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Visible-light-promoted photoredox synthesis of thioacetylenes by dehydrogenation coupling of thiophenols and alkynes

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Herein, by applying visible-light photoredox catalysis, we achieved the first example of catalytic dehydrogenative coupling of thiophenols and alkynes for the synthesis of thioacetylenes at room temperature under mild reaction conditions. The advantages of our catalytic system mainly lie in the use of air instead of atmospheric oxygen with photoredox catalysis at room temperature.

Introduction

Aromatic sulfur-containing compounds are commonly found in natural products, bioactive molecules,[1] pharmaceutical molecules,[2,3] organic materials[4] and polymers.[5] Therefore, constructing C–S bonds using environmentally friendly and atomically economical synthetic methods is of great significance.[6–8] In traditional transition metal catalyzed cross-coupling reactions, a cross coupling reaction involving thiols and aryl halides is one of the effective methods for C–S bond formation.[9] However, traditional methods have shortcomings such as the use of strong bases (such as ^{t}BuONa), complex ligands that are sensitive to air and high-temperature reaction conditions as well as substrate applicability limitations such as narrow scope and poor compatibility with functional groups.[10–13] Besides, the toxicity of sulfides towards transition metals often hinders catalytic recycling, which is also a disadvantage. Correspondingly, developing a new catalytic system for C–S bond formation has become a priority for synthetic chemists, as it addresses the disadvantages of traditional methods.

Over the past decades, visible-light photoredox catalysis has emerged as a powerful synthetic approach, providing numerous possibilities for organic synthesis.[14–20] These reactions mainly focus on C–C and C–E (E = N, S, Cl, Br, Si, B, and Se) bond formation.[21–27] It should be emphasized that in the research on C–S bond formation, these methods mainly focus on C(sp^3)–S[28–33] and C(sp^2)–S bond formation,[34–38] while the C(sp)–S bond formation has been less reported.[39] Besides, in the literature on C(sp)–S bond formation for the direct synthesis of thioalkynes with thiophenols and phenylacetylenes, to the best of our knowledge, only one example using 1 atm of oxygen at 70 °C (Scheme 1A) has been reported, requiring heating conditions and strict conditions of atmospheric oxygen.[40] Consequently, the development of a milder and more convenient approach for the direct synthesis of thioalkynes with thiophenols and alkynes remains underdeveloped. Herein, we report the first example of a general dehydrocoupling of thiophenols with alkynes enabled by photoredox catalysis under visible-light irradiation to produce a series of thioalkynes (Scheme 1B).

Results and discussion

We chose ethynylbenzene (**1a**) (0.2 mmol) coupled with 4-methylbenzenethiol (**2a**) (0.4 mmol) as reactants, MeCN (1 mL) as solvent and CuBr (10 mol%) as the photoredox catalyst (see Table 1, entry 1–6 for base screening), under air conditions, with a 25 W white LED plate as the light source at room temperature. The results of our initial investigations revealed that in reactions screened using organic bases (such as TEA, DBU and DIPEA, Table 1, entries 1–3), the yields are approximately close with the product containing no more than 60% of **3a.** When it turned to Cs_2CO_3, 85% of **3a** was obtained with a relatively satisfactory yield (Table 1, entry 4), slightly higher than the K_2CO_3 with 82% yield of **3a** (Table 1, entry 5). It should be pointed out that we only got a trace amount of **3a** without base (Table 1, entry 6). With Cs_2CO_3 as the best base in hand, we turned to optimizing photocatalysts(Table 1, entry 4 and entry 7–10). With CuCl as the photocatalyst, we obtained a 75% yield of **3a** (Table 1, entry 7). Coincidentally, CuI and $Cu(OAc)_2\cdot H_2O$ had an equal catalytic effect with 60% yield of **3a** (Table 1, entry 8–9). Only 56% yield of 3a was obtained when $CuCl_2$ was used as the photocatalyst (Table 1, entry 10). Finally, the economic viability of the catalyst was under consideration, and we turned to reduce the amount of catalyst (CuBr) used (Table 1, entry 11–13), when the amount of CuBr were reduced to 1%, 2% and 5%, we obtained the yield of **3a** as 43%, 44% and 47% respectively, which were far less than 10 mol% CuBr was used, while it is worth to mention that 20 mol% CuBr as the catalyst also gave a lower result with 65% yield of **3a** (Table 1, entry 14).

