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Photocatalytic selective synthesis of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones using $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as the catalyst†

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Selectively producing a variety of valuable compounds using controlled chemical reactions starting from a common material is an appealing yet complex concept. Herein, a photocatalytic approach for the selective synthesis of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones from allenamides and sodium sulfinates was established. This reaction exhibits the traits of an eco-friendly solvent and adjustable amide cleavage, and can accommodate a diverse range of substrates with exceptional functional group tolerance. Based on control experiments and deuterium labeling experiments, a plausible radical reaction pathway is proposed.

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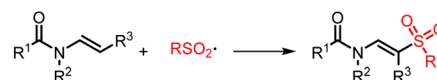
Introduction

In the field of pharmaceutical and organic chemistry, significant advancements in recent years have paved the way for the recognition of the diverse biological activities of β -amino vinyl sulfone skeletons¹ and their potential in organic transformation.² Consequently, the development of methods for the selective construction of these skeletons is gaining significant attention. Sulfonylation *via* the addition of sulfonyl radicals to enamides and their derivatives is a prevalent method for chemical transformation (Scheme 1a).³ This process typically involves the use of various aryl sulfonyl halides and sodium sulfinates under specific conditions. Another effective approach to synthesizing aminovinyl sulfones is *via* C(sp³)-H functionalization of amines (Scheme 1b).^{4,5} Researchers such as Yuan,^{4a} Xia,^{4b} and Talbot^{4c} have reported direct C(sp³)-H sulfonylation of tertiary amines to β -amidovinyl sulfones *via* catalysis with excessive oxidants. Visible-light photoredox catalysis has also been used for this purpose by Zheng,^{5a} Rueping,^{5b} and Sun.^{5c} Despite recent advances, there remains a need for developing innovative building blocks to simplify the preparation of β -aminovinyl sulfones. This includes expanding the range of substrates while avoiding expensive catalysts and hazardous

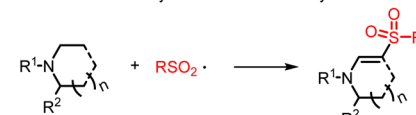
additives, which is vital for the safe and efficient practice of organic synthetic chemistry.

As a highly versatile and potent building block, allenamides have garnered extensive usage in the synthesis of aminovinyl derivatives *via* catalysis by either Brønsted acids or transition metals.⁶ To the best of our knowledge, there have been limited investigations into the radical reaction of allenamides, particularly the precise chemo-, regio-, and stereoselective radical

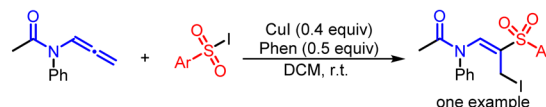
(a) Generation of amidovinyl sulfones from enamides



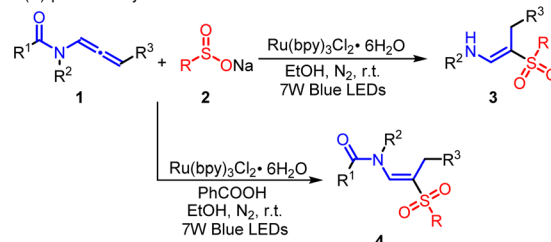
(b) Generation of aminovinyl sulfones from tertiary amines



(c) Copper-catalyzed iodosulfonation of allenamides with sulfonyl iodides



(d) This work: Photocatalytic selective synthesis of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones



Scheme 1 General strategy for the synthesis of aminovinyl sulfone.

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sulfonylation of allenamides. In 2018, Zhang *et al.* reported a novel iodosulfonylation of allenamides using sulfonyl iodides, CuI, and 1,10-phenanthroline. The approach resulted in highly regioselective iodination of the allenamide backbone, affording *I*- α -iodomethyl amidovinyl sulfones.⁷ At the same time, studies have shown that visible light-induced sulfonylation is an effective method for the synthesis of sulfone-containing compounds.⁸ However, until now, no reports have described the photoredox-catalyzed hydrosulfonylation of allenamides to efficiently produce β -aminovinyl sulfones or β -aminovinyl sulfones with high regio- and stereoselectivity. Selectively producing a variety of valuable compounds using controlled chemical reactions starting from a common material is an appealing yet complex concept.⁹ As part of our ongoing research aimed at developing efficient strategies for the synthesis of sulfone-containing compounds,¹⁰ we propose a straightforward and generalized photocatalytic method for the production of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones from allenamides and sodium sulfinates (Scheme 1d).

