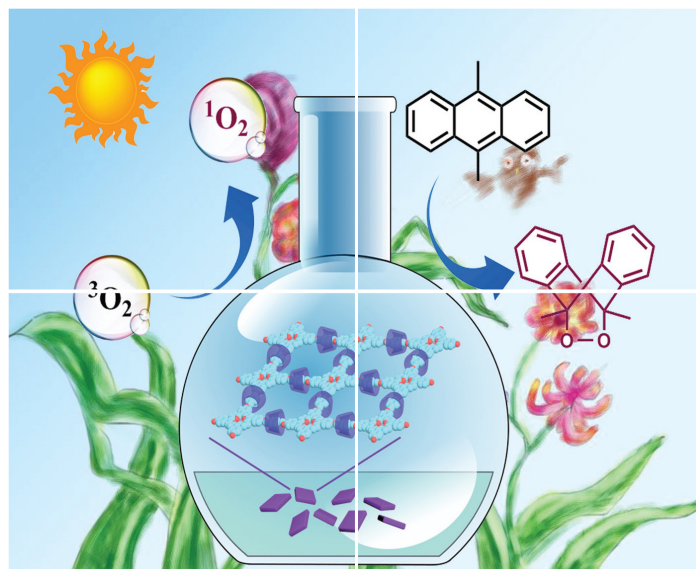


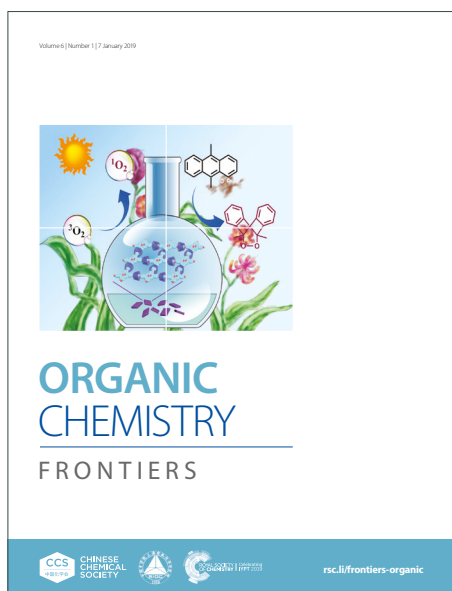
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ARTICLE

Photoinduced Sulfanyloximation of Styrenes Using *N*-Nitrosamines and Thiols

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Molecules featuring both sulfur and nitrogen atoms are privileged scaffolds in medicinal chemistry and biological systems. However, methods for the direct and regioselective installation of these heteroatoms onto alkenes remain limited. Herein, we report a visible-light-induced, three-component sulfanyloximation of styrenes utilizing thiols and *N*-nitrosamine as a bench-stable nitrogen oxide (NO) surrogate. This regioselective protocol operates under mild conditions with remarkable functional group tolerance. The synthetic utility of this methodology is further demonstrated by its extension to the synthesis of 2,3-disubstituted indoles and the divergent downstream derivatization of α -sulfanyl ketoxime products via imidoyl fluoride intermediates. An extensive mechanistic investigation supports a pathway initiated by thiyl radical addition to alkenes followed by radical coupling with in situ generated NO.

Introduction

Molecules incorporating both sulfur and nitrogen atoms are ubiquitous in nature and represent privileged scaffolds in modern medicinal chemistry.¹ These heteroatom-rich motifs are central to a wide range of biologically active compounds, including thiofanox, benzthiazide, and erdosteine (Scheme 1A). One representative example is the amino acid L-cysteine, which features a 1,2-aminothiol unit, and this is a structural pattern that is among the most frequent and vital motifs observed in biological systems.² Consequently, the development of efficient, regioselective, and atom-economical methods to construct molecules featuring dual sulfur and nitrogen functionalities remains a high-priority goal in synthetic organic chemistry.

Oximes serve as versatile synthetic intermediates and bioactive components.³ They are considered essential functional group for the construction of complex molecules via the Beckmann rearrangement that can provide facile access to amides, nitriles, and various *N*-heterocycles.⁴ Furthermore, the oxime moiety has gained significant prominence as a powerful directing group in C–H activation reactions.⁵ Despite their utility, current synthetic methods to obtain highly decorated ketoximes remains relatively limited, often requiring pre-functionalized precursors.

