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One-Step Copper-Assisted Synthesis of α-(Styrylsulfonyl) amides via SO_2 Incorporation Under Visible Light

Nejc Petek[1,2] | Till Opatz[1]

[1]Department of Chemistry, Johannes Gutenberg University, Mainz, Germany | [2]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Correspondence: Nejc Petek (Nejc.Petek@fkkt.uni-lj.si) | Till Opatz (opatz@uni-mainz.de)

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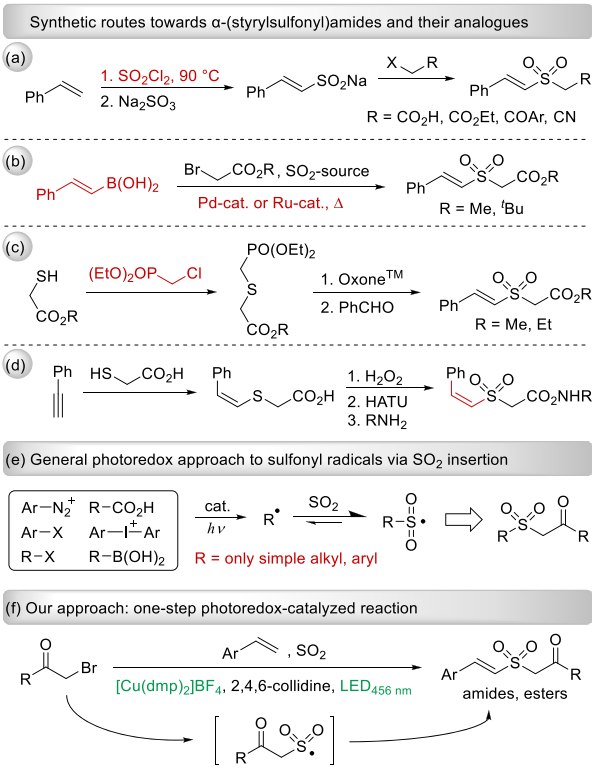
ABSTRACT

α-(Styrylsulfonyl)amides and their related ester analogs are an important class of substances that have been widely used as precursors toward bioactive compounds. While most existing methods for the preparation of related compounds include either multiple steps or the use of precious metals, the method presented in this paper utilizes copper and visible light to produce α-(styrylsulfonyl)amides and α-(styrylsulfonyl)esters from α-bromoamides or esters, SO_2 and styrenes in moderate to high yield in a single step. The mechanism of the newly developed method is investigated and likely differs from related methods for the photocatalyzed fixation of SO_2 into organic scaffolds.

1 | Introduction

α-(Styrylsulfonyl)amides and their related ester and carboxylic acid analogs are an important class of compounds that have been widely used as precursors of compounds possessing antimicrobial, antituberculosis, antioxidant and anti-inflammatory activity [1–5]. Vinyl sulfone moiety in general is of an importance in drug design and reactive dyes [6, 7]. α-(Styrylsulfonyl)amides, esters, nitriles, and carboxylic acids were previously synthesized by different routes, including by the condensation of sodium styrylsulfinate with chloroacetic acid or other α-bromocarbonyl compounds (Scheme 1a) [8–10]. α-(Styrylsulfonyl)esters were also prepared by a metal-catalyzed coupling reaction from (*E*)-styrylboronic acid (Scheme 1b) or by a Horner–Wadsworth–Emmons reaction from a sulfone-based reagent (Scheme 1c) [11–14]. While these methods enable the synthesis of (*E*)-isomers, the reaction between phenylacetylene and sodium thioglycolate, followed by oxidation, activation and addition of amines, produces (*Z*)-isomers of (styrylsulfonyl)acetamides (Scheme 1d) [4, 15, 16]. While most of these procedures are composed of multiple steps and isolations or are catalyzed by precious metals, we envisioned a plausible one-step photoredox-catalyzed procedure for the synthesis of α-(styrylsulfonyl)amides via SO_2 incorporation.

Photochemical and electrochemical incorporation of SO_2 into small organic molecules via radical pathways have received much attention in the past decade as the fixation of SO_2 represents a sustainable and atom economical way of synthesizing compounds containing a sulfonyl moiety [17–20]. Moreover, SO_2 can even be considered a waste product and methods for its valorization are attractive [21]. One of the first examples of SO_2 fixation into photochemically generated C-centered radicals utilized arenediazonium salts [17, 19, 22, 23]. The resulting arenesulfonyl radicals were shown to participate in a variety of reactions, mainly radical additions [22–27]. Other radical intermediates derived from aryl and alkyl halogenides, diaryliodonium salts, carboxylic acids and their derivatives, borate salts,



SCHEME 1 | Overview of methods for the preparation of α-(styrylsulfonyl)carboxylic acid derivatives and general photoredox-catalyzed SO_2 insertion reactions. (a) sulfonylation/reduction/alkylation; (b) boron/sulfur exchange and alkylation; (c) Horner reaction; (d) alkyne hydrothiolation/oxidation; (e) general photoredox approach to SO_2 incorporation; and (f) this work.

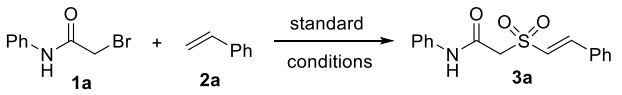
cyclobutanone oxime esters, and Katritzky salts have also been shown to react with SO_2 and generate sulfonyl radicals (Scheme 1e) [28–35]. Meanwhile, styrylsulfinate ions could only be generated from styrylboronic acid and SO_2 through nonradical, metal-catalyzed reactions. [11–13, 36, 37]

Inspired by these seminal works on photoredox-catalyzed SO_2 incorporation, we developed a strategy for the synthesis of α-(styrylsulfonyl)amides and esters via a radical pathway from styrenes, SO_2 and α-bromoamides or esters, using an inexpensive copper complex (Scheme 1f).