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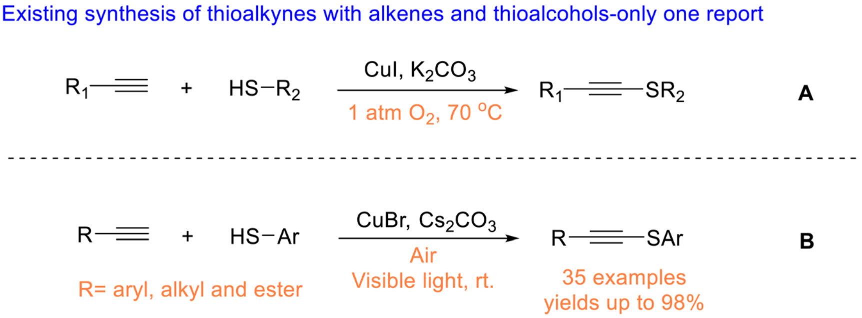
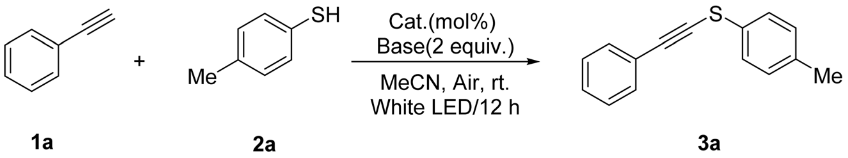


Scheme 1 (A): Synthesis of thioalkynes using a catalyst of CuI and base of K_2CO_3 with 1 atm of oxygen at 70 °C; (B): our current work using a photocatalyst of CuBr and base of Cs_2CO_3 under visible light conditions at room temperature and air atmosphere.

Table 1 Condition optimizations[a]

