

Selective C–S Bond Constructions Using Inorganic Sulfurs via Photoinduced Electron Donor–Acceptor Activation

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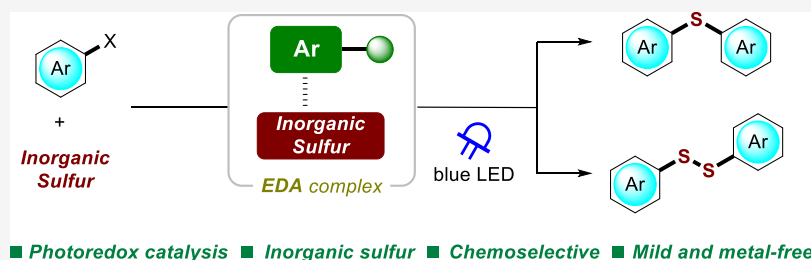
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ABSTRACT: By complementing traditional transition metal catalysis, photoinduced catalysis has emerged as a versatile and sustainable way to achieve carbon–heteroatom bond formation. This work discloses a visible-light-induced reaction for the formation of a C–S bond from aryl halides and inorganic sulfuration agents via electron donor–acceptor (EDA) complex photocatalysis. Divergent formations of organic sulfide and disulfide have been demonstrated under mild conditions. Preliminary mechanistic studies suggest that visible-light-induced intracomplex charge transfer within the monosulfide-anion-containing EDA complex permits the C–S bond construction reactivity.

INTRODUCTION

Aryl sulfides and disulfides are prevalent in a wide range of bioactive natural products¹ and pharmaceuticals,² including Lissoclibadin 7,^{1b} Arbidol,^{1d} and Vortioxetine^{2g} (Scheme 1A). Furthermore, aromatic sulfides and disulfides are also valuable architectures in drug development,³ organic materials,⁴ and polymers.⁵ Therefore, the development of environmentally friendly methods for constructing a C–S bond is of significant importance with a broad impact across the areas of small-molecule synthesis and materials.

Traditionally, active organosulfur reagents are required to synthesize aryl sulfides using the following two main strategies (Scheme 1B): (a) Transition-metal-catalyzed coupling⁶ of aryl halides, arylboronic acids, or other active metal reagents with thiophenols, disulfides, or functionalized sulfurs. The use of precious metals, strong bases, or high temperature is generally indispensable for these protocols. (b) Photoinduced C–S bond formation has become a powerful strategy for the development of aryl sulfide construction under mild conditions.⁷ However, most of these organic sulfuration agents need to be prepared in advance from inorganic sulfuration agents. Moreover, some of them are easily oxidized or deactivate the transition metal catalysts.

As clean and sustainable sulfur sources, inorganic sulfuration agents ($\text{Na}_2\text{S}_2\text{O}_3$, KSCN, AcSK, etc.) have been developed for aryl sulfide synthesis under transition metal catalysis (Scheme 1C).⁸ However, some inherent issues, such as expensive

transition metal catalysts or substrates presynthesis still exist. Moreover, visible-light-driven methods using inorganic sulfuration agents still remain underdeveloped. Therefore, the development of more environmentally friendly and more atom-economical methods is still in great need. As our ongoing interest in photocatalysis,⁹ we herein developed visible-light-induced C–S bond construction by employing inorganic sulfides as both a donor of an EDA complex and a sulfur donor. Through simple control of the type of sulfides and the photoredox catalyst, (hetero)aryl halides were selectively transformed into (hetero)aryl sulfides and (hetero)aryl disulfides in high efficiency (Scheme 1D). Notably, these divergent C–S bond formations also feature abundant starting materials, mild conditions, and transition metal free and scalable preparation.

RESULTS AND DISCUSSION

Initially, we commenced our investigations by exploring visible-light-induced direct C–S bond construction between 4-bromobenzonitrile **1a** and Li_2S . In the absence of a photoredox