2 | Results and Discussion

According to the reaction design outlined above, we began our investigation by screening suitable reaction conditions. Model substrate **1a**, styrene (**2a**) and a solution of SO_2 in acetonitrile were used in initial screening, with the addition of $[Cu(dmp)_2]BF_4$ as a photoredox catalyst (dmp = 2,9-dimethylphenanthroline). The choice of the catalyst was based on its good performance in reactions involving sulfonyl radicals, as well as its availability [38–40]. Initially, neither product **3a** nor its precursor **3a-II** (Scheme 2) could be detected in the reaction mixture by liquid chromatography-mass spectrometry (LC-MS, Table 1, entry 1), which led us to consider adding base to the reaction mixture. Anticipating an unfavorable interaction between SO_2

TABLE 1 | Optimization study of the reaction conditions.[a]



Entry	Deviation from standard conditions	3a (%)[b]
1	no base	n.d.
2	no deviation	55
3	Et_3N	n.d.
4	pyridine	n.d.
5	K_2HPO_4	n.d.
6	2,6-di-*tert*-butylpyridine	n.d.
7	$[Cu(dmp)_2Cl]Cl$	53
8	$[Cu(DPEphos)(dmp)]BF_4$	47
9	$[Cu(Xantphos)(dmp)]BF_4$	44
10	$[Cu(Xantphos)(bq)]BF_4$	37
11	$[Cu(DPEphos)(bq)]BF_4$	18
12	$[Cu(bq)_2]BF_4$	traces
13	*fac*-$[Ir(ppy)_3]$	n.d.
14	$[Ru(bpy)_3](PF_6)_2$	n.d.
15	40 h	68
16	2,4,6-collidine	68
17	2,4,6-collidine, 40 h	84

[a]Standard reaction conditions: **1a** (0.4 mmol), **2a** (0.52 mmol), $[Cu(dmp)_2]BF_4$ (1 mol%), MeCN (anhydrous, degassed, 1.8 mL), 2,6-lutidine (1.6 mmol), SO_2 (0.8 mmol as a 4 M solution in MeCN), LED_{456nm}, 35°C, 20 h. n.d. = not detected;
[b]Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

and alkyl amines or inorganic bases, 2,6-lutidine was used instead. Gratifyingly, we observed the formation of the target product **3a** in 55% NMR yield after 20 h of irradiation under 456 nm light (Table 1, entry 2). Replacing 2,6-lutidine with triethylamine or pyridine prevented the reaction from taking place (Table 1, entries 3 and 4, see also SI 4.8.1.). Based on our previous reports [39, 40], K_2HPO_4 was also tested as a potential base, resulting in an unsuccessful reaction (Table 1, entry 5). Interestingly, when 2,6-di-*tert*-butylpyridine was used instead of 2,6-lutidine, intermediate **3a-II** (Scheme 2) was detected in the reaction mixture by LC-MS and nuclear magnetic resonance (NMR) analysis, but no formation of **3a** was observed. This can be explained by the lower basicity of this pyridine derivative due to steric hindrance (Table 1, entry 6).

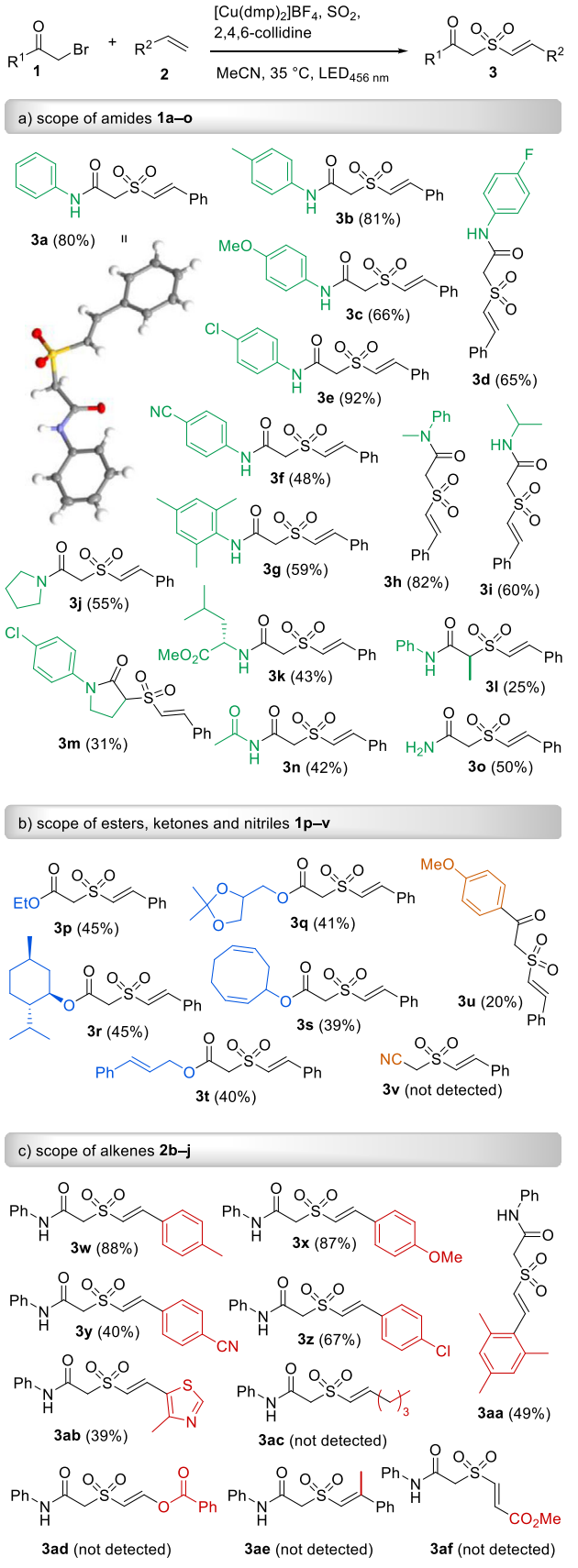
Next, multiple catalysts were tested and while other photoredox-active copper complexes (bq = 2,2′-biquinoline; DPEphos = [oxydi(2,1-phenylene)]bis(diphenylphosphane); Xantphos = (9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(diphenylphosphane)) performed well with somewhat diminished yields, ruthenium and iridium complexes as well as organic catalysts and photoredox-inactive copper complexes failed to produce the desired product (Table 1, entries 7–14 and Table S1, entries 17–21). The reaction time was then increased to ensure complete conversion of the starting material **1a**, which led to an increase in the yield of **3a**

