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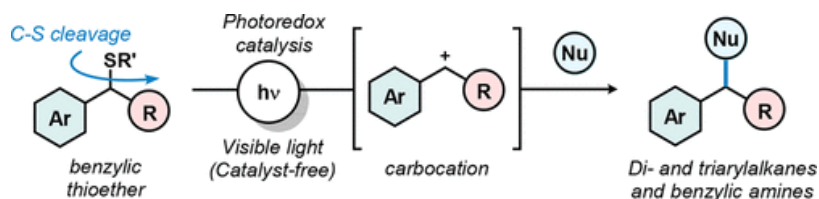
# Visible light-triggered C-C and C-N bonds formation by C-S bonds cleavage of benzylic thioethers

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## ABSTRACT:

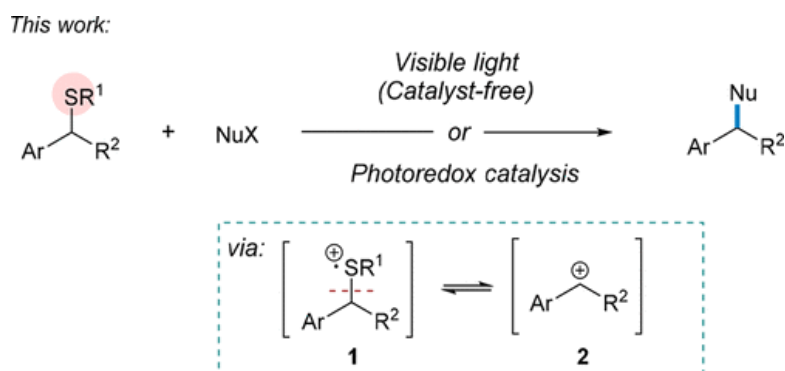
The cleavage of sulfidic C–S bonds under visible-light irradiation was harnessed to generate carbocations under neutral conditions and synthesize valuable di- and triarylalkanes as well as benzyl amines. To this end, photoredox catalysis and direct photoinduced C–S bond cleavage are used as complementary approaches and participate in the versatility of the general strategy. Extensive mechanistic studies have demonstrated the diversity of the reaction mechanism at work in these different reactions.

Sulfides are ubiquitous and simple functional groups constitutive of many bioactive molecules(1) and commercially available compounds. Synthetic sequences involving the cleavage of sulfidic C–S bonds followed by the new formation of C–C or C–heteroatom bonds are then anticipated as highly suitable to achieve last-stage transformations or increase the molecular complexity. Moreover, the sulfur atom is hardly electronegative and the C–S bond is poorly polarized, making thioethers insensitive to soft Brønsted acids and bases. As a consequence, C–S bond cleavages can constitute highly chemoselective transformations. Great achievements have been made to perform the catalytic activation of sulfidic C–S bonds relying on transition metal complexes(2) and Lewis acids.(3) However, most of these approaches display a narrow scope due to the ability of the Lewis basic sulfur atom to poison electron-deficient catalysts.(4)

In the meantime, the selective oxidation of thioethers is efficiently ensured by photoredox catalysis since it does not proceed by coordination of the sulfur atom to the catalyst. Even if this approach has been extensively studied to synthesize sulfoxides,(5) it remains a surprisingly underexplored strategy concerning the fragmentation of thioethers.(6) Only in 2013, Bowers and co-workers made a proof of this concept with the first example of photocatalyzed glycosylation of thioglycosides induced by selective oxidation of a

thioether.(7) More recently, our group reported an efficient synthesis of  $\alpha$ -substituted amides by photoredox-catalyzed C–S bond cleavages of  $\alpha$ -amidodisulfides.(8) Despite these few examples,(9) the synthetic potential of the visible light photoredox catalyzed fragmentation of thioethers remains surprisingly underexplored.

