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Tuning Selectivity in the Visible-Light-Promoted Coupling of Thiols with Alkenes by EDA *vs* TOCO Complex Formation

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ABSTRACT: The visible-light-promoted catalyst-free condition has been demonstrated for self- and cross-coupling reactions of thiols in an ambient atmosphere. Further, synthesis of β-hydroxysulfides is accomplished under very mild conditions involving the formation of an electron donor−acceptor (EDA) complex between a disulfide and an alkene. However, the direct reaction of thiol with alkene *via* the formation of a thiol−oxygen co-oxidation (TOCO) complex failed to produce the desired compounds in high yields. The protocol was successful with several aryl and alkyl thiols for the formation of disulfides. However, the formation of β-hydroxysulfides required an aromatic unit on the disulfide fragment, which supports the formation of the EDA complex during the course of the reaction. The approaches presented in this paper for the coupling reaction of thiols and the synthesis of β-hydroxysulfides are unique and do not require toxic organic or metal catalysts.
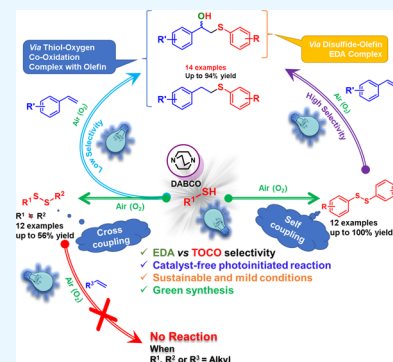
INTRODUCTION

In the last decade, research on light-induced organic transformations has moved forward tremendously[1a] because of simple, mild, sustainable, and greener methods.[1b] Recently, the direct use of photons for chemical transformations drew much attention from researchers due to the low-cost, rapid, sustainable, and green outcomes.[2a] The increasing interest in the photoinduced methodologies for the step-economic synthesis of highly stained rigid molecules is due to their potential industrial applications in the near future.[2b−d]

Sulfur-based organic compounds are essential for antimicrobials and pathology from the medicinal chemistry and chemical biologist point of view (Figure 1).[3] Sulfur linkers are also responsible for the stability of proteins and peptides in biological systems due to their high redox potential.[4] In the recent pandemic, asymmetric disulfides were found to be the central unit of protein present in the COVID-19 virus.[5] Sulfur-incorporated heterocyclic scaffolds act as prodrugs such as cysteine,[6a] polycarpamines B,[6b] lissoclibadin 5[6c] and are highly distributed in nature.[6d] The self- and cross-coupled S−S bond-based disulfide motifs[6e] such as disulfiram act as agrochemicals[6g] and have played a vital role as vulcanizing agents.[6f] As a result of the high demand for a simple and sustainable synthetic route for S−S bond formation, traditional metal-catalyzed, aerial-oxidative, and thermal protocols are being developed (Scheme 1).[7] Recently, Lie et al. developed an electro-oxidative technique for direct S−S bond construction.[7c] The first successful report on photoinduced thiol coupling was done by Wu and co-workers in 2014,[8a] where CdSe quantum dot-based photocatalysts have been used. Several reports on thiol self- and cross-coupling have been published in the last

ten years, but all of them require toxic dye-based photocatalysts such as eosin Y, rose Bengal, chlorophyll, and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or costly metal- and nanocomposite-based photocatalysts such as GO-FePc, CoOx-C, N@CeO$_2$, Cu$_2$(OH)PO$_4$, PhTePh@Rose Bengal, TiO$_2$, fac-Ir(ppy)$_3$, CsPbBr$_3$, etc.[8] Because of the ongoing interest in the development of eco-friendly organic synthetic routes known as "green synthesis," the first works on the subject were published in 2019[8j] by the Yadav group and the second in 2020[8k] by Lang et al., where chlorophyll and TEMPO were used as catalysts, respectively. Both protocols, despite being limited to aromatic and small thiol systems, were inapplicable in the aliphatic system. In a recent report, Kokotos demonstrated a phenyl glyoxylic acid-photoinitiated thiol coupling reaction,[8l] but the protocol does not have any control over the huge waste generation. Therefore, catalyst-free, sustainable, and light-promoted S−S coupling protocol development, which can be extended up to aliphatic thiols, will overcome the problems of metal-catalyzed or toxic organic dye-based photocatalyzed synthetic routes.
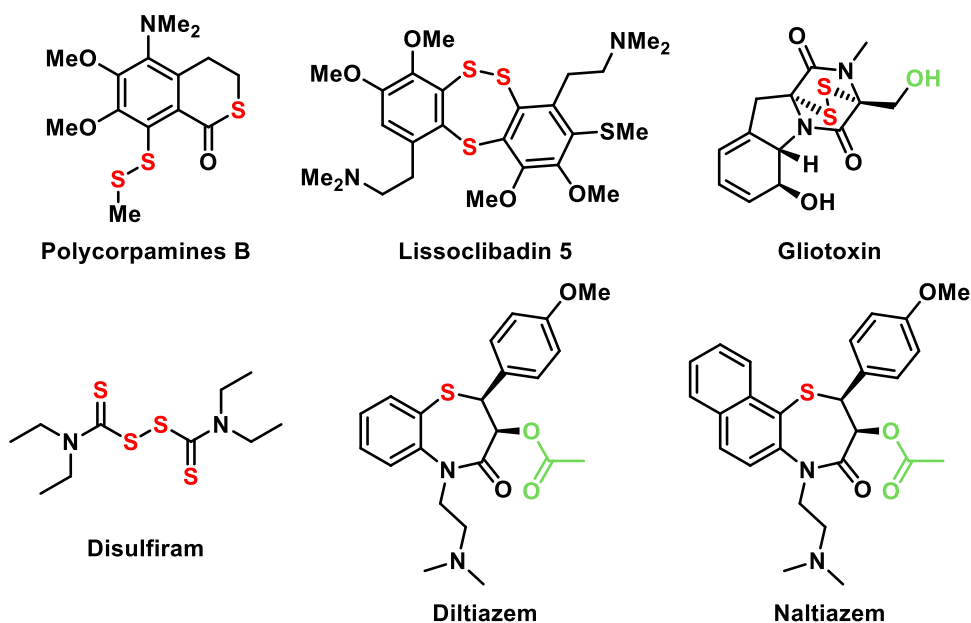
Moreover, β-hydroxysulfides are also well known for their biological activities and use in pharmaceutical applications.[9] In natural products[10] as well as in asymmetric synthesis,[10,11] they are used as a very important building block. Due to this high

Figure 1. Selected biologically active compounds and natural products containing disulfide and β-hydroxysulfide moieties.

importance, there has been a lot of work done over the years to develop methodologies for producing β-hydroxysulfide derivatives,[12] but the majority of them are produced through the thiol−oxygen co-oxidation (TOCO) reaction between thiols and olefins.[13] However, drawbacks such as the need for a large excess of thiols, the possibility of thiol-ene click side reactions, low regioselectivity, and low yield necessitated the development of a new methodology to avoid the TOCO-based β-hydroxysulfide synthetic route.[14] As a result, the Movassagh group developed the first alternative route for β-hydroxysulfide construction using Zn/AlCl₃ in 2008, starting with disulfide and alkene derivatives.[15a] But over the decade, only a few more alternative thermal routes were developed, including rongalite-promoted,[15b] I₂-catalyzed,[15c,e] HBr/H₂O₂-mediated,[15d] and copper-catalyzed[15f] conditions. The hydroxyl group came from the reaction between CBr₄ and water in light-induced β-hydroxysulfide synthesis via the TOCO complex-free disulfide−olefin route first developed by Wang et al. in 2017.[16] However, the olefin−disulfide EDA complex-mediated additive-free photoinitiated protocol can still solve the problem of side reactions. Toward this goal, in this paper, we report the first-ever examples of catalyst-free light-induced self- and cross-coupling of thiols. We also report one-pot β-hydroxysulfide synthesis via EDA complex formation between disulfide and olefins (Scheme 1).

