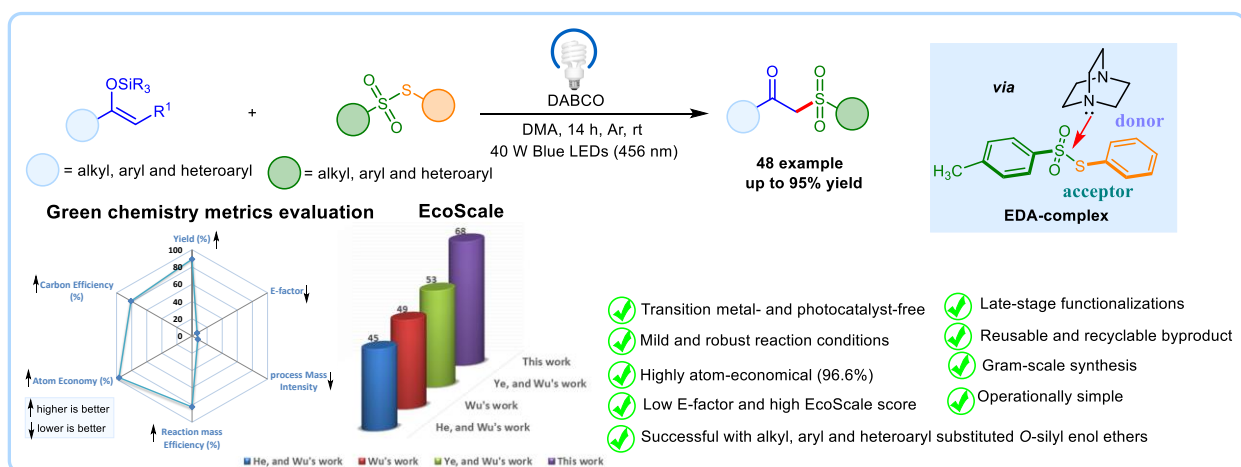


Visible Light Driven α -Sulfonylation of Ketone-Derived Silyl Enol Ethers *via* Electron Donor-Acceptor Complex

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Abstract: The diverse utility of β -ketosulfones in pharmaceuticals and bioactive compounds has generated considerable interest in their synthesis. However, existing synthetic approaches often depend on transition-metal catalysts, which require extensive purification and low yields. Herein, we present a cost-effective, metal-, photocatalyst-free, visible light electron donor-acceptor (EDA) complex-mediated sulfonylation of ketone-derived silyl enol ethers with thiosulfonates (acceptor) and DABCO as an electron donor under mild conditions, offering a more efficient and straightforward approach. Our method enables the synthesis of a diverse range of β -keto sulfone derivatives, including biologically active and late-stage molecules, in good yields. Our strategy offers several significant advantages over existing techniques, which include (i) transition-metal and photoredox catalyst-free; (ii) external SO_2 -source-free; (iii) broad substrate scope; (iv) recyclable and reusable by-product; (v) excellent atom economy, reaction mass efficiency, process mass intensity, and *E*-factor and EcoScale scores, highlighting its efficiency and economic sustainability. Detailed mechanistic studies confirm the involvement of an EDA-complex mediated radical process that operates without a catalyst.



Keywords: Electron-donor-acceptor (EDA)-complex, *O*-Silyl Enol ethers, β -ketosulfones, α -sulfonylation.

Introduction:

Organosulfones are essential in synthetic and medicinal chemistry, particularly in modulating and controlling drug metabolism and biotransformation rate.¹ Several clinically approved drugs containing sulfone groups are shown in Fig 1A. Among these, β -ketosulfones have garnered significant attention from synthetic chemist due to their versatile applications in organic synthesis and their considerable pharmaceutical relevance.² These compounds demonstrate a wide array of biological activities, making them particularly valuable in organic synthesis. As a result, extensive efforts have been devoted to synthesizing β -ketosulfones, underscoring their importance in chemical and biological contexts. Several methods have been developed for the synthesis of β -ketosulfones. These include the acylation of alkyl sulfones with acid chlorides, esters, or N-acyl benzotriazoles,³ the oxidation of β -ketosulfides or β -hydroxysulfones with stoichiometric oxidants,⁴ and the alkylation of metallic arene sulfinates with α -halo- or α -tosyloxy ketones.⁵ All these methods are impregnated with drawbacks such as use of costly transition metal catalysis, hazardous oxidants, and elevated temperatures. In this regard, radical sulfonylation has gained attention as an effective approach for synthesizing β -ketosulfones. This method typically involves the reaction of alkenes,⁶ alkynes⁷ or activated alkenes⁸ with various radical sulfonylation reagents. Although traditional methods are useful, they often require cumbersome multi-step prefunctionalization or preactivation of the starting materials, have limited substrate scopes, yield low results, or involve harsh reaction conditions, all of which present significant challenges.

In the past decade, visible-light-promoted photoredox reactions have achieved significant milestones in organic synthesis.⁹ Amongst these, three methods involving visible light-promoted synthesis of β -ketosulfones have been reported involving the reaction between silyl enol ethers, external sulfur dioxide (SO₂) source, and an alkyl/aryl radical source. The first of these was disclosed by Ye, Wu, and co-workers in 2019, who reported a visible light Ir-catalyzed sulfonylation of silyl enol ethers using amine-derived Katritzky salts as alkyl radical precursors with K₂S₂O₅ as a SO₂ source (Fig. 1B, a).¹⁰ However, the substrate scope was limited and did not include aryl radical intermediates and alkyl-substituted *O*-silyl enol ethers. Moreover, the reaction produced 2,4,6-triphenylpyridine as a non-reusable by-product. The following year, Wu and co-workers developed a Ru-catalyzed synthesis of β -ketosulfones *via* a three-component reaction using aryldiazonium tetrafluoroborates, Na₂S₂O₅, and 2,2-difluoroenol silyl ethers under photochemical conditions (Fig. 1B, b).¹¹ Additionally, this method also suffers from a narrow substrate scope due to using unstable diazonium salts with an expensive photocatalyst. Later in 2022, He, Wu, and co-workers introduced an Ir-catalyzed sulfonylation of silyl enol ethers with DABCO·(SO₂)₂ and arene or alcohol-derived thianthrenium salts (Fig. 1B, c).¹² Despite its innovation, the method has limitations, including its restriction to aryl-substituted *O*-silyl enol ethers, reliance on an expensive photoredox catalyst, the use of a complex and costly SO₂ surrogate, and a long reaction time of 48 h. Typically, in these methods, the photoexcited catalyst (*PC) reduces the starting substrate *via* single electron transfer (SET), generating a radical intermediate (Fig. 1B, d). This radical then reacts with the SO₂ surrogate, forming a sulfonyl radical intermediate, which adds to the silyl enol ethers, followed by SET reduction and subsequent hydrolysis, yielding the β -ketosulfone product. Consequently, developing a method for β -ketosulfone synthesis that eliminates the need for any transition metal,