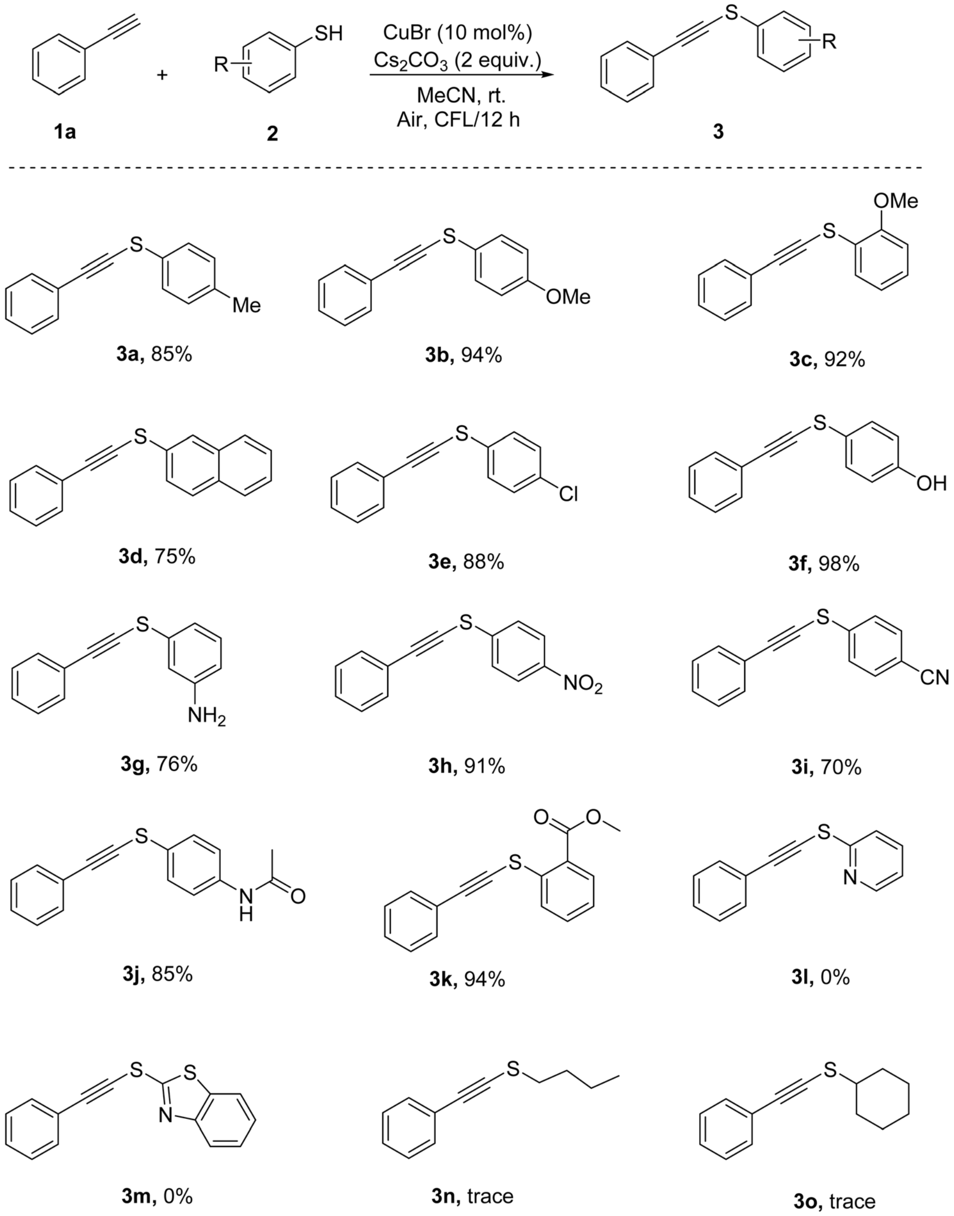


Entry	Cat.(mol%)	Base	Yield(%)[b]
1	CuBr (10 mol%)	TEA	60
2	CuBr (10 mol%)	DBU	55
3	CuBr (10 mol%)	DIPEA	58
4	**CuBr** (10 mol%)	**Cs_2CO_3**	**85**
5	CuBr (10 mol%)	K_2CO_3	82
6	CuBr (10 mol%)	None	Trace
7	CuCl (10 mol%)	Cs_2CO_3	75
8	CuI (10 mol%)	Cs_2CO_3	60
9	$Cu(OAc)_2 \cdot H_2O$ (10 mol%)	Cs_2CO_3	60
10	$CuCl_2$ (10 mol%)	Cs_2CO_3	56
11	CuBr (1 mol%)	Cs_2CO_3	43
12	CuBr (2 mol%)	Cs_2CO_3	44
13	CuBr (5 mol%)	Cs_2CO_3	47
14	CuBr (20 mol%)	Cs_2CO_3	65

[a] Reaction conditions: the reactions were performed in 25 mL vials with **1a** (0.2 mmol), **2a** (0.4 mmol), MeCN 1.0 mL and the vial was placed under air conditions with irradiation for 12 h at room temperature. [b] Yields were determined by isolation.