In the course of a research program, we became interested in the synthesis of di- and triarylalkanes since these moieties are prevalent in numerous pharmaceuticals and natural products.(10) As a complementary approach to the existing methods,(11) we envisioned the photocatalyzed oxidative C–S bond cleavage of benzyl thioethers(12) as a potential soft route to access such molecules (Scheme 1). The generation of radical cation **1** by single electron oxidation of the substrates should, in principle, lead to the formation of benzylic carbocation **2**. This intermediate could then undergo the addition of various nucleophiles under neutral conditions. We report herein the achievement of a photoredox-catalyzed synthesis of di- and triarylalkanes. Additionally, we set up a complementary catalyst-free process in which the C–S bond cleavage was induced by simple visible-light irradiation of the substrate.

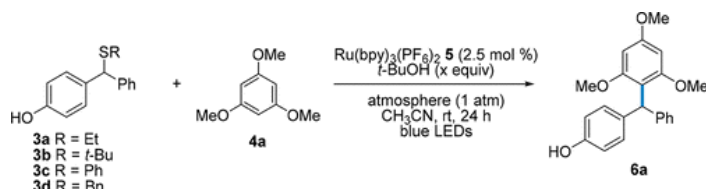


**Scheme 1.** Work hypothesis.

On the basis of our previous work,(8) we initially attempted to functionalize 4-ethylthio(phenylmethyl)phenol **3a** with 1,3,5-trimethoxybenzene **4a** in the presence of photocatalyst **5** in acetonitrile/*t*-BuOH (8:2, v/v) under visible light irradiation (5 W blue LEDs) with molecular oxygen as an oxidant. To our delight, we were able to isolate the desired triarylmethane derivative **6a** in 81% yield after 24 h (Table 1, entry 1). The nature of the thioether moiety has demonstrated a crucial influence on the reaction outcome. Indeed, when R is a *tert*-butyl (**3b**) or a phenyl (**3c**) group, the substitution efficiency was significantly decreased (entries 2–3). However, S-benzyl derivative **3d** afforded **6a** in a nearly quantitative yield (entry 4). Unlike our previous study,(8) the presence of *t*-BuOH does not have a prominent effect when **3d** and **4a** constitute the reaction partners (entry 5). Pleasingly, the reaction can be performed on a 1 mmol scale without any change in rates or yields (entry 6). Control experiments showed that the reaction failed to proceed in the absence of light (entry 7). A slower substitution was observed in an open-air flask (entry 8), highlighting the positive effect of O<sub>2</sub> on the reaction rate. This observation was supported by a dramatic conversion drop when the arylation was performed under an argon atmosphere (entry 9). Then, we found that when the flask was irradiated for 24 h in the absence of catalyst, **6a** was isolated in 11% yield (entry 10). This

striking observation suggested a potential, although poorly efficient, direct photoactivation of substrate **3d** under blue LED irradiation.<sup>(13)</sup>

**Table 1. Optimization of the Desulfitative Arylation Process**



Entry <sup>[a]</sup>	3	atmosphere	X eq.	6a %
1	3a	O <sub>2</sub>	10	84
2	3b	O <sub>2</sub>	10	71
3	3c	O <sub>2</sub>	10	56
4	3d	O <sub>2</sub>	10	99
5	3d	O <sub>2</sub>	0	94
6	3d	O <sub>2</sub>	0	94 <sup>c</sup>
7	3d	O <sub>2</sub>	0	0 <sup>d</sup>
8	3d	air	0	83
9	3d	Ar	0	14
10	3d	O <sub>2</sub>	0	11 <sup>e</sup>

