

## Metal free photoinduced C(sp<sup>3</sup>)-H thioarylation

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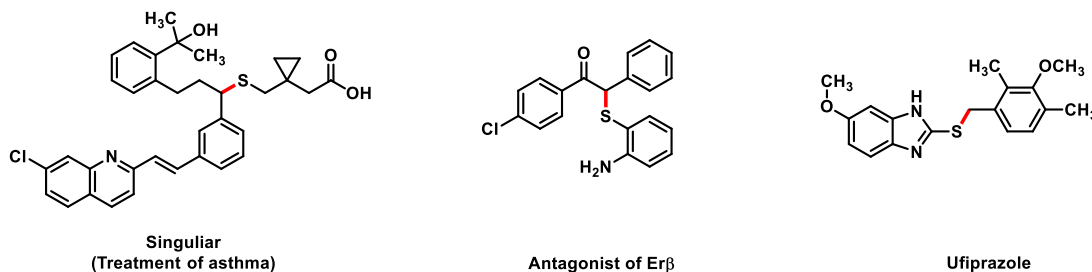
<sup>#</sup>These authors contributed equally.

**Abstract:** C-H thioarylation of hydrocarbon building blocks is a highly desirable synthetic transformation attributed to its prevalence in various pharmaceuticals and organic functional materials. However, all the developments till date majorly rely on peroxide mediated transformations. Unfortunately, harsh reaction conditions of these reactions cause severe functional group intolerance. To surpass these issues, photo-induced radical coupling reactions have gained significant attention as a sustainable way out, which require either metal based photosensitizers or the use of an organophotocatalyst. Herein, we demonstrated a mild metal free approach for C(sp<sup>3</sup>)-H thioarylation using thioxanthone as a photo-catalyst. The protocol is compatible with various arenes, heteroarenes, as well as unactivated alkanes and cycloalkanes. The post-synthetic modifications of thioarylated compounds are also demonstrated through cross coupling reactions as well as functional group interconversions.

Organosulfur compounds are prevalent in many natural products and drug molecules.<sup>1</sup> Therefore, C-S bond formation carries a key position in the quest to synthesize important synthetic compounds.<sup>2</sup> Direct conversion of C-H bond to C-X (X= O, N and S) bond not only allow the facile synthesis of heteroatom containing organic compounds with high atom economy but also provide new insights towards the mechanistic understanding of these reactions.<sup>3</sup> In particular, C(sp<sup>3</sup>)-S bond formation has gained significant attention due to its omnipresence in a variety of drug molecules (Scheme 1a).<sup>4</sup> In general, C(sp<sup>3</sup>)-S bond is formed *via* S<sub>N</sub>2 reaction between thiophenol with haloalkanes. Haloalkanes like benzyl bromides have lachrymatory properties which limits its applicability at large scale. On the other hand, direct C-H thioarylation of alkanes requires super stoichiometric amount of peroxide initiator under harsh reaction conditions and thus many functional groups are not compatible.<sup>5</sup> Therefore, the involvement of mild reaction conditions to generate C-H thioarylation is a formidable and desirable challenge to synthetic community. In this regard, photo-induced radical coupling reactions have become quite promising for the generation of radical species.<sup>6</sup> Ir, Ru, and W based metal photocatalysts are widely used in this domain by Macmillan, Doyle, Noel and other groups.<sup>7</sup> Along the line, Martin, Reuping and other groups have demonstrated that biaryl ketone photosensitizers can promote C(sp<sup>3</sup>)-H functionalization through the use of hydrogen atom transfer.<sup>8</sup> Upon irradiation with visible light, simple organic molecule like biaryl ketones get excited to its triplet excited state and abstract hydrogen atom to generate aliphatic radical species. Harnessing this concept, various aliphatic C-H functionalizations have been realised by using biaryl ketone derivatives as photosensitizer. However, in majority of transformations, metals such as Nickel or Copper are predominantly required as the catalyst.<sup>9</sup> Later on, some other groups came up with new carbonyl based photosensitizers which can perform C-H