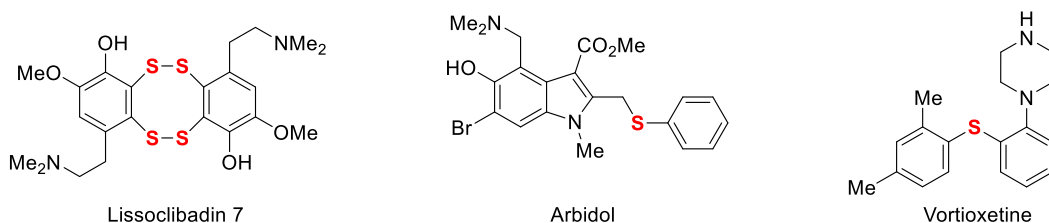
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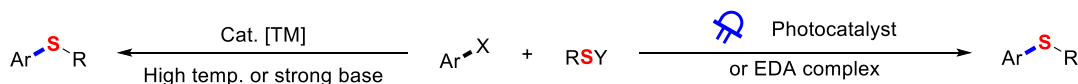


Scheme 1. Representative Sulfur-Containing Bioactive Compounds and Classic Methods for the Formation of Aryl Sulfides

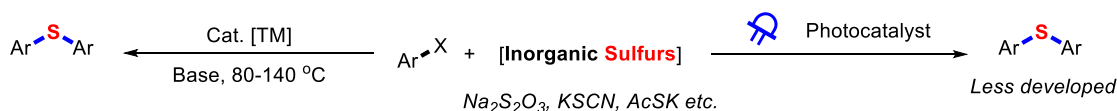
A | Sulfur-containing bioactive compounds



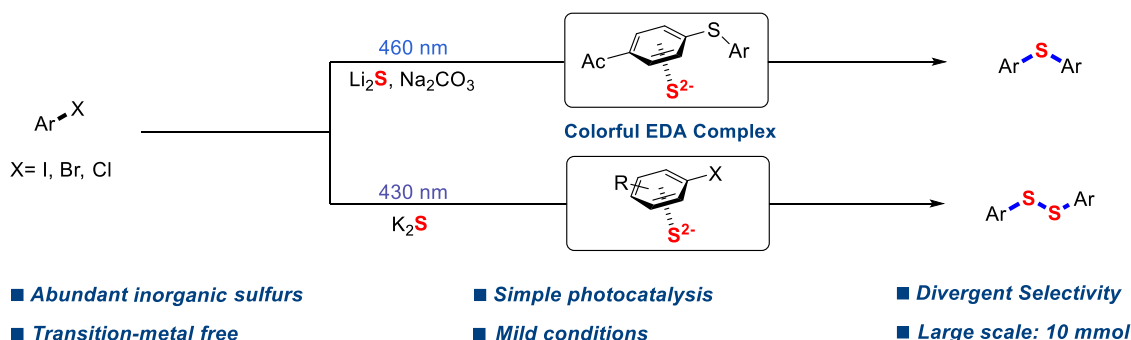
B | C-S bond constructions from organic sulfuration agents



C | C-S bond constructions from inorganic sulfuration agents



D | This work: photocatalytic C-S constructions from inorganic sulfurs



catalyst, the reaction mixture containing 4-bromobenzonitrile **1a** and Li_2S under blue LEDs (440 nm) irradiation did not give any desired product **2a** at room temperature (Table 1, entry 1). The evaluation of photoredox catalysts (entries 2–6) suggested that simple aryl sulfide **PC3** was the best choice for the formation of sulfide **2a** with respect to yields (entry 4). A decrease in yields of **2a** was observed when using Na_2S or K_2S instead of Li_2S (entries 7–8). Cheaper Na_2CO_3 emerged as the optimal base for this transformation (entries 9–10). The reactivity was maintained with lower catalyst loading (entries 11 vs 10). The irradiation with longer wavelength blue LEDs (460 nm) resulted in an excellent yield (entries 13 vs 11–12).

The optimization of less developed aryl disulfide synthesis was subsequently carried out to divert the chemoselectivity (Table 1, entry 8). Replacement of 4-bromobenzonitrile **1a** with 4-bromoacetophenone **1b** significantly improved the outcome delivering the aryl disulfide product **3b** in a moderate yield (entry 14). The control experiments revealed that desired product **3b** was also obtained with a better yield and chemoselectivity (3/2) in the absence of the organic photoredox catalyst and the base when 3.0 equiv of K_2S was used (entries 16 vs 14–15).

