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## ARTICLE

**Organic photoredox catalysis enabled cross-coupling of arenediazonium and sulfinate salts: synthesis of (un)symmetrical diaryl/alkyl aryl sulfones†**Received 00th January 20xx,  
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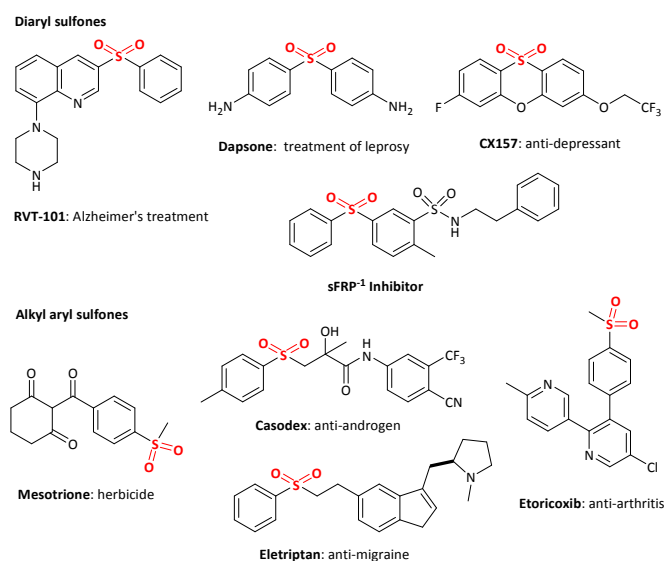
We disclose herein the first transition-metal- and external oxidant/reductant-free visible-light-mediated synthesis of (un)symmetrical diaryl/alkyl aryl sulfones from arenediazonium tetrafluoroborates and sodium sulfinate salts using eosin Y as an organic photoredox catalyst. The utilization of visible light as an inexpensive and ecosustainable energy source, operational simplicity, ambient temperature and clean reaction in aqueous acetonitrile are the salient features of the developed protocol. The desired sulfones were also synthesized via a one-pot, two-step process directly from anilines and sulfinate salts in good to excellent yields.

**Introduction**

Assembling the sulfone functionality in a molecule is among the highly desirable goals for an organic chemist. It not only imparts incredible biological properties (Fig. 1)<sup>1</sup> to the designed molecules but also transforms them into important building blocks via Julia olefination,<sup>2</sup> Ramberg Backlund reaction<sup>3</sup> and Smiles rearrangement.<sup>4</sup> The significance of organosulfones can be easily estimated from their high degree of prevalence in agrochemicals, pharmaceuticals and functional materials.<sup>5</sup> Given their importance, a number of routes have been devised for the synthesis of this class of compounds.<sup>6</sup> The most common among these methods are the oxidation of sulfides and sulfoxides, sulfonylation of arenes and transition-metal (palladium and copper) catalyzed arylation of sulfinate salts.<sup>6,7</sup> These routes are either multiple-step, require oxidizing agents in over-stoichiometric amount or employ high temperature, expensive and difficult-to-remove transition-metals (Pd and Cu), solvents (e.g. DMSO and DMF) and obnoxious-smelling toxic thiols. Therefore, the development of a greener metal-free approach for the synthesis of sulfones is substantially appealing.

The revival of visible-light photoredox catalysis (VLPC) in the last decade has led to the development of new synthetic protocols and also to the improvisation of the existing ones.<sup>8</sup> Environmental sustainability and cost-effectiveness are the key benefits associated with the use of VLPC. Although sulfones have been synthesized via VLPC<sup>9</sup> (Scheme 1), to the best of our knowledge, there is no report in