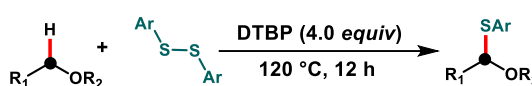
functionalization without the use of any metal catalyst.<sup>10</sup> In this domain, metal-free benzylic mono- and difluorination, hydroperoxidation, amination, carboxylation, oxygenation *etc* were performed under photo-induced radical conditions using organophotocatalysts.<sup>11</sup>

**a. Pharmaceuticals containing C(sp<sup>3</sup>)-S bond**

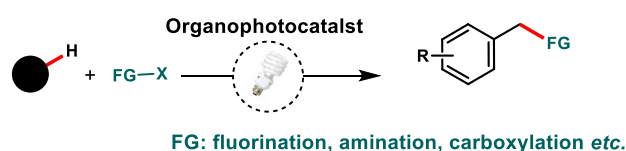


**Previous works:**

**b. C(sp<sup>3</sup>)-S bond formation via radical coupling**

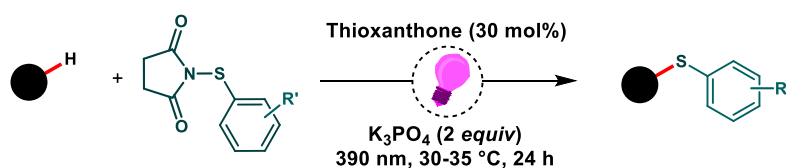


**c. Organophotocatalyzed C(sp<sup>3</sup>)-H functionalization**



**Present work:**

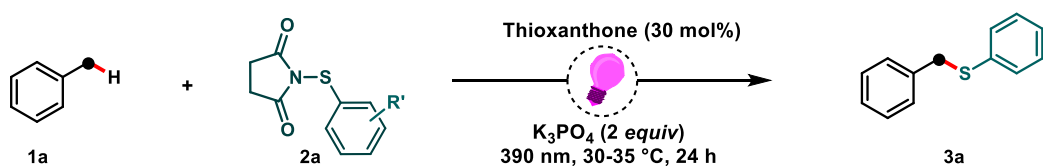
**d. Metal free C(sp<sup>3</sup>)-H thioarylation**



**Scheme 1. Common approaches for radical mediated aliphatic C-H functionalization.**

Considering the significance of C-S bond formation, we envisioned that the biaryl ketone as photosensitizer and HAT agent in the presence of a suitable thioaryl radical source can perform the desired aliphatic C-H thioarylation.

With this hypothesis, toluene (**1a**) was considered as model substrate was irradiated in presence of 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) as the thioaryl coupling partner, benzophenone (20 mol %) as photosensitizer, and 2,6-lutidine as base (2 equiv) in the presence of purple LEDs for 24 hours. The reaction setup was cooled up with a fan to keep the temperature around 30-35 °C. Pleasingly, our desired thioarylated product **3a** was formed in 35% yield (**S1**). Furthermore, different biaryl ketones based photosensitizers known in literatures were screened (**S1**).



| Entry | Variation | GC Yield of 3a (%) |
|-------|-----------|--------------------|
|-------|-----------|--------------------|

|   |  |       |
|---|--|-------|
| 1 | none   | 68    |
| 2 | no thioxanthone  | ND    |
| 3 | no Base  | 21    |
| 4 | without light at RT  | trace |
| 5 | PhSH instead of <i>N</i> -SPh                                | ND    |
| 6 | with Ph <sub>2</sub> S <sub>2</sub> instead of <i>N</i> -SPh | 25    |
| 7 | with TEMPO or BHT  | ND    |
| 8 | 2,6-lutidine instead of K <sub>3</sub> PO <sub>4</sub>       | 60    |
| 9 | 4,4'-dichloro benzophenone instead of thioxanthone           | 57    |

Reaction conditions: 1a (1 mL), 2a (0.2 mmol), PC (30 mol %), Base (2 equiv), 24 h purple LEDs irradiation. ND = Not Detected. For yield calculation deodecane was used as internal standard.