Traditionally, the synthesis of α -sulfanyl ketoximes, which contains the 1,2-aminothiol unit, has relied on the functionalization of pre-existing carbonyl compounds.^{6,7} A common route involves the use of α -haloketones, which are converted to oximes using hydroxylamine, followed by the

nucleophilic displacement of the halide with thiols (Scheme 1B, eq. 1). An alternative method involves the prefunctionalization of nitroalkanes via double silylation to generate *N,N*-bis(oxy)enamines that serve as highly electrophilic reagents towards thiols (Scheme 1B, eq. 2).^{6d} Despite the reliability of this strategy, this stepwise logic is inherently constrained by its reliance on pre-functionalized starting materials, which often suffer from poor accessibility and limited functional group tolerance due to harsh conditions required for halogenation. Moreover, these protocols frequently generate stoichiometric chemical waste, detracting from the overall atom economy of the process.⁸

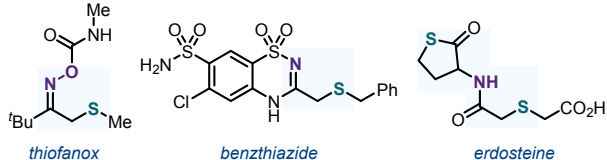
The direct 1,2-difunctionalization of styrenes represents a more streamlined alternative, as these alkenes are abundant, inexpensive feedstock chemicals.⁹ While significant strides have been made in the simultaneous installation of two heteroatoms, the catalytic sulfanyloximation of alkenes has not been reported. To date, alkyl nitrites such as ^tBuONO have served as the standard reagents for radical nitrosation; however, their practical utility is often hampered by thermal instability and side reactions.¹⁰ In 2001, Motherwell and co-workers reported the synthesis of α -sulfanyl ketoximes via the addition of trityl thionitrite (TrSNO) to alkenes (Scheme 1C).¹¹ However, a major drawback of this approach lies in the inherent instability and challenging preparation of primary and secondary *S*-nitrosothiols, which significantly restricts the reaction scope to trityl derivatives.¹² To address these limitations, we envisioned that the combination of thiols with a bench-stable *N*-nitrosamine as nitrogen oxide (NO) surrogate could provide a robust and versatile platform for the sulfanyloximation of alkenes.¹³

Here we report a photoinduced sulfanyloximation of styrenes using *N*-nitrosamines as a stable NO source and thiols (Scheme 1D). In this three-component coupling, the bench

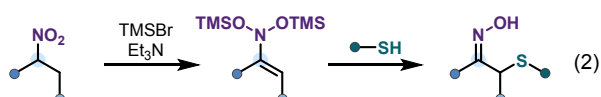
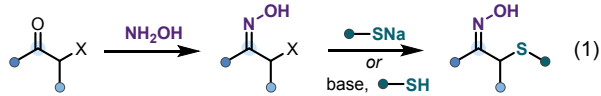
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stable and commercially available *N*-nitrosodiphenylamine (NDPhA) undergoes a single-electron reduction to release NO, which is subsequently trapped by a benzylic radical to furnish a wide range of α -sulfanyl ketoximes with excellent functional group tolerance. Furthermore, α -sulfanyl ketoximes are converted into various nitrogen and sulfur containing compounds through mild downstream derivatization.

A - 1,2-Aminothiol unit in biologically active compounds

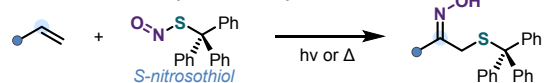


B - Conventional synthesis of α -sulfanyl ketoximes



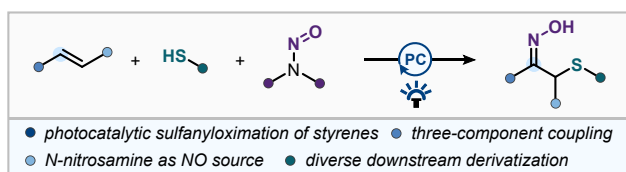
● pre-functionalized starting materials ● multi-step synthesis

C - *S*-Nitrosothiol for α -sulfanyl ketoximes synthesis



● unstable *S*-nitrosothiols (sensitive to heat, light, and pH) ● limited to trityl group

D - This work: Photoinduced sulfanyloximation of styrenes



Scheme 1. Prevalence of 1,2-aminothiol units in biologically relevant molecules and synthetic approaches.