RESULTS AND DISCUSSION

The preliminary investigation for selecting the best base was started with 1,4-diazabicyclo[2.2.2]octane (DABCO) under blue LED light irradiation, which gave 100% self-coupled product (**2a**) starting from thiophenol (**1a**) (Table 1, entry 1). When other organic bases such as tetramethylethylenediamine (TMEDA), triethylamine (TEA), and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were used, 1,2-diphenyldisulfane (**2a**) was obtained in moderate 56−82% yields (entries 2−4). Therefore, DABCO was further used as a base for finding the best reaction conditions.
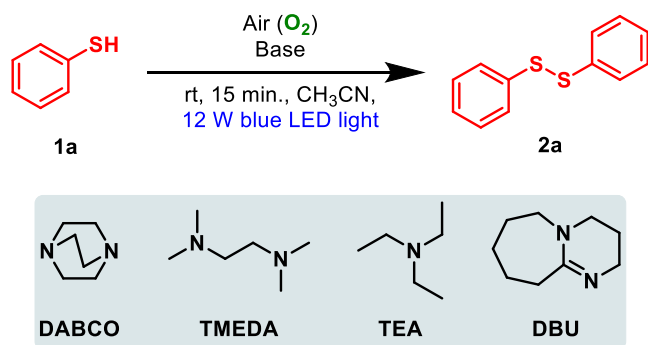
With the chosen base in hand, we further investigated to find the best reaction conditions as listed in Table 2. In an attempt

to improve the yield, solvents such as EtOAc, dichloromethane (DCM), MeOH, water, dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) were used in the reaction without much success (entries 2−7). >99% yield was observed only for CH₃CN as a solvent (entry 1). Among the various amounts of DABCO, starting from 0.1 to 0.75 equiv (entries 1 and 8−10), 0.5 equiv (entry 1) was the optimized base loading for maximum yield. We also optimized the light irradiation time, where 15 min of light irradiation gave a maximum yield of >99% (entry 1). Any lesser light irradiation time than 15 min only leads to a lesser yield (entries 13−14), while more than 15 min of light irradiation was not found more beneficial (entries 11−12). Finally, one experiment was also done under dark conditions, which failed to produce any product (entry 15). Other light sources, such as 18 W CFL light and 30 W fluorescent black light (385−390 nm), gave 81 and >99% yields, respectively (entries 16 and 17).

With the best reaction conditions, we explored the substrate scope for a variety of aromatic as well as aliphatic thiols as depicted in Scheme 2 (condition A). We achieved self-coupling of aromatic thiols with excellent functional group tolerance for both electron-donating and electron-withdrawing groups. Thiophenols containing electron-donating groups such as −Me and −OMe (**1b**, **1c**, and **1d**), and electron-withdrawing groups such as −Cl, −Br, and −F (**1e**, **1f**, and **1g**) gave 94−100% yields. In the case of 2-amino-thiophenol, 82% of the self-coupled product **2h** was obtained. For phenylmethanethiol (**1i**), a satisfactory result of 94% was achieved. Unfortunately, thiophen-2-ylmethanethiol (**1j**) gave only 78% of disulfide (**2j**). The protocol also worked well for aliphatic thiols such as 2-mercaptoethanol (**1'a**) and cyclo-hexanethiol (**1'b**), giving 76−80% of their respective disulfides (**2k** and **2l**).

Encouraged by the synthetic importance of the cross-coupling reaction of thiols, we also explored the heterocoupling between the 1:1 ratio of thiophenol (**1a**) and 2-mercaptoethanol (**1'a**) in the presence of the equivalent amount of DABCO as a base (Table S2, Supporting Information (SI)). However, only 16% of 2-

Scheme 1. Protocols for the Synthesis of Disulfide and β-Hydroxysulfides

(phenyldisulfaneyl)ethan-1-ol (**2m**) was produced after 15 min of light irradiation (entry 1). Additionally, increments of light irradiation time up to 60 min leads to 40% of **2m** (entry 3).

Any additional light irradiation did not improve the yield (entry 4). Even any further concentration increases of **1'a** and DABCO did not affect the yield (entry 5).

Table 1. Optimization of the Base in Photoinduced Self-Coupling of Thiophenol[a]

entry	base (loading)	yield of 2a (%)[b]
1	**DABCO (0.5 equiv)**	>99
2	TMEDA (0.5 equiv)	82
3	TEA (1 equiv)	77
4	DBU (0.5 equiv)	56

[a]Reaction conditions: **1a** (0.90 mmol), **base** (0.45 mmol), CH$_3$CN (3 mL), 15 min, air atmosphere, and 12 W blue LED light. [b]Isolated yield.

Table 2. Optimization of Photoinduced Self-Coupling of Thiophenol[a]
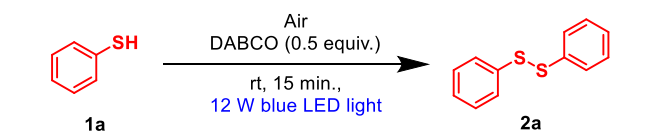
entry	variation from the standard condition	yield of 2a (%)[b]
1	**None**	>99
2	EtOAc as solvent	trace
3	DCM as solvent	trace
4	MeOH as solvent	8
5	H$_2$O as solvent	trace
6	DMSO as solvent	trace
7	THF as solvent	10
8	0.75 equiv DABCO	>99
9	0.25 equiv DABCO	79
10	0.1 equiv DABCO	54
11	60 min light irradiation	>99
12	30 min light irradiation	>99
13	10 min light irradiation	82
14	5 min light irradiation	52
15	under dark	trace
16	18 W CFL light	81
17	30 W fluorescent black light	>99

[a]Reaction conditions: **1a** (0.90 mmol), **DABCO** (0.45 mmol), CH$_3$CN (3 mL), 15 min, air atmosphere, and 12 W blue LED light. [b]Isolated yield.

We also explored the substrate scope of cross-coupling of thiols in Scheme 2 (B). In all of the examples, a nonpolar thiol was used with a polar thiol to obtain the chemoselective cross-coupled disulfide products (**2m–2x**) under optimal reaction conditions. The result was only a reflection of the battle between self- and the cross-coupling reaction of thiols. In the literature, there were only limited examples of metal or toxic catalyst-promoted cross-coupling reactions of thiols. In comparing those protocols, we achieved a catalyst-free, light-promoted green method with decent yields (39–56%) of

respective cross-coupled disulfides. Though the yield was moderate in some cases, from the point of view of replacing the requirement of toxic and metal catalyst-based protocols, the present method could be highly impactful.

A model reaction between thiophenol (**1a**) and styrene (**3a**) was used to determine the most suitable and selective reaction conditions for the synthesis of β-hydroxysulfide, with the key intermediate being 1,2-diphenyldisulfane (**2a**). In this reaction, after the conversion of thiophenol (**1a**) to 1,2-diphenyldisulfane (**2a**), styrene (**3a**) was added to the reaction mixture and further irradiated for the required time (Table 3). It was observed that a 1:2:1 ratio of styrene (**3a**), thiophenol (**1a**), and DABCO under 5 h 45 min of light irradiation in the second step gave the maximum yield of 87% (entry 1). Any more enhancement in light irradiation time did not affect the yield (entry 4), but lower light irradiation gave only a lesser yield (entries 2 and 3). Also, decrement in the reagent quantities reduced the yield (entry 5), whereas any increase in the equivalent amount of the reagent does not affect productivity (entry 6). Other light sources, such as 18 W CFL light and 30 W fluorescent black light (385–390 nm), gave 65 and 88% yields, respectively (entries 7 and 8). Experiments for a complete one-pot reaction of styrene (**3a**) and thiophenol (**1a**) to construct β-hydroxysulfide **4a** were also explored, but the path showed very low selectivity with a maximum yield of 56% only (Table S4, SI).

Using the best reaction conditions, we have investigated the substrate scope for a variety of olefins (**3**) and thiols (**1**) to construct β-hydroxysulfide (**4**). In this finding, we used both the EDA complex pathway (condition A) and the TOCO complex pathway (condition B) to look at the range of olefins (**3**) and thiols (**1**) with different functional groups in the moiety. In Scheme 3, two different conditions (conditions A and B) were used to establish competition data for the formation of β-hydroxysulfide (**4**). Unfortunately, by using condition B, less selectivity was achieved. Since the stability and availability of thiol radical species depend upon the nature of substituents present in the aromatic ring, the aromatic thiols with electron-donating substituents such as −Me and −OMe (**4c**, **4d**, and **4g**) gave a slightly higher yield (80–92%) in comparison with those with electron-withdrawing substituents such as −Br, −Cl, and −F (**4b**, **4e**, and **4f**) by condition A. But a reverse trend was observed when condition B was used for the same because of less selectivity by the TOCO complex path. For 2-amino-thiophenol (**1h**), a slight decrement in yield (62%) was observed by condition A, but a comparatively moderate yield of 51% was achieved by condition B. During the exploration of the olefin scope, a slightly higher yield of 86–90% by condition A and 57–65% by condition B was observed with the olefins with electron-donating groups such as −Me and −OMe (**4i** and **4j**). On the other side, the electron-deficient olefins with −Cl and −Br functional groups (**4k** and **4l**) gave a slightly lower yield of 81–85% by condition A and 40–43% by condition B. Styrene with the −OMe group (**3i**) produced 90% of **4m** when 3-methylbenzenethiol (**1d**) was used in condition A, whereas styrene with the −Me group (**3j**) produced 86% of **4n** with 4-bromobenzenethiol (**1f**). But for the same combinations, **4m** and **4n** were formed with 68 and 61% yields, respectively, by condition B. Unfortunately, neither protocol was active in β-hydroxysulfide (**4o-4t**) synthesis from aliphatic olefins or thiols.