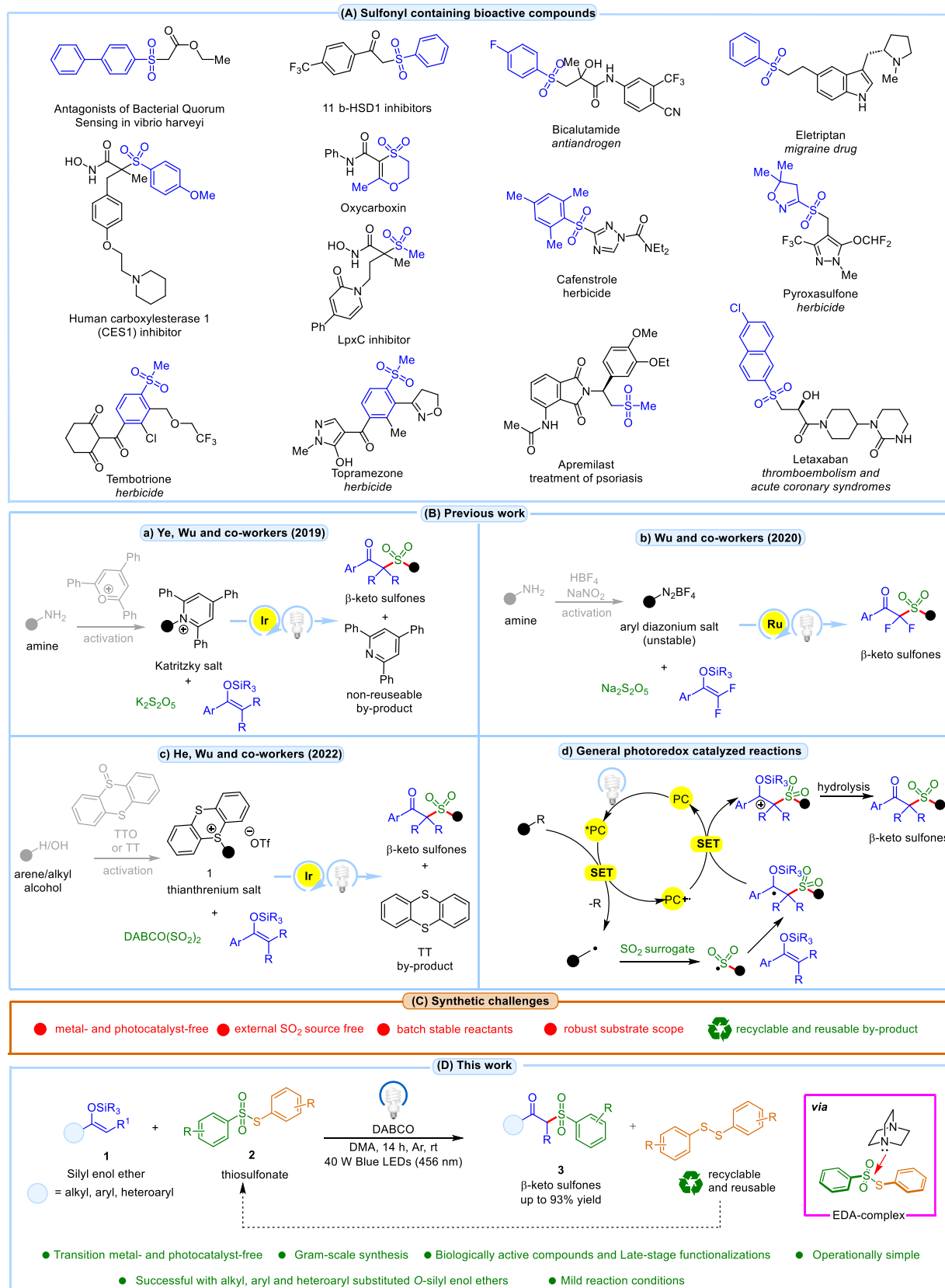
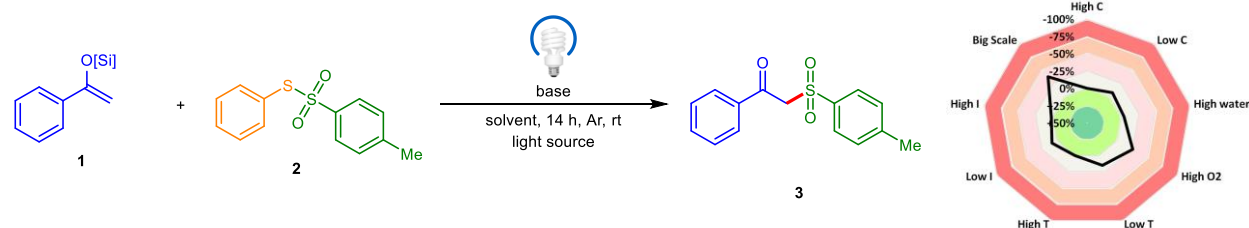


Figure 1. (A) Sulfonyl containing bioactive drugs; (B) previous work; (C) synthetic challenges; (D) this work.

photocatalyst, and directly leads to the sulfonyl radical intermediate would be a significant breakthrough and a major advancement in β -ketosulfone synthesis.

In this context, electron donor-acceptor (EDA) complex-based reactions have garnered significant interest in organic synthesis.¹³ Such EDA complexes, formed in the ground state, can absorb visible light, triggering an intermolecular single electron transfer (SET) event and eliminating the critical need for a customary redox potential matching in such reactions.