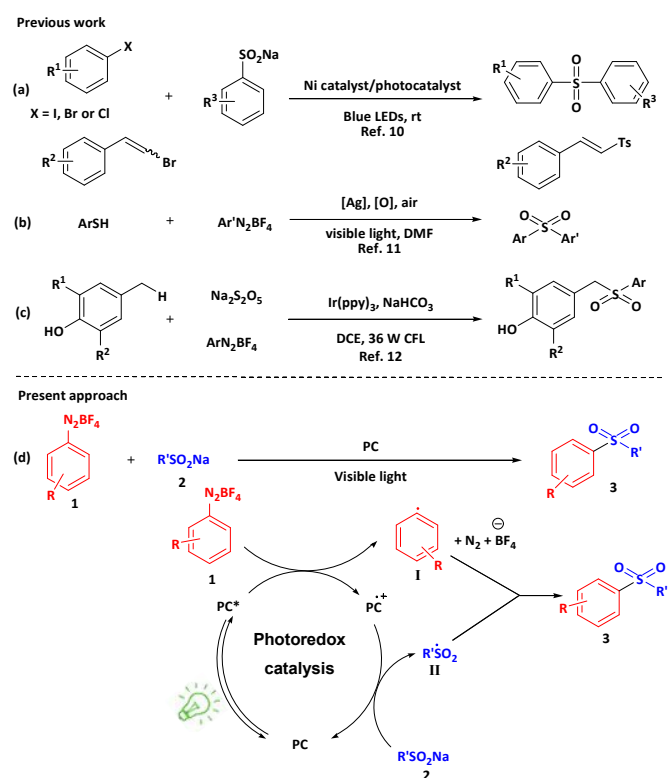
the literature on the metal-free visible-light-mediated synthesis of diaryl/alkyl aryl sulfones which is striking. The previous methods mainly rely on dual photoredox/nickel catalysis to synthesize these compounds from aryl halides and sulfinate salts (Scheme 1a).<sup>10</sup> Also, Lee and co-workers have recently reported the visible-light driven silver catalyzed one-pot synthesis of diaryl sulfones using aryl thiols and aryldiazonium salts (Scheme 1b).<sup>11</sup> More recently, Wu et al have developed visible-light-mediated iridium catalyzed three-component synthesis of sulfones (Scheme 1c).<sup>12</sup> All these methods suffer from one or more drawbacks mentioned earlier in the first paragraph and most of them lead only to the synthesis of diaryl sulfones and not alkyl aryl sulfones. With this background in mind and in continuation of our work on VLPC<sup>13</sup> and synthesis of

**Fig. 1** Examples of biologically active sulfones.

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sulfones,<sup>14</sup> we envisioned the synthesis of diaryl/alkyl aryl sulfones via a visible-light-mediated photoredox relay between sulfinate and arenediazonium salts (Scheme 1d). A recent work by Suryavanshi and co-workers describes the copper-catalyzed synthesis of diaryl sulfones using the same starting materials in methanol.<sup>7e</sup> As arylating agents, diazonium salts are easy to handle stable solids and are exceptional alternatives to haloarenes and boronic acids because of the ease of their reduction.<sup>15a</sup> We envisaged that the diazonium and sulfinate salts can prove to be excellent reaction partners in our designed protocol because both are known for the facile generation of radicals via visible-light-mediated reduction and oxidation, respectively.<sup>15,16</sup> According to our hypothesis, the SET from the excited state of photocatalyst (PC) to diazonium salt **1** would generate the aryl radical **I** and the complementary SET from the sulfinate salts **2** to PC<sup>+</sup> would complete the photoredox catalytic cycle forming the sulfonyl radical **II**, obviating the need of any external sacrificial reductant. Cross-coupling of radicals **I** and **II** would lead to the formation of the desired sulfones **3** (Scheme 1d).



**Scheme 1** Visible-light-mediated synthesis of diaryl/alkyl aryl sulfones.

## Results and discussion

In order to test the viability of our hypothesis, a model reaction was performed using benzenediazonium salt **1a** and *p*-toluenesulfinate **2a**. Eosin Y was chosen as a photocatalyst for the reaction as it very easily generates radicals of both the salts **1a** and **2a** under visible-light irradiation.<sup>16</sup> The oxidation potentials of the diazonium salt (benzenediazonium tetrafluoroborate -0.06 V vs. SCE)<sup>15a,16f,17</sup> and the sulfinate salt (sodium *p*-toluenesulfinate 0.45 V vs. SCE)<sup>16b,c,e</sup> are both accessible by the eosin Y catalyst such that