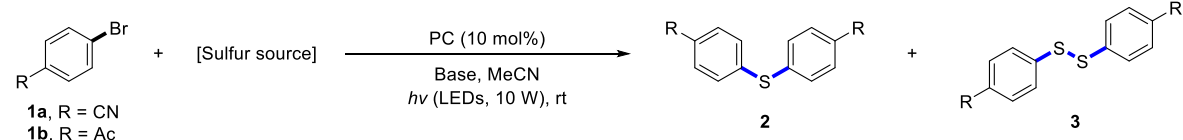
Having optimized the reaction conditions, the substrate scope of this visible-light-induced thioetherification was first inves-

tigated (Scheme 2a). Reactions of benzonitrile with *para*-halide substituents provided excellent yields of the aryl sulfide **2a** (83–87%). The aryl halides with some sensitive groups, such as CHO , CO_2R , and NO_2 at the *para*-position of the phenyl ring, all could be performed smoothly and gave the desired products in moderate to good yields (**2c–2f**, 53–83%). In addition, these sensitive groups at the *meta*- or *ortho*-position of aryl halides **1** were also well tolerated to deliver the corresponding sulfides (**2g–2l**) in 32–62% yields. In contrast, the electron-donating methyl group on the phenyl ring was not applicable to this transformation (**2m**). Notably, several heterocyclic aryl halides were feasible to afford the desired products with up to a 97% yield (**2n–2r**).

Next, we further assessed the visible-light-induced preparation of aryl disulfide transformation (Scheme 2b). The *para*-haloacetophenone, including bromo and iodo, could provide **3b** in decent yields. The nitril on different positions of the substrate could be compatible in this reaction as well (**3c–3e**). It was observed that substituents at the *meta*- or *ortho*-position gave slightly decreased yields. In addition, the aryl aldehyde substrates could be readily converted to the corresponding disulfides in moderate yields (**3f**, **3g**).

To gain insight into the reaction mechanism of the photoinduced sulfuration process, several control experiments

Table 1. Optimization for the Formation of Aryl Sulfides and Disulfides^{abc}

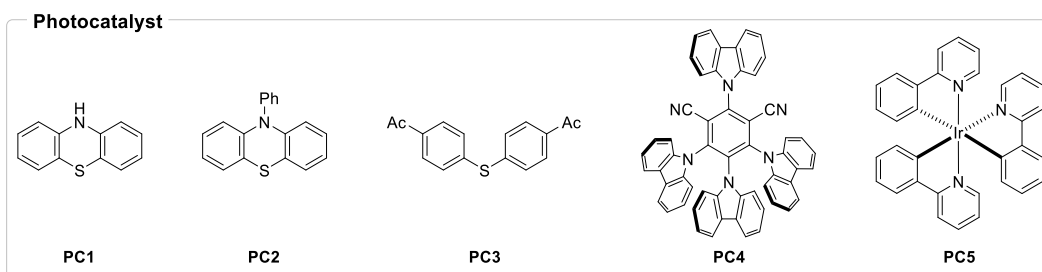


1a, R = CN
1b, R = Ac

2

3

Entry	1	PC (mol%)	[S] (equiv.)	Base (2.0 equiv.)	LED (nm)	Yield of 2 (%)	Yield of 3 (%)
1	1a	--	Li ₂ S (1.0)	Cs ₂ CO ₃	440	N.D.	N.D.
2	1a	PC1 (10)	Li ₂ S (1.0)	Cs ₂ CO ₃	440	10	N.D.
3	1a	PC2 (10)	Li ₂ S (1.0)	Cs ₂ CO ₃	440	39	N.D.
4	1a	PC3 (10)	Li ₂ S (1.0)	Cs ₂ CO ₃	440	46	N.D.
5	1a	PC4 (10)	Li ₂ S (1.0)	Cs ₂ CO ₃	440	2	N.D.
6	1a	PC5 (2)	Li ₂ S (1.0)	Cs ₂ CO ₃	440	43	N.D.
7	1a	PC3 (10)	Na ₂ S (1.0)	Cs ₂ CO ₃	440	40	N.D.
8	1a	PC3 (10)	K ₂ S (1.0)	Cs ₂ CO ₃	440	33	2
9	1a	PC3 (10)	Li ₂ S (1.0)	K ₂ CO ₃	440	44	N.D.
10	1a	PC3 (10)	Li ₂ S (1.0)	Na ₂ CO ₃	440	72	N.D.
11	1a	PC3 (5)	Li ₂ S (1.0)	Na ₂ CO ₃	440	72	N.D.
12	1a	PC3 (5)	Li ₂ S (1.0)	Na ₂ CO ₃	405	56	N.D.
13	1a	PC3 (5)	Li ₂ S (1.0)	Na ₂ CO ₃	460	91(87) ^c	N.D.
14 ^b	1b	PC3 (10)	K ₂ S (3.0)	K ₂ CO ₃	430	18	61
15 ^b	1b	--	K ₂ S (3.0)	K ₂ CO ₃	430	19	60
16 ^b	1b	--	K ₂ S (3.0)	--	430	18	67(65) ^c