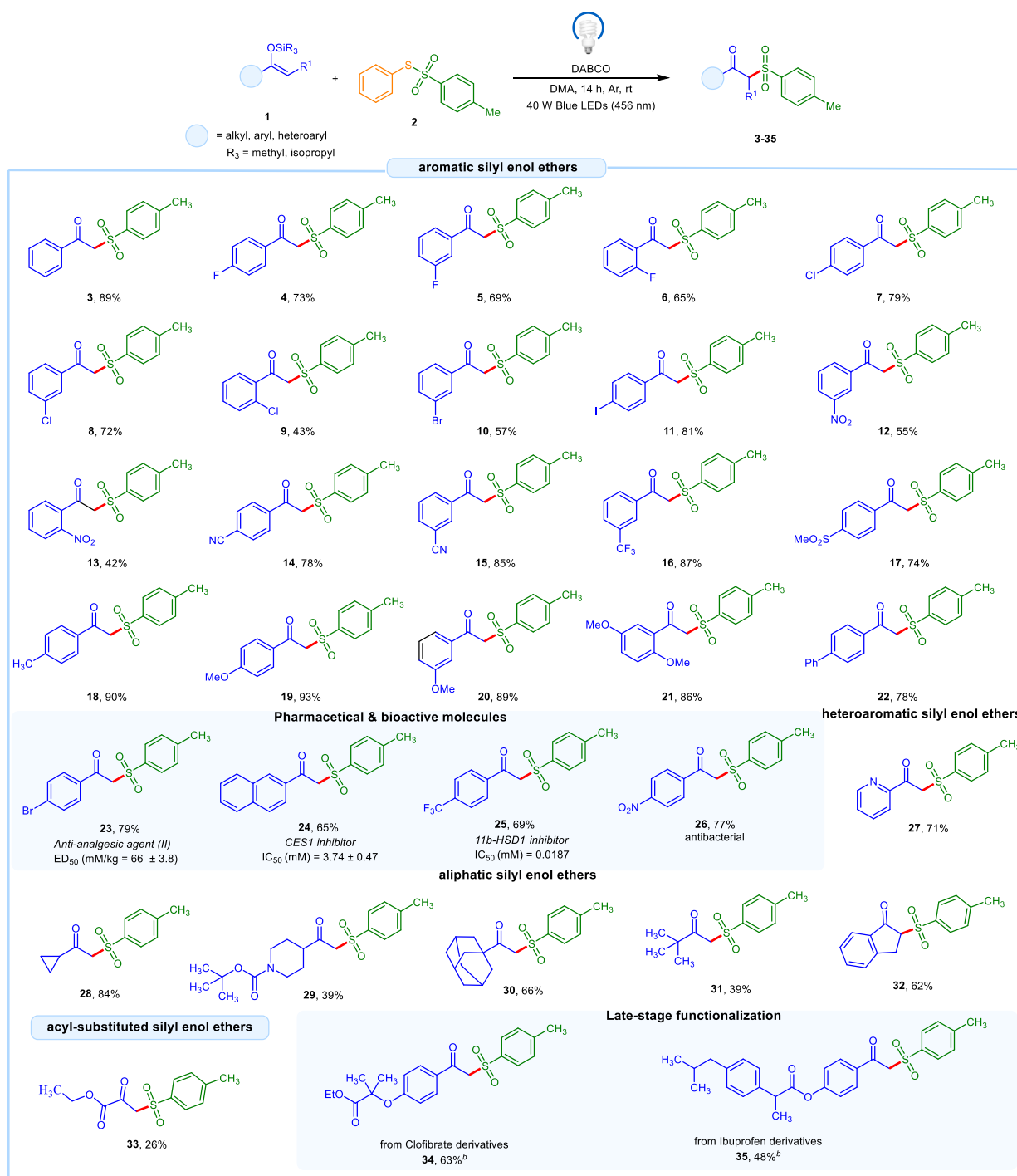
ENTRY	BASE (2.0 EQUIV.)	SOLVENT	LIGHT	YIELD (%)	ENTRY	BASE (2.0 EQUIV.)	SOLVENT	LIGHT	YIELD (%)
1	DBU	MeCN	456	52	14	DABCO	THF	456	42
2	TMEDA	MeCN	456	48	15	DABCO	MeOH	456	N.D
3	DMAP	MeCN	456	30	16 ^b	DABCO	DMA	456	55
4	Et ₃ N	MeCN	456	trace	17 ^c	DABCO	DMA	456	89
5	Triphenylamine	MeCN	456	trace	18 ^d	-	DMA	456	N.D
6	DABCO	MeCN	456	67	19 ^e	DABCO	DMA	dark	N.D
7	DABCO	DMSO	456	72	20	DABCO	DMA	23W CFL bulb	40
8	DABCO	Acetone	456	38	21	DABCO	DMA	427	65
9	DABCO	DCM	456	52	22	DABCO	DMA	390	55
10	DABCO	DMF	456	70	23	DABCO	DMA	Green LED	72
11	DABCO	DMA	456	81	24 ^f	DABCO (TIPS)	DMA	456	52
12	DABCO	EtOH	456	N.D	25 ^g	DABCO (TES)	DMA	456	0
13	DABCO	DCE	456	55	26 ^h	DABCO (TBS)	DMA	456	0

Scheme 1. (a) Reaction conditions: A mixture of *O*-silyl enol ether [Si] = TMS (trimethylsilyl) **1a** (0.2 mmol), and *S*-phenyl 4-methylbenzenesulfonylthioate **2a** (0.24 mmol, 1.2 equiv.), base (0.4 mmol, 2.0 equiv.) solvent (0.5 mL) under visible light irradiation (light source) for 14 h under Ar atmosphere at rt; (b) base (0.2 mmol 1.0 equiv.) (c) base (0.6 mmol 3.0 equiv.); (d) No base (e) in the dark; (f) [Si] = TIPS (triisopropylsilyl) (g) [Si] = TES (triethylsilyl), (h) [Si] = TBS (*ter*-butyldimethylsilyl).

Building on our ongoing research into green and sustainable photoinduced EDA-complex reactions,¹⁴ we present a practical method for the synthesis of β -ketosulfone using silyl enol ethers with thiosulfonates (acceptor) and DABCO (donor) under visible light irradiation (Fig. 1D). We hypothesize that an EDA-complex forms between thiosulfonates (acceptor) and DABCO (donor), leading to the generation of an S-centered radical intermediate. This intermediate reacts with the silyl enol ether to yield the desired β -ketosulfone product and an aryl disulfide by-product. The use of an inexpensive base as an electron donor and thiosulfonate as a sulfonyl source under photochemical conditions facilitates the synthesis of β -keto sulfones, a challenging feat to achieve without the need for expensive photoredox catalysis and external SO₂ source. Additionally, the aryl disulfide by-product generated in the reaction is recyclable and reusable, offering additional advantages in terms of economic sustainability. Our method also enables the synthesis of various bioactive molecules and late-stage modification of pharmaceutical complexes, thus significantly benefiting industrial and academic research.