to 68% (Table 1, entry 15). Finally, changing the base to 2,4,6-collidine further increased the yield to 84% after a prolonged reaction time (Table 1, entry 17). Additional screening experiments, including solvent, SO_2 surrogates, and concentration variations, are gathered in the Supporting Information (Table S1). Next, we explored the scope of the reaction (Table 2). Substituted aniline-derived bromoacetamides gave the corresponding products **3a–g** in yields up to 92%. Bromoacetamides derived from secondary and aliphatic amines also produced products **3h–k** in satisfactory yields of up to 82%, including the L-leucine-derived compound **3k**. Unfortunately, 2-bromopropanamide **1l** gave only 25% of the corresponding product **3l**, indicating a significant effect of steric hindrance of the additional methyl group on the reaction. Similarly, γ-lactam-based substrate **2m** was converted to the sulfone **3m** in 31% yield. Imide-based product **3n** and *N*-unsubstituted compound **3o** were also synthesized.

Expanding the scope from amides to esters, compounds **3p–t** were prepared in diminished yields up to 45%, whereas the ketone-derived product **3u** was isolated in a modest 20% yield. While all the side products could not be identified, the corresponding Katritzky salt of **1t** and 2,4,6-collidine was detected in the crude reaction mixture after irradiation, indicating a possible explanation for the diminished yields compared to amides **1**. The role of Katritzky salts is further discussed in the mechanistic section and in SI (SI 4.8.1.). The main side product arising from ketone **1u** was identified as 4-methoxyacetophenone. It should be noted that bromoacetonitrile remained unconverted under the employed reaction conditions and the target product **3v** was not detected in the reaction mixture. Despite the presence of an internal double bond in bromoacetates **1s** and **1t**, no cyclization products arising from radical attack to the double bond could be detected when styrene (**2a**) was omitted from the reaction mixture. However, when substituted styrenes **2b–f** were used, compounds **3w–aa** were successfully isolated in yields ranging from 40%–88%. Gratifyingly, the heterocyclic thiazole-derived alkene **2g** could also be converted to the corresponding sulfone **3ab**. 1-Hexene (**2h**), vinyl benzoate (**2i**), α-methylstyrene (**2j**) and methyl acrylate (**2k**) failed to give the corresponding products **3ac–af**. Lastly, the model reaction between **1a** and **2a** was scaled up to a 4 mmol scale, providing product **3a** in 66% yield. Additionally, the structure of the product **3a** was confirmed by X-ray crystallography (CCDC number: 2 425 291, Figure S11), supporting the observation of a sole (*E*)-isomer of styryl sulfones **3** in the reaction mixture, which is consistent with various reports on vinyl sulfone syntheses [39, 41, 42].

Having established the scope of the reaction, we commenced the investigation of its mechanism. In the absence of light, no product **3a** was detected, even at elevated temperature (Table S1, entries 35, 36). The addition of the radical scavenger TEMPO prior to irradiation caused the yield of **3a** to drop below the detection limit (SI 4.1.), supporting the involvement of radical intermediates. The most widely accepted pathway for photoredox catalyzed incorporation of SO_2 involves generation of C-centered radical species, followed by the formation of sulfonyl radicals [17, 19, 22–36]. In our study, the representative substrate **1a** would therefore need to be reduced by the catalyst in its excited state to form α-carbonyl radical species **1a-II** (Scheme 2). While many of the tested copper complexes gave appreciable yields

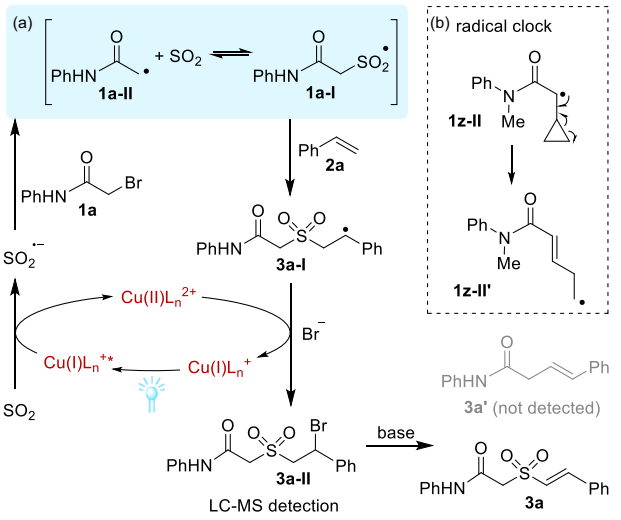
TABLE 2 | Scope of α-bromocarbonyl compounds **1** and alkenes **2**.