Results and discussion

We began our investigation for the sulfanyloximation by using *para*-methylstyrene (**1a**), [4-(*tert*-butyl)phenyl]methanethiol (**2a**), and *N*-nitrosodiphenylamine (NDPhA, **3a**) as the model substrates for three-component coupling reaction. After an extensive reactivity search, pleasingly, the desired product **4a** was formed in 89% NMR yield with 1,2,3,5-tetrakis(carbazol-9-yl)4,6-dicyanobenzene (4CzIPN) as the photocatalyst and *N,N*-diisopropylethylamine (DIPEA) as the base under visible light irradiation (470 nm) (Table 1, entry 1). The reaction is *Z*-selective (*Z/E* = 11.3/1), and the major isomer can be easily separated by flash column chromatography (77% isolated yield). The use of different bases such as K_2CO_3 , Na_2CO_3 , 2,6-lutidine, or pyridine resulted in diminished product yields and *Z/E* selectivities (Table 1, entries 2-5). Decreasing the amount of DIPEA to 30 mol% had a minimal effect on the product yield (Table 1, entry 6). Although the common nitrosating reagent

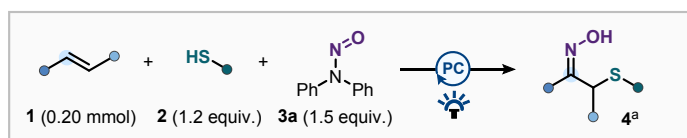
t BuONO also afforded the product **4a**, both the yield and *Z/E* selectivity were inferior to those obtained with *N*-nitrosamine **3a** (Table 1, entry 7). This result highlights the effectiveness of *N*-nitrosamines as a superior NO source for nitrosation reactions. Comparative studies using *N*-nitrosomethylphenylamine (NMPA, **3b**) and *N*-nitrosodicyclohexylamine (NDCHA, **3c**) demonstrated that an aromatic ring adjacent to nitrogen atom is indispensable for the transformation, as trace product **4a** was observed with dialkyl *N*-nitrosamine substrate **3c** (Table 1, entries 8 and 9). Control experiments revealed that the reaction proceeded in the absence of DIPEA, albeit with low efficiency (Table 1, entry 10). However, both the photocatalyst and light irradiation were found to be essential for achieving high yields (Table 1, entries 11-12). Furthermore, while the product **4a** was formed under thermal conditions, the yield remained poor, underscoring the necessity of the photochemical pathway (Table 1, entry 13).

Table 1. Optimization of reaction conditions.

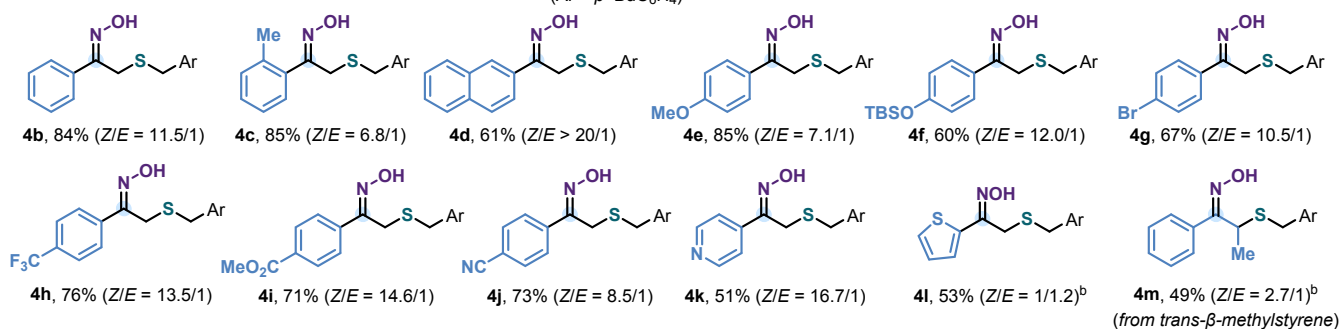
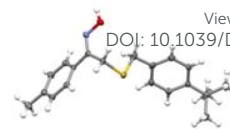
Table 1. Optimization of reaction conditions.

entry ^a	deviations	4a (%) ^b	<i>Z/E</i> ^d
1	none	89 (77) ^c	11.3 / 1
2	K_2CO_3 instead of DIPEA	79	4.0 / 1
3	Na_2CO_3 instead of DIPEA	39	9.4 / 1
4	2,6-lutidine instead of DIPEA	59	9.6 / 1
5	pyridine instead of DIPEA	50	6.3 / 1
6	DIPEA (30 mol%)	87	10.3 / 1
7	t BuONO instead of 3a	73	4.0 / 1
8	3b instead of 3a	92	8.9 / 1
9	3c instead of 3a	trace	n.d.
10	no DIPEA	44	4.9 / 1
11	no 4CzIPN	19	>20 / 1
12	no light	0	n.d.
13	no 4CzIPN, no light, 60 °C	39	>20 / 1