Results and discussion

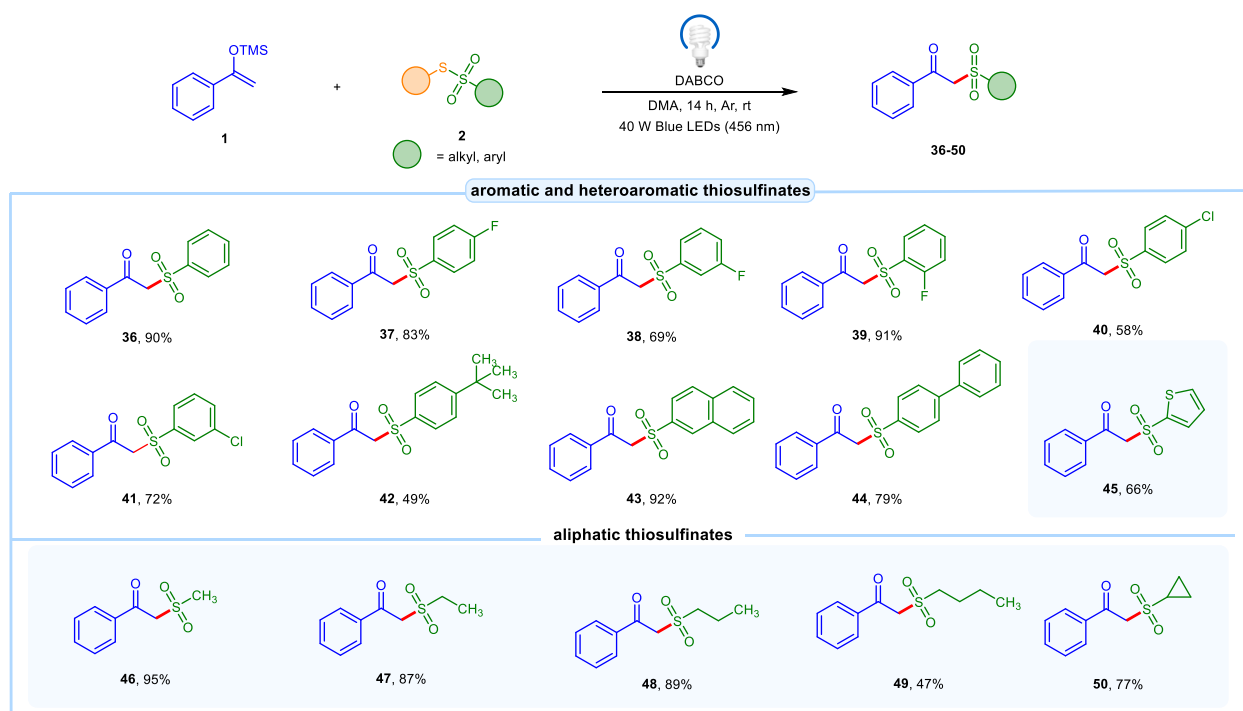
We initiated our study using trimethylsilyl enol ether of acetophenone **1a** and S-phenyl 4-methylbenzenesulfonothioate **2a** as model substrates in MeCN solvent, with DBU as a base, under 456 nm Kessil lamp irradiation. To our satisfaction, the desired product was obtained in 52% yield (entry-1). Further screening of other bases proved unproductive (entries 2-6) except for DABCO, which emerged as the optimal base, delivering the highest yield of 67% (entry 6). We then tested various solvents, including DMSO, acetone, DCM, DMF, DCE, EtOH, and MeOH (entries 7-15). Among these, the reaction achieved an 81% yield in DMA solvent (entry-11), likely due to the efficient solubilization of the reaction components (**1a** and **2a**). Notably, mixing **1a** and **2a** led to an intense yellow color change in the reaction mixture, suggesting the formation of an EDA-complex. The reaction yielded 55% yield when 1.0 equiv. of DABCO was used (entry 16). However, the yield increased to 89% when 3.0 equiv. of DABCO was used (entry-17). The reaction did not proceed without DABCO, underscoring its critical role in product formation (entry 18). Additionally, the reaction failed without light, confirming the necessity of light irradiation (entry 19). Screening of other light sources resulted in reduced yields (entries 20-23), indicating that 456 nm Kessil lamp irradiation is optimal for product formation. Lastly, we investigated compound **1**, which features a sterically more demanding triisopropylsilyl (TIPS), triethylsilyl (TES), *ter*-butyldimethylsilyl (TBS) groups in place of the trimethylsilyl (TMS) group of acetophenone-derived enol ether under the optimized conditions led to reduced yields or complete failure (entries 24-26), indicating that the TMS group in enol ethers is crucial for a high yield of this reaction. In a condition-based sensitivity assessment, our EDA-protocol transformation was sensitive to high oxygen concentration, low temperature, and low light intensity. However, it generally exhibited tolerance to variations in substrate concentration, high reaction temperature, high light intensity, and water (see the radar diagram in Scheme 1 and the ESI[†] for details).



Scheme 2. ^aReaction conditions: *O*-Silyl enol ethers **1** (0.2 mmol, where R = Me), *S*-phenyl 4-methylbenzenesulfonothioate **2a** (1.2 equiv., 0.24 mmol), DABCO (3 equiv., 0.6 mmol) in 0.5 mL DMA, were irradiated with 456 nm Kessil Lamp at room temperature under argon for 14 h. ^bR = isopropyl.

After establishing the optimized reaction conditions, we applied the protocol to various *O*-silyl enol ethers of acetophenone bearing alkyl, aryl, and heteroaryl functionalities, using *S*-phenyl 4-methylbenzenesulfonothioate **2a** as the coupling partner with DABCO. *O*-silyl enol ether of acetophenone