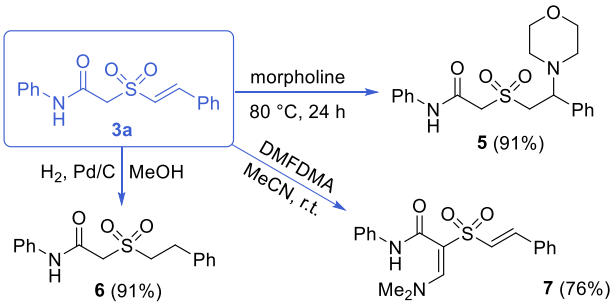
Reaction conditions: **1** (1.0 mmol), **2** (1.3 mmol), $[Cu(dmp)_2]BF_4$ (1 mol%), MeCN (anhydrous, degassed, 3.67 mL), 2,4,6-collidine (4.0 mmol), SO_2 (2.0 mmol as a 1.5 M solution in MeCN), $LED_{456\,nm}$, 35°C, 40 h. Isolated yields are reported.

of **3a** (Table 1, entries 2,8–11), only the excited state redox potentials of $[Cu(dmp)_2]BF_4$ and $[Cu(Xantphos)(dmp)]BF_4$ are suitable for the reduction of substrate **1a**, while others are not reducing enough to generate intermediate **I** (Table S2). This could indicate that formation of **1a-II** is not the first step of the reaction. Meanwhile, SO_2 can easily be reduced by all the excited states of these catalysts to generate $SO_2^{\bullet-}$ (Table S2) – a more likely event according to the approximately two orders of magnitude larger quenching rate constant of SO_2 compared to that of **1a** (Stern–Volmer quenching experiments Figures S8–S9). It is therefore probable that the generation of the $SO_2^{\bullet-}$ anion represents the first step of the reaction, which is followed by nucleophilic substitution to generate intermediate **1a-I** from substrate **1a** (Scheme 2a). Such substitution is also in line with the reactivity of α-halocarbonyl compounds **1a**, **1w**, and **1x** in the synthesis of compound **3a**, which decreases from iodo- to bromo- and chloro-analog (Table S3), reflecting the ability of halide ions to act as leaving groups. Next, the radical addition of sulfonyl radical **1a-I** to styrene (**2a**) is likely followed by oxidation of **3a-I** to benzylic cation and bromide ion inclusion or, alternatively, by copper-mediated halogen atom transfer to form **3a-II** (which was detected by LC-MS when 2,6-di-*tert*-butylpyridine was used as a base) [43–46]. Alternating irradiation and darkness showed no reaction in the dark phases (SI 4.3.) and the relative quantum yield of the reaction was determined to be as low as 3.4%, ruling out the possibility of an efficient radical chain mechanism (SI 4.4.). Lastly, elimination of HBr by base forms the final product **3a**.

Interestingly, as substrate **1z** only gave the product **3af** (Table 2, SI 4.2.) under standard conditions, indicating the radical clock transformation from intermediate **1z-II** to **1z-II'** (Scheme 2b), a possible equilibrium between intermediates **1a-I** and **1a-II** should also be considered (Scheme 2a). Moreover, as no alternative product **3a'**, originating from intermediate **1a-II**, was detected in the reaction mixture, either this equilibrium is shifted toward **1a-I** or the reaction of the latter with **2a** is preferred. It should be noted that free α-carbonylsulfonyl radicals were so far only detected at low temperatures and are known to eliminate SO_2 due to the low singly occupied



SCHEME 2 | Proposed reaction mechanism. (a) mechanistic hypothesis and (b) radical clock experiment.



SCHEME 3 | Some transformations of compound **3a**.

molecular orbital (SOMO) energy of the C-centered radicals involved [47]. As only the copper-based complexes among the tested photoredox catalysts led to the formation of product **3a** (Table S1, entries 9–21), it appears plausible that copper plays a crucial role in the reaction, possibly through chelation. While similar observations are not unprecedented in the field of photoredox catalysis, further investigation of the exact role of copper is required to better understand the reaction mechanism [48, 49].

The necessity for 2,4,6-collidine (or 2,6-lutidine) in the reaction should also be addressed, as other tested bases proved unsuitable for the reaction (Table S1, entries 3–8). Both the involvement of the Katritzky salt **1y**, formed from 2,4,6-collidine and **1a**, and the formation of a charge transfer complex between 2,4,6-collidine and **1a**, were ruled out experimentally, contrasting previously reported related methods (SI 4.8.1.) [50, 51]. However, absorption spectra show that 2,4,6-collidine forms a charge transfer complex with SO_2, similar to other amine-SO_2 complexes (SI 4.8.1.) [52–55]. Furthermore, when the reaction was performed under otherwise standard conditions (Table 1) but in the absence of a catalyst absorbing at 456 nm, no product **3a** was detected in the reaction mixture, while only 8% and 10% NMR yields of product **3a** were achieved at 427 and 390 nm irradiation wavelength, respectively (Table S1, entries 34, 37, 38). It is therefore possible that the 2,4,6-collidine–SO_2 charge transfer complex plays a role in the reaction although the involvement of complexes such as $[S_3O_6]^{2-}$ and $[S_2O_4]^{\bullet-}$ cannot be ruled out entirely [56]. The possibility for the additional role of base besides deprotonation of intermediate **3a-II** (Scheme 2) is therefore still under scrutiny.

The synthetic utility of the representative product **3a** was demonstrated (Scheme 3) in a reaction with morpholine, yielding 91% of amine **5**. Additionally, hydrogenation of styryl sulfone **3a** resulted in a 91% yield of saturated derivative **6**. Finally, reaction with dimethyl formamide dimethyl acetal (DMFDMA) produced compound **7** in a 76% yield. Compounds **3** can therefore react as an electrophile or nucleophile as needed.