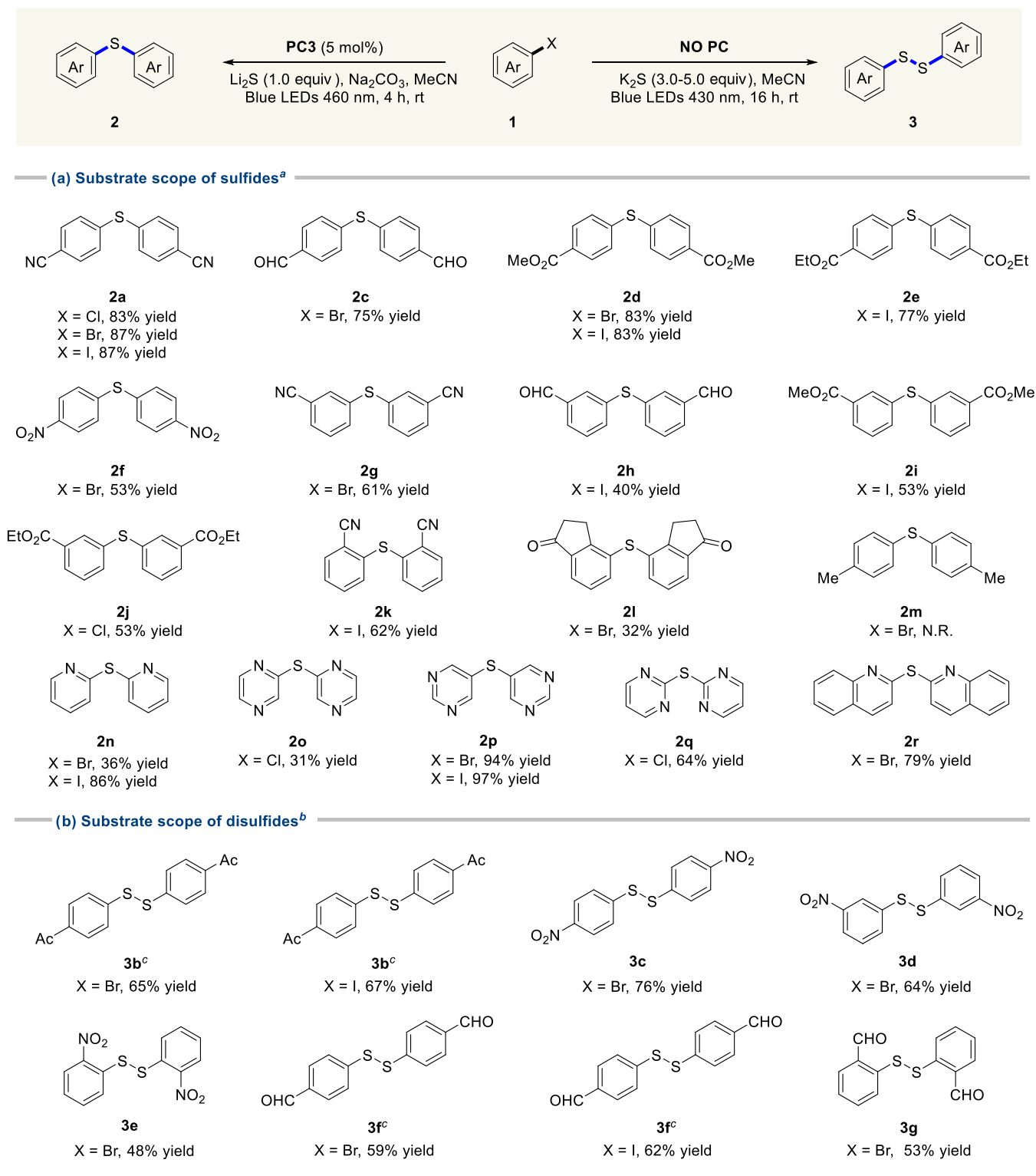


^aConditions: 1a (0.20 mmol), [S] (0.10 mmol), PC (10 mol%), base (0.20 mmol), MeCN (1.0 mL), 440 nm LED, 10 W, N₂ atmosphere, rt, and 4 h. Yields were determined by ¹H NMR analysis of the crude reaction mixture. ^bConditions: 1b (0.10 mmol), [S] (0.30 mmol), PC (10 mol%), MeCN (1.0 mL), 430 nm LED, 10 W, N₂ atmosphere, rt, and 16 h. Yields were determined by ¹H NMR analysis of the crude reaction mixture. ^cIsolated yield.