<sup>a</sup>

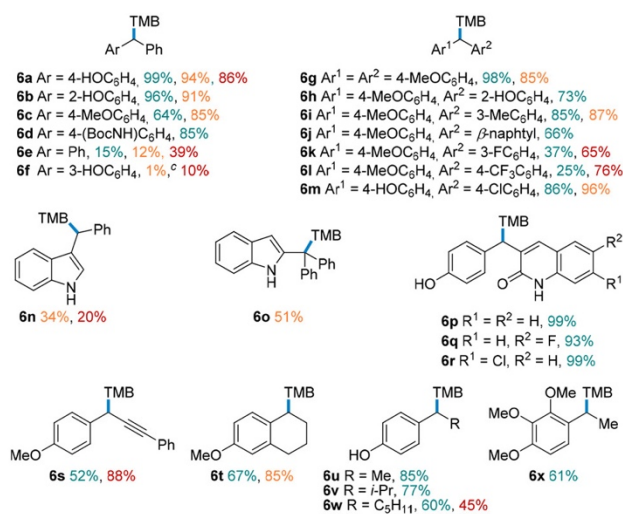
General conditions: **3** (0.10 mmol, 1 equiv), **4a** (0.15 mmol), **5** (0.025 equiv), *t*-BuOH (0 or 10 equiv) in CH<sub>3</sub>CN (0.5 mL) irradiated with 5 W blue LEDs at rt for 24 h. <sup>b</sup> Isolated yields. <sup>c</sup> Reaction performed on a 1 mmol scale (of **3d**). <sup>d</sup> Reaction performed in the dark. <sup>e</sup> Reaction performed without catalyst.

With the optimized reaction conditions, the scope of the photocatalyzed arylation of benzylthioethers with **4a** was then explored (Scheme 2a). Diarylmethanes bearing strong donating (+M) substituents provided triarylmethanes **6a–6d** with good to excellent yields. In contrast, products **6e** and **6f** were isolated in 12% and 1% yields, respectively. For this last product the hydroxyl in the *meta* position does not participate in the carbocation stabilization and only –I destabilizing effect is operating. In the synthesis of **6e** and **6f**, sulfoxides arising from the oxygenation of the radical cation intermediate **1** were identified as the main reaction products (see Supporting Information (SI)). A similar trend was brought to light for anisole derivatives, since the photocatalytic arylation was found efficient for electron-donating aromatic substituents (**6g–j**). On the other

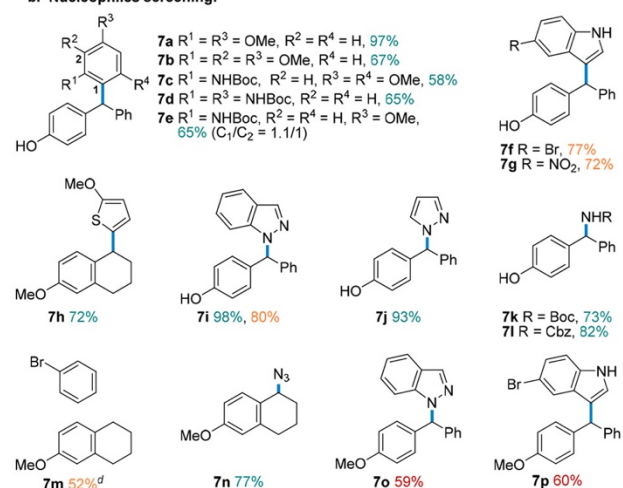
hand, the presence of electron-withdrawing groups as *m*-F and *p*-CF<sub>3</sub> resulted in the formation of products **6k** and **6l** in low yields. The reaction proceeded smoothly when combining highly electron-rich phenols with electron-poor arenes (**6m**). Heteroaromatic substituents such as the 3-indolyl or 3-quinolinonyl group were also competent reaction partners, delivering products (**6n–r**) that have potential applications in medicinal chemistry. Extension of this novel photocatalyzed protocol to diverse secondary benzylic thioethers was also successful providing efficient access to biologically relevant diarylalkanes.(10) The desulfurative arylation can be efficiently applied to propargylic thioethers as well as cyclic and acyclic benzylic substrates **6s–w**. Additionally, this transformation provides an efficient route to anticancer isoeirinin analogue **6x**.(14) It has to be noticed that the presence of *t*-BuOH can have a slight impact on the reaction efficiency without us being able to establish a clear relationship with the structure of the substrate.