3 | Conclusion

A detailed account of the formation of α-(styrylsulfonyl)amides and their ester analogs in a Cu-catalyzed three-component photoreaction is presented. The developed method is best suited for the synthesis of α-(styrylsulfonyl)amides with no substituents in the α-position. Their ester analogs were prepared by the same

method, albeit in lower yields, while the ketone analog was isolated only with a poor yield. Among the tested olefins, only vinyl(hetero)arenes could successfully be used as coupling partners. Based on experimental data, an alternative mechanism for the fixation of SO_2 is proposed. This work opens new opportunities for the utilization of the copper–SO_2 system, which will be explored further, while investigating the exact roles of copper complexes and base in the process.

4 | Experimental Section

4.1 | General Procedure for the Synthesis of Sulfones 3a–af

A dried 8 mL vial was charged with **1** (1.0 mmol), **2** (1.3 mmol), $[Cu(dmp)_2]BF_4$ (5.7 mg, 1.0 mol%), MeCN (anhydrous, degassed, 3 mL), 2,4,6-collidine (529 µL, 4.0 mmol), and SO_2 solution in anhydrous acetonitrile (2 mmol, 1.34 mL of 1.5 M or equivalent amount). The vial was then sealed under argon with a septum. The reaction mixture was stirred under light emitting diode irradiation at 456 nm ($LED_{456\ nm}$) for 40 h at 30°C. The reaction mixture was then quenched with 0.5 M aqueous citric acid (10 mL) and extracted with DCM (15 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and the filtrate concentrated under reduced pressure to afford crude **3**, which was purified by column chromatography. Due to the instability of sulfones **3** on silica gel, their purification should be carried out rapidly to avoid a decrease in yield.

[CCDC 2 425 291 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Author Contributions

Nejc Petek: conceptualization, investigation, methodology, data curation, formal analysis, writing – original draft, writing – review & editing, visualization. **Till Opatz**: conceptualization, funding acquisition, project administration, resources, supervision, writing – review & editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article. Additional data is available from the corresponding author upon reasonable request.

References

1. G. Sravya, G. Yamini, V. Padmavathi, and A. Padmaja, "Synthesis and Antimicrobial Activity of Styryl/Pyrrolyl/Pyrazolyl Sulfonylmethyl-1,3,4-Oxadiazolyl Amines and Styryl/Pyrrolyl/Pyrazolyl Sulfonylmethyl-1,3,4-Thiadiazolyl Amines," *European Journal of Medicinal Chemistry* 122 (2016): 647–655, https://doi.org/10.1016/j.ejmech.2016.06.014.

2. S. Gundala, N. Ummadi, P. Venkatapuram, et al., "Antioxidant and Anti-Inflammatory Activities of 5-((styrylsulfonyl) Methyl)-1,3,4-Oxadiazol/Thiadiazol-2-Amine Derivatives," *Letters in Drug Design & Discovery* 16, no. 11 (2019): 1233–1247, https://doi.org/10.2174/1570180816666181102114529.

3. M. M. Shulaeva, M. A. Kravchenko, and V. E. Semenov, "Synthesis and Antimycobacterial Activity of Pyridinium Compounds with Sulfonylacetamide Substituent in N-Alkyl Chain," *Chemistry of Heterocyclic Compounds* 54, no. 9 (2018): 868–874, https://doi.org/10.1007/s10593-018-2362-3.

4. T. Bhanu Prakash, L. Mallikarjuna Reddy, A. Padmaja, and V. Padmavathi, "Synthesis and Antimicrobial Activity of Azole Derivatives," *Chemical and Pharmaceutical Bulletin* 61, no. 5 (2013): 516–523, https://doi.org/10.1248/cpb.c12-00975.

5. P. B. Jones, N. M. Parrish, T. A. Houston, et al., "A New Class of Antituberculosis Agents," *Journal of Medicinal Chemistry* 43, no. 17 (2000): 3304–3314, https://doi.org/10.1021/jm000149l.

6. R. Ahmadi and S. Emami, "Recent Applications of Vinyl Sulfone Motif in Drug Design and Discovery," *European Journal of Medicinal Chemistry* 234 (2022): 114255, https://doi.org/10.1016/j.ejmech.2022.114255.

7. K. Venkataraman, The Chemistry of Synthetic Dyes V6: Reactive Dyes (Academic Press, 1971).

8. M. V. Ramana Reddy, D. B. Reddy, P. V. Ramana Reddy, and S. Vijayalakshmi, "Synthesis of (E,E)-bis(arylcyclopropyl) Sulfones from Novel (E,E)-bis(styryl) Sulfones.," *Organic Preparations and Procedures International* 23, no. 5 (1991): 633–638, https://doi.org/10.1080/00304949109457916.

9. M. R. Mallireddigari, V. R. Pallela, E. P. Reddy, and M. V. R. Reddy, "Sequential Reduction and Dehydration of Phenacyl-(E)-Styryl Sulfones to Unsymmetrical (E, E)-Bis(styryl) Sulfones," *Synthesis* 2005, no. 20 (2005): 3639–3643, https://doi.org/10.1055/s-2005-918450.

10. J. Yu, H. Zhang, X. Wu, and C. Zhu, "Intermolecular Radical Fluoroalkylative Olefination of Unactivated Alkenes," *CCS Chemistry* 4, no. 4 (2022): 1190–1198, https://doi.org/10.31635/ccschem.021.202100944.

11. H. Zhu, Y. Shen, Q. Deng, J. Chen, and T. Tu, "Pd(NHC)-Catalyzed Alkylsulfonylation of Boronic Acids: A General and Efficient Approach for Sulfone Synthesis," *Chemical Communications* 53, no. 92 (2017): 12473–12476, https://doi.org/10.1039/C7CC05851A.

