Letter

Sulfonylation of Aryl Halides by Visible Light/Copper Catalysis

Qiuli Yan, Wenwen Cui, Xiuyan Song, Guiyun Xu, Min Jiang, Kai Sun, Jian Lv, and Daoshan Yang*



ABSTRACT: An efficient visible-light-assisted, copper-catalyzed sulfonylation of aryl halides with sulfinates is reported. In our protocol, a single ligand Cu^I photocatalyst formed in situ was used in the photocatalytic transformation. Diverse organosulfones were obtained in moderate to good yields. This strategy demonstrates a promising approach toward the synthesis of diverse and useful organosulfones.

O rganosulfones, one of the most valuable sulfurcontaining molecules, are pivotal structural motifs found in several biologically active molecules and argochemicals (Figure 1).¹ Additionally, sulfones are also versatile



Figure 1. Examples of organosulfones in biologically active molecules.

chemical building blocks widely utilized in synthetic chemistry.² Therefore, the development of efficient and sustainable approaches toward the construction of organo-sulfones is highly desirable. Conventionally, there are five methods for the synthesis of these valuable molecules: (a) oxidation of sulfoxide or ssulfides;³ (b) cross-coupling reactions of sulfinate salts with aryl haildes under transition-metal-catalyzed conditions;⁴ (c) difunctionalization of alkynes and alkenes with sulfinate salts or sulfinic acids;⁵ (d) sulfur dioxide fixation with a SO₂ surrogate;⁶ (e) sulfonyaltion of arenes via a Friedel–Crafts-type pathway.⁷ These methods are successful; however, the use of foul-smelling sulfides or sulfoxides, strong oxidants, and harsh reation conditions can

limit their wide applications, which thus stimulates chemists to search for more efficient and practical processes.

Recently, tremendous progress has been made in the field of photocatalytic organic transformations since it provides a green and sustainable means for building carbon-heteroatom and carbon-carbon bonds.8 In this respect, diverse and efficient photocatalysts, including transition metal complexes based on iridium(III) and ruhenium(II), and organic dyes, have been extensively developed.9 Nevertheless, most of these photocatalysts still have some drawbacks, such as potential toxicity, high cost, the scarity of the metal salts, and lower photostability, which might impede their wide applications. Therefore, copper complexes are gaining more attention for visiblelight-promoted transformations. Copper complexes, especially copper-phenanthroline derivatives, usually have long excited state lifetimes and strong photoexcited reducing ability and also tend to undergo structural redistribution and ligand exchange which provide unique reaction pathways.¹⁰ In addition to being an economically attractive alternative to iridium or ruthenium photocatalysts, Cu¹ complexes also have a special role in facilitating electron transfer to organic substrates. In 2012, Hwang et al. initially developed an efficient CuCl-catalyzed, visible-light-induced Sonogashira cross-coupling reaction under mild conditions (Scheme

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1a).¹¹ Since the pioneering work by the Hwang group, visiblelight-promoted copper catalyst systems have been extensively

Scheme 1. Strategies for the Copper-Catalyzed Coupling Reactions under Visible-Light Conditions



studied. In the past few years, a large number of copper(I) complexes have been studied as visible light catalysts.¹² For instance, Fu's group demonstrated a green and efficient visiblelight-induced enantioselective C-N cross-coupling using a copper complex as the precursor of the photocatalyst (Scheme 1b).¹³ In 2018, Lalic and co-workers reported a mild coppercatalyzed visible-light-promoted alkylation of terminal alkynes with alkyl iodides (Scheme 1c).¹⁴ Very recently, Zhang et al. described an efficient visible-light-induced, copper-catalyzed asymmetric alkylation of azoles (Scheme 1d).¹⁵ The key step in the transformations mentioned above is the photoexcitation of the copper-nucleophile complex (LCuNu*) followed by electron transfer to an alkyl halide. It still remains a formidable challenge to establish different catalytic models for diverse organic transformations by using copper complexes as photocatalysts under visible light irradiation.

On the other hand, although great progress has been made in the area of visible-light-promoted C-S bond forming reactions, only limited examples of arylation of sulfinate salts under visible-light irradiation have been sporadically reported.¹⁶ Additionally, ultraviolet (UV) light-induced coupling of sulfinates with aryl halides was reported.¹⁷ However, these developed methods could possess some limitations, including the use of expensive and toxic Ir/Ru organometallic complexes, bases, and high-energy UV irradiation. Therefore, there is still ample room for innovation, and the development of alternative visible-light promoted strategies for the construction of organosulfones as supplements to the existing methods still remains very attractive. As a part of our continuing interest in photochemical transformations,¹⁸ we herein disclose a visiblelight-promoted method for the synthesis of organosulfones from aryl halides and sulfinate salts using [(BINAP)Cu-(NCMe) [PF₆] generated in situ as the photocatalyst under mild conditions (Scheme 1d).