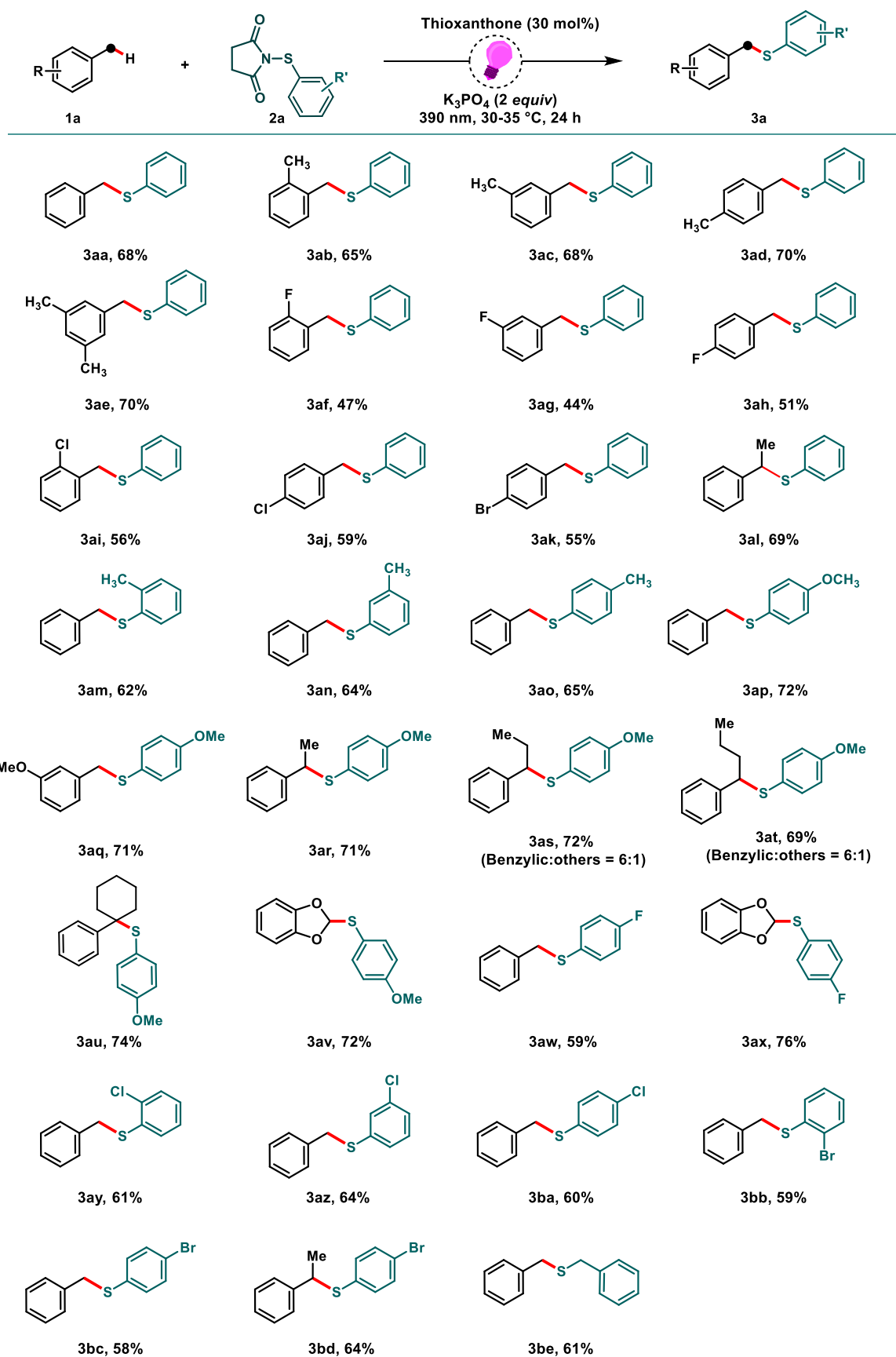
**Table 1. Summary of optimization of reaction conditions.**