12. A. S. Deeming, C. J. Russell, and M. C. Willis, "Palladium(II)-Catalyzed Synthesis of Sulfinates from Boronic Acids and DABSO: A Redox-Neutral, Phosphine-Free Transformation," *Angewandte Chemie International Edition*, 55, no. 2 (2016): 747–750, https://doi.org/10.1002/anie.201508370, (accessed 2025/08/06).

13. K. Gulbe and M. R Turks, "Synthesis of Sulfones via Ru(II)-Catalyzed Sulfination of Boronic Acids," *The Journal of Organic Chemistry* 85, no. 8 (2020): 5660–5669, https://doi.org/10.1021/acs.joc.9b03403.

14. S. T. Nguyen and N. P. Peet, "A New Method for the Preparation of (E)-2-(Styrylsulfonyl)acetic Acid Esters and Their Reactions with Hydrazine Hydrate," *Synthesis* 2011, no. 08 (2011): 1205–1207, https://doi.org/10.1055/s-0030-1259974.

15. M. V. R. Reddy and S. Reddy, "A Novel Synthesis of (E)-Substituted Styryl (Z)-Styryl Sulfones," *Synthesis* 1984, no. 04 (1984): 322–323, https://doi.org/10.1055/s-1984-30827.

16. M. R. Guda, S. Gundala, V. Padmavathi, and A. Padmaja, "An Efficient Synthesis of Styryl 1,3,4-Thiadiazoles Using Lawesson's Reagent and Propylphosphonic Anhydride-Precursors for Bis Heterocycles," *Arabian Journal of Chemistry* 7 (2014): 947. https://doi.org/10.1016/j.arabjc.2014.08.013.

17. K. Hofman, N.-W. Liu, and G. Manolikakes, "Radicals and Sulfur Dioxide: A Versatile Combination for the Construction of Sulfonyl-Containing Molecules," *Chemistry – A European Journal* 24, no. 46 (2018): 11852–11863, https://doi.org/10.1002/chem.201705470.

18. G. Qiu, K. Zhou, L. Gao, and J. Wu, "Insertion of Sulfur Dioxide via a Radical Process: An Efficient Route to Sulfonyl Compounds," *Organic Chemistry Frontiers* 5, no. 4 (2018): 691–705, https://doi.org/10.1039/C7QO01073G.

19. S. P. Blum, K. Hofman, G. Manolikakes, and S. R. Waldvogel, "Advances in Photochemical and Electrochemical Incorporation of Sulfur Dioxide for the Synthesis of Value-Added Compounds," *Chemical Communications* 57, no. 67 (2021): 8236–8249, https://doi.org/10.1039/D1CC03018C.

20. S. Ye, X. Li, W. Xie, and J. Wu, "Photoinduced Sulfonylation Reactions through the Insertion of Sulfur Dioxide," *European Journal of Organic Chemistry* 2020, no. 10 (2020): 1274–1287, https://doi.org/10.1002/ejoc.201900396.

21. G. Liu, C. Fan, and J. Wu, "Fixation of Sulfur Dioxide into Small Molecules," *Organic & Biomolecular Chemistry* 13, no. 6 (2015): 1592–1599, https://doi.org/10.1039/C4OB02139H.

22. M. Májek, M. Neumeier, and A. Jacobi von Wangelin, "Aromatic Chlorosulfonylation by Photoredox Catalysis," *ChemSusChem* 10, no. 1 (2017): 151–155, https://doi.org/10.1002/cssc.201601293.

23. M. Yu, S. Lin, S. Zhang, X. Lin, and X. Huang, "Direct C–H Sulfonylation of Hydrazones Involving the Insertion of SO_2," *Organic Chemistry Frontiers* 11 (2024): 4284–4289, https://doi.org/10.1039/D4QO00835A.

24. J. Zhang, F. Zhang, L. Lai, J. Cheng, J. Sun, and J. Wu, "Generation of Sulfonated 1-Isoindolinones through a Multicomponent Reaction with the Insertion of Sulfur Dioxide," *Chemical Communications* 54, no. 31 (2018): 3891–3894, https://doi.org/10.1039/C8CC01124A.

25. D. Zheng, Y. An, Z. Li, and J. Wu, "Metal-Free Aminosulfonylation of Aryldiazonium Tetrafluoroborates with DABCO·$(SO_2)_2$ and Hydrazines," *Angewandte Chemie International Edition* 53, no. 9 (2014): 2451–2454, https://doi.org/10.1002/anie.201309851.

26. D. Louvel, A. Chelagha, J. Rouillon, et al., "Metal-Free Visible-Light Synthesis of Arylsulfonyl Fluorides: Scope and Mechanism," *Chemistry – A European Journal* 27, no. 34 (2021): 8704–8708, https://doi.org/10.1002/chem.202101056.

27. S. Ghosh, S. Samanta, A. K. Ghosh, S. Neogi, and A. Hajra, "Advances in Oxosulfonylation Reaction," *Advanced Synthesis & Catalysis* 362, no. 21 (2020): 4552–4578, https://doi.org/10.1002/adsc.202000647.

28. Y. Li, D. Zheng, Z. Li, and J. Wu, "Generation of N-Aminosulfonamides via a Photo-Induced Fixation of Sulfur Dioxide into Aryl/Alkyl Halides," *Organic Chemistry Frontiers* 3, no. 5 (2016): 574–578, https://doi.org/10.1039/C6QO00060F.