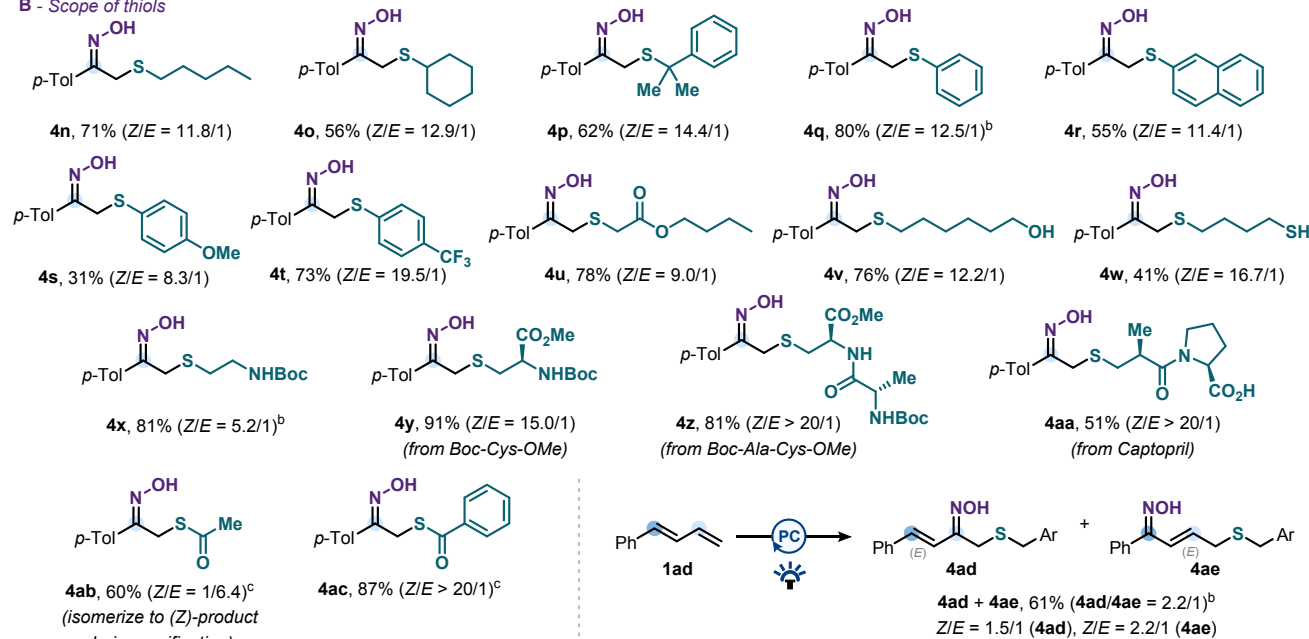
[a] General conditions: **1a** (0.20 mmol), **2a** (0.24 mmol, 1.2 equiv.), **3a** (0.30 mmol, 1.5 equiv.), 4CzIPN (2.0 μ mol, 1.0 mol%), DIPEA (0.12 mmol, 60 mol%), MeCN, 14 h, blue LEDs (470 nm). [b] ¹H NMR analysis using 1,1,2,2-tetrabromoethane as an internal standard. [c] Isolated yield for the major isomer. [d] *Z/E* selectivities determined by crude ¹H NMR. n.d. = not determined.