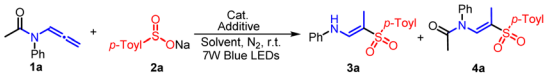
Results and discussion

Our investigation began by evaluating the model reaction between *N*-phenyl-*N*-(propa-1,2-dien-1-yl) acetamide (**1a**)¹¹ and sodium *p*-toluenesulfinate (**2a**)¹² using 3 mol% eosin Y as catalyst and dried ethanol (EtOH) as solvent. After 8 hours of irradiation with 7 W blue LEDs at room temperature, we isolated (*E*)-*N*-(2-tosylprop-1-en-1-yl) aniline **3a** with a yield of 37% (Table 1, entry 1). Encouraged by this result, we screened other

photocatalysts such as Na₂-eosin Y, 4-CzIPN, (Ir[p-Fppy]₂(dtbpy))PF₆ and Ru(bpy)₃Cl₂·6H₂O to improve the conversion rate (entries 2–5). Interestingly, all of these catalysts showed better catalytic efficiency than before, with Ru(bpy)₃Cl₂·6H₂O showing the highest yield of 92%. However, when we changed the solvent from EtOH to other alcohol solvents like methanol (MeOH), isopropyl alcohol (*i*-PrOH), and *tert*-butanol (*t*-BuOH), we observed lower conversions (entries 6–8). Likewise, other solvents like trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) completely inhibited the reaction (entries 9 and 10). Consequently, we selected additives such as bases (K₂HPO₄) or acids (CH₃COOH). The **3a** yield did not increase when excess base amounts were added (entry 11). However, when we added acetic acid as an additive, the product **4a** was selectively generated whereas the formation of **3a** was completely inhibited (entry 12). We further screened other Brønsted acids, including formic acid (HCOOH), trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (TsOH), and benzoic acid (PhCOOH), and identified benzoic acid as exhibiting good selectivity, with yields of up to 75% for **4a** (entries 13–16). Significantly, no desired product was detected in the absence of either Ru(bpy)₃Cl₂·6H₂O or the irradiation of visible light, which both play an essential role in the generation of the sulfonyl radical (entries 18 and 19).

After optimizing the photoredox conditions, the scope and limitations of the developed method for hydrosulfonylation and amide cleavage of allenamides with sodium sulfinates were examined (Scheme 2). Initially, we examined the impacts of various amides on the reaction, including acetamide,

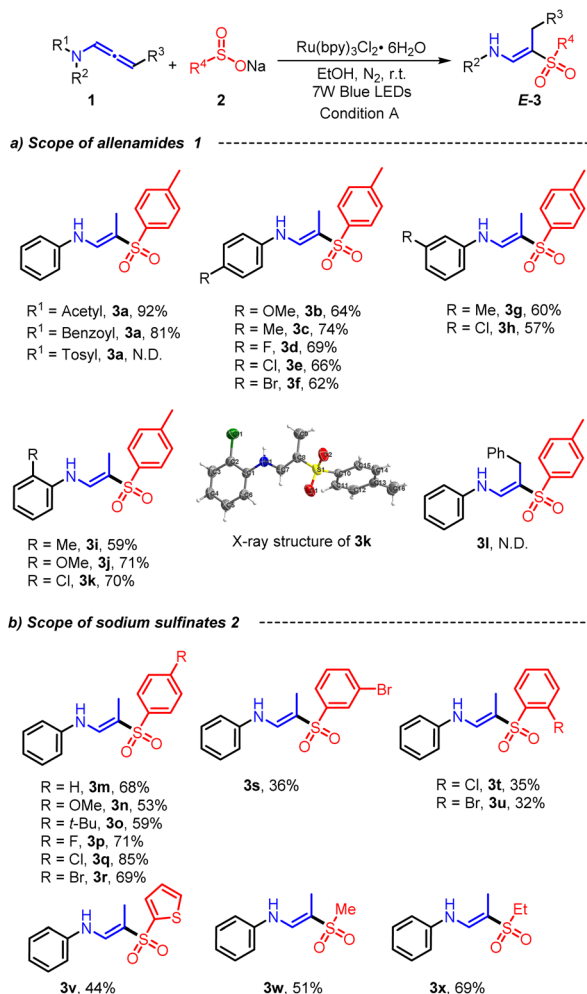
Table 1 Optimization of reaction conditions^a