were performed (Scheme 3). When 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was added to the model reaction, an aryl radical was captured by TEMPO with only a trace amount of target product 2a could be detected (Scheme 3a). The addition radical suppressed experiment with butylated hydroxytoluene (BHT) further supports that a radical process is probably involved in the reaction (Scheme 3b). Ultraviolet–visible (UV–vis) spectroscopic measurements on various combinations of 1f, PC3, and Li₂S in MeCN were performed to figure out the active photo-responded species (Scheme 3c). It shows that there was no strong light absorbance for the solution of 4-bromoni-

trobenzene 1f (I) or PC3 (II). The mixture of aryl halide 1f or PC3 with Li₂S in the presence of Na₂CO₃ showed significant visible-light absorptions (IV and V). It is believed that Li₂S could trigger this reaction through the formation of the EDA complex, which induces the single-electron transfer (SET) upon the irradiation of visible light to produce radical ion pairs.¹⁰ In addition, the hypothetical benzenethiol intermediate 4-nitrobenzenethiol 1f' (III) shows a small absorption band, while the mixture of PC3-1f'-Na₂CO₃ (VI) or 1f-1f'-Na₂CO₃ (VII) exhibited an obvious increase in visible-light absorption. These

Scheme 2. Substrate Scope of Sulfides and Disulfides



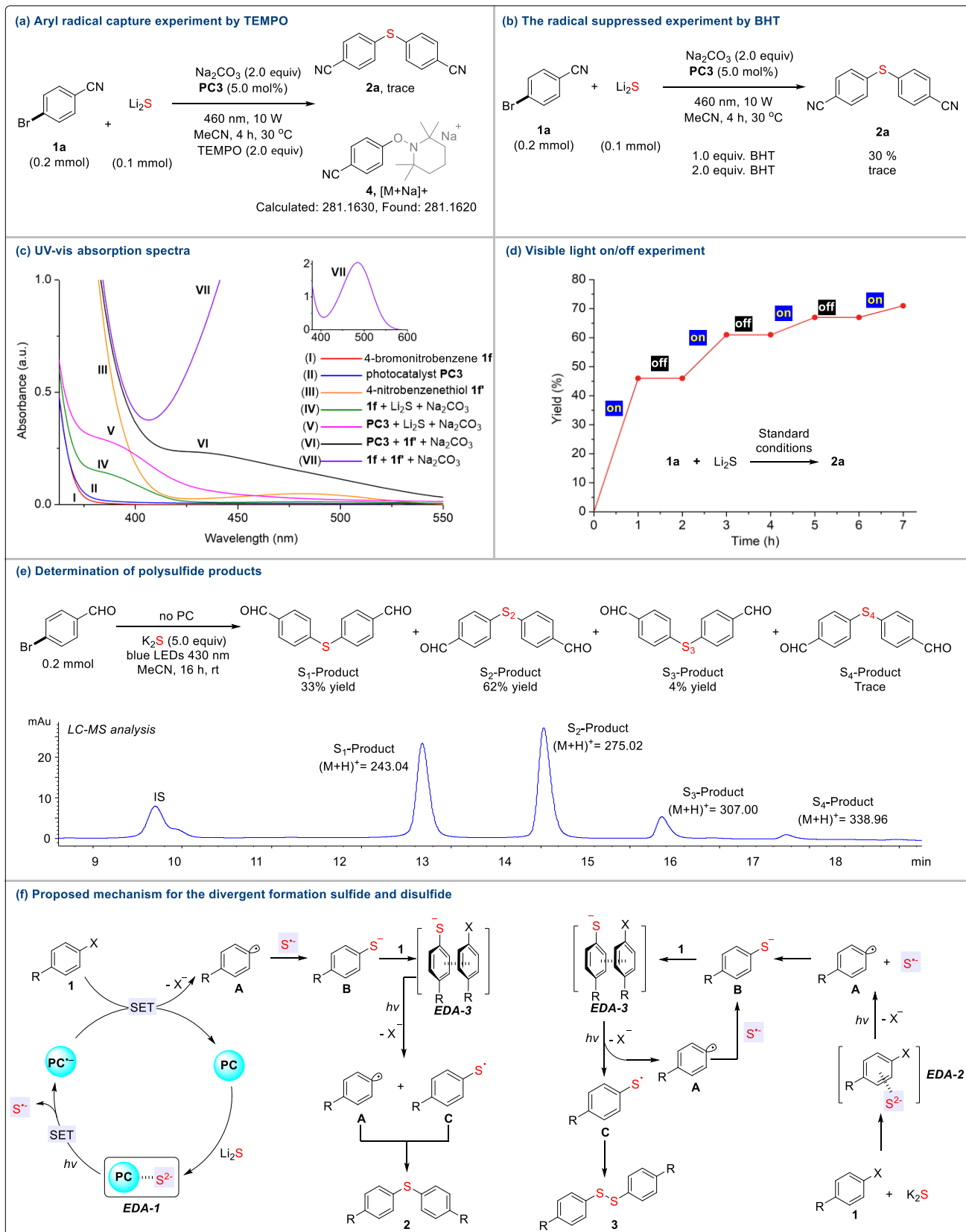
^aConditions: **1** (0.20 mmol), Li_2S (0.10 mmol), **PC3** (5.0 mol%), Na_2CO_3 (0.20 mmol), MeCN (1.0 mL), 460 nm LEDs (10 W), N_2 atmosphere, rt, and 4 h. An isolated yield was given. ^bConditions: **1** (0.10 mmol), K_2S (0.30–0.50 mmol), MeCN (3.0 mL), 430 nm LEDs (10 W), N_2 atmosphere, rt, and 16 h. An isolated yield was given. ^cAccompanied by a small amount of inseparable corresponding sulfide **2**; the yield of the product has been adjusted accordingly.