Initially, we selected 4-bromoacetophenone (1a) and sodium 4-methylbenzenesulfinate (2a) as the coupling partners to explore the optimized reaction conditions (Table 1).





^{*a*}Reaction condions: **1a** (0.3 mmol), **2a** (0.45 mmol), [Cu-(CH₃CN)₄PF₆] (10 mol %), ligand (15 mol %), Cs₂CO₃ (0.6 mmol) and degassed DMSO (2 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 16 h. ^{*b*}The yields were determined by ¹H NMR with CH₂Br₂ as an internal standard. ^{*c*}**1a/2a** = 1:3. ^{*d*}No light.

Delightedly, a 30% yield of cross-coupling product **3a** was obtained in the presence of 10 mol % $Cu(CH_3CN)_4PF_6$, 15 mol % 2,2'-dipyridyl (**A**), and Cs_2CO_3 in DMSO at room temperature for 16 h under an irradiation of visible light with a 20 W blue LED (455 nm). Next, other ligands, bases, and solvents were also investigated (see Table S1 in the Supporting Information (SI) for the details). According to the results from optimization of the reaction conditions, we determined that $Cu(CH_3CN)_4PF_6$ as the catalyst, BINAP as the ligand, and DMSO as the solvent are suitable in the present photocatalytic sulfonylation pathway.

After obtaining the optimized conditions, the substrate scope of this sulfonylation transformation was explored (Scheme 2). To our delight, diverse aryl halides smoothly reacted with various sulfinates, delivering the desired organosulfones in moderate to good yields. For this photocatalytic system, the aryl iodides possessing electron-withdrawing functional groups generally have higher reactivity, while those bearing electron-donating ones generally have lower



Scheme 2. Substrate Scope of Aryl halides with Sulfinates^{*a,b*}

^{*a*}Reaction condions: **1** (0.2 mmol), **2** (0.6 mmol), [Cu- $(CH_3CN)_4PF_6$] (10 mol %), BINAP (15 mol %), and degassed DMSO (2 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 16 h. ^{*b*}Isolated yield. ^{*c*}At 60 °C.

reactivity (3g-3i). In addition, the investigated compounds did not have an obvious steric effect; aryl halides bearing formyl or cyano groups at different positions reacted with sulfinates to afford the desired products (3f, 3g, 3q, and 3v) smoothly. Other heteroaryl halides such as 2-bromopyrimidine and 3-iodoquinoline were tested. Satisfactorily, these substrates also gave sulfonylated products 3w, 3ac, and 3ah in 46-90% yield. Notably, heteroaryl sulfinates including sodium pyridine-3-sulfinate and sodium thiophene-2-sulfinate were also examined, which delivered the cross-coupling products (3x, 3y, 3z, 3aa, 3af, and 3ag) in moderate yields. It should be noted that the aryl sulfinates show higher reactivity than the alkyl ones (3an and 3ao). In addition, vinyl bromides could also be applied in our developed photocatalytic conditions (3aj and 3ak). Furthermore, other nucleophiles including 4methylbenzenethiol, p-tolylmethanamine, p-cresol, p-tolylmethanol, and p-toluidine were also tested under the standard conditions. Unfortunately, no desired products were observed (see the SI for details). Diverse functional groups such as aldehyde, methoxy, cyano, methyl, and ester were compatible in the visible-light conditions.

A gram-scale synthesis of 3a using 4-bromoacetophenone (1a) and sodium 4-methylbenzenesulfinate (2a) was performed (Scheme 3a). Under the standard conditions, the desired product 3a was constructed in 81% yield (5.0 mmol scale). In addition, this protocol could be applied to the postmodification of biologically related molecules. As shown in Scheme 3b, an L-menthol derivative 1h could be transformed

Scheme 3. Synthetic Applications



to the desired sulfonylated products **3ap** and **3aq** in moderate yields.

In order to verify the role of the Cu¹-based photocatalyst, the copper complex (6) was synthesized according to the previous literature.¹⁹ Then, this copper catalyst (6) was then applied in place of the combination of $Cu(MeCN)_4PF_6$ and BINAP as the photocatalyst for the sulfonylation transformation. To our delight, the desired product (3a) was obtained in almost the same yield as that under the standard conditions (Scheme 4).

Scheme 4. Control Experiments



However, treatment of the copper complex (6) with sodium 4methylbenzenesulfinate (2a) did not afford the LCuNu complex (7) (see the SI for detail). These preliminary experimental results showed that this Cu^{I} photocatalyst generated in situ was the active photocatalyst in the present transformation.

To further illuminate the photoreactivity of the Cu^I photocatalyst, we measured the UV/vis absorptions of the in situ formed [(BINAP)Cu(NCMe)]PF₆], as well as other components in the reaction system, such as **1a**, **2a**, Cu-(CH₃CN)₄PF₆, BINAP, and their combination (Figure 2a; see the SI for details), respectively. [(BINAP)Cu(NCMe)]PF₆] and the in situ generated [Cu(CH₃CN)₄PF₆ + BINAP] showed almost the same absorption circumstances which extended into the visible region. For **1a**, **2a**, Cu(CH₃CN)₄PF₆, and BINAP, the absorptions all had wavelengths of <300 nm.