bearing halide groups, such as fluoro-, chloro-, bromo-, and iodo-substituents, reacted smoothly, producing the desired products in moderate to good yields (**4-11**). Additionally, Aryl substituted *O*-silyl enol ethers with both electron-withdrawing and electron-donating substituents, such as nitro-, cyano-, trifluoromethyl-, methylsulfonyl-, methyl, and methoxy groups, were well tolerated under the optimized conditions, resulting in moderate to excellent yields (**12-21**). Additionally, biphenyl β -keto sulfone **22** was obtained with a 78% yield. We were pleased to discover that this mild protocol demonstrated good reactivity towards the synthesis of pharmaceutical and bioactive molecules under the optimized conditions. For example, β -keto sulfone **23**, known for its excellent anti-analgesic properties, was synthesized with a 79% yield. Furthermore, β -keto sulfone **24** and **25**, which function as carboxylesterase 1 and 11 β -hydroxysteroid dehydrogenase type I inhibitors, were obtained with yields of 65% and 69%, respectively. Additionally, β -Keto sulfone **26**, which exhibits anti-bacterial properties, was synthesized with a 77% yield. Furthermore, a heteroaryl *O*-silyl enol ether containing a pyridine group reacted well, producing the desired product **27** in 71% yield. To further assess the versatility of this method, a series of alkyl-substituted *O*-silyl enol ethers was subjected under the EDA-protocol, resulting in the desired products in moderate to good yields (**28-31**). Next, an internal silyl enol ether derivative was successfully applied under the reaction protocol, yielding the desired product **32** in 62% yield. Additionally, an acyl-substituted *O*-silyl enol ether was evaluated, resulting in the targeted product **33** in 26% yield. Finally, the utility of this method was further demonstrated through the late-stage functionalization of silyl enol ether derivatives derived from the hypertriglyceridemia drug clofibrate and the anti-inflammatory drug ibuprofen, yielding the desired products in 63% and 48% yield, respectively.



Scheme 3. ^aReaction conditions: *O*-Silyl enol ether **1** (0.2 mmol), thiosulfonates **2a** (1.2 equiv., 0.24 mmol), DABCO (3.0 equiv., 0.6 mmol) in 0.5 mL DMA, were irradiated with 456 nm Kessil Lamp at room temperature under argon for 14 h.

To further diversify our strategy, we employed various thiosulfonates **2a** with alkyl and aryl functionalities under the optimized condition with *O*-silyl enol ether **1**. These thiosulfonates **2a** reacted efficiently with *O*-silyl enol ether **1**, yielding the corresponding β -ketosulfones **36-50** in moderate to excellent yields, as illustrated in Scheme 3. Simple, non-substituted thiosulfonates **2** reacted well with *O*-silyl enol ether **1** to yield the desired product **36** in 90% yield. Furthermore, thiosulfonates **2** bearing halide groups (F, Cl) were well tolerated under the reaction conditions, yielding the corresponding β -ketosulfones **37-41** in 58-91% yield. Notably, thiosulfonates **2** with a *t*-butyl group on the benzene ring afforded the β -ketosulfones product **42** in 49% yield. This method was also compatible with polyaromatic thiosulfonates, such as those with a naphthalene ring, affording the required product **43** in 92% yield. Conversely, biphenyl derived β -ketosulfone **44** was obtained in 79% yield. Impressively, heteroaromatic thiosulfonates were also well tolerated under the optimized conditions, resulting in the desired product **45** in 66% yield. Moreover, aliphatic thiosulfonates **2** were subjected to our EDA-complex protocol with *O*-silyl enol ethers **1**. Aliphatic thiosulfonates **2** with primary alkyl chain (C1 to C4) were well tolerated under the reaction protocol, producing the desired products **46-49** in 47-95% yield. Additionally, thiosulfonates **2** with secondary alkyl chains proved compatible, yielding the target product **50** in 77% yield.

Mechanistic insights

Next, a series of mechanistic studies were conducted to elucidate the reaction mechanism, as illustrated in Fig. 2. UV/Vis-absorption analysis of individual components and the reaction mixture in DMA was measured, as shown in Fig. 2a. Neither Silyl enol ether **1a** nor DABCO displayed an absorption band beyond 400 nm. However, the mixture of **1a** and **2a** exhibited a significant bathochromic shift (brown line). Additionally, the mixture of **2a** and DABCO (green line), as well as the reaction mixture of **1**, **2a**, and DABCO (purple line), displayed a notable bathochromic shift with visible light absorption in the range of 425-500 nm, indicating the formation of an EDA-complex. The intense yellow color observed in the reaction mixture, further suggested the formation of an EDA-complex aggregate, as depicted in Fig. 2a. Additionally, a molar absorption of 1:1 for the mixture of **2a** and DABCO was proven by Job's plot study (Fig. 2b). Next, $^1\text{H-NMR}$ titration experiment between *S*-phenyl 4-methylbenzenesulfonothioate **2a** and DABCO in CDCl_3 revealed that the ^1H -proton signals of **2a** shifted upfield, thus indicating the formation of an EDA-complex between **2a** and DABCO (Fig. 2c). Subsequently, a Benesi-Hildebrand experiment¹⁵ was performed, yielding an association constant of 4.55 M^{-1} in DMA, which confirmed the formation of a visible light-active EDA complex (Fig. 2d). Following this, radical trapping experiment was performed under standard conditions using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), butylated hydroxytoluene (BHT) and 1,1-diphenylethylene. The reactions were quenched, and the resulting radical trapped adducts were successfully detected by high-resolution mass spectrometry (HRMS), indicating the involvement of a radical pathway. Next, the reaction was irradiated with natural sunlight, resulting in the formation of the desired product **3a** in 59% yield (Fig. 2f). The reaction was scaled up to the gram scale, achieving a yield of 68% yield of the target product **3a** (Fig. 2g). Thereafter, light-on and on/off experiment were performed, demonstrating that continuous visible-light irradiation is necessary for the reaction to proceed (Fig. 2h). Lastly, a quantum yield experiment was performed and was measured to be $\Phi = 0.82$, which indicates a closed chain pathway (See ESI[†] for detailed discussion).