To demonstrate the potential of our protocol, a gram-scale experiment was conducted for all three reactions (Scheme 4).

Scheme 2. Substrate Scope for Photoinduced Self- and Cross-Coupling of Thiols[a,b]
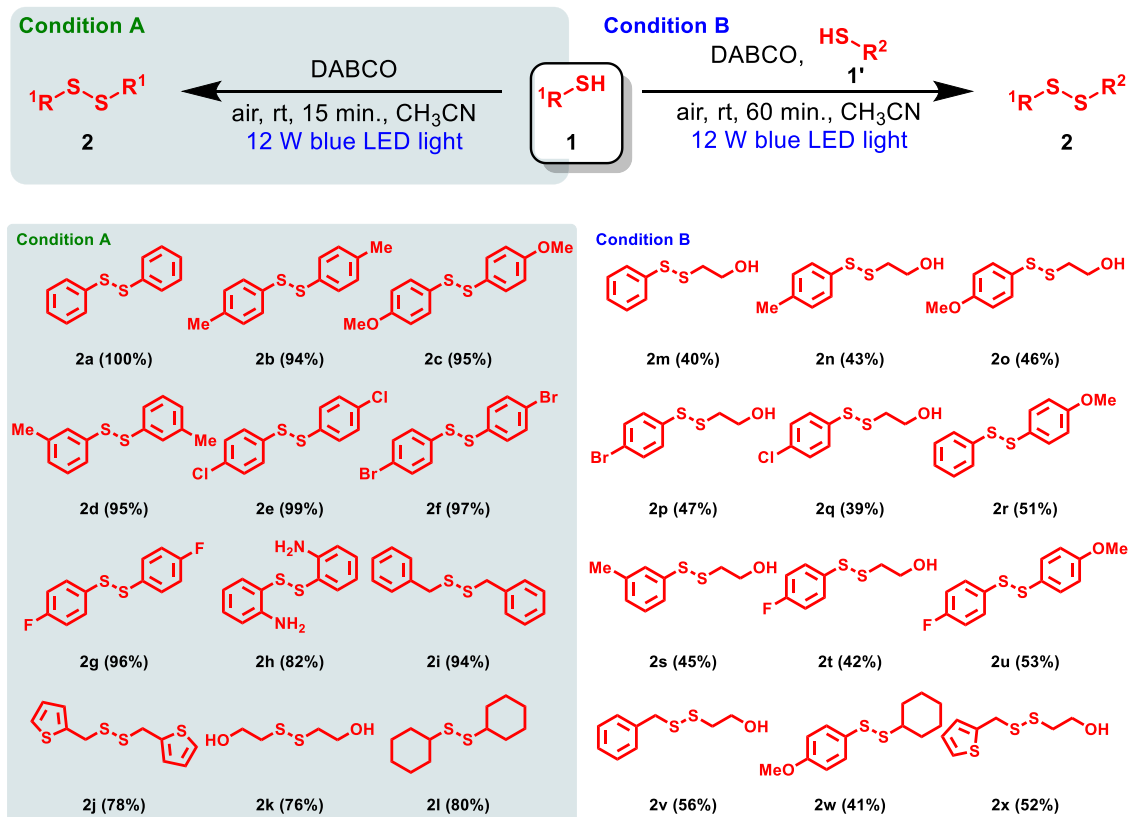
[a]Reaction conditions: condition A. **1a** (0.90 mmol), **DABCO** (0.45 mmol), CH$_3$CN (4 mL), 15 min, and 12 W blue LED light. [b]Condition B. **1a** (0.90 mmol), **1′a** (0.90 mmol), **DABCO** (0.90 mmol), CH$_3$CN (4 mL), 60 min, and 12 W blue LED light.
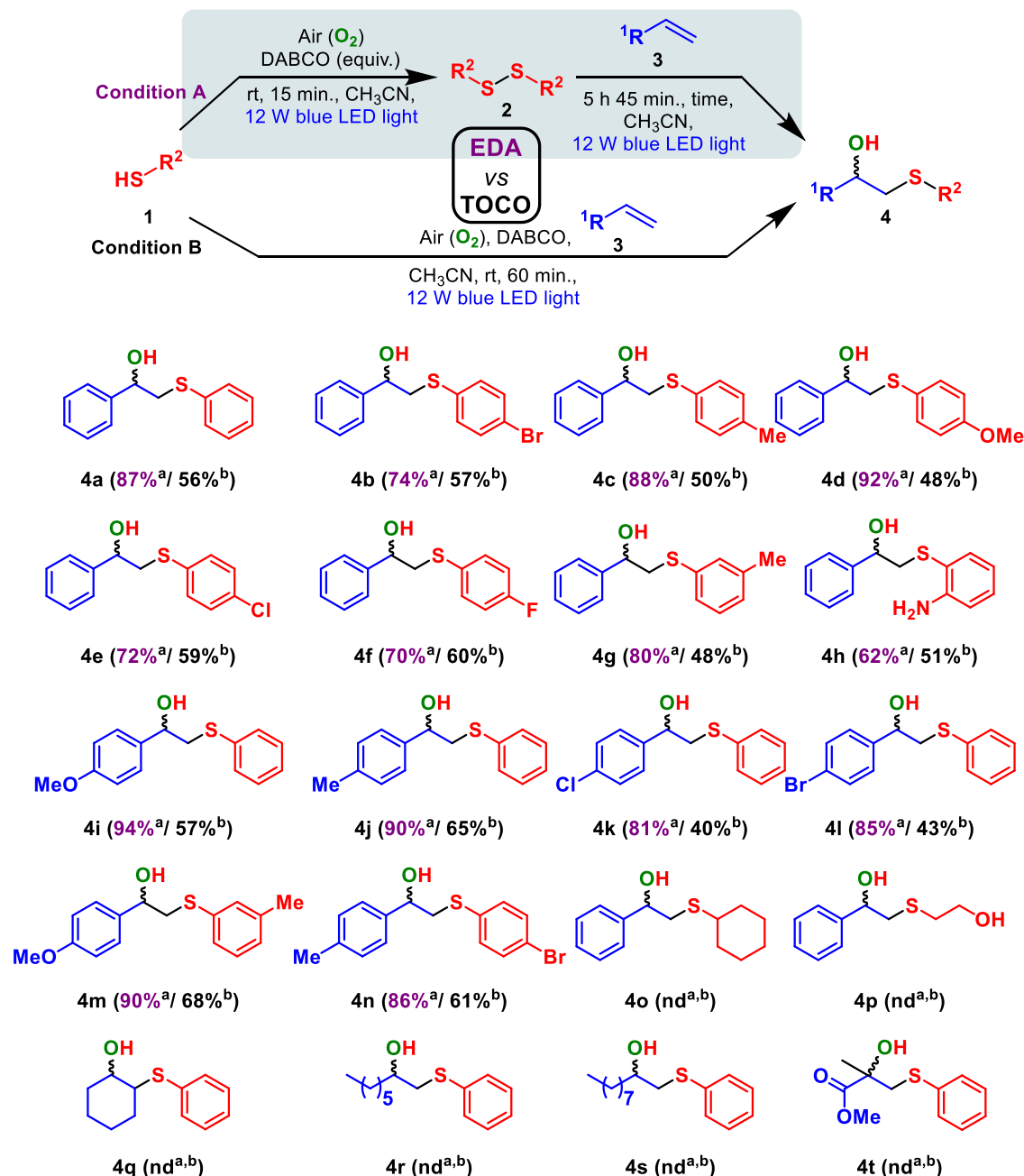
Table 3. Optimization of β-Hydroxysulfide Synthesis[a]

entry	variation from the standard condition	yield of **4a** (%)[b]
1	**none**	**87**
2	1 h 45 min light irradiation	64
3	3 h 45 min light irradiation	77
4	7 h 45 min light irradiation	87
5	1.5 equiv **1a** and 0.75 equiv **DABCO**	80
6	2.5 equiv **1a** and 1.25 equiv **DABCO**	87
7	18 W CFL light	65
8	30 W fluorescent black light	88

[a]Reaction conditions: (i) **1a** (1.91 mmol), **DABCO** (0.95 mmol, 1.0 equiv), CH$_3$CN, 15 min, 12 W Blue LED light; (ii) **3a** (0.96 mmol), 5 h 45 min, and 12 W blue LED light. [b]Isolated yield.