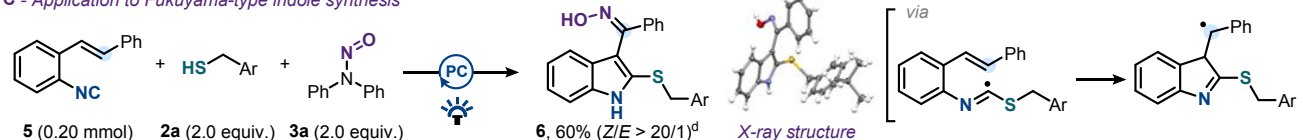
A - Scope of styrenes

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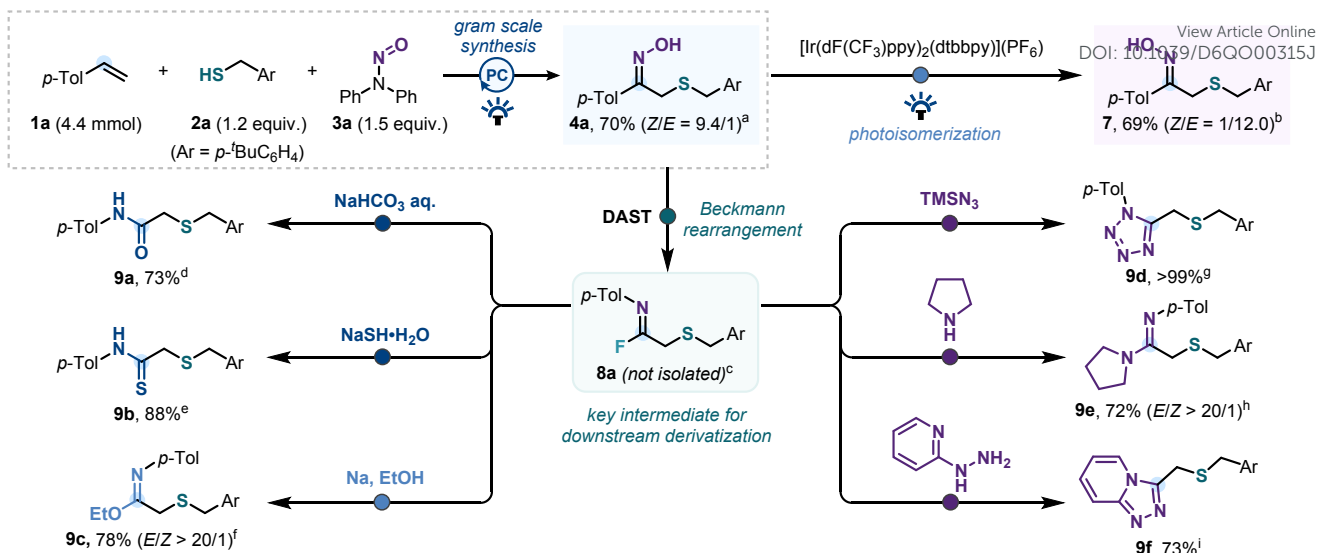
B - Scope of thiols



C - Application to Fukuyama-type indole synthesis



Scheme 2. Substrate scope of photoinduced sulfanyloximation of styrenes. [a] General conditions: **1** (0.20 mmol), **2** (0.24 mmol, 1.2 equiv.), **3a** (0.30 mmol, 1.5 equiv.), 4CzIPN (2.0 μ mol, 1.0 mol%), DIPEA (0.12 mmol, 60 mol%), MeCN, 14 h, blue LEDs (470 nm). Isolated yields for major isomers are shown. Z/E selectivities were determined by crude ¹H NMR. [b] Isolated yields as E/Z mixtures. [c] **1** (0.20 mmol), **2** (0.40 mmol, 2.0 equiv.), **3a** (0.40 mmol, 2.0 equiv.), 4CzIPN (2.0 μ mol, 1.0 mol%), 2,6-lutidine (0.12 mmol, 60 mol%), THF, 14 h, blue LEDs (470 nm). [d] 24 h reaction time.



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Scheme 3. Gram scale synthesis and product derivatization. Isolated yields for major isomers are shown. [a] Reaction carried out for 37 h. [b] $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ (0.5 mol%), AcOEt, rt, 5 h, blue LEDs (425 nm). [c] DAST (1.5 equiv.), THF, rt, 20 min. [d] sat. NaHCO_3 aq. [e] $\text{NaSH}\cdot\text{H}_2\text{O}$ (10 equiv.), DMF, 0 °C to rt, 1 h. [f] Na (3.2 equiv.), EtOH, 0 °C to rt, 16 h. [g] TMSN_3 (4.0 equiv.), THF, 0 °C to rt, 3 h. [h] pyrrolidine (3.0 equiv.), THF, rt, 21 h. [i] 2-hydrazinopyridine (3.0 equiv.), toluene, rt to 50 °C, 8 h.