While dimethyl substituted benzophenone led to a diminished yield of around 29%, dimethoxy benzophenone increased the yield to 43%. On the variation of other halide containing benzophenones, 4,4'-dichloro was found to be superior than others (**S1**). However, the reaction was completely silent on the application of diamine containing benzophenone and anthraquinone based photosensitizers (**S1**). Finally, on stringent optimization thioxanthone was found out to be the most efficient giving the desired product in 60% yield (**S1**). Base optimization studies revealed that among different inorganic bases, K<sub>3</sub>PO<sub>4</sub> is the optimum base for this transformation giving the desired product in 68% yield (**S4**). Higher loadings of base were also tested. However, it didn't prove out to be beneficial. Controlled experiments revealed that all the reagents are crucial for the transformation (**Table 1**).

With the optimized condition in hand, we screened toluene based substrates first. Both electron donating (OMe-, Me-) as well as electron withdrawing groups (F-, Cl-, Br-) were well tolerated under the reaction conditions, producing the desired thioarylated product in good yields.

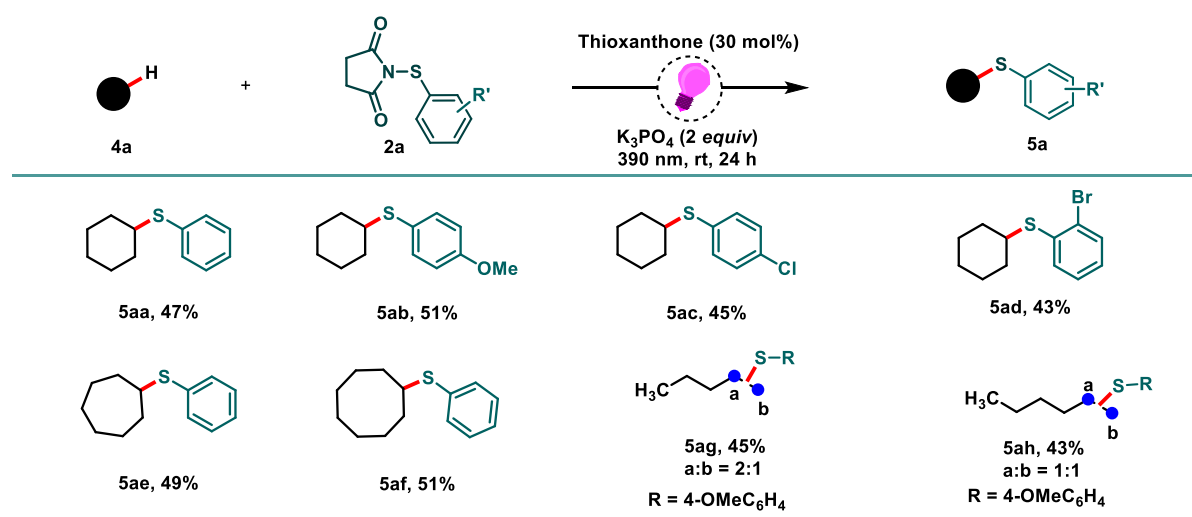
Even the *di*- and *tri*- substituted toluenes *viz ortho*-, *meta*-, *para*-, xylenes and mesitylene produced mono thioarylated products in moderate to good yields ranging from 60-70% (**3ab-3ae**). Steric hindrance posed by *ortho*- and *meta*- substituents was found not to affect the outcome of reaction. Halogen containing toluenes also worked well to produce the desired product in moderate yields 40-60% (**3ae-3ak**). Position of halogen substituent was not found to exhibit any particular effect on the progress of reaction.