Under standard conditions, 9.07 mmol of thiophenol (**1a**) gave 94% of the self-coupled product **2a** (Scheme 4a) and 36% of the cross-coupled product **2m** (Scheme 4b). In the case of the reaction between thiophenol (**1a**, 19.2 mmol) and styrene (**3a**, 9.6 mmol), 82% of 1-phenyl-2-(phenylthio)ethan-1-ol (**4a**) was produced (Scheme 4c).

To find out the steps involved in the reaction, two sets of control experiments were conducted where one was for S–S bond formation (Table 4) of phenylmethanethiol (**1i**) and another was the second step leading to 1-phenyl-2-

(phenylthio)ethan-1-ol (**4a**) synthesis (Table 5). Both reactions under dark conditions failed to produce any product (Table 4, entry 1/Table 5, entry 1). In the case of self-coupling of phenylmethanethiol (**1i**), without DABCO, no progress in the reaction was observed (Table 4, entry 2). Under an inert atmosphere, no progress in the reaction for self-coupling of thiol was observed (Table 4, entry 3). But in the case of β-hydroxysulfide synthesis, only a negligible decrement in yield was observed under the nitrogen atmosphere (Table 5, entry 2). This indicates the necessity of an air atmosphere in the first

Scheme 3. Substrate Scope for Photoinduced β-Hydroxysulfide Synthesis[a,b]

4a (87%[a]/ 56%[b])   4b (74%[a]/ 57%[b])   4c (88%[a]/ 50%[b])   4d (92%[a]/ 48%[b])

4e (72%[a]/ 59%[b])   4f (70%[a]/ 60%[b])   4g (80%[a]/ 48%[b])   4h (62%[a]/ 51%[b])

4i (94%[a]/ 57%[b])   4j (90%[a]/ 65%[b])   4k (81%[a]/ 40%[b])   4l (85%[a]/ 43%[b])

4m (90%[a]/ 68%[b])   4n (86%[a]/ 61%[b])   4o (nd[a,b])   4p (nd[a,b])

4q (nd[a,b])   4r (nd[a,b])   4s (nd[a,b])   4t (nd[a,b])

[a]Reaction conditions: condition A. (i) **1a** (1.91 mmol), **DABCO** (0.95 mmol, 1.0 equiv), CH₃CN (4 mL), 15 min, 12 W Blue LED light; (ii) **3a** (0.96 mmol), 5 h 45 min, and 12 W blue LED light. [b]Condition B. **1a** (1.91 mmol), **3a** (0.96 mmol), **DABCO** (0.95 mmol, 1.0 equiv), CH₃CN (4 mL), 60 min, and 12 W blue LED light.

step and also denies the requirement of an air atmosphere in the second step. In the presence of radical scavengers such as TEMPO and butylated hydroxytoluene (BHT),[81] a tremendous decrement in yield was observed in both reactions (Table 4, entries 4 and 5/Table 5, entries 3 and 4). This confirmed the presence of a radical pathway in the reactions. The generation of superoxide radical anion during β-hydroxysulfide synthesis was proved by the quenching experiment with p-benzoquinone[17a] (Table 5, entry 7). However, no role of a superoxide radical anion was found during the coupling reaction of thiols (Table 4, entry 7). In the presence of sodium azide as a singlet oxygen scavenger,[17a] a noticeable decrement of yield was observed for the coupling reaction of thiols (Table

4, entry 6), but for the β-hydroxysulfide synthesis step, not much depression of yield was observed (Table 5, entry 5). Thus, in the first step, the role of singlet oxygen was proved but not in the second step of β-hydroxysulfide synthesis. The generation of H₂O₂ in the first step and quenching of that H₂O₂ in the second step of β-hydroxysulfide synthesis were also proved by the I₂−starch experiments (Figure S1, SI). On the other side, in the presence of KI, only a trace amount of 1-phenyl-2-(phenylthio)ethan-1-ol (**4a**) was formed because of the quenching of H₂O₂ (Table 5, entry 6).[17b]

To understand the origin of the C−S cross-coupling reaction, we performed UV−vis spectroscopic measurements on various combinations of reactants **1a**, **2a**, **3a**, and **DABCO**
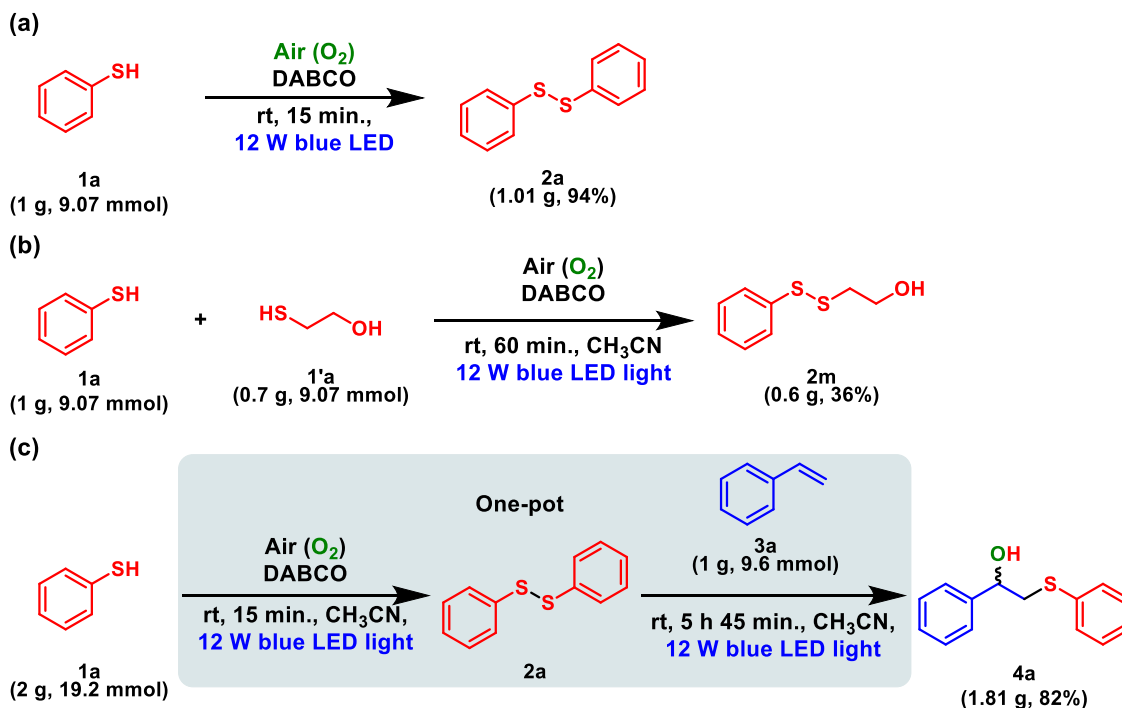
Scheme 4. Gram Scale Reactions

(a)

1a
(1 g, 9.07 mmol)

Air (O₂)
DABCO
rt, 15 min.,
12 W blue LED

2a
(1.01 g, 94%)

(b)

1a
(1 g, 9.07 mmol)

+

1'a
(0.7 g, 9.07 mmol)

Air (O₂)
DABCO
rt, 60 min., CH₃CN
12 W blue LED light

2m
(0.6 g, 36%)

(c)

One-pot

1a
(2 g, 19.2 mmol)

Air (O₂)
DABCO
rt, 15 min., CH₃CN,
12 W blue LED light

2a

3a
(1 g, 9.6 mmol)
rt, 5 h 45 min., CH₃CN,
12 W blue LED light

4a
(1.81 g, 82%)

Table 4. Control Experiments for Self-Coupling of Thiols

1i

Air (O₂)
DABCO
rt, 120 min., CH₃CN,
12 W blue LED light

2i (94%)

| entry	variation from the standard condition	notes	yield of 2i (%)[a]
1	dark	importance of light	nd
2	no DABCO	importance of base	nd
3	N₂ atmosphere	importance of air oxygen	nd
4	TEMPO (2.0 equiv)	radical scavenger	trace
5	BHT (2.0 equiv)	radical scavenger	12
6	NaN₃ (2.0 equiv)	singlet oxygen scavenger	42
7	p-benzoquinone (2.0 equiv)	superoxide radical anion scavenger	94

[a]Isolated yield (nd = not detected).