**a. Thioethers screening** (TMB = 1,2,3-trimethoxybenzene)



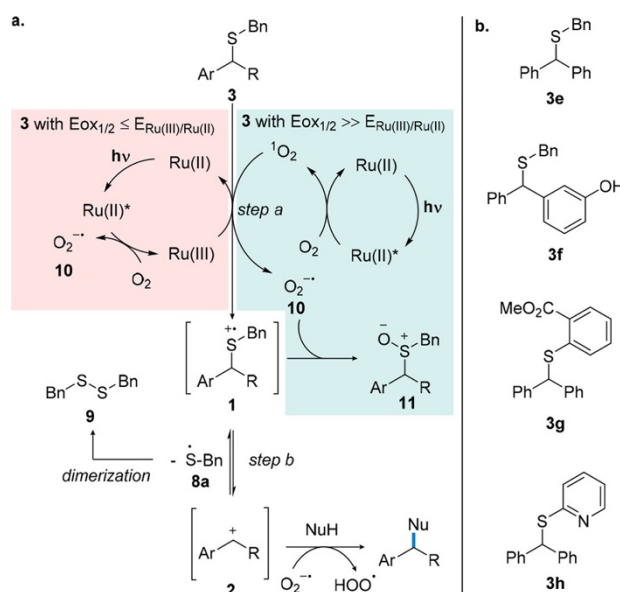
**b. Nucleophiles screening:**



**Scheme 2.** Substrates Scope of the Desulfitative Arylation. <sup>a</sup>Isolated yields. <sup>b</sup>Temperature measured in a reaction tube at 3 cm of the bulb. <sup>c</sup>Yields determined by <sup>1</sup>H NMR. <sup>d</sup>Reaction performed over 48 h

Encouraged by these results, we turned our efforts toward extending this protocol to other nucleophiles (Scheme 2b). Diversely substituted arenes and heteroarenes readily participated in C–C bond formation to afford the expected triarylmethanes **7a–7h** in good yields. Moreover, the construction of C–N bonds can also be achieved thanks to this method. Various azole derivatives were successfully incorporated giving rise to important drugs building blocks **7i** and **7j**.<sup>(15)</sup> Nonaromatic *N*-nucleophiles such as carbamates, anilines, and azides were also found to be viable reagents (**7k–7n**).

To gain insight into the mechanism of the photoredox-catalyzed thioether C–S bond cleavage, we first determined the redox potential of several thioethers. Model substrate **3d** displayed an oxidation potential  $E_{1/2} = +0.85$  V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN (see SI) that makes a direct SET thermodynamically unlikely from the excited state of **5a** (Ru(II)\*<sup>+</sup>/Ru(I):  $E_0 = +0.37$  V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN).<sup>(16)</sup> This was confirmed by Stern–Volmer experiments in which no significant fluorescence quenching was observed in the presence of **3d** or trimethoxybenzene **4a** (see SI). Based on these observations and the requirement of O<sub>2</sub> for the reaction to proceed efficiently, we assumed that Ru(III) (Ru(III)/Ru(II):  $E_0 = +0.89$  V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN) could be the active oxidant of electron-rich substrates (Scheme 3, *red square*).



**Scheme 3.** Suggested reaction mechanism.

The mesolytic cleavage of the C–S bond in radical cation **1** was supported by several experimental proofs. The involvement of a carbocation intermediate (S<sub>N</sub>1-type process) was unambiguously demonstrated by the complete loss of enantiomeric excess through the arylation of optically pure thioether **3d** (see SI). Also, disulfide **9** resulting from the dimerization of thiyl radical **8a** was isolated in 83% yield when **3d** was reacted with **4a** (Scheme 3).<sup>(17)</sup> This fast dimerization prevents radical propagation as demonstrated by kinetic

experiments involving alternation of irradiation and dark (see SI). In a final step, the addition of the nucleophile onto the carbocation could be assisted by the basic superoxide radical **10**.