both oxidation and reduction can operate simultaneously (EY<sup>•+</sup>/EY<sup>+</sup> 1.11 V vs. SCE, EY<sup>•-</sup>/EY<sup>-</sup> 0.78 V vs. SCE).<sup>16c</sup> Since the reduction potential of diazonium salts is much lower than the oxidation potential of sulfonates, they are more likely to generate the radical **I** first in comparison to sulfinate salts via SET from EY<sup>•+</sup>. To our utmost satisfaction, the use of 1 mol% of the catalyst under irradiation with green light emitting diodes (LEDs; 2.50 W,  $\lambda = 535$  nm) produced the target sulfone **3a** in 72% yield in DMF as a solvent after 10 hours (Table 1, entry 1). Further, it was imperative to test the necessity of photocatalyst and visible-light in the reaction. It was observed that in the absence of either of the two reaction parameters, the desired product was formed in traces (entries 2 and 3). In fact, in the absence of the photocatalyst (entry 2) and visible light (entry 3), aryldiazo sulfone was obtained as the major product under our reaction conditions.<sup>18</sup> This excluded the possibility of the formation of **3a** from the corresponding aryldiazo sulfone on irradiation with 2.50 W green LEDs, which is in conformity with the earlier observation that irradiation of an aryldiazo sulfone with 12 W blue LEDs produced only traces of the product (Table 1, entry 3 of Ref. 19). With these results in hand, we began our expedition of deciding the best conditions for our reaction. A range of solvents and solvent systems were screened (entries 1, 4-10). No product formation could be detected in water probably due to the reactivity of the aryl radical-water system under irradiation leading to other products (entry 4).<sup>20</sup> Similarly, no reaction took place in dry acetonitrile which can be attributed to the solubility issues of salts **1a** and **2a** in the solvent (entry 6). However, the solvent combination of acetonitrile/water (10:1) gave the best yield of the desired product (entry 8). As far as the photocatalyst is concerned, eosin Y worked more efficiently than Rose Bengal, whereas the catalytic activity of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was comparable to eosin Y (entries 8, 11 and 12), but we opted to use eosin Y in view of our goal to develop a transition-metal-free protocol. Increment in the reaction time from 10 to 12 h led to no significant increase in the yield of the product (entry 13). The optimum catalyst loading for the developed photocatalytic protocol was found to be 1 mol% (entry 8 versus 14 and 15). A decrease in the amount of solvent led to the slight decrease in the yield of the desired product (entry 16). This observation may be attributed to the fact that a higher concentration of radicals leads to the increase in the formation of side products (dimers of radicals **I** and **II**).

After establishing the optimum conditions for our reaction, we explored the scope of the reaction with respect to the arenediazonium salts **1** using sodium *p*-toluenesulfinate **2a** (Table 2). Both electron-withdrawing and electron-donating substituents on the aromatic ring of diazonium salts provided the corresponding diaryl sulfones in good to excellent yields (**3a-o**). The diazonium salts bearing different functional groups such as -OCH<sub>3</sub>, -Cl, -F, -CH<sub>3</sub>, -NO<sub>2</sub> and -CN were compatible with our reaction conditions. It was observed that electron-withdrawing group on the aromatic ring gave slightly better yield of the products in shorter reaction time in comparison to those having an electron-donating group (Table 2, products **3b-e** versus **3f-l**). The presence of an electron-withdrawing substituent at the *p*-position exhibits greater reactivity than that on

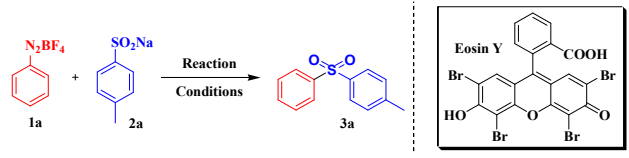
the *o*- or *m*-position (**3g** versus **3h**, and **3j** versus **3k** and **3l**). The substrate 2-naphthyl diazonium salt also gave decent yield of the corresponding sulfone (**3m**). Disubstituted arenediazonium salts such as 3,4-dichloro and 3,5-dichloro arenediazonium salts also smoothly coupled with **2a** and excellent yields of corresponding products were obtained (**3n** and **3o**).