Following that, the reactivity of different thioaryl coupling partners were also tested. Electron withdrawing groups like F-, Cl-, Br-, as well as electron releasing substituents like Me-, and OMe- containing thioaryl coupling partner were well tolerated producing the desired product in synthetically useful yields. Benzylic radical was not formed on the methyl substituted thioarylated reagent (**3am-3ao**). The statistical advantage of toluene over the limiting reagents should be responsible for this chemo-selectivity. Even the benzylic thioaryl partner was also found to suitably couple with toluene (**3be**).



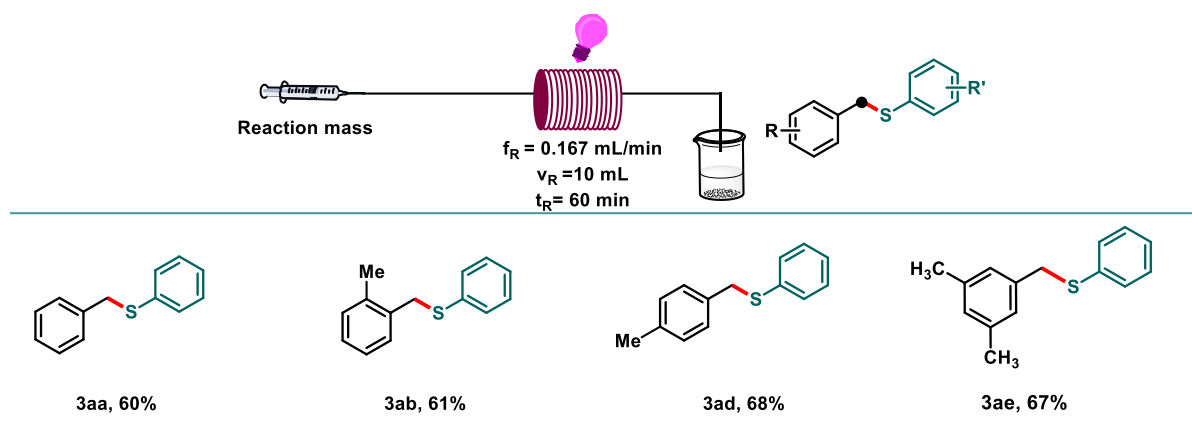
Scheme 2. Substrate scope with respect to C( $sp^3$ )-H containing arenes.

Benzene ring bearing aliphatic substituents like ethyl, propyl, butyl and cyclohexyl were also thioarylated at the benzylic position (**3ar-3au**). However, selectivity issues were observed in the cases of propyl and butyl benzene (6:1) due to the possible radical migration (**3as, 3at**). Other aliphatic C–H containing substrates like benzodioxoles were also thioarylated at alpha position to hetero atom (most stabilized radical position) using *para* substituted F- and OMe-containing thioaryl coupling partner (**3av, 3ax**). Moderately good yields were observed which is due to extra high radical stability which enhances the product formation. Next, we expanded the scope of the reaction to unactivated aliphatic substrates like alkanes and cycloalkanes. Under the same reaction conditions, cyclohexane was thioarylated with various thioaryl coupling partners (**5aa-5ad**). Expanding the ring size from cyclohexane to cycloheptane to cyclooctane, didn't affect the reaction much, showing almost similar yields of desired product (**5ae, 5af**). Common laboratory solvents like *n*-pentane and *n*-hexane were also thioarylated using methoxy containing thioaryl partner (**5ag, 5ah**). However, mixture of regiomers were observed in both of these cases.