Correlations between the Hammett parameters ( $\sigma$ ) of aromatic substituents and the corresponding yields obtained after 24 h (see SI) have highlighted a drop in yields in the presence of substituents with  $\sigma$  values  $\geq 0$ . This could be explained by a dramatic increase in the oxidation potentials of the related substrates. As a matter of fact, oxidation potentials of **3e** (precursor of **6e**) ( $E_{1/2} = +1.18$  V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN) and **3k** (precursor of **6k**) ( $E_{1/2} = +1.14$  V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN) are elusive for Ru(III) suggesting another reaction mechanism for this work (Scheme 3, *green square*). In this case, the sulfur oxidation (step a) could rely on the formation of singlet oxygen <sup>1</sup>O<sub>2</sub> by energy transfer between Ru(II)\* and O<sub>2</sub>.<sup>(18)</sup> In order to shatter this main scope limitation, photocatalysts with higher oxidation potentials were tested in the arylation of **3e** without significant improvement of the yields (see SI). On the other hand, these disappointing results could be explained by poor stabilization of the carbocation intermediate **2**, which slows C–S bond cleavage favoring the oxygenation of the radical cation **1**. Unfortunately, the use of alternative oxidants to prevent the formation of sulfoxide **11** uniformly resulted in no conversion. Additionally, our attempts to improve the nucleofugality of thiyl radicals **8** (Scheme 3b, compounds **3g** and **3h**) remained unsuccessful (see SI).

With the desire to set up a complementary strategy and based on our previous observation that the benzylthioethers participate in arylation C–S bond cleavage under catalyst-free conditions (Table 1, entry 14), we hypothesized that an appropriate choice of conditions would allow the formation of triarylalkanes while preventing the competing overoxidation. Even if **3e** remained unreactive under 5 W blue LED irradiation an optimization stage (see SI) revealed that the use of a more intense 25 W CFL bulb and higher dilution supported the formation of desired product **6e** in 39% yield (Scheme 2). The synthetic potential of this new set of conditions was then explored. Electron-rich substrates underwent the smooth addition of **4a** although in lower yields compared to the Ru-catalyzed process. However, the catalyst-free substitution furnishes enhanced efficiency in the case of more electron-deficient substrates. Fluorinated products **6k** and **6l** were then obtained in 65% and 76% yields, respectively. This highlights the complementarity between the two methodologies described herein. Highly deactivated thioether was converted to triarylmethane **6f** in 10% yield only. However, this remains 10 times higher than with the photoredox approach. The photoinduced desulfidation also turned out to be more suitable to access diarylalkyne **6s**. Various arenes and heteroarenes can be used as the reaction partners, as demonstrated by the formation of compounds **7a**, **7o**, **7p** in rather good yields. Even if the mechanism of this transformation is not fully understood, it is expected to involve a visible-light-induced homolytic cleavage of the C–S bond (see SI).<sup>(19,20)</sup>

To conclude, we have described an unprecedented visible-light photoredox catalyzed synthesis of diarylalkane and triarylmethane derivatives under neutral conditions. The reported strategy relied on the oxidative weakening of sulfidic C–S bonds allowing the *in situ* generation of the reactive carbocations. An appreciable range of substrates and nucleophiles can be engaged in this transformation that uses O<sub>2</sub> as a terminal oxidant. Extensive mechanistic studies allowed us to understand the initial limitations in term of substrate electronic properties. This work finally revealed the possibility of inducing homolytic C–S bonds cleavage under direct



visible-light irradiation. This catalyst-free approach efficiently complemented the first methodology since it ensures the formation of C–C and C–N bonds from more electron-deficient substrates. We hope this work will highlight the synthetic potential of the low oxidation state sulfur photoactivation.

## ASSOCIATED CONTENT:

### Supporting Information

Experimental details, complete modeling data, characterization of products, copies of NMR spectra, XYZ coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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