at 2×10^{-5} (M) and 0.001 (M) concentrations in each sample and reactant mixtures (Figure 2a−c). When a 1:1 ratio of **3a** and **2a** as well as **1a** and **3a** was taken, a red shift of the absorption band was observed when compared to the respective individual molecules (Figure 2b). This indicated that both **3a** and **2a**, as well as **1a** and **3a**, formed a complex when mixed. It was already proven in the literature that, in contact with **1a**, styrene (**3a**) could form a TOCO complex, whereas, in contact with disulfide (**2a**), styrene (**3a**) could form an EDA complex.[18a,b] Therefore, in both cases, a new absorption band was observed. Additionally, the Yoe and Jones mole ratio method confirmed the formation of a 1:1 EDA complex between **3a** and **2a** (Figure 2d).[18c,d] Further, we conducted a ¹H NMR titration experiment between **2d** and **3i** (Figure 2e).[18a,b] The upfield shift of the **2d** methyl protons with increasing **3i** concentration justified the formation of an EDA complex between styrene and disulfide. Finally, the

Table 5. Control Experiments for β-Hydroxysulfide Synthesis

One-pot

1a

Air (O₂)
DABCO (equiv.)
rt, 15 min., CH₃CN,
12 W blue LED light

2a (100%)

3a
5 h 45 min., time,
CH₃CN,
12 W blue LED light

4a (87%)

entry	variation from the standard condition (second step)	notes (second step)	yield of 4a (%)[a]
1	dark	importance of light	trace
2	N₂ atmosphere	importance of air oxygen	79
3	TEMPO (2.0 equiv)	radical scavenger	trace
4	BHT (2.0 equiv)	radical scavenger	21
5	NaN₃ (2.0 equiv)	singlet oxygen scavenger	86
6	KI (2.0 equiv)	H₂O₂ scavenger	trace
7[b]	p-benzoquinone (2.0 equiv)	superoxide radical anion scavenger	16

[a]Isolated yield. [b]p-Benzoquinone was added at the beginning of the reaction.
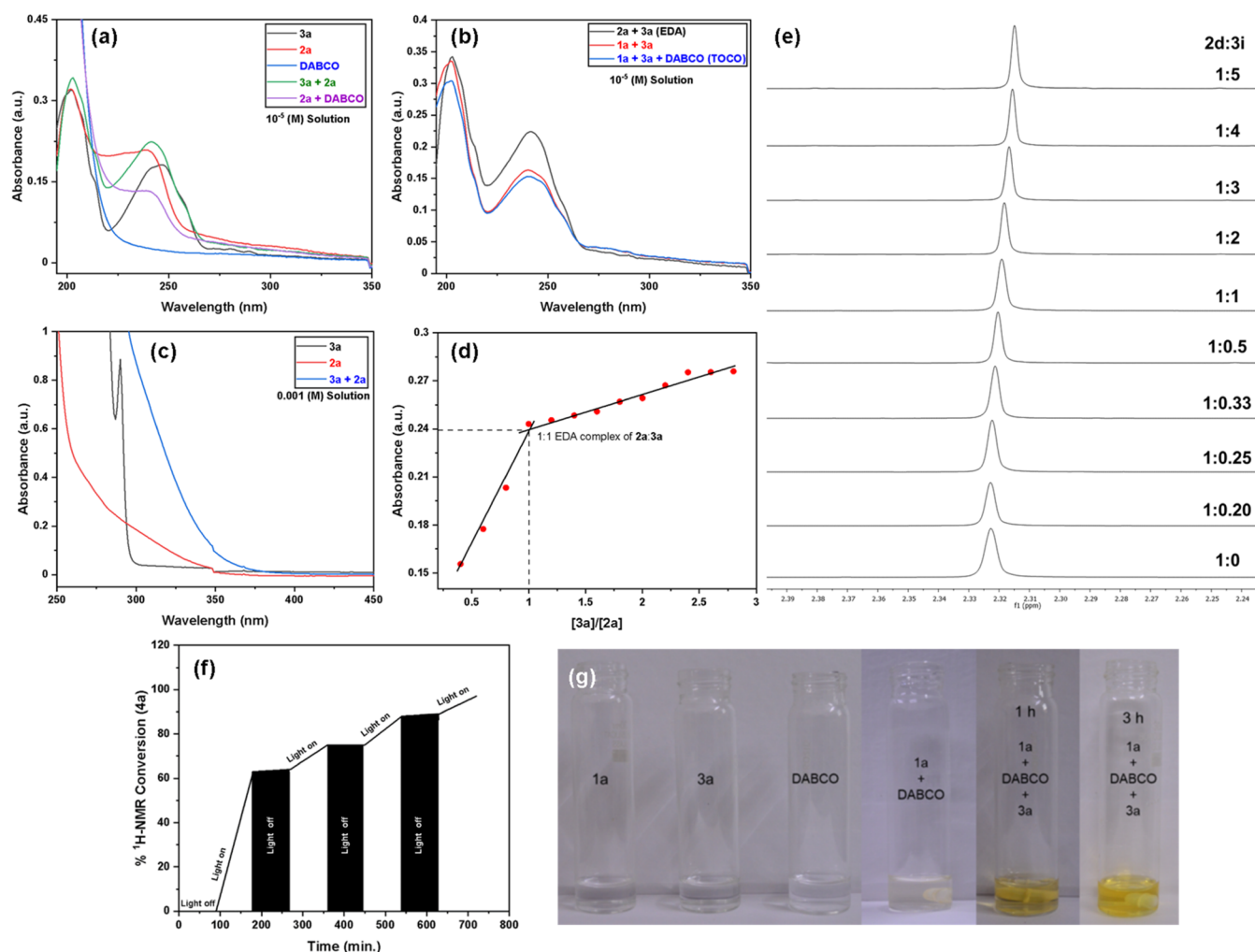
Figure 2. (a) UV−vis absorption spectra of **3a**, **2a**, **DABCO**, and respective mixtures in 10^{-5} (M) concentration. (b) Comparison of UV−vis absorption spectra between the EDA complex and the TOCO complex. (c) UV−vis absorption spectra of **3a**, **2a**, and respective mixture in 0.001 (M) concentration. (d) Yoe and Jones mole ratio plot. (e) ^{1}H NMR titration experiment between **2d** and **3i**. (f) Light on−off experiment. (g) Color change of the reaction mixture.

presence of a radical path and absence of radical chain propagation possibility was proved by a light on−off experiment where not much improvement in the yield was observed when the light was turned off (Figure 2f). Even the physical confirmation of EDA complex formation was done by the yellow color that appeared when disulfide **2a** (obtained by 15 min light irradiation of thiophenol, **1a**) was mixed with styrene (**3a**) and further irradiated for 1 to 3 h (Figure 2g).[18c]

In Scheme 5, a possible mechanism for both thiol coupling and β-hydroxysulfide synthesis in the presence of aromatic alkenes was identified based on literature evidence[18,19] and control experiments. DABCO first deprotonates thiophenol (**1a**), which is then oxidized by active oxygen molecules in the presence of light to produce thiol radical intermediates **A**.[19a] In the next step, **A** undergoes a self-coupling reaction to produce 1,2-diphenyldisulfane (**2a**). **2a** is further involved in EDA complex formation with styrene (**3a**) to produce the carboradical species **E** along with a thiol radical **A**. Now **E** can react with the hydroxyl radical[19b−e] generated from H_2O_2 to produce 1-phenyl-2-(phenylthio)ethan-1-ol (**4a**).

CONCLUSIONS

In conclusion, a visible-light-induced, catalyst-free, green approach for S−S bond formation *via* thiol self- and cross-coupling reactions, as well as β-hydroxysulfides synthesis *via* EDA complex formation between disulfide and styrene, has been developed. Within 15 min of light irradiation, a self-coupled product with a high yield was obtained, and 60 min of light irradiation produced a cross-coupled product of thiols with a moderate yield. The EDA complex between the disulfide and styrene leads to the formation of β-hydroxysulfides with a 94% yield after only 6 h of light irradiation. The green environment, such as aerial oxygen and acetonitrile solvent with blue light irradiation, as well as high regioselectivity and high functional group tolerance, makes the protocol easily accessible to wide industrial applications.

EXPERIMENTAL SECTION

General Information. The analytical grade solvents and commercially available reagents were purchased from SDFCL, AVARICE, Fisher Scientific, MERCK, THOMAS BAKER, Spectrochem, AVRA, and LOBA Chemie. All of the purchased reagents were used without further purification. Noncommer-

Scheme 5. Proposed Reaction Mechanism

cially available starting materials were synthesized by known literature procedures, and their physical and spectroscopic data were compared with the reported values. Purification of the derivatives was done by column chromatography on silica gel (100−200 mess sizes well as 200−400 mess size). D'Mak LED Ceiling COB spotlight 3 Watt (dimensions: 7L × 4W × 10H cm) and Gesto 2835 Cove LED strip Light 6 Watt (5 meters) with a combined wavelength of 429 nm were used in the photoreactor setup. NMR spectra were acquired on a BRUKER 500 MHZ and JOEL 400 MHZ spectrometer for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl$_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR/DMSO-d_6: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). ^{13}C NMR spectra were acquired on a broadband decoupled mode. The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septuplet), m (multiplet), dd (doublet of doublet), and br.s (broad singlet).