With the optimized reaction conditions in hand (Table 1, entry 4), we evaluated the generality of our methodology for the synthesis of various thioacetylenes. First, thiophenols with different substituents on the phenyl ring were applied in the reaction with ethynylbenzene (**1a**) (Scheme 2). In general, good to excellent yields were obtained except **3l** and **3m** with 0% yield. For example, thiophenols with 4-Me, 4-OMe, 2-OMe and naphthalene ring reacted smoothly with **1a** and afforded the corresponding thioacetylenes **3a–3d** in yields ranging from 75% to 94%, thiophenols with –OH, $-NO_2$, –CN in the para position and $-NH_2$ in the meta position of the phenyl ring, we obtained **3e–3i** in yields ranging from 70% to 98%. With an acetamide group in the para position and methylate in the ortho position of the phenyl ring, we got 85% yield of **3j** and 94% yield of **3k**, respectively. It should be pointed out that only trace amounts of **3n** and **3o** were obtained when phenylacetylene reacted with *n*-butanethiol and cyclohexanethiol, which is similar to the results for **3l** and **3m.**

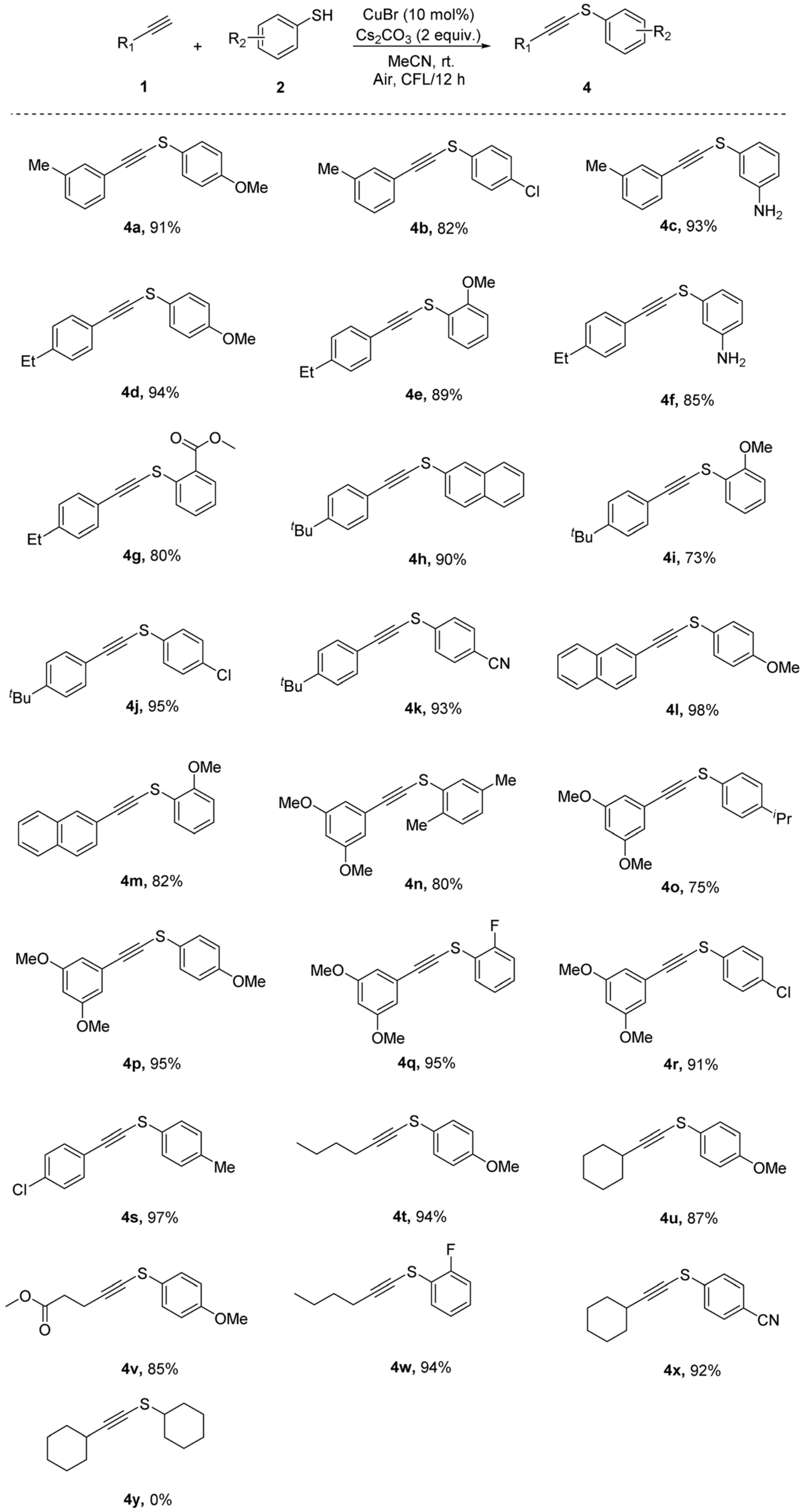
We then turned our attention to the dehydrogenative coupling of different alkynes with various thiophenols under visible-light irradiation. Firstly, –Me, –Et and –^{t}Bu of alkyl substituents on the phenyl rings at different positions of the acetylenes reacted with thiophenols, we obtained products **4a–4k** in yields ranging from 73% to 95% (Scheme 3). Subsequently, we reacted 2-ethynylnaphthalene with –OMe on the para position and ortho position of the phenyl ring at the thiophenols, we got **4l** and **4m** with yields of 98% and 82% respectively. Two-substituted benzyl acetylenes of –OMe with thiophenols, the yields of product **4n–4r** ranged from 75% to 98% with relatively satisfactory results. Next, we got 97% **4s**



