



Visible-light-promoted synthesis of diaryl sulfides under air



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ABSTRACT

A convergent, organocatalytic visible-light-mediated process for the synthesis of diaryl sulfides has been developed. A broad range of aryl thiols reacted with various aryl diazonium salts in the presence of eosin Y under air atmosphere to afford the desired diaryl sulfides in high yields. This novel and environmentally friendly method provides an alternative route to established synthetic approaches.

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Introduction

Sulfur-containing compounds are found in numerous natural products and pharmaceuticals.¹ In particular, diaryl sulfides and their derivatives are important structural motifs in natural and synthetic molecules and have shown interesting biological activities such as HIV protease inhibition, anti-hepatitis C activity, anti-depression activity, anti-inflammatory and anti-histamine properties (Scheme 1).^{1e,2} Moreover, diaryl sulfides have been employed as organic materials in the field of materials science.³ Furthermore, they are precursors to other sulfur-containing compounds comprising higher-oxidation state-sulfur, which have similar important bioactive properties.^{2f,4}

Given the significance of these compounds as important structural scaffolds in natural products and drug candidates, it is very important to develop an efficient process for synthesizing diaryl sulfides. Previous approaches for the synthesis of diaryl sulfides utilized various transition metals such as Pd,⁵ Cu,^{1d,6} Fe,⁷ Ni,⁸ Rh,⁹ Co¹⁰ and In.¹¹ These methods provide powerful tools for the synthesis of diaryl sulfides. However, metal-catalyzed reactions have some limitations such as using expensive and/or toxic metal catalysts and sensitive or harsh reaction conditions. A number of metal-free processes were also investigated; for example, condensation of arenethiols with aryl halides, and nucleophilic substitution of activated aryl halides with thiols.¹² Early studies for the synthesis of diaryl sulfides reported by the Petrillo group used metal-free processes that included the use of various aryl

diazonium salts and thiolates.¹³ In these studies, the reactions were performed carefully under nitrogen since the intermediate diazosulfide is a potent explosive.

Recently, metal-free C–H thioarylation of electron rich arenes and heteroarenes using electrophilic sulfur reagents such as sulfonyl chlorides,¹⁴ sulfonyl hydrazines,¹⁵ *N*-(thio)succinimides,¹⁶ sodium sulfinates,¹⁷ thiols,¹⁸ disulfides,¹⁹ sulfoxides^{2f} and others²⁰ has been developed. Despite these recent advances, a direct process for the synthesis of diaryl sulfides via photocatalysis would offer a complementary strategy to the existing synthesizing methods.

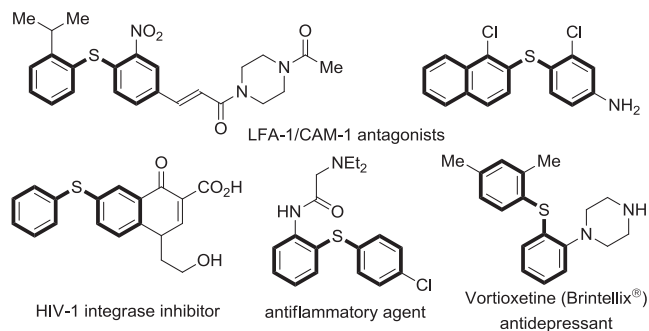
Recently, visible-light-mediated photoredox catalysis has emerged as a powerful tool in organic synthesis. Ruthenium and iridium polypyridyl complexes are widely employed in visible light photocatalysis with great reported success.²¹ However, based on the limitations of utilizing transition metals, the development of green activation modes in photoredox system is very important. Organic dyes have been used as an attractive alternative to transition metal photoredox catalysts;²² especially, eosin Y was widely employed as an organocatalyst in various photoredox processes.²³ Herein, we report a mild convergent approach for the synthesis of diaryl sulfides in the presence of eosin Y via visible light photocatalysis (Scheme 2).

Results and discussion

To develop a metal-free protocol, we designed a reaction model with thiophenol **1a** and 4-methoxybenzenediazonium tetrafluoroborate **2a** in the presence of organo-photocatalysts at room temperature under air atmosphere (Table 1). Various organic dyes

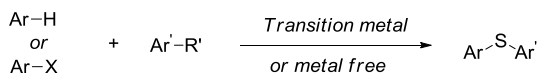
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Scheme 1. The diaryl sulfide moiety in bioactive compounds.

■ Previous approaches



X = halide, B(OH)₂

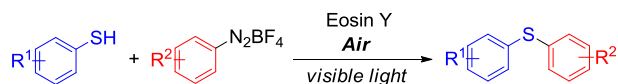
R' = SH, SSAr, S(O)₂Cl, S(O)₂NHNH₂,

SO₂Na, SCl, SBn, SO₂H, S(O)Me

■ **harsh / air sensitive conditions**

■ **prefunctionalized SM**

■ This work



■ **organo-photocatalysis**

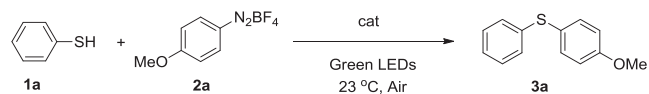
■ **neutral pH / mild conditions**

■ **air stable conditions**
: open air

■ **pretreated thiols**
: not necessary

Scheme 2. Strategies for the synthesis of diaryl sulfides.