We next evaluated the scope of sulfinate salts **2** under the present reaction conditions and a broad range of substituents were found to be tolerated (Table 3). In particular, aryl sulfonates proved to be suitable substrates, and a range of electron-donating and electron-withdrawing substituents could be included on the aromatic rings (**4a-g**). Even alkyl sulfinate salts were found to be befitting reaction partners and the corresponding alkyl aryl sulfones were obtained in moderate yields (**4h-k**). Linear as well as cycloalkyl sulfonates could also be clubbed with diazonium salt but a longer reaction time was needed for the product formation (**4j** and **4k**) in their case.

**Table 2** Scope of arenediazonium salts in VLPC enabled arylation of sulfonates<sup>a</sup>

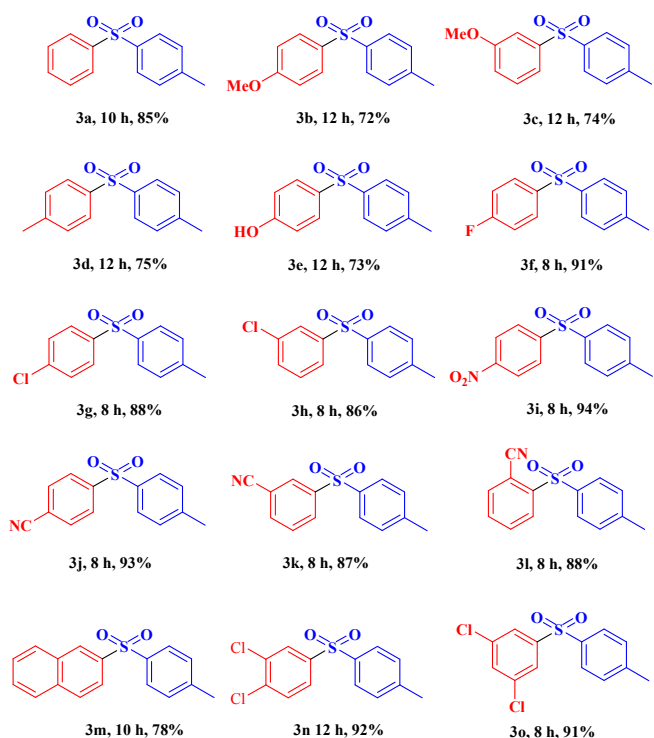
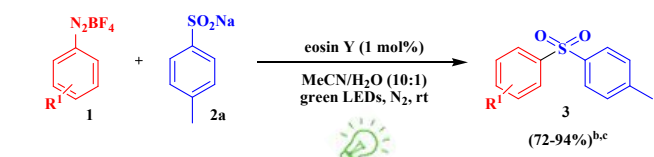
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**Table 1** Optimization of experimental conditions<sup>a</sup>



Entry	Photocatalyst (mol%)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	Eosin Y (1 mol%)	DMF	10	72
2	-	DMF	15	Traces
3 <sup>c</sup>	Eosin Y (1 mol%)	DMF	15	Traces
4	Eosin Y (1 mol%)	H <sub>2</sub> O	15	Nil
5	Eosin Y (1 mol%)	DMSO	10	65
6	Eosin Y (1 mol%)	MeCN	15	Traces
7	Eosin Y (1 mol%)	MeCN/H <sub>2</sub> O (5:1)	10	70
8	Eosin Y (1 mol%)	MeCN/H <sub>2</sub> O (10:1)	10	85
9	Eosin Y (1 mol%)	DMF/H <sub>2</sub> O (10:1)	10	81
10	Eosin Y (1 mol%)	DMSO/H <sub>2</sub> O (10:1)	10	78
11	Rose Bengal (1 mol%)	MeCN/H <sub>2</sub> O (10:1)	12	53
12 <sup>d</sup>	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (1 mol%)	MeCN/H <sub>2</sub> O (10:1)	10	86
13	Eosin Y (1 mol%)	MeCN/H <sub>2</sub> O (10:1)	12	85
14	Eosin Y (0.5 mol%)	MeCN/H <sub>2</sub> O (10:1)	10	58
15	Eosin Y (2 mol%)	MeCN/H <sub>2</sub> O (10:1)	10	86
16 <sup>e</sup>	Eosin Y (1 mol%)	MeCN/H <sub>2</sub> O (10:1)	12	79