significant absorptions are probably derived from the charge transfer of newly formed EDA complexes.

The reactivity profile of this protocol was obtained from visible light on/off control experiments (Scheme 3d). It is found

that constant light irradiation is essential for the formation of the desired product. Besides sulfide and disulfide products, trace amounts of trisulfide and tetrasulfide products were also observed when 4-bromobenzaldehyde was subjected to the

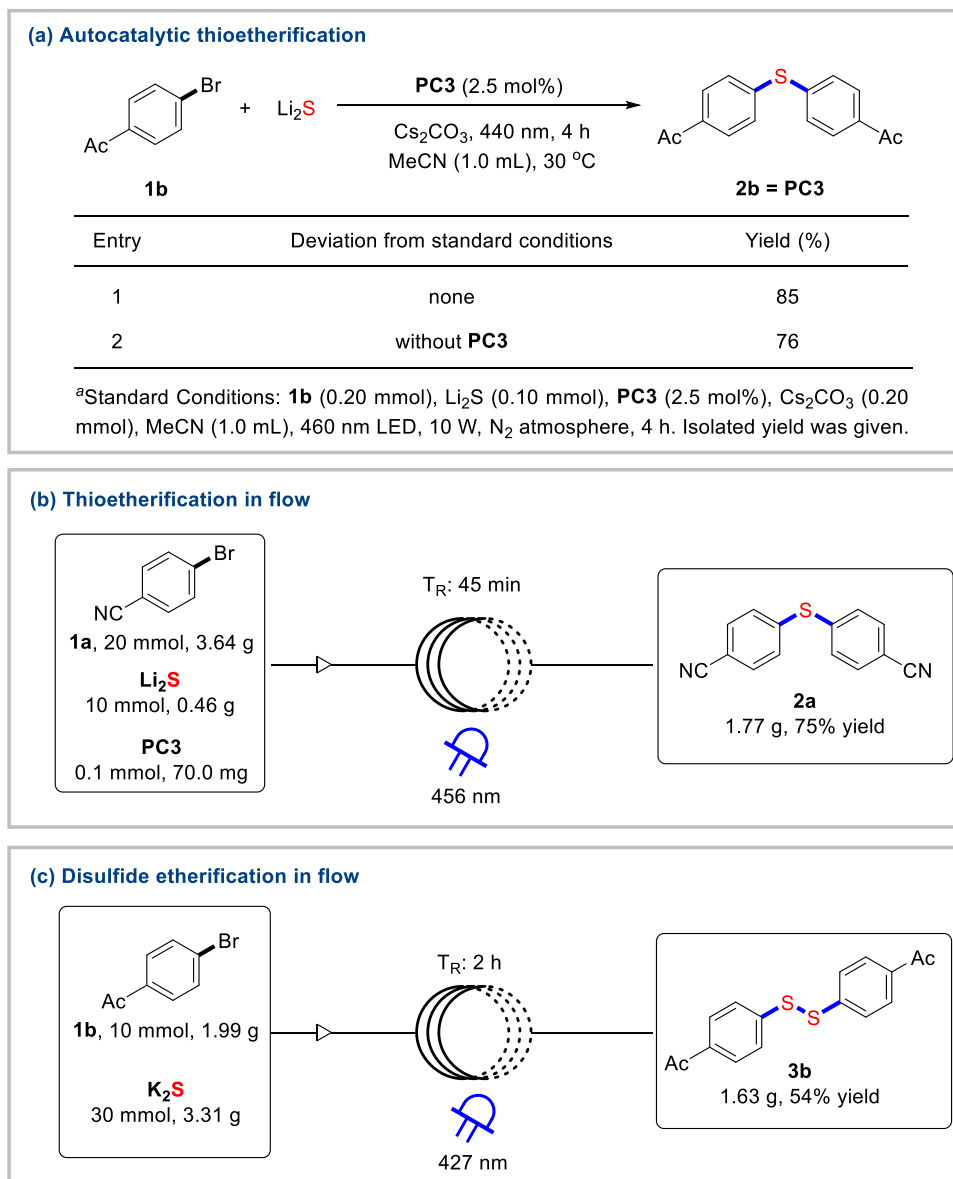
Scheme 3. Mechanistic Investigations and the Proposed Mechanism



visible-light-induced process with 5.0 equiv of K_2S . It suggested that a monosulfide anion radical might be transformed to polysulfides subsequently (Scheme 3e).^{7h,11}

Based on the aforementioned mechanistic studies, a proposed mechanism for visible-light-induced C–S bond construction is shown in Scheme 3f. In the presence of external photocatalyst PC, an association of electron-rich anion S^{2-} with electron-poor

Scheme 4. Autocatalytic Thioetherification and the Photoinduced Scale-Up Reaction in Flow