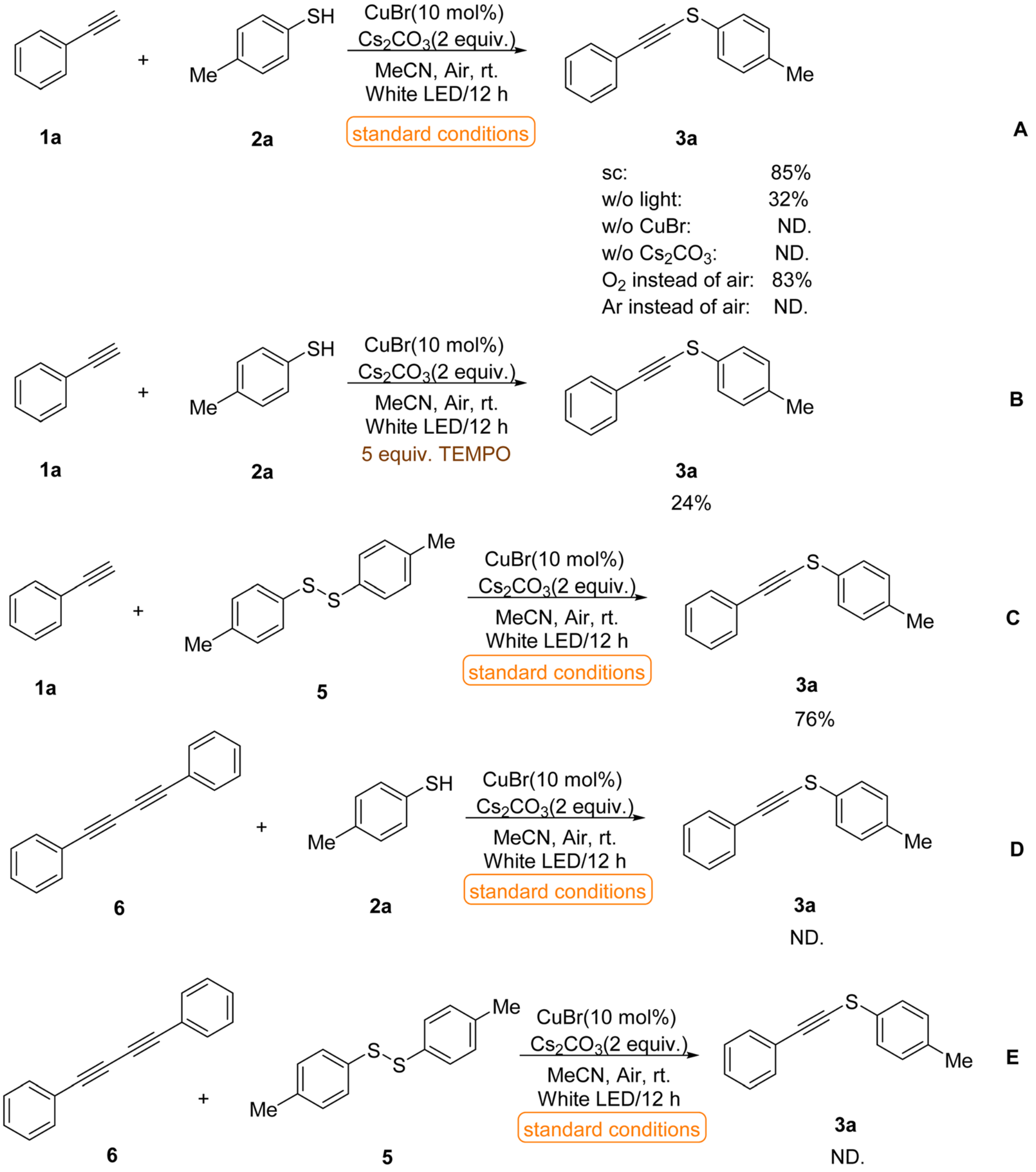
Scheme 2 Dehydrogenative coupling of ethynylbenzene with various thiophenols under visible-light irradiation: the reactions were performed in 25 mL vials with **1a** (0.2 mmol), **2** (0.4 mmol), CuBr (10 mol%), Cs_2CO_3 (0.4 mmol), MeCN 1.0 mL and the vial were placed under air conditions with irradiation for 12 h at room temperature, yields were determined by isolation.