Synthesis of Starting Materials. Phenylmethanethiol (**1i**) and thiophene-2-ylmethanethiol (**1j**) were prepared according to a published procedure; spectral data were in agreement with literature values.[20] Noncommercially available alkenes (**3b−e**)[21a,b] were synthesized by known literature procedures, and their physical and spectroscopic data were compared with the reported values.

General Procedure for the Photoinduced Self-Coupling Reaction of Thiols. An oven-dried glass vial was charged with thiol **1** (0.90 mmol) and DABCO (0.45 mmol). 4 mL of CH$_3$CN was added to the reaction mixture and stirred

under 12 W blue LED light for 15 min. After the complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to give product **2**.

Characterization. *1,2-Diphenyldisulfane (2a).* White solid; yield: 100%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, J = 7.9 Hz, 4H), 7.31 (t, J = 7.6 Hz, 4H), 7.23 (t, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.10, 129.17, 127.56, 127.24. Spectral data are in agreement with literature values.[22]

1,2-Di-p-tolyldisulfane (2b). White solid; yield: 94%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 (d, J = 8.2 Hz, 4H), 7.11 (d, J = 8.1 Hz, 4H), 2.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.54, 134.02, 129.90, 128.65, 21.17. Spectral data are in agreement with literature values.[22]

1,2-Bis(4-methoxyphenyl)disulfane (2c). Light yellow liquid; yield: 95%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, J = 8.7 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 160.03, 132.77, 128.54, 114.73, 55.47. Spectral data are in agreement with literature values.[22]

1,2-Di-m-tolyldisulfane (2d). Light yellow liquid; yield: 95%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (d, J = 7.4 Hz, 4H), 7.19 (t, J = 7.9 Hz, 2H), 7.03 (d, J = 7.7 Hz, 2H), 2.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.02, 137.04, 129.01, 128.12, 124.68, 21.48. Spectral data are in agreement with literature values.[23]

1,2-Bis(4-chlorophenyl)disulfane (2e). White solid; yield: 99%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.29, 133.79, 129.48, 129.44. Spectral data are in agreement with literature values.[22]

1,2-Bis(4-bromophenyl)disulfane (2f). White solid; yield: 97%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.5 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.87, 132.36, 129.54, 121.68. Spectral data are in agreement with literature values.[22]

1,2-Bis(4-fluorophenyl)disulfane (2g). Colorless Liquid; yield: 96%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46−7.42 (m, 4H), 7.01 (t, J = 8.6 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.73, 161.76, 132.33, 132.30, 131.44, 131.38, 116.50, 116.32. Spectral data are in agreement with literature values.[22]

2,2′-Disulfanediyldianiline (2h). Yellow solid; yield: 82%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17−7.14 (m, 4H), 6.71 (d, J = 8.3 Hz, 2H), 6.59 (t, J = 7.5 Hz, 2H), 4.26 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.73, 136.94, 131.72, 118.89, 118.37, 115.37. Spectral data are in agreement with literature values.[24]

1,2-Dibenzyldisulfane (2i). Colorless Liquid; yield: 94%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 (t, J = 7.1 Hz, 4H), 7.31−7.25 (m, 6H), 3.62 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.53, 129.56, 128.63, 127.57, 43.46. Spectral data are in agreement with literature values.[71,22]

1,2-Bis(thiophen-2-ylmethyl)disulfane (2j). Colorless Liquid; yield: 78%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25−7.24 (m, 2H), 6.96−6.94 (m, 4H), 3.87 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.83, 127.29, 127.05, 125.76, 37.77. Spectral data are in agreement with literature values.[71]

2,2′-Disulfanediylbis(ethan-1-ol) (2k). Colorless Liquid; yield: 78%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.91 (t, J = 5.7 Hz, 4H), 2.88 (t, J = 5.7 Hz, 4H), 2.12 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 60.48, 41.32. Spectral data are in agreement with literature values.[25]

1,2-Dicyclohexyldisulfane (2l). Colorless Liquid; yield: 80%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.70−2.66 (m, 2H), 2.05−2.03 (m, 4H), 1.79−1.77 (m, 4H), 1.63−1.60 (m, 2H), 1.35−1.21 (m, 10H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 50.08, 32.97, 26.22, 25.82. Spectral data are in agreement with literature values.[23]

General Procedure for Photoinduced Cross-Coupling Reaction of Thiols. An oven-dried glass vial was charged with thiol **1** (0.90 mmol), **1′** (0.90 mmol), and DABCO (0.90 mmol). 4 mL of CH$_3$CN was added to the reaction mixture and stirred under 12 W blue LED light for 60 min. After the complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to give product **2**.

Characterization. *2-(Phenyldisulfaneyl)ethan-1-ol (2m).* Colorless Liquid; yield: 40%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 5.5 Hz, 1H), 3.88 (t, J = 5.7 Hz, 2H), 2.92 (t, J = 5.7 Hz, 2H), 1.89 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.07, 129.21, 127.95, 127.26, 60.01, 41.23. Spectral data are in agreement with literature values.[81]

2-(p-Tolyldisulfaneyl)ethan-1-ol (2n). Colorless Liquid; yield: 43%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.85 (t, J = 5.7 Hz, 2H), 2.89 (t, J = 5.7 Hz, 2H), 2.34 (s, 3H), 1.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.77, 133.67, 130.07, 129.03, 59.99, 41.33, 21.18. Spectral data are in agreement with literature values.[26]

2-((4-Methoxyphenyl)disulfaneyl)ethan-1-ol (2o). Colorless Liquid; yield: 46%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.87 (t, J = 5.7 Hz, 2H), 3.81 (s, 3H), 2.89 (t, J = 5.7 Hz, 2H), 1.83 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.97, 132.37, 127.91, 114.95, 60.01, 55.53, 41.31. Spectral data are in agreement with literature values.[27]

2-((4-Bromophenyl)disulfaneyl)ethan-1-ol (2p). Colorless Liquid; yield: 47%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46−7.41 (m, 4H), 3.85 (t, J = 5.8 Hz, 2H), 2.89 (t, J = 5.8 Hz, 2H), 1.85 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 136.33, 132.22, 129.38, 121.14, 60.01, 41.23. Spectral data are in agreement with literature values.[8g]

2-((4-Chlorophenyl)disulfaneyl)ethan-1-ol (2q). Colorless Liquid; yield: 39%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 3.86 (t, J = 5.7 Hz, 2H), 2.89 (t, J = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 135.67, 133.29, 129.33, 129.30, 60.02, 41.26.

1-(4-Methoxyphenyl)-2-phenyldisulfane (2r). Colorless Liquid; yield: 51%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, J = 7.3 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.94, 137.60, 131.89, 129.14, 128.34, 128.14, 127.34, 114.83, 55.49. Spectral data are in agreement with literature values.[28]

2-(m-Tolyldisulfaneyl)ethan-1-ol (2s). Colorless Liquid; yield: 45%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37−7.35 (m, 2H), 7.23 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 3.86 (t, J = 5.7 Hz, 2H), 2.90 (t, J = 5.7 Hz, 2H), 2.35 (s, 3H), 1.73 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.17, 136.90, 129.08, 128.64, 128.23, 125.17, 60.11, 41.38, 21.43.

2-((4-Fluorophenyl)disulfaneyl)ethan-1-ol (2t). Colorless Liquid; yield: 42%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.55−7.52 (m, 2H), 7.04 (t, J = 8.5 Hz, 2H), 3.87 (t, J = 5.8 Hz, 2H), 2.90 (t, J = 5.8 Hz, 2H), 1.70 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.54, 161.57, 132.46, 132.43, 131.06, 131.00, 116.51, 116.33, 60.15, 41.38.

