain insights about the reaction mechanism. In an attempt to trap radical intermediates, we performed an experiment in the presence of TEMPO and discovered that the reaction was completely suppressed (Scheme 2). Although we were unable to isolate the TEMPO adduct, we detected the presence of species **4** upon GC–MS analysis of the reaction mixture. When

Scheme 2. (a,b) Mechanistic Investigation

(a) Investigative experiments



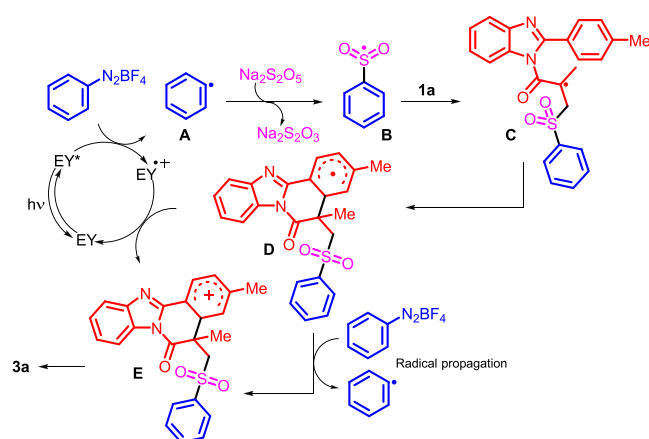
(b) Extended cascade employing intramolecular olefin trap



BHT was employed with the intent to trap radicals, the original product was obtained in only a 20% yield, although no BHT adduct could be isolated. We also performed a potential competition experiment by adding 1,1-diphenylethylene to the reaction under otherwise identical reaction conditions. We observed that only a trace amount of the product formed, and the species **5** and **6** could be detected upon the GC–MS analysis of the reaction mixture, indicating that the phenyl and phenylsulfonyl radicals were trapped by the olefin (Scheme 2). We designed a radical clock experiment wherein the *O*-allylated phenyldiazonium salt (**2w**) was employed under standard conditions. The product **3w** was obtained in a 63% yield, implying that the intramolecular trapping of the phenyl radical by the allyl double bond preceded the alkylsulfonate formation and subsequent steps. The results obtained from the above reactions provide evidence to indicate that the reaction likely follows a radical pathway. We also determined that the Eosin Y fluorescence was being quenched by the diazonium salt **2a**.

Based on abovementioned experimental observations and literature information,^{31,52,53} we proposed a plausible mechanism of the reaction as depicted in Scheme 3. Initially, the

Scheme 3. Proposed Mechanism



phenyl radical is generated from the diazonium ($E_{1/2} = -0.2$ V)^{54–56} by the oxidative quenching of the photoexcited catalyst ($E_{1/2} = -1.11$ V),⁵⁷ which is trapped by either Na₂S₂O₅ or SO₂ (thermally generated from Na₂S₂O₅)⁵⁸ to form the phenylsulfonyl radical B. This radical intermediate further reacts with the precursor 1a to generate the alkyl radical C, which is trapped by the aryl ring to generate the intermediate D. Finally, the photocatalytic cycle is being terminated by the oxidation of D to afford E. Alternatively, E could be generated by the single electron oxidation with the diazonium salt *via* chain propagation,⁵⁹ which then results in the final product 3a.

In conclusion, we have developed a photochemical cascade cyclization that results in the formation of two C–S bonds and one C–C bond in a single operation. A collection of sulfonylated benzimidazo/indolo[2,1-*a*]iso-quinolin-6(*5H*)-ones were accessed in an expeditious manner utilizing this transformation that does not require transition metals, oxidants, or additives and employs a readily available SO₂ surrogate. The preliminary potential of this reaction manifold to access even more complex moieties was demonstrated through a functionalized diazonium precursor, and further studies in this area are ongoing in our labs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02302>.

Experimental procedures, complete optimization data, and characterization data including copies of ¹H and ¹³C NMR spectra for all new compounds (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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