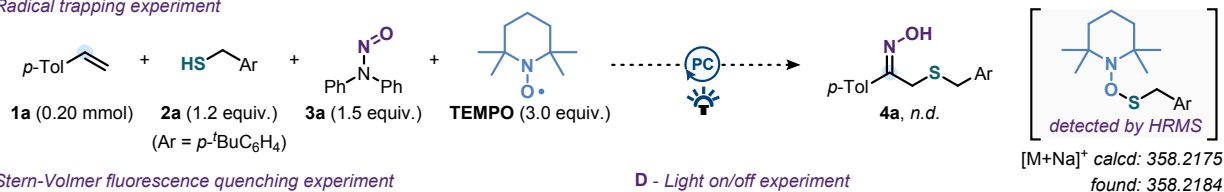
With the optimal conditions in hand, we next investigated the substrate scope of the photocatalytic sulfanyloximation reaction (Scheme 2). Initially, we explored the generality of this transformation with respect to various substituted styrenes (Scheme 2A). The presence of an *ortho*-methyl group in **4c** did not impede the reaction, indicating that the transformation is compatible with sterically hindered substrates. The introduction of a naphthyl group significantly improved the *Z/E* selectivity and only the (*Z*)-isomer of **4d** was observed. Styrenes bearing various electron-donating and electron-withdrawing groups on the aromatic ring were well tolerated, giving the corresponding α -sulfanyl ketoximes **4e–j** in high yields and *Z/E* selectivities. Pleasingly, heteroaromatic substrates, including those containing pyridine and thiophene rings, afforded the corresponding products **4k** and **4l** in good yields. Notably, the *Z/E* selectivity for **4l** was significantly altered, which can likely be attributed to the existence of an intramolecular hydrogen bonding interaction. Substituents at the β -position were also tolerated, affording the product **4m** in 49% yield. This result demonstrates that the transformation can be extended to the synthesis of highly functionalized α -sulfanyl ketoximes. Next, we turned our attention to exploring the scope of various thiols (Scheme 2B). Notably, primary, secondary, and tertiary alkyl thiols all proved to be suitable substrates, affording the desired products **4n–p** in consistently good yields. Similarly, aromatic thiols were well tolerated, providing the corresponding α -sulfanyl ketoximes **4q–t** in moderate to high yields. However, a diminished yield was observed for substrate **4s**, which bears an electron-donating group on the phenyl ring. Furthermore, various potentially reactive moieties were well tolerated under these conditions. A variety of functional groups, including ester, alcohol, hydrosulfide, and Boc-protected amine, were well tolerated, providing the corresponding products **4u–x** in good yields. Importantly, the transformation was successfully applied

to biologically relevant molecules. Both the protected cysteine derivative (Boc-Cys-OMe) and the dipeptide (Boc-Ala-Cys-OMe) were well tolerated, affording the corresponding α -sulfanyl ketoximes **4y** and **4z** in high yields. Notably, these substrates exhibited improved *Z/E* selectivities compared to simple alkyl thiols. The reaction was further extended to the angiotensin-converting enzyme (ACE) inhibitor captopril, which contains an unprotected carboxylic acid moiety. Despite the presence of this acidic group, the reaction proceeded smoothly to afford the desired product **4aa** in 51% yield as a single isomer. Beyond various thiols, the reaction was successfully extended to thioacids. Thioacetic acid and thiobenzoic acid were compatible under the photocatalytic conditions with minor modifications, affording the corresponding products **4ab** and **4ac** in 60% and 87% yields, respectively. When 1,3-diene was used as a starting material, both 1,2- and 1,4-adducts were obtained in 61% combined yield (**4ad/4ae** = 2.2/1).

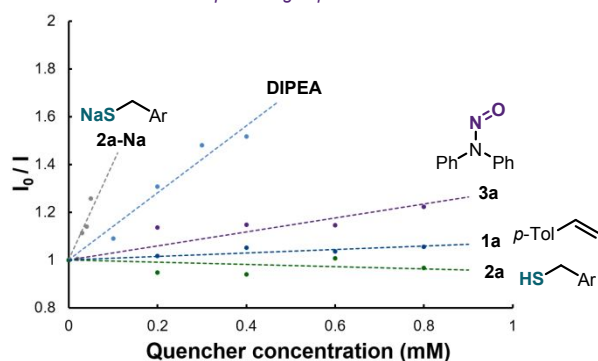
To further extend this multicomponent coupling reaction, we investigated the reactivity of the isonitrile-substituted stilbene **5** (Scheme 2C).¹⁴ We were pleased to find that the substrate **5** underwent an intramolecular cyclization to afford an indole derivative **6** in 60% yield as a single isomer. This Fukuyama-type indole synthesis is most likely initiated by the preferential addition of the thiyl radical to the isocyano group rather than the alkene moiety. The resulting imidoyl radical then undergoes intramolecular cyclization, followed by trapping of the radical intermediate with nitric oxide generated *in situ* from **3a**. Finally, the tautomerization affords the 2,3-disubstituted indole **6**.