<sup>a</sup>Reaction conditions: **1a** (1.0 mmol), **2a** (1.3 mmol), catalyst (1 mol%), solvent (5 mL), green LEDs, 10-15 h, under a nitrogen atmosphere. <sup>b</sup>Isolated yield. <sup>c</sup>No light. <sup>d</sup>Irradiation with blue LEDs. <sup>e</sup>Solvent (4 mL).

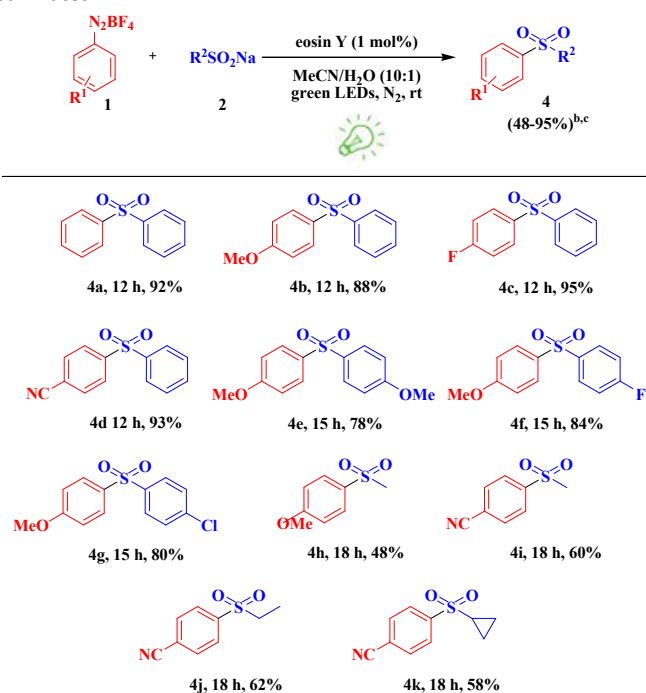


<sup>a</sup>Reaction conditions: **1** (1.0 mmol), **2a** (1.3 mmol), eosin Y (1 mol%), CH<sub>3</sub>CN/H<sub>2</sub>O (10:1, 5 mL), green LEDs, 8-12 h, under a nitrogen atmosphere. <sup>b</sup> Isolated yield of the purified products **3**. <sup>c</sup> All compounds are known in literature<sup>7,10</sup> and gave satisfactory spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS) data (see ESI).

Furthermore, we were also very keen to test the compatibility of our protocol with the *in situ* generation of the diazonium salts starting from anilines in order to circumvent the stability issues of aryldiazonium salts and to skip the separate diazotization step. Based on previous reports,<sup>16d,21</sup> 20 mol% of methanesulfonic acid and 1.5 equiv. *tert*-butyl nitrite were added to aniline and sodium *p*-toluenesulfonate in acetonitrile/water (10:1) along with 1 mol% of eosin Y under 2.50 W green LED irradiation. To our delight, the corresponding sulfone **3a** was obtained in good yield in this one-pot, two-step transformation. Several other anilines **5** were also applied and the results are presented in Table 4.