Table 1
Optimization of reaction conditions.^a



Entry	Catalyst (mol%)	Solvent	Yield (%) ^b
1 ^c	Rose Bengal (5)	CH ₃ CN	10
2 ^c	Rose Bengal (5)	DMF	30
3	Rose Bengal (5)	DMF	31
4	Rhodamin B (5)	CH ₃ CN	Trace
5	Rhodamin B (5)	DMF	Trace
6	Eosin Y (5)	CH ₃ CN	37
7	Eosin Y (5)	DMF	51
8	Eosin Y (5)	THF	35
9	Eosin Y (5)	MeOH	33
10	Eosin Y (5)	DMSO	90
11	Eosin Y (2)	DMSO	68
12	Eosin Y (4)	DMSO	84
13 ^d	Eosin Y (5)	DMSO	10
14	None	DMSO	11
15 ^e	Eosin Y (5)	DMSO	13

^a Conditions: **1a** (0.5 mmol, 1.0 equiv), **2a** (1.2 equiv), catalyst, solvent (0.2 M) at 23 °C for 5 h.

^b Yields are of isolated product after column chromatography.

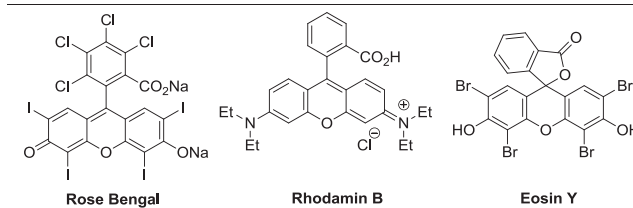
^c The reaction was conducted under blue LED light irradiation.

^d The reaction was performed in the dark.

^e The reaction was conducted under N₂ atmosphere.

including rose bengal, eosin Y, and rhodamine B were examined. The reaction yield was low in the case of rose bengal (entries 1–3). Eosin Y was found to be more effective for this transformation, with a 90% yield for the desired product **3a** (entry 10). In the case of solvents, dimethyl sulfoxide provided the best results in terms of

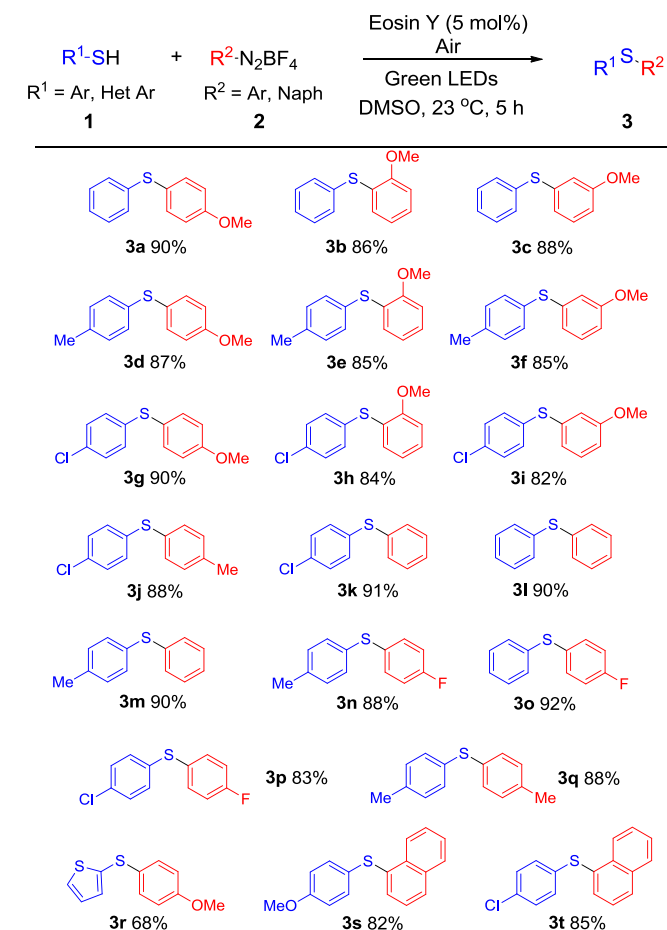
reaction yield; other solvents such as acetonitrile, dimethylformamide, methanol and tetrahydrofuran resulted in lower yields (entries 6–9). Poor conversion was observed when the reaction was performed in the absence of either the photocatalyst or light (entries 13 and 14). Furthermore, we carried out the reaction under nitrogen atmosphere where low yield was observed (entry 15). These results indicated that photocatalyst, visible light, and air are necessary for this transformation process.



After determining the optimized reaction conditions, the scope of this transformation was explored (Table 2). The reaction was found to tolerate a wide range of aromatic thiols and aryl diazonium salts to afford the desired diaryl sulfides in good to high yields.

Both electron-rich and electron-deficient aryl thiols provided the products in high yields (82–91%, **3d–3k**, **3m–3n**, **3p–3q**, **3s–3t**). Ortho and meta-substituted aryl diazonium salts were well-tolerated as well (82–88%, **3b–3c**, **3e–3f**, **3h–3i**). Electron-deficient

Table 2
Substrate scope.^a



^a Reactions conducted on 0.5 mmol scale. Yields are of isolated product after column chromatography. For details, see the Supporting Information.

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