29. X. Gong, Y. Ding, X. Fan, and J. Wu, "Synthesis of β-Keto Sulfones via Coupling of Aryl/Alkyl Halides, Sulfur Dioxide and Silyl Enolates through Metal-Free Photoinduced C–X Bond Dissociation," *Advanced Synthesis & Catalysis* 359, no. 17 (2017): 2999–3004, https://doi.org/10.1002/adsc.201700525.

30. S. Zhang, Q. Zhang, S. Lin, X. Lin, and X. Huang, "Photoredox-Catalyzed Sulfonylation of Diaryliodonium Salts with DABSO and Silyl Enolates Involving the Insertion of SO_2," *Rsc Advances* 14, no. 21 (2024): 14697–14701, https://doi.org/10.1039/D4RA02773F.

31. V. T. Nguyen, G. C. Haug, V. D. Nguyen, N. T. H. Vuong, H. D. Arman, and O. V. Larionov, "Photocatalytic Decarboxylative Amidosulfonation Enables Direct Transformation of Carboxylic Acids to Sulfonamides," *Chemical Science* 12, no. 18 (2021): 6429–6436, https://doi.org/10.1039/D1SC01389K.

32. Z.-D. Chen, X. Zhou, J.-T. Yi, et al., "Catalytic Decarboxylative Fluorosulfonylation Enabled by Energy-Transfer-Mediated Photocatalysis," *Organic Letters* 24, no. 13 (2022): 2474–2478, https://doi.org/10.1021/acs.orglett.2c00459.

33. T. Liu, Y. Li, L. Lai, J. Cheng, J. Sun, and J. Wu, "Photocatalytic Reaction of Potassium Alkyltrifluoroborates and Sulfur Dioxide with Alkenes," *Organic Letters* 20, no. 12 (2018): 3605–3608, https://doi.org/10.1021/acs.orglett.8b01385.

34. J. Zhang, X. Li, W. Xie, S. Ye, and J. Wu, "Photoredox-Catalyzed Sulfonylation of O-Acyl Oximes via Iminyl Radicals with the Insertion of Sulfur Dioxide," *Organic Letters* 21, no. 13 (2019): 4950–4954, https://doi.org/10.1021/acs.orglett.9b01323.

35. X. Wang, Y. Kuang, S. Ye, and J. Wu, "Photoredox-Catalyzed Synthesis of Sulfones through Deaminative Insertion of Sulfur Dioxide," *Chemical Communications* 55, no. 99 (2019): 14962–14964, https://doi.org/10.1039/C9CC08333B.

36. J. Hong, C. Li, K. Zhao, et al., "Fluorosulfonylation of Vinylboronic Acids for (E)-Vinyl Sulfonyl Fluorides with Copper Participation," *Organic Letters* 26, no. 11 (2024): 2332–2337, https://doi.org/10.1021/acs.orglett.4c00711.

37. M. A. Idris and S. Highly Lee, "Reactive Palladium-Catalyzed and Acetonitrile-Mediated Three-Component Reactions for Arylsulfone Synthesis," *Organic Letters* 24, no. 46 (2022): 8520–8525, https://doi.org/10.1021/acs.orglett.2c03430.

38. S. Engl and O. Reiser, "Making Copper Photocatalysis Even More Robust and Economic: Photoredox Catalysis with [CuII$(dmp)_2$Cl]Cl," *European Journal of Organic Chemistry* 2020, no. 10 (2020): 1523–1533, https://doi.org/10.1002/ejoc.201900839, (accessed 2021/04/22).

39. N. Petek, H. Brodnik, U. Grošelj, J. Svete, and B. Štefane, "Access to β-Lactam Sulfonamides from Sulfamoyl Chlorides via Photoredox Catalyzed C–S Bond Formation," *Advanced Synthesis & Catalysis* 366, no. 15 (2024): 3310–3315, https://doi.org/10.1002/adsc.202400311.

40. N. Petek, H. Brodnik, O. Reiser, and B. Copper- Štefane, "Copper- and Photoredox-Catalyzed Cascade to Trifluoromethylated Divinyl Sulfones," *The Journal of Organic Chemistry* 88, no. 10 (2023): 6538–6547, https://doi.org/10.1021/acs.joc.2c02422.

41. Y. Fang, Z. Luo, and X. Xu, "Recent Advances in the Synthesis of Vinyl Sulfones," *Rsc Advances* 6, no. 64 (2016): 59661–59676, https://doi.org/10.1039/C6RA10731A.

42. A. Hossain, S. Engl, E. Lutsker, and O. Reiser, "Visible-Light-Mediated Regioselective Chlorosulfonylation of Alkenes and Alkynes: Introducing the Cu(II) Complex [Cu(dap)Cl_2] to Photochemical ATRA Reactions," *Acs Catalysis* 9, no. 2 (2019): 1103–1109, https://doi.org/10.1021/acscatal.8b04188.

43. X.-J. Tang and W. R. DolbierJr, "Efficient Cu-Catalyzed Atom Transfer Radical Addition Reactions of Fluoroalkylsulfonyl Chlorides with Electron-Deficient Alkenes Induced by Visible Light," *Angewandte Chemie International Edition* 54, no. 14 (2015): 4246–4249, https://doi.org/10.1002/anie.201412199.

44. D. B. Bagal, G. Kachkovskyi, M. Knorn, T. Rawner, B. M. Bhanage, and O. Reiser, "Trifluoromethylchlorosulfonylation of Alkenes: Evidence for an Inner-Sphere Mechanism by a Copper Phenanthroline Photoredox Catalyst," *Angewandte Chemie International Edition* 54, no. 24 (2015): 6999–7002, https://doi.org/10.1002/anie.201501880.