from the reaction of 1-chloro-4-ethynylbenzene with 4-methylbenzenethiol. Finally, we have expanded the reaction between different substituted alkyl alkynes and *p*-methoxyphenylthiophenol, product **4t**, **4u** and **4v** were obtained with excellent yields: 94%, 97% and 85% yield, respectively. The reactions with 2-fluorophenylthiophenol (**2w**) and 4-cyanophenylthiophenol (**2x**) led to the desired products **4w** and **4x** in 94% and 92% yields. Regretfully and imagined, we still cannot obtain the desired product from the reaction of alkanethiol with acetylene in 0% yield of product **4y**.

To understand the reaction mechanism, we carried out several control experiments. First, we observed that the omission of light yielded a lower amount of **3a** at 32%, without CuBr or Cs_2CO_3, product **3a** was not detected, hence indicating the crucial role of light, photocatalyst and base in the reaction (Scheme 4A). In the study of the atmosphere of the reaction, when air was replaced with oxygen, we got **3a** with a similar yield, Ar instead of air; however, the product **3a** was not detected, and this indicated the key role of oxygen or oxygen in the air (Scheme 4A). Second, the addition of 5 equiv. of TEMPO to the reaction largely suppressed the reaction, with only 24% of **3a** obtained (Scheme 4B). In addition, disulfide reacted with phenylacetylene to produce **3a** in 76% yield, with a similar result compared with "standard conditions" (Scheme 4C). It should be pointed out that, no product of **3a** were detected from 1,4-diphenylbutadiyne **6** reacted with thiophenol **2a** and



Scheme 3 Dehydrogenative coupling of alkynes with various thiophenols under visible-light irradiation: the reactions were performed in a 25 mL vial with **1** (0.2 mmol), **2** (0.4 mmol), CuBr (10 mol%), Cs_2CO_3 (0.4 mmol), and MeCN 1.0 mL, and the vial were placed under air conditions with irradiation for 12 h at room temperature, yields were determined by isolation.