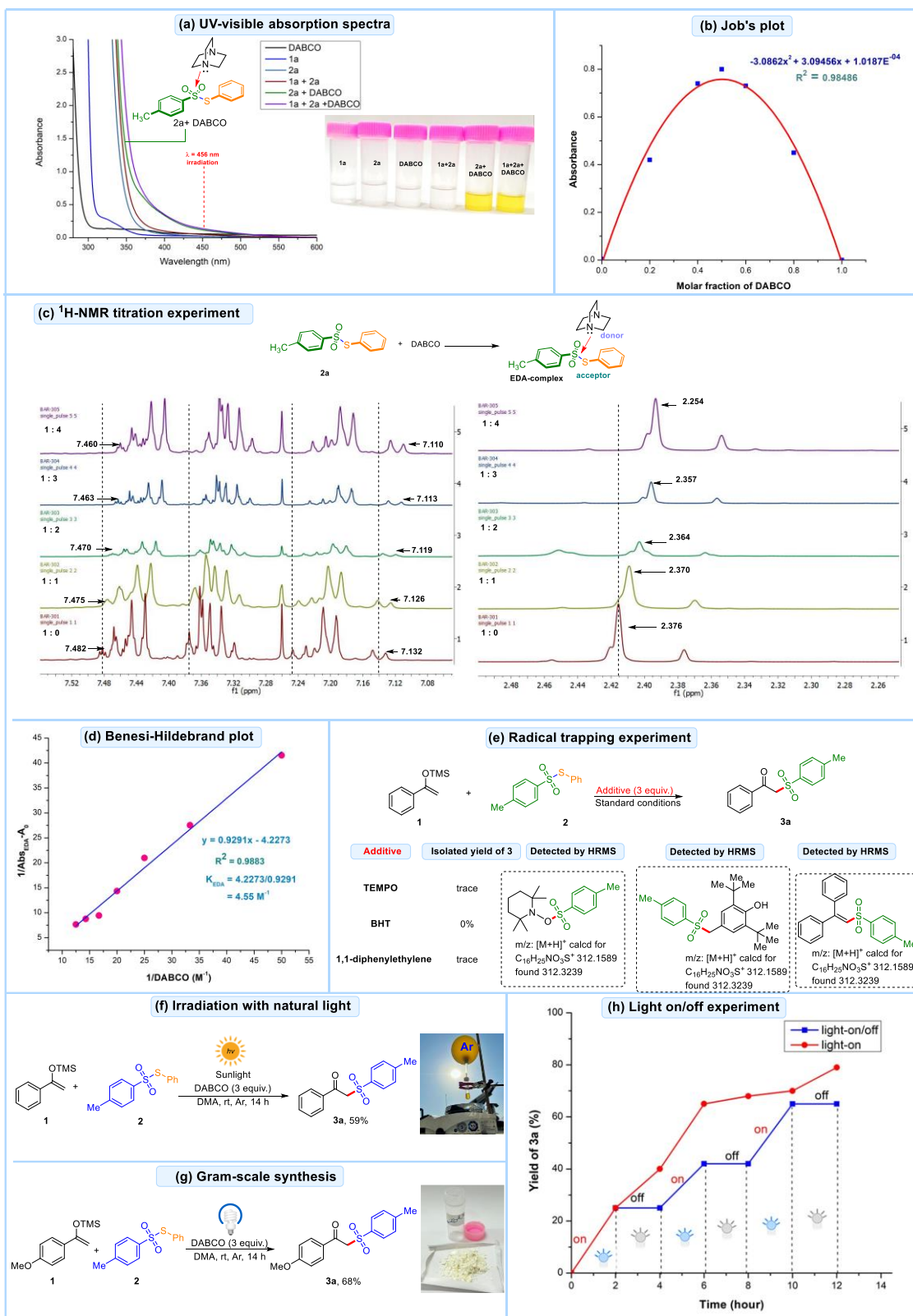


Figure 2. (a) UV-visible absorption spectra; (b) Job's plot; (c) ¹H-NMR titration experiment; (d) Benesi-Hildebrand plot; (e) radical trap experiment; (f) irradiation with natural light; (g) gram scale synthesis; (h) light on/off experiment.