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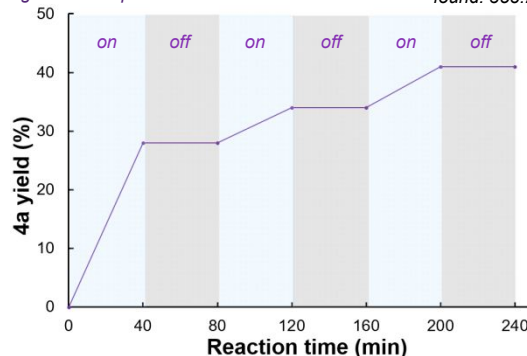
A - Radical trapping experiment



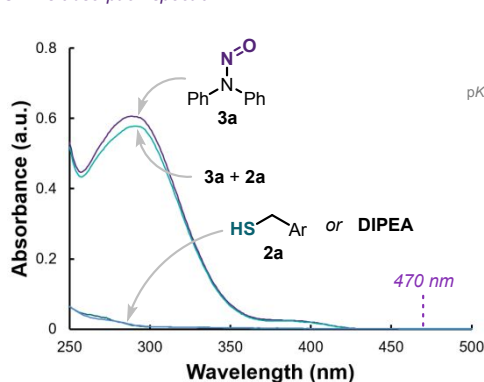
B - Stern-Volmer fluorescence quenching experiment



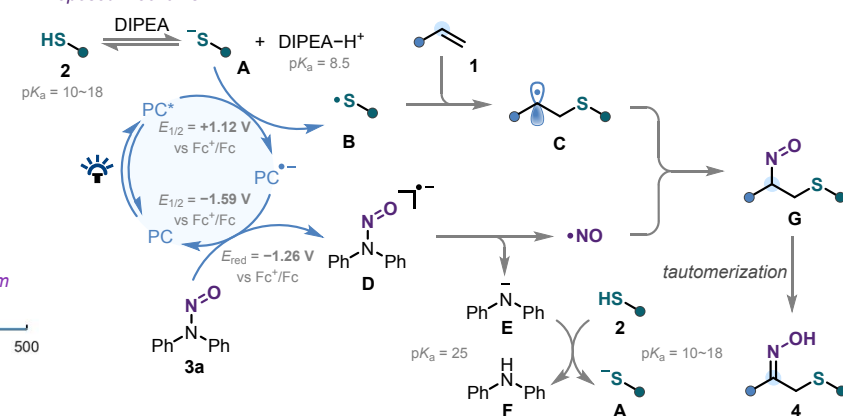
D - Light on/off experiment



C - UV-vis absorption spectra



E - Proposed mechanism



Scheme 4. Mechanistic studies. n.d. = not detected.

To substantiate the scalability of this methodology, the reaction of **1a** and **2a** was performed on a gram scale (Scheme 3). The transformation was successfully scaled up to 4.4 mmol, furnishing the product **4a** in a comparable yield and *Z/E* selectivity, albeit with an extended reaction time. While the present reaction conditions selectively afford the (*Z*)-product **4a**, it can be readily isomerized to the (*E*)-isomer **7**. By employing [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆) as a photocatalyst, **7** was obtained in 69% yield with high *E/Z* selectivity.¹⁵ In order to further showcase the synthetic utility of our products, we investigated the transformation of the hydroxyimino group for the synthesis of various 1,2-aminothiol units. Utilizing (diethylamino)sulfur trifluoride (DAST) as a mild promoter for the Beckmann rearrangement allows for the rapid formation of

the imidoyl fluoride **8a** at room temperature within 20 min.^{16,17} This species serves as a versatile intermediate that can be used without purification, enabling the efficient construction of diverse functional groups using various nucleophiles. For example, an aqueous workup with NaHCO₃ solution or treatment with NaSH as a nucleophile furnished the amide **9a** and the thioamide **9b** in 73% and 88% yields, respectively. The use of NaOEt as a nucleophile, prepared *ex situ* from sodium metal and ethanol, afforded the imidate **9c** in 78% yield as a single isomer. Furthermore, the reaction with TMSN₃ delivered the tetrazole product **9d** in quantitative yield. Pyrrolidine also proved to be an effective nucleophile, affording the amidine **9e** in 72% yield as a single isomer. Notably, the reaction with 2-hydrazinopyridine enabled access to the [1,2,4]triazolo[4,3-

α]pyridine scaffold of **9f** in 73% yield via a sequential double-nucleophilic attack involving the terminal and pyridine nitrogen atoms of the nucleophile. Overall, the α -sulfanyl ketoxime products synthesized via our photocatalytic transformation from readily accessible starting materials serve as highly versatile building blocks for the construction of diverse and complex molecular frameworks.