1-(4-Fluorophenyl)-2-(4-methoxyphenyl)disulfane (2u). Colorless Liquid; yield: 53%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46−7.44 (m, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.00 (t, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.69, 161.72, 160.23, 132.56, 132.55, 132.53, 131.75, 131.68, 128.00, 116.35, 116.17, 114.91, 55.51. Spectral data are in agreement with literature values.[28]

2-(Benzyldisulfaneyl)ethan-1-ol (2v). Colorless Liquid; yield: 56%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34−7.27 (m, 5H), 3.91 (s, 2H), 3.73−3.72 (m, 2H), 2.52 (t, J = 5.7 Hz, 2H), 1.84 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.34, 129.45, 128.72, 127.71, 60.34, 43.66, 41.06. Spectral data are in agreement with literature values.[81]

1-Cyclohexyl-2-(4-methoxyphenyl)disulfane (2w). Colorless Liquid; yield: 41%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.82−2.77 (m, 1H), 2.05−2.00 (m, 2H), 1.77−1.74 (m, 2H), 1.61−1.56 (m, 1H), 1.38−1.19 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.31, 130.86, 129.54, 114.69, 55.51, 49.84, 32.73, 26.13, 25.79. Spectral data are in agreement with literature values.[29]

2-((Thiophen-2-ylmethyl)disulfaneyl)ethan-1-ol (2x). Colorless Liquid; yield: 52%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.26−7.25 (m, 1H), 7.02−7.01 (m, 1H), 6.95−6.94 (m, 1H), 4.12 (s, 2H), 3.77 (t, J = 5.7 Hz, 2H), 2.62 (t, J = 5.7 Hz, 2H), 1.76 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.87, 127.27, 127.10, 125.86, 60.33, 41.17, 38.02.

General Procedure for Photoinduced β-Hydroxysulfide Synthesis by EDA Complex Formation. An oven-dried glass vial was charged with thiol **1** (1.91 mmol) and DABCO (0.95 mmol). 4 mL of CH$_3$CN was added to the reaction mixture and stirred under 12 W blue LED light for 15 min. After 15 min, **3** (0.96 mmol) was added to the reaction mixture and further stirred under 12 W blue LED light for 5 h 45 min. After the complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to give product **3**.

Characterization. *1-Phenyl-2-(phenylthio)ethan-1-ol (4a).* Colorless Liquid; yield: 87%^{a}/56%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, J = 7.2 Hz, 2H), 7.36−7.28 (m, 7H), 7.24−7.23 (m, 1H), 4.75−4.71 (1H), 3.33 (dd, J = 13.8, 3.5 Hz, 1H), 3.10 (dd, J = 13.8, 9.5 Hz, 1H), 2.83 (d, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.29, 135.06, 130.36, 129.26, 128.68, 128.11, 126.91, 125.98, 71.83, 44.15. Spectral data are in agreement with literature values.[19f]

2-((4-Bromophenyl)thio)-1-phenylethan-1-ol (4b). Pale yellow Liquid; yield: 74%^{a}/ 57%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.38−7.26 (m, 7H), 4.73 (dd, J = 9.2, 3.6 Hz, 1H), 3.28 (dd, J = 13.8, 3.7 Hz, 1H), 3.11 (dd, J = 13.8, 9.3 Hz, 1H), 2.74 (br.s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.08, 134.48, 132.21, 131.60, 128.69, 128.20, 125.93, 120.67, 71.94, 43.82. Spectral data are in agreement with literature values.[30]

1-Phenyl-2-(p-tolylthio)ethan-1-ol (4c). Colorless Liquid; yield: 88%^{a}/ 50%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36−7.27 (m, 7H), 7.14 (d, J = 7.9 Hz, 2H), 4.68 (dd, J = 9.7, 3.3 Hz, 1H), 3.28 (dd, J = 13.8, 3.3 Hz, 1H), 3.03 (dd, J = 13.8, 9.7 Hz, 1H), 2.92 (br.s, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.28, 137.18, 131.12, 131.06, 130.03, 128.60, 127.99, 125.96, 71.59, 44.85, 21.15. Spectral data are in agreement with literature values.[30]

2-((4-Methoxyphenyl)thio)-1-phenylethan-1-ol (4d). Colorless Liquid; yield: 92%^{a}/ 48%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 7.35−7.27 (m, 5H), 6.87 (d, J = 8.6 Hz, 2H), 4.63 (dd, J = 9.7, 3.2 Hz, 1H), 3.82 (s, 3H), 3.20 (dd, J = 13.8, 3.3 Hz, 1H), 2.97 (dd, J = 13.8, 9.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.47, 142.25, 134.02, 128.58, 127.95, 125.97, 124.85, 114.90, 71.44, 55.44, 46.12. Spectral data are in agreement with literature values.[30]

2-((4-Chlorophenyl)thio)-1-phenylethan-1-ol (4e). Colorless Liquid; yield: 72%^{a}/ 59%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37−7.27 (m, 9H), 4.72 (dd, J = 9.3, 3.6 Hz, 1H), 3.28 (dd, J = 13.8, 3.6 Hz, 1H), 3.11 (dd, J = 13.8, 9.3 Hz, 1H), 2.62 (br.s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.09, 133.76, 132.82, 131.50, 129.30, 128.68, 128.18, 125.93, 71.92, 44.04. Spectral data are in agreement with literature values.[30]

2-((4-Fluorophenyl)thio)-1-phenylethan-1-ol (4f). Colorless Liquid; yield: 70%^{a}/ 60%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44−7.41 (m, 2H), 7.36−7.28 (m, 5H), 7.02 (t, J = 8.6 Hz, 2H), 4.68 (dd, J = 9.4, 3.5 Hz, 1H), 3.25 (dd, J = 13.8, 3.5 Hz, 1H), 3.06 (dd, J = 13.8, 9.4 Hz, 1H), 2.78 (br.s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.21, 161.25, 142.13, 133.30, 133.24, 129.96, 128.66, 128.13, 125.96, 116.44, 116.26, 71.80, 45.19. Spectral data are in agreement with literature values.[30]

1-Phenyl-2-(m-tolylthio)ethan-1-ol (4g). Colorless Liquid; yield: 80%^{a}/ 48%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36−7.28 (m, 5H), 7.24−7.19 (m, 3H), 7.05 (d, J = 6.8 Hz, 1H), 4.72 (dd, J = 9.5, 3.4 Hz, 1H), 3.32 (dd, J = 13.8, 3.4 Hz, 1H), 3.08 (dd, J = 13.8, 9.6 Hz, 1H), 2.88 (br.s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.30, 139.06, 134.66, 131.02, 129.08, 128.65, 128.06, 127.79, 127.31, 125.97, 71.75, 44.12, 21.44. Spectral data are in agreement with literature values.[30]

2-((2-Aminophenyl)thio)-1-phenylethan-1-ol (4h). Yellow Liquid; yield: 62%^{a}/ 51%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, J = 7.7 Hz, 1H), 7.33−7.25 (m, 5H), 7.17 (t, J = 7.7 Hz, 1H), 6.80−6.74 (m, 2H), 4.62 (dd, J = 9.6, 3.0 Hz, 1H), 3.14 (dd, J = 13.7, 3.1 Hz, 1H), 2.89 (dd, J = 13.7, 9.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.23, 142.39, 136.52, 130.43, 128.57, 127.90, 125.98, 119.49, 117.33, 115.74, 72.11, 44.79. Spectral data are in agreement with literature values.[31]

1-(4-Methoxyphenyl)-2-(phenylthio)ethan-1-ol (4i). Pale yellow Liquid; yield: 94%^{a}/ 57%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, J = 7.5 Hz, 2H), 7.33−7.27 (m, 4H), 7.23 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 4.68 (dd, J = 9.3, 3.4 Hz, 1H), 3.80 (s, 3H), 3.29 (dd, J = 13.8, 3.6 Hz, 1H), 3.10 (dd, J = 13.8, 9.4 Hz, 1H), 2.78 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.46, 135.09, 134.39, 130.26, 129.24, 127.25, 126.84, 114.06, 71.43, 55.42, 43.98. Spectral data are in agreement with literature values.[19f]

2-(Phenylthio)-1-(p-tolyl)ethan-1-ol (4j). Pale yellow Liquid; yield: 90%^{a}/ 65%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.25−7.22 (m, 3H), 7.16 (d, J = 7.8 Hz, 1H), 4.70 (d, J = 9.2 Hz, 1H), 3.31 (dd, J = 13.8, 3.5 Hz, 1H), 3.09 (dd, J = 13.8, 9.5 Hz, 1H), 2.78 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.29, 137.84, 135.09, 130.22, 129.34, 129.22, 126.80, 125.91, 71.63, 43.97, 21.27. Spectral data are in agreement with literature values.[15b]