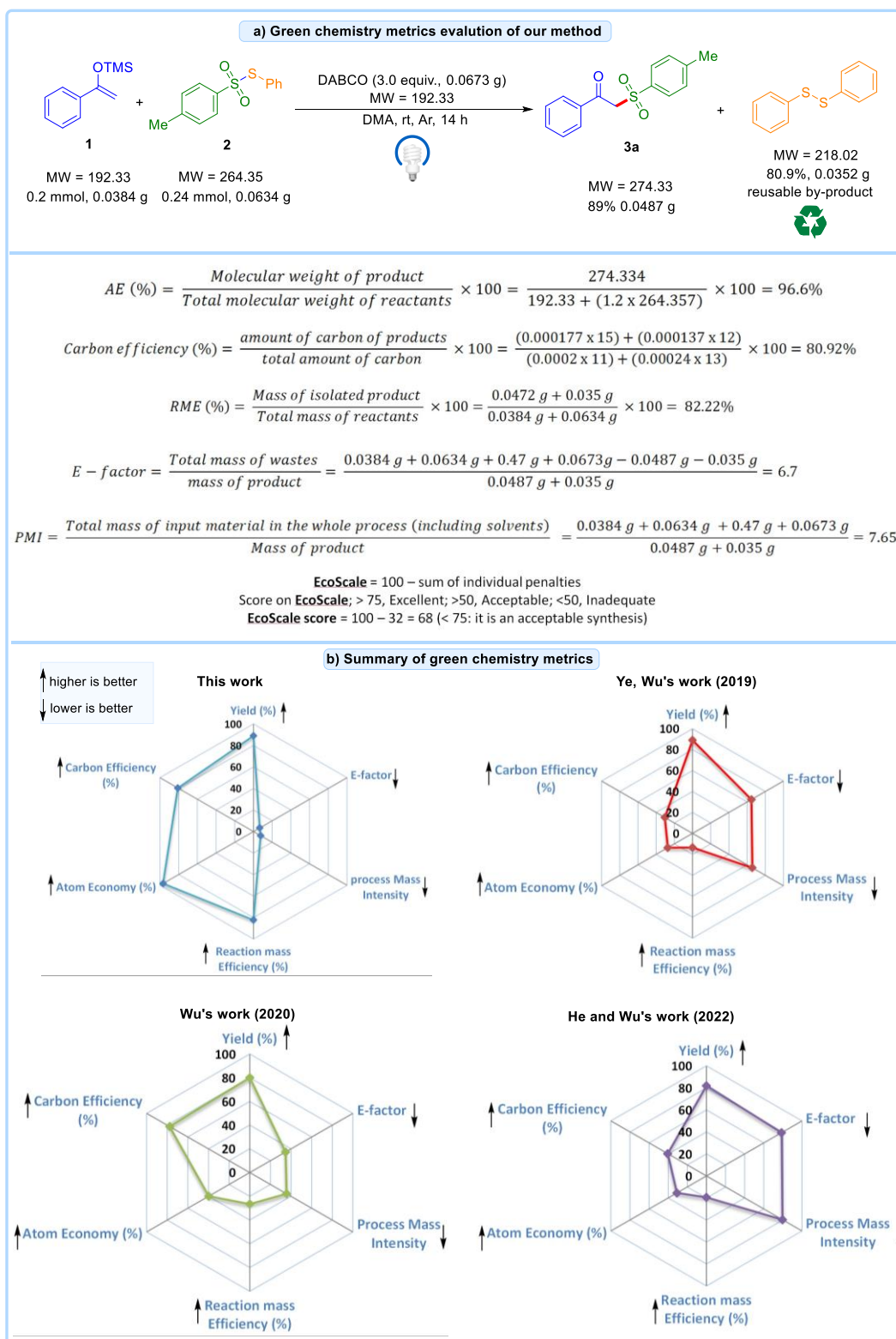


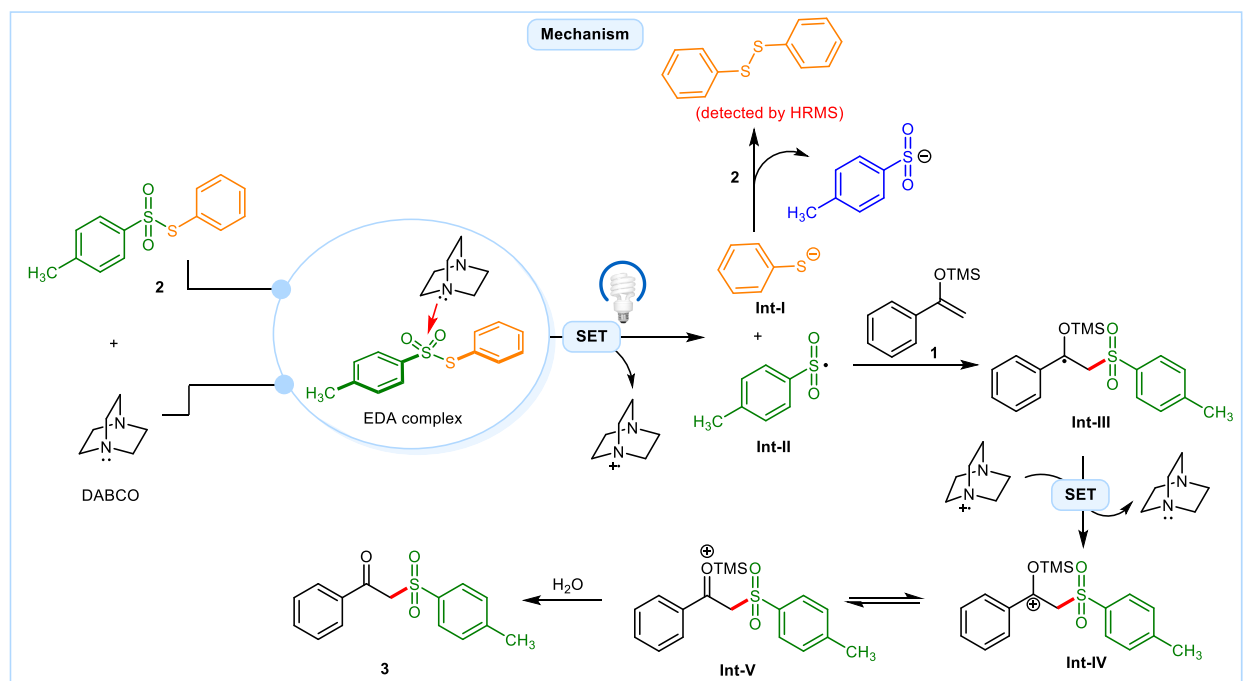
Figure 3. Green chemistry metrics analysis (a) Green chemistry metrics evaluation of our method; (b) Summary of green chemistry metrics of our method compared to previous methods (see ESI† for detailed

calculation). Note; Atom Economy (AE), Reaction Mass Efficiency (RME), Process Mass Intensity (PMI), Carbon efficiency, and *E*-factor. (↑) higher is better, (↓) lower is better.

Green Chemistry metrics

To assess the environmental impact of our EDA-strategy,¹⁶ we evaluated the green chemistry metrics for the synthesis of compound **3a** (0.0487 g, 89%), starting from **1a** (0.2 mmol, 0.0384 g) and *S*-phenyl 4-methylbenzenesulfonylthioate **2a** (0.24 mmol, 0.0634 g), using DABCO (3.0 equiv., 0.0673 g) under visible light conditions. The results are depicted in Figure 3a. Our method demonstrates outstanding green chemistry metrics. Specifically, the atom economy was calculated to be 96.6%, the reaction mass efficiency at 82.22%, and the process mass intensity at 7.65, all of which indicate a highly efficient process. Additionally, the *E*-factor was determined to be 6.7, the lowest among comparable methods. The EcoScale score was calculated to be 68 (see ESI[†] for detailed calculation), which is acceptable and reflects a favorable balance of safety, economic, and ecological considerations. Overall, the green chemistry metrics of our method indicate a strong alignment with sustainability goals. The comparison between the green chemistry metrics of our strategy and other reports is shown in Figure 3b. (see ESI[†] for detailed calculation).

Mechanism



Scheme 3: Possible reaction mechanism

Based on the experimental observations and prior literature,¹⁷ a plausible mechanism for this photochemical EDA-complex mediated transformation is depicted in Scheme 3. Initially, an EDA-complex aggregate is formed between **2** and DABCO. In the presence of visible light irradiation, this EDA complex undergoes a single-electron transfer (SET) event from DABCO to the *S*-phenyl 4-

methylbenzenesulfonylthioate **2**, generating thioyl anion intermediate **Int-I**, S-centered radical intermediate **Int-II**, and DABCO radical cation. The generated sulfonyl radical intermediate **Int-II** reacts with silyl enol ether **1**, leading to the formation of the radical intermediate **Int-III**, which subsequently undergoes SET with DABCO radical cation to generate cation intermediate **Int-IV**. Lastly, tautomerization, followed by hydrolysis, yields the desired product **3**.