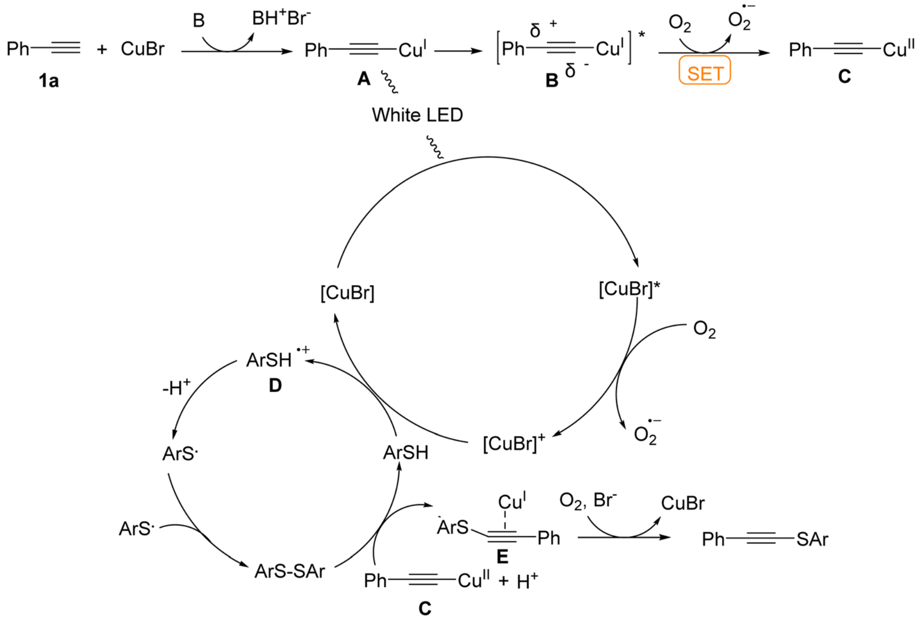


Scheme 4 Mechanism study reactions.

disulfide **5** under "standard conditions" severally (Schemes 4D and E). This might already indicated the cyclic pathway of this catalytic reaction.

Based on the above control experiments and previous reports,[20,41,42] a plausible mechanism is proposed in Scheme 5. The photo irradiation of *in situ* generated copper(I)-phenylacetylide **A** generates a long-lived triplet photoexcited copper(I)-phenylacetylide **B**. The electron donor behavior of photoexcited **B** has undergone the SET process with O_2 and results in the intermediate super oxide radical anion as well as electron-deficient copper(II) phenylacetylide **C**. [CuBr] was excited under visible light to yield its excited state species, [CuBr]*, which then undergoes a single electron transfer with benzaldehyde to yield [CuBr]$^+$ and super oxide radical anion. Then, [CuBr]$^+$ was reduced by thiophenol to regenerate [CuBr] and produce the radical cation of thiophenol **D**, which produced the S-based radical after deprotonation. Coupling of S-based radical generated ArS–SAr, which reacted with copper(II) phenylacetylide **C** and H$^+$ to generate Cu(I)-amino thiophenol complex **E** and thiophenol. Finally, complex **E** reacted with Br$^-$ and O_2 to give the C(sp)–S coupling product thioacetylenes and regeneration of CuBr (Scheme 5).

In conclusion, we have developed the first visible-light-promoted photoredox dehydrogenative coupling of alkynes with thiophenols. Our system offers the milder conditions (without atmospheric O_2 and at room temperature) for the dehydrogenative coupling of thiophenols and alkynes. Moreover, a series of thioacetylenes was successfully synthesized with



Scheme 5 Plausible reaction mechanism for photoredox dehydrocoupling of thiophenols and alkynes.

excellent yields (up to 98%) and excellent tolerance of functional groups.

Author contributions

Xianya Wang, administration of the funding project and writing the manuscript; Xun Wu, conducting the experiments; Yong Zhu and Yaowu Liu, analysis of the experimental results. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

The data supporting this article have been included as part of the SI. Supplementary information: all experimental procedures, characterization data and NMR spectra for all new compounds. See DOI: https://doi.org/10.1039/d5ra05631d.

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