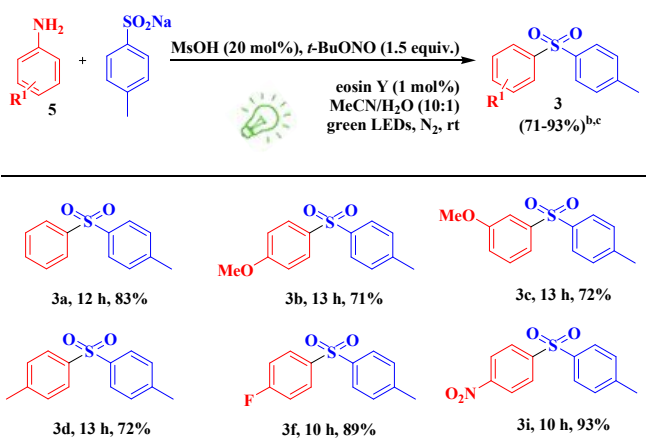
As regards the mechanism of the developed protocol, no diaryl sulfone formation could be detected when three equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) were added to the reaction mixture under standard conditions which supported our proposed radical pathway (Scheme 2). The formation of phenyl-TEMPO adduct **6** was confirmed by its MS (HRMS (EI): calcd for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O [M]<sup>+</sup> 243.1497, found 243.1495). We also attempted the radical trapping experiment with 1,1-diphenylethylene and the

**Table 3** Scope of sulfinate salts in VLPC enabled arylation of sulfonates<sup>a</sup>



<sup>a</sup>Reaction conditions: **1** (1.0 mmol), **2** (1.3 mmol), eosin Y (1 mol%), CH<sub>3</sub>CN/H<sub>2</sub>O (10:1, 5 mL), green LEDs, 12-18 h, under a nitrogen atmosphere. <sup>b</sup> Isolated yield of the purified products **4**. <sup>c</sup> All compounds are known in literature<sup>7,10</sup> and gave satisfactory spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS) data (see ESI).

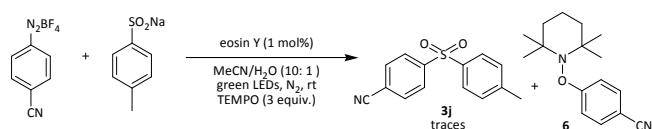
**Table 4.** Scope of anilines for one-pot, two-step sulfonylation process<sup>a</sup>



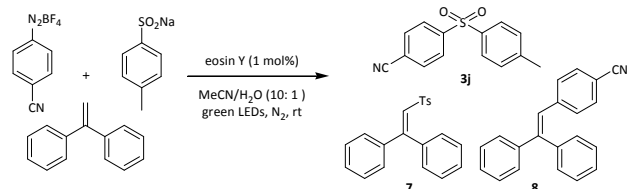
<sup>a</sup>Reaction conditions: **5** (1.0 mmol), MsOH (20 mol%), *t*-BuONO (1.5 mmol), **2a** (1.3 mmol), eosin Y (1 mol%), CH<sub>3</sub>CN/H<sub>2</sub>O (10:1, 5 mL), green LEDs, 10-13 h, under a nitrogen atmosphere. <sup>b</sup> Isolated yield of the purified products **3**. <sup>c</sup> All compounds are known in literature<sup>7,10</sup> and gave satisfactory spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS) data.

compounds **7** and **8** were detected by GC-MS along with the formation of the corresponding sulfone **3j**. This further confirmed the generation of the aryl and sulfonyl radical in the reaction (Scheme 2). Radical chain SRN pathway was excluded on the basis of light turn-ON/OFF experiment (See ESI).

## Radical inhibiting experiment



## Radical trapping experiment



Scheme 2 Mechanistic investigations.

## Conclusions

In summary, we have developed a transition-metal- and external oxidant/reductant-free visible-light-mediated approach for the synthesis of diaryl/alkyl aryl sulfones from aryl diazonium and sulfinate salts employing eosin Y as an organophotoredox catalyst under mild conditions. The protocol is operationally very simple and utilizes visible light as an inexpensive and ecosustainable energy source in aqueous acetonitrile as an acceptable green solvent at ambient temperature. The developed method overcomes a number of limitations of the previously reported methods and qualifies well as an applaudable entry in the arena of green synthetic methods for the procurement of sulfones. Moreover, the desired diaryl/alkyl aryl sulfones were also synthesized by a one-pot, two-step process involving an *in situ* diazotization of a number of anilines followed by VLPC enabled arylation of sulfinate salts.

## Conflicts of interest

"There are no conflicts to declare".

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