Applications

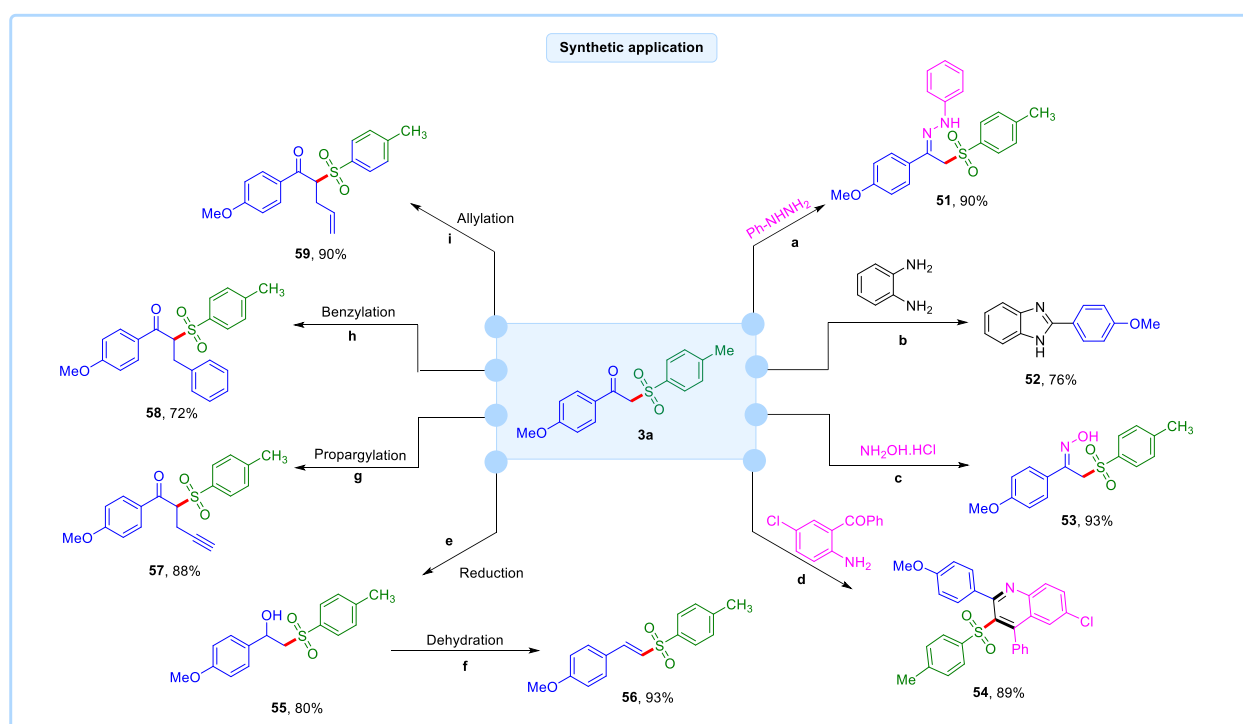


Figure 4: Reaction conditions: (a) **3a** (0.2 mmol), phenylhydrazine (1.0 equiv.), acetic acid (cat. amount), ethanol (1.0 ml), reflux, 1h; (b) **3a** (0.2 mmol), *o*-phenylenediamine (1 equiv.), AcOH, 120 °C, 10 h; (c) **3a** (0.2 mmol) hydroxylamine hydrochloride (1.5 equiv.) and NaOAc (1.5 equiv.) ethanol (1 mL), water (3ml), reflux, 5 h; (d) **3a** (0.2 mmol), (2-amino-5-chlorophenyl)(phenyl)methanone (1.5 equiv.), TfOH (20 mol%), PhCl, 150 °C, 10 h. (e) **3a** (0.2 mmol), NaBH₄ (1.5 equiv.), methanol (2.0 mL), 25°C, 1h; (f) **55** (0.1 mmol), BF₃.Et₂O (0.2 mmol), DCM, 25°C, 20 h (g) **3a** (0.2 mmol), K₂CO₃ (2.0 equiv.), propargylic bromide (1.1 equiv.), acetone (2.0 mL), reflux, 12h; (h) **3a** (0.2 mmol), K₂CO₃ (3.5 equiv.), BnBr (1.1 equiv.), acetone, reflux; (i) **3a** (0.2 mmol), K₂CO₃ (2.0 equiv.), allyl bromide (1.1 equiv.), acetone (2.0 mL), reflux, 16 h.

To broaden the synthetic application, various reactions were conducted using compound **3a** as shown in fig. 4. The reaction of **3a** with phenylhydrazine produced the required product **51** in 90% yield.¹⁸ Additionally, the reaction with *o*-phenylenediamine yielded the corresponding product **52** in 76% yield.¹⁹ Similarly, the reaction with hydroxylamine hydrochloride gave the oxime product **53** product in 93% yield.¹⁸ Conversely, the reaction with (2-amino-5-chlorophenyl)(phenyl)methanone yielded a six-membered ring product **54** in 89% yield.²⁰ The carbonyl group of the β-ketosulfone was smoothly reduced to compound **55** using NaBH₄ in methanol.²¹ The resulting hydroxyl group was then dehydrated to produce vinyl sulfone **56**, with an approximate yield of 93%.²² Finally, we also demonstrated the propargylation,²³ benzylation,²⁴ and allylation²⁵ of compound **3a**, resulting in the corresponding products (**57-59**) was good to excellent yields.

Conclusion

In summary, we reported a transition metal- and photocatalyst-free method for the visible light-induced synthesis of β -ketosulfones *via* sulfonylation of ketone-derived silyl enol ethers with thiosulfonates (electron acceptor) and DABCO (electron donor) under mild conditions. This method facilitates the synthesis of a wide range of β -ketosulfone derivatives, including biologically active and late-stage molecules, from structurally diverse silyl enol ethers, including alkyl, aryl, and heteroarylsilyl enol ethers. Extensive mechanistic studies, including UV-visible absorption studies, Job's plot, $^1\text{H-NMR}$ titration experiment, Benesi-Hildebrand plot, radical trapping experiment, light on/off experiment, and quantum yield experiment confirm the involvement of an EDA complex-mediated radical process. Additionally, our method offers several advantages over existing literature. This includes (i) transition-metal and photoredox catalyst-free; (ii) external SO_2 -source free; (iii) accommodates a diverse range of substrates; (iv) recyclable and reusable by-product; (v) demonstrates excellent atom economy, reaction mass efficiency, process mass intensity, *E*-factor, and EcoScale score, highlighting its efficiency and economic sustainability. Moreover, the versatility of β -ketosulfones was demonstrated by their successful conversion into various of aromatic and heteroaromatic compounds, showcasing their broad utility as intermediates and making them a practical solution for academic research and industrial applications.

Data availability

Experimental data has been provided as ESI.†

Author contributions

B. Saxena optimized the reaction conditions and synthesized all the derivatives. R. I. Patel synthesized the thiosulfonates. B. Saxena and R. I. Patel performed the mechanistic studies and wrote the manuscript with the helpful insights of Prof. A. Sharma. Prof. A. Sharma supervised the whole work, interpreted the results, and edited the manuscript. All the authors have given their approval to the final version of the manuscript.

Conflicts of interest

The authors declare the following competing interests that one patent has been registered (No: 202411058425) in India.

Acknowledgements

Financial support from SERB (CRG/2022/002691), Govt. of India is gratefully acknowledged. We also acknowledge DST-FIST (SR/FST/CSII/2018/72(C) for the NMR and HRMS facilities in the Chemistry Department, IIT Roorkee. B. S. and R. P. thank CSIR and UGC for the SRF Fellowship, respectively.

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