**Scheme 3.** Scope with respect to unactivated aliphatic substrates.

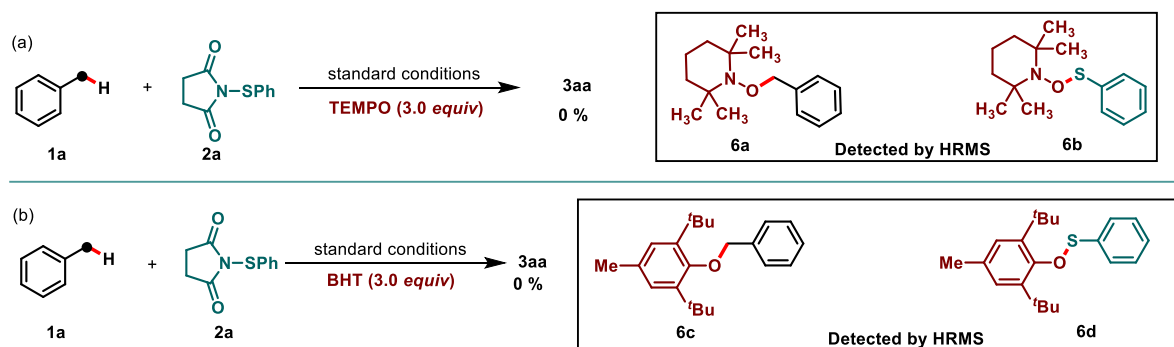
In an attempt, to shorten the reaction time and to enhance the reaction scale, we tested our methodology in continuous flow. However, insolubility of thioxanthone and K<sub>3</sub>PO<sub>4</sub> in toluene limits its applicability to micro flow photo-reactor. Therefore, we opted for our second best optimized photosensitizer *i.e.* 4,4'-dichlorobenzophenone, and 2,6-lutidine as base, which were completely homogeneous in the reaction medium. After optimizing the various parameters in flow, 60 min residence time was found to be optimum (see Supporting Information, page S41). Toluene, *ortho*-xylene, *para*-xylene, and mesitylene were thioarylated in continuous flow reactor using a modified reaction condition producing > 0.24 g/h of **3aa** which corresponds to 5.7 g in a day.



Reaction mass: 2a (2 mmol), 4,4'-diCIBP (30 mol%), 2,6-lutidine (2.0 equiv) in 10 mL toluene.

#### Scheme 4. Scale up reaction using continuous flow reactor.

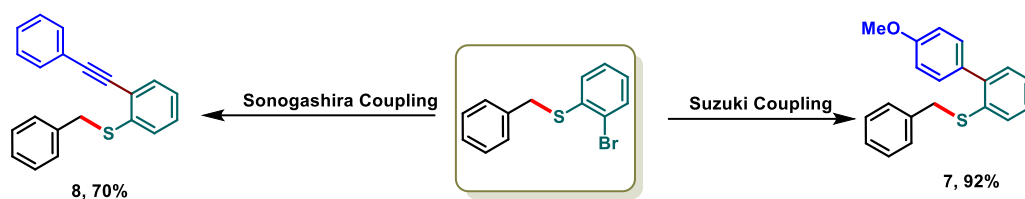
To probe the radical mechanism, the experiments were performed using stoichiometric amount of radical scavengers like TEMPO and BHT (Scheme 5). In both of the cases, reaction was completely silent and the TEMPO- and BHT- adduct with both coupling partners could be detected by mass spectroscopy.



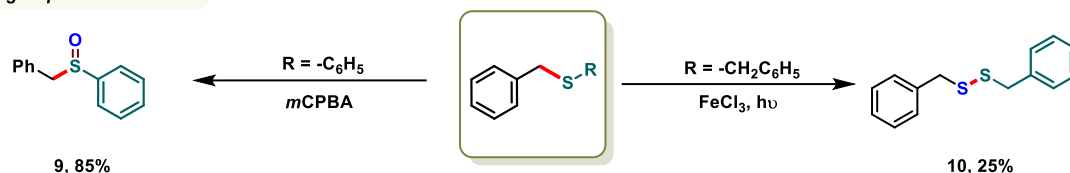
#### Scheme 5. Radical trapping studies.