To further understand the redox states of the Cu^I photocatalyst that might be involved in this photocatalytic sulfonylation process, mechanistic studies by EPR spectroscopy were performed. When 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), a well-known free radical spin-trapping agent, was added to the solution of $Cu(CH_3CN)_4PF_{60}$, BINAP, and 1a,



Figure 2. (a) Fluorescence quenching experiments. (b) EPR spectra of the DMPO-radical adduct.

obvious carbon-centered radical signals was observed (g = 2.004, AN = 1.46 mT, $A_{\rm H} = 2.24$ mT) under irradiation with 20 W blue LED (455 nm) for 5 min (Figure 2b, red line). Notably, no sulfonyl radical signal was observed in the present transformation. To our delight, a Cu(II) signal ($g_{\parallel} = 2.22$, $g_{\perp} = 2.03$) was also detected under irradiation with 20 W blue LED (455 nm) for 20 min (see Figure S16, SI). However, no radical signal was observed without light irradiation (Figure 2b, black line). These results preliminarily support the SET process between Cu^I complex and **1a**.

To investigate the mechanism further, Stern–Volmer fluorescence quenching experiments were carried out. The fluorescence intensity of the excited state of the in situ formed $[(BINAP)Cu(NCMe)]PF_6]$ was significantly reduced when the solution of 1a was added (Figure 3a). Moreover, Figure 3b



Figure 3. Fluorescence quenching experiments.

showed an obvious linear relationship between the concentrations of la and the fluorescence intensities. However, further experiments indicated that 4-methylbenzenesulfinate (2a) did not quench the fluorescence of the [(BINAP)Cu-(NCMe)]PF₆] (see the SI for details). These preliminary results indicated that the excited state of the Cu^I complex was quenched by the substrate 1a. The excited redox potential of Cu^I complex [(BINAP)Cu(NCMe)]PF₆] (-3.04 V vs Ag/ AgCl) and the reductive potential of 1a (-2.00 V vs Ag/AgCl) suggested that a single electron transfer (SET) event was presumably engaged in the present reaction. In addition, we envisioned that sodium sulfinate 2 (TsNa, E_{ox} = +1.0 V vs Ag/AgCl in CH₃CN) could not react with Cu^{II}L ([(BINAP)Cu- (CH_3CN)]PF₆], $E_{1/2} = 0.14$ V vs Ag/AgCl in CH₃CN) to give a sulfonyl radical through an SET pathway in the present system.20 An on/off experiment showed that continuous irradiation with blue light is necessary (Figure S14). Furthermore, the apparent quantum efficiency (455 nm) values (AQE) for the model reaction was calculated to be 0.14% showing that a radical-chain process might not be involved (see the SI for details).

Based on these preliminary experimental results above, a plausible reaction pathway is proposed in Scheme 5. First, the

Scheme 5. Possible Reaction Mechanism



in situ generated Cu^I complex [(BINAP)Cu(NCMe)]PF₆] was excited by visible light irradiation leading to the excited species CuL*. Next, an SET process from the excited species CuL* to aryl halides afforded the radical anion I and LCu^{II} species. Fragmentation of Ar–X^{•–} (I) gave the aryl radical II, which subsequently reacted with the Cu^{II} complex to produce Ar–Cu^{III} intermidate III. Then, the intermidate III reacted with sulfinates through a ligand exchange process to furnish intermidate IV. Finally, reductive elimination of IV would afford the sulfones 3 and regenerated the catalytic species LCu^{II}.

In conclusion, we have successfully disclosed an elegant visible-light-promoted, copper-catalyzed sulfonylation of aryl halides with sulfinates. This method has demonstrated mild conditions and a broad substrate scope. A series of organosulfones can be effectively obtained in moderate to good yields with good functional group tolerance. In addition, satisfactory results were also obtained in gram scale experiments. We anticipate that the current strategy can provide more insights to design a copper complex for visible-light promoted organic transformations. Further studies to determine the mechanistic details of this process and to expand the applications of this synthetic strategy are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01050.

General experimental procedures, mechanistic experiments, and compound characterization data, including the ${}^{1}\text{H}/{}^{13}\text{C}$ NMR spectra, and HRMS date spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

 Daoshan Yang – Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China;
 orcid.org/0000-0002-3047-5416; Email: yangdaoshan@ tsinghua.org.cn

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Authors

- Qiuli Yan Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China
- Wenwen Cui Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China
- Xiuyan Song Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China
- Guiyun Xu Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China
- Min Jiang College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, P. R. China
- Kai Sun College of Chemistry and Chemical Engineering, YanTai University, Yantai 264005, P. R. China; orcid.org/0000-0002-0041-6044
- Jian Lv Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China;
 orcid.org/0000-0001-7641-5411

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c01050

Notes

The authors declare no competing financial interest.

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