1-(4-Chlorophenyl)-2-(phenylthio)ethan-1-ol (4k). Colorless Liquid; yield: 81%^{a}/ 40%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, J = 7.5 Hz, 2H), 7.36−7.28 (m, 7H), 4.70 (d, J = 9.2 Hz, 1H), 3.31 (dd, J = 13.9, 3.5 Hz, 1H), 3.05 (dd, J = 13.9, 9.5 Hz, 1H), 2.92 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 140.68, 134.58, 133.75, 130.57, 129.34, 128.81, 127.37, 127.14, 71.05, 44.23. Spectral data are in agreement with literature values.[15b]

1-(4-Bromophenyl)-2-(phenylthio)ethan-1-ol (4l). Colorless Liquid; yield: 85%^{a}/ 43%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 4.9 Hz, 1H), 7.19 (d, J = 8.3 Hz, 2H), 4.64 (dd, J = 9.4, 3.3 Hz, 1H), 3.25 (dd, J = 13.9, 3.5 Hz, 1H), 3.00 (dd, J = 13.9, 9.4 Hz, 1H), 2.88 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.22, 134.56, 131.76, 130.59, 129.35, 127.71, 127.16, 121.89, 71.09, 44.21. Spectral data are in agreement with literature values.[15b]

1-(4-Methoxyphenyl)-2-(m-tolylthio)ethan-1-ol (4m). Colorless Liquid; yield: 90%^{a}/ 68%^{b}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 (d, J = 8.5 Hz, 2H), 7.22−7.18 (m, 3H), 7.04 (d, J = 7.0 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 4.69 (d, J = 8.6 Hz, 1H), 3.80 (s, 3H), 3.29 (dd, J = 13.7, 3.7 Hz, 1H), 3.09 (dd, J = 13.7, 9.3 Hz, 1H), 2.76 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.44, 138.96, 134.95, 134.54,

130.90, 129.01, 127.63, 127.23, 127.21, 114.03, 71.53, 55.35, 43.94, 21.38.

2-((4-Bromophenyl)thio)-1-(p-tolyl)ethan-1-ol (4n). Colorless Liquid; yield: 86%[a]/ 61%[b]; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.72 (dd, *J* = 9.0, 3.8 Hz, 1H), 3.27 (dd, *J* = 13.7, 3.9 Hz, 1H), 3.13 (dd, *J* = 13.7, 9.1 Hz, 1H), 2.62 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.22, 137.97, 134.73, 132.20, 131.60, 129.37, 125.90, 120.61, 71.94, 43.81, 21.24. Spectral data are in agreement with literature values.[14c]

General Procedure for Photoinduced β-Hydroxysulfide Synthesis by TOCO Complex Formation. An oven-dried glass vial was charged with alkene **3** (0.96 mmol), thiol **1** (1.92 mmol), and DABCO (0.96 mmol). 4 mL of CH$_3$CN was added to the reaction mixture and stirred under 12 W blue LED light for 60 min. After the complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to give products **4** and **5**, respectively.

Characterization. *Phenethyl(phenyl)sulfane (5a).* Colorless Liquid; yield: 25%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.32−7.29 (m, 4H), 7.24−7.18 (m, 4H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 8.3 Hz, 2H). Spectral data are in agreement with literature values.[32]

(4-Bromophenyl)(phenethyl)sulfane (5b). Colorless Liquid; yield: 23%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25−7.18 (m, 5H), 3.15 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 8.2 Hz, 2H). Spectral data are in agreement with literature values.[33]

Phenethyl(p-tolyl)sulfane (5c). Colorless Liquid; yield: 36%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31−7.26 (m, 4H), 7.23−7.18 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 3.13 (t, *J* = 7.3 Hz, 2H), 2.90 (t, *J* = 8.4 Hz, 2H), 2.33 (s, 3H). Spectral data are in agreement with literature values.[34]

(4-Methoxyphenyl)(phenethyl)sulfane (5d). Colorless Liquid; yield: 40%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22−7.16 (m, 3H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H). Spectral data are in agreement with literature values.[35]

(4-Chlorophenyl)(phenethyl)sulfane (5e). Colorless Liquid; yield: 19%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31− 7.17 (m, 9H), 3.14 (t, *J* = 7.4 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H). Spectral data are in agreement with literature values.[36]

(4-Fluorophenyl)(phenethyl)sulfane (5f). Colorless Liquid; yield: 20%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38−7.35 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 12), 3.12 (t, *J* = 7.4 Hz, 2H), 2.89 (t, *J* = 8.3 Hz, 2H). Spectral data are in agreement with literature values.[36]

Phenethyl(m-tolyl)sulfane (5g). Colorless Liquid; yield: 37%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.24−7.15 (m, 6H), 7.00 (d, *J* = 7.0 Hz, 1H), 3.16 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H), 2.33 (s, 3H).

2-(Phenethylthio)aniline (5h). Yellow Liquid; yield: 28%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.22−7.11 (m, 4H), 6.75−6.69 (m, 2H), 3.00 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 8.3 Hz, 2H); [13]C

NMR (125 MHz, CDCl$_3$) δ 148.36, 140.42, 135.91, 129.78, 128.65, 128.52, 126.42, 118.60, 117.78, 115.03, 36.14, 36.06. Spectral data are in agreement with literature values.[33]

(4-Methoxyphenethyl)(phenyl)sulfane (5i). Colorless Liquid; yield: 41%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 8.2 Hz, 2H). Spectral data are in agreement with literature values.[32]

(4-Methylphenethyl)(phenyl)sulfane (5j). Colorless Liquid; yield: 30%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12− 7.08 (m, 4H), 3.15 (d, *J* = 7.7 Hz, 2H), 2.89 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 3H). Spectral data are in agreement with literature values.[34]

(4-Chlorophenethyl)(phenyl)sulfane (5k). Colorless Liquid; yield: 44%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34− 7.32 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.25−7.24 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 8.1 Hz, 2H). Spectral data are in agreement with literature values.[37]

(4-Bromophenethyl)(phenyl)sulfane (5l). Colorless Liquid; yield: 45%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.36−7.34 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 8.1 Hz, 2H). Spectral data are in agreement with literature values.[38]

(4-Methoxyphenethyl)(m-tolyl)sulfane (5m). Colorless Liquid; yield: 22%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20− 7.11 (m, 5H), 7.01−6.98 (m, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.87 (t, *J* = 8.6 Hz, 2H), 2.33 (s, 3H).

(4-Bromophenyl)(4-methylphenethyl)sulfane (5n). Colorless Liquid; yield: 21%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.12−7.07 (m, 4H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.33 (s, 3H).

Cyclohexyl(phenyl)sulfane (5q). Colorless Liquid; yield: 24%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 3.12−3.07 (m, 1H), 2.00−1.97 (m, 2H), 1.79−1.76 (m, 2H), 1.63−1.60 (m, 1H), 1.40−1.22 (m, 5H). Spectral data are in agreement with literature values.[32]

Octyl(phenyl)sulfane (5r). Colorless Liquid; yield: 16%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.67−1.61 (m, 2H), 1.45−4.39 (m, 2H), 1.31−1.26 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). Spectral data are in agreement with literature values.[32]

Decyl(phenyl)sulfane (5s). Colorless Liquid; yield: 14%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (d, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.67−1.61 (m, 2H), 1.43−1.39 (m, 2H), 1.30−1.26 (m, 12 H), 0.88 (t, *J* = 6.9 Hz, 3H). Spectral data are in agreement with literature values.[32]

Methyl 2-Methyl-3-(phenylthio)propanoate (5t). Colorless Liquid; yield: 9%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.28−3.24 (m, 1H), 2.94−2.90 (m, 1H), 2.73− 2.66 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H). Spectral data are in agreement with literature values.[32]

Control Experiment Synthesis Procedure of (1-Phenylethane-1,2-diyl)bis(phenylsulfane) (6a). An oven-dried glass

vial was charged with thiol **3a** (0.96 mmol) and **2a** (1.92 mmol). 4 mL of CH_3CN was added to the reaction mixture and purged by nitrogen gas for 15 min. After that, it was stirred under 12 W blue LED light for 6 h under a nitrogen atmosphere. After 6 h, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to give product **6a**.

Characterization. *(1-Phenylethane-1,2-diyl)bis-(phenylsulfane) (6a).* Colorless Liquid; yield: 57%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 5H), 7.30–7.19 (m, 10H), 4.30–4.27 (m, 1H), 3.53 (dd, J = 13.6, 4.9 Hz, 1H), 3.39 (dd, J = 13.6, 10.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.81, 135.69, 134.34, 133.05, 130.17, 129.07, 129.05, 128.65, 128.23, 127.90, 127.77, 126.55, 52.61, 39.90. Spectral data are in agreement with literature values.[39]

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02070.

> Experimental procedure and characterization of new compounds (^{1}H and ^{13}C NMR spectra) (PDF)

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Notes

The authors declare no competing financial interest.

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