To gain insight into the reaction pathway for this photocatalytic sulfanyloximation, a series of mechanistic studies were conducted (Scheme 4). Initially, a radical trapping experiment was performed by adding 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) under the standard conditions (Scheme 4A). The reaction was completely suppressed, and the thiol-TEMPO adduct was detected by mass spectrometry, thereby confirming the existence of a thiyl radical. Next, the Stern-Volmer fluorescence quenching studies revealed that the sodium thiolate **2a-Na** quenched the excited photocatalyst more effectively than DIPEA or NDPhA **3a** (Scheme 4B). In contrast, the neutral thiol **2a** exhibited no quenching effect and showed a flat slope. These results indicate that an *in situ* generated thiolate via deprotonation facilitates the single-electron transfer (SET) from the excited state photocatalyst. The effect of visible light irradiation was further demonstrated through the UV-vis absorption spectra that showed no significant absorption by the reactants at 470 nm, indicating that the photocatalyst is the sole species excited under the standard reaction conditions (Scheme 4C). Furthermore, a light on/off experiment demonstrated that sustained irradiation is essential for the reaction to proceed, with no product formation observed during the dark periods (Scheme 4D). This result suggests that a radical chain mechanism is likely not involved.

Based on these mechanistic insights, a plausible catalytic cycle is proposed as shown in Scheme 4E.¹⁸ Initially, the photocatalyst (PC) is excited upon visible light irradiation. The resulting excited state (PC*) undergoes SET to oxidize thiolate **A**, which exists in an equilibrium with thiol **2** via deprotonation by DIPEA. This oxidative quenching process generates the thiyl radical **B** and the corresponding radical anion of the photocatalyst (PC⁻). Subsequently, the thiyl radical **B** undergoes regioselective addition to the β -position of styrene **1** and generates the benzylic radical **C**. Concurrently, the radical anion PC⁻ reduces the *N*-nitrosamine **3a** via SET, furnishing the corresponding radical anion **D** and regenerating the ground state photocatalyst. The facile dissociation of nitric oxide from radical anion **D** generates aminyl anion **E**, which subsequently deprotonates another molecule of thiol **2**. This step regenerates thiolate **A**, thereby sustaining the catalytic cycle and explaining why only a catalytic amount of base is required. Finally, the radical-radical coupling between benzylic radical **C** and NO yields the nitroso intermediate **G**, which undergoes spontaneous tautomerization to afford the α -sulfanyl ketoxime product **4**.

Conclusions

In conclusion, we have developed a robust and efficient photocatalytic sulfanyloximation of styrenes. By employing *N*-nitrosamines as a superior and stable NO source, this three-component coupling overcomes the limitations associated with traditional nitrosating agents, offering a streamlined approach to highly functionalized α -sulfanyl ketoximes under mild visible-light irradiation. This method demonstrates exceptional functional group tolerance, including biologically relevant molecules and thioacids, while further showcasing its versatility through the synthesis of 2,3-disubstituted indoles and divergent downstream derivatization. Mechanistic investigations clarified that the reaction proceeds through a thiolate-mediated oxidative quenching cycle, where a thiyl radical addition initiates the process followed by a radical-radical coupling with NO. Given its operational simplicity, scalability, and broad synthetic utility, this methodology provides a powerful tool for the construction of complex molecular architectures in modern synthetic and medicinal chemistry.

Conflicts of interest

There are no conflicts to declare.

Data availability

A data availability statement (DAS) is required to be submitted alongside all articles. Please read our [full guidance on data availability statements](#) for more details and examples of suitable statements you can use.

Acknowledgements

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- The data supporting this article have been included as part of the Supplementary Information. Supplementary information: NMR spectra and further experimental details. Crystallographic data for compounds 4a, 6 and 9 has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under CCDC 248789, CCDC 2487892 and CCDC 2487894, respectively, and can be obtained from www.ccdc.cam.ac.uk/data_request/cif.

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