^aStandard Conditions: **1b** (0.20 mmol), Li_2S (0.10 mmol), **PC3** (2.5 mol %), Cs_2CO_3 (0.20 mmol), MeCN (1.0 mL), 460 nm LED, 10 W, N_2 atmosphere, and 4 h. An isolated yield was given.

PC forms aggregate **EDA-1**. Irradiation of the **EDA-1** complex under the blue LED triggers an intracomplex electron transfer from anion S^{2-} to **PC**, generating monosulfide radical anion $\text{S}^{\bullet-}$ and radical anion $\text{PC}^{\bullet-}$. A subsequent single-electron reduction of aryl halide **1** by the resulting reductant $\text{PC}^{\bullet-}$ promotes the generation of aryl radical **A** and regenerates photocatalyst **PC**. The transient radical **A** could couple with monosulfide radical anion $\text{S}^{\bullet-}$ to form thiolate anion **B**. Based on Miyake's C–S cross-coupling study^{7b} and the significant absorption of **1f-1f'**- Na_2CO_3 (**VII**), it is feasible to propose that the association of thiolate anion **B** with aryl halide **1** could form **EDA-3**. Subsequently, photoexcitation of the **EDA-3** complex gives rise to thiyl radical **C** and aryl radical **A** via a SET process. The coupling of the resulting thiyl radical **C** with aryl radical **A** produces target aryl sulfide **2**.