45. L. N. Pham, A. Olding, C. C. Ho, A. C. Bissember, and M. L. Coote, "Investigating Competing Inner- and Outer-Sphere Electron-Transfer Pathways in Copper Photoredox-Catalyzed Atom-Transfer Radical Additions: Closing the Cycle," *Angewandte Chemie*

International Edition 64, no. 3 (2024): e202415792, https://doi.org/10.1002/anie.202415792.

46. A. Reichle, M. Koch, H. Sterzel, et al., "Photocatalyzed Bromonitroalkylation of Olefins: Evidence for Highly Efficient Inner-Sphere Pathways," *Angewandte Chemie International Edition* 62, no. 16 (2023): e202219086, https://doi.org/10.1002/anie.202219086.

47. J. S. Hwang and C. P. Tsonis, "Radicals in the Synthesis of Sulphur Dioxide-Based Copolymers," *Journal of Polymer Science: Part A* 31, no. 6 (1993): 1417–1421, https://doi.org/10.1002/pola.1993.080310608.

48. M. Zhang, L. Liu, B. Wang, et al., "Direct Synthesis of Sulfonamides via Synergetic Photoredox and Copper Catalysis," *Acs Catalysis* 13, no. 17 (2023): 11580–11588, https://doi.org/10.1021/acscatal.3c03096.

49. T. Liu, Y. Ding, X. Fan, and J. Wu, "Photoinduced Synthesis of (E)-Vinyl Sulfones through the Insertion of Sulfur Dioxide," *Organic Chemistry Frontiers* 5, no. 21 (2018): 3153–3157, https://doi.org/10.1039/C8QO00965A.

50. R. N. Lima, J. A. C. Delgado, D. I. Bernardi, et al., "Post-Synthetic Functionalization of Tryptophan Protected Peptide Sequences through Indole (C-2) Photocatalytic Alkylation," *Chemical Communications* 57, no. 47 (2021): 5758–5761, https://doi.org/10.1039/D1CC01822A.

51. E. Fuks, L. Huber, T. Schinkel, and O. Trapp, "Photoinduced Alkylations of Electron-Rich Heterocompounds with Electron-Deficient Alkyl Bromides in the Sole Presence of 2,6-Lutidine," *European Journal of Organic Chemistry* 2020, no. 39 (2020): 6192–6198, https://doi.org/10.1002/ejoc.202001003.

52. T. Hata and S. Kinumaki, "Reactions of Ammonia and Aliphatic Amines with Sulphur Dioxide," *Nature* 203, no. 4952 (1964): 1378–1379, https://doi.org/10.1038/2031378b0.

53. N. M. Monezi, A. C. Borin, P. S. Santos, and R. A. Ando, "The Thermochromic Behavior of Aromatic Amine-SO_2 Charge Transfer Complexes," *Spectrochimica Acta Part A* 173 (2017): 462–467, https://doi.org/10.1016/j.saa.2016.09.043.

54. A. V. Leontiev and D. M. Rudkevich, "Revisiting Noncovalent SO_2−Amine Chemistry: An Indicator−Displacement Assay for Colorimetric Detection of SO_2," *Journal of the American Chemical Society* 127, no. 41 (2005): 14126–14127, https://doi.org/10.1021/ja053260v.

55. J. F. King and M. Aslam, "Organic Sulfur Mechanisms. 21. The Reaction of Arylsulfenes with Sulfur Dioxide," *Canadian Journal of Chemistry* 57, no. 24 (1979): 3278–3291, https://doi.org/10.1139/v79-536.

56. D. Knittel, "Electrolytically Generated Sulfur Dioxide Anion Radical $S_2O_4^{\cdot-}$, Its Absorption Coefficient and Some of Its Decay Reactions," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 195, no. 2 (1985): 345–356, https://doi.org/10.1016/0022-0728(85)80054-1.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. **Supporting Scheme S1:** Control experiments on the possible involvement of Katritzky salt **1y** in reaction mechanism. **Supporting Scheme S2:** Control experiments on the possible involvement of a base in reaction mechanism. **Supporting Scheme S3:** Proposed generation of side product **4a**. **Supporting Fig. S1:** Standard photochemical setup. **Supporting Fig. S2:** Substrates **1a–z** and **2a–k** used in this study. **Supporting Fig. S3:** Rate of formation of **3a** with irradiation (white) or in the dark (gray). For the first 30 minutes, the reaction mixture was irradiated. **Supporting Fig. S4:** Cyclic voltammogram of **1a** with ferrocene standard. **Supporting Fig. S5:** Cyclic voltammogram of **1w** with ferrocene standard. **Supporting Fig. S6:** Cyclic voltammogram of **1x** with ferrocene standard. **Supporting Fig. S7:** Cyclic voltammogram of **1y** with ferrocene standard. **Supporting Fig. S8:** Stern–Volmer plot of [Cu(Xantphos)(dmp)]BF_4 quenching by **1a**. **Supporting Fig. S9:** Stern–Volmer plot of [Cu(Xantphos)(dmp)]BF_4 quenching by SO_2. **Supporting Fig. S10:** Absorption spectra of acetonitrile solutions of 2,4,6-collidine (in blue), sulfur dioxide (in green), **1a** (in black), 2,4,6-collidine with **1a** (in orange) and sulfur dioxide with 2,4,6-collidine (in red). **Supporting Fig. S11:** Chemical structures of some of the copper complexes used in this study. **Supporting Fig. S12:** Molecular structure of product **3a**. Thermal ellipsoids are shown at 50% probability. CCDC number: 2425291. **Supporting Table S1:** Optimization study of the reaction conditions. **Supporting Table S2:** Redox potentials of **1a**, SO_2 and some of the employed copper complexes in their excited states. **Supporting Table S3:** Effect of halide substituent on the reaction progress.