Post synthetic modification was performed using our produced thioarylated product (**3aa**, **3bb** and **3be**). Bromo containing thioarylated product (**3bb**) was found to be suitably compatible for Suzuki-Miyaura and Sonogashira cross-coupling reactions (Scheme 6). Benzyl(phenyl)sulfane (3aa) was successfully oxidized to sulfoxide, a structurally important chromophore in many natural products. Dibenzylsulfane (**3be**) was converted to corresponding dibenzyldisulfide which is itself a popular reagent for C–H thioarylation.

### Post-synthetic applications

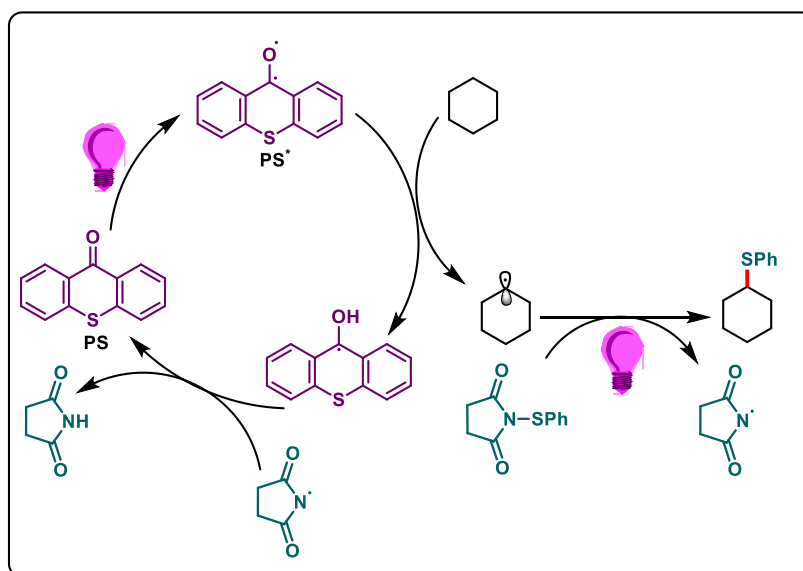


### Functional group interconversion



Scheme 6. Post-synthetic modifications.

Based on our radical trapping experiments and related literature studies, a plausible mechanism is outlined (Scheme 7), in which upon irradiation with 390 nm light, thioxanthone (PS) gets excited from ground state to triplet  $PS^*$ , which initiates the reaction *via* hydrogen abstraction from  $C(sp^3)$ -H bond. 1-(phenylthio)pyrrolidine-2,5-dione gets homolytically cleaved into thioaryl and succinyl radical species under light irradiation. Then, thioaryl radical couples with  $C(sp^3)$  radical generated from the substrate. Succinyl radical regenerates thioxanthone and commences the catalytic cycle further.



Scheme 7. Plausible mechanism of thioxanthone catalysed C-H thioarylation.

### Conclusion:

In summary, we have established a mild protocol for direct  $C(sp^3)$ -H thioarylation which is applicable on a wide variety of substrates. Electron withdrawing as well as electron releasing groups containing thioaryl partners were well tolerated under the reaction protocol.

Thioxanthone as photosensitizer plays the dual role of hydrogen atom transfer as well as energy transfer. This transformation proceeds *via* radical pathway as confirmed by radical trapping studies. Formed benzylphenyl sulfane derivatives can also undergo cross coupling reactions and can also be converted to sulfoxide or corresponding disulfides, which reflects their synthetic utility. Further, scale up was performed using continuous flow photo-reactor under slightly modified reaction conditions. More mechanistic investigations are currently underway in our lab.

### Author Contributions

J. G. and G. P. conceived the project. J. G., and G. P., completed the experimental work. D. M. and G. K. L. supervised the work. All authors contributed in writing the manuscript.

### Conflicts of interest

The authors declare no conflict of interest.

### Acknowledgements

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