In the absence of external photocatalyst **PC**, monosulfide anion S^{2-} of K_2S associates with aryl halide **1** to generate **EDA-2** in the ground state. The visible-light-induced intracomplex SET

event of the **EDA-2** complex produces aryl radical **A** and monosulfide radical anion $\text{S}^{\bullet-}$.^{7h} A subsequent radical coupling of each other produces thiolate anion **B**. Similarly, aryl halide **1** could interact with thiolate anion **B** to generate the **EDA-3** complex and undergo another SET process to form aryl radical **A** and thiyl radical **C**. Aryl radical **A** could be captured by monosulfide radical anion $\text{S}^{\bullet-}$ to yield thiolate anion **B**. A final self-quench of two molecules of thiyl radical **C** produces the desired aryl disulfide **3** product. In general, it is supposed that the photocatalyst might interact more easily with Li_2S than K_2S to achieve selective thioetherification, while the excess K_2S is more feasible to interact with substrate aryl halides to generate thiyl radical **C** to produce disulfide products.

Inspired by the catalyst-free synthesis of aryl disulfides, we found that photocatalyst **PC3** could be easily accessed from the coupling of 4-bromoacetophenone **1b** and Li_2S under autocatalysis (Scheme 4a). When the visible-light-induced reaction was carried out under standard conditions, the target

product obtained an 85% yield (entry 1). Furthermore, only a slight decrease in the product yield of PC3 was observed under photocatalyst-free conditions (entry 2).

To further test the scalability of these protocols, the photoinduced C–S bond constructions have been demonstrated in flow. The reaction between 1a and Li₂S was efficiently promoted in a homogeneous system using PC3 as a photoredox catalyst in an operationally simple microtubing continuous-flow reactor. Desired product 2a was obtained in a 75% yield (1.77 g) with 45 min as the residence time (Scheme 4b). Disulfide 3b could also be produced in the same flow reactor in a 54% yield (1.63 g) with 2 h as the residence time (Scheme 4c).

CONCLUSIONS

In summary, a mild and efficient visible-light-induced protocol has been developed for C–S bond constructions without the use of a transition metal catalyst. This strategy uses sustainable and readily available Li₂S or K₂S as both the sulfuration agents and the trigger for photocatalysis. The UV–vis spectroscopic measurements suggest the formation of a key EDA complex between the monosulfide anion and aryl halide with an electron-withdrawing group. Photoexcitation of the EDA complex by visible light is the key process to promoting intracomplex electron transfer. Moreover, the scalability of these protocols has been demonstrated in flow. Overall, the current strategy could act as an important complement to traditional approaches to the preparation of useful aryl sulfides and disulfides.

EXPERIMENTAL SECTION

General Procedure for the Photoinduced Synthesis of Aryl Sulfides. To an oven-dried 4 mL borosilicate glass vial, aryl halides 1 (0.2 mmol, 2.0 equiv), lithium sulfide (0.1 mmol, 1.0 equiv), PC3 (0.005 mmol, 5.0 mol %), Na₂CO₃ (0.2 mmol, 2.0 equiv), and MeCN (1.0 mL) were added in a nitrogen glovebox. The vial was capped with a septum and wrapped with parafilm. The reaction mixture was stirred for 4 h and positioned approximately 4 cm from a visible-light source (WATTCAS WP-TEC-1020HSL, λ = 460–465 nm, 10 W, irradiation temperature maintained between 25 and 30 °C). After the reaction was completed, the crude product was neutralized with an acetic acid solution (2% v/v) and extracted with ethyl acetate–water. The organic layer was washed with a brine solution and dried over anhydrous Na₂SO₄. The removal of the organic solvent in a vacuum rotavapor followed by flash silica gel column chromatographic purification (hexane/ethyl acetate) afforded the desired product.

General Procedure for the Photoinduced Synthesis of Aryl Disulfides. To an oven-dried 4 mL borosilicate glass vial, aryl halides 1 (0.1 mmol, 1.0 equiv), potassium sulfide (0.3–0.5 mmol, 3.0–5.0 equiv), and MeCN (3.0 mL) were added in a nitrogen glovebox. The vial was capped with a septum and wrapped with parafilm. The reaction mixture was stirred for 16 h and positioned approximately 4 cm from a visible-light source (WATTCAS WP-TEC-1020HSL, λ = 430–435 nm, 10 W, irradiation temperature maintained between 25 and 30 °C). After the reaction was completed, the crude product was extracted with ethyl acetate–water. The organic layer was washed with a brine solution and dried over anhydrous Na₂SO₄. The removal of the organic solvent in a vacuum rotavapor followed by flash silica gel column chromatographic purification (hexane/ethyl acetate) afforded the desired disulfide product.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.2c01750>.

Experimental procedures; characterization data; spectroscopic data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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