| Entry | Photocatalyst | Solvent | Additive | Yield ^b 3a (%) | Yield ^b 4a (%) |
|-----------------|---|----------------|---------------------------------|----------------------------------|----------------------------------|
| 1 | Eosin Y | EtOH | — | 37 | N.D. |
| 2 | Na ₂ -eosin Y | EtOH | — | 46 | N.D. |
| 3 | 4-CzIPN | EtOH | — | 64 | N.D. |
| 4 | (Ir[p-Fppy] ₂ (dtbpy))PF ₆ | EtOH | — | 85 | N.D. |
| 5 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | — | 92 | N.D. |
| 6 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | MeOH | — | 88 | N.D. |
| 7 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | <i>i</i> -PrOH | — | 74 | N.D. |
| 8 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | <i>t</i> -BuOH | — | 70 | N.D. |
| 9 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | TFE | — | N.D. | N.D. |
| 10 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | HFIP | — | N.D. | N.D. |
| 11 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | K ₂ HPO ₄ | 71 | N.D. |
| 12 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | CH ₃ COOH | N.D. | 54 |
| 13 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | HCOOH | N.D. | 56 |
| 14 | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | TFA | N.D. | 66 |
| 15 ^c | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | TsOH | N.D. | 57 |
| 16 ^d | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | PhCOOH | N.D. | 75 |
| 17 ^e | Ru(bpy) ₃ Cl ₂ ·6H ₂ O | EtOH | PhCOOH | N.D. | 64 |
| 18 | — | EtOH | PhCOOH | N.D. | N.D. |
| 19 | — | EtOH | — | N.D. | N.D. |

^a Reaction conditions are as follows: **1a** (0.2 mmol), **2a** (0.4 mmol), cat. (3 mol%), additive (0.4 mmol), solvent (2 mL), under 7 W blue LEDs, at room temperature, N₂, 8 h. ^b Isolated yield based on **1a**. ^c Cat. (1 mol%). ^d **2a** (0.5 mmol), additive (0.5 mmol). ^e **2a** (0.3 mmol), additive (0.3 mmol). N.D., not detected. TFE, 2,2,2-trifluoroethanol. TFA, trifluoroacetic acid.





Scheme 2 Substrate scope of (*E*)-β-aminovinyl sulfones **3**. Reaction condition A: **1** (0.2 mmol), **2** (0.4 mmol), Ru(bpy)₃Cl₂·6H₂O (3 mol%), EtOH (2 mL), under 7 W blue LEDs, at room temperature, N₂, 8 h.

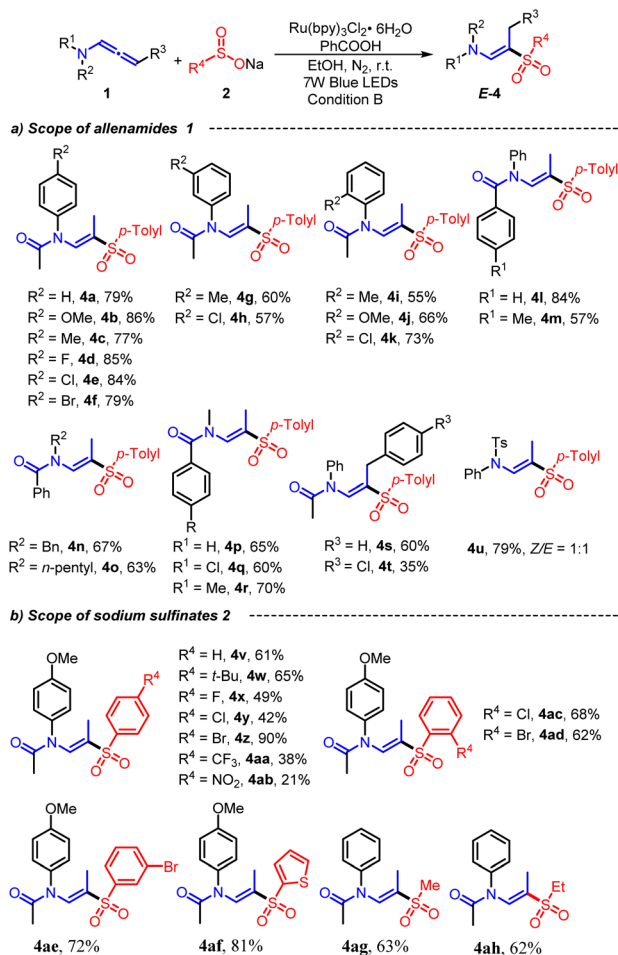
benzamide, and *p*-toluenesulfonamide. Out of these, the acetamide group exhibited superior selectivity, yielding up to 92% for **3a**. Conversely, the *p*-toluenesulfonamide group failed to produce the intended final product. Next, sodium *p*-toluenesulfinate (**2a**) was reacted with allenamides (**1**) featuring varied electronic properties and aryl substitution positions. The photocatalytic transformations were successfully accomplished with all of them. Different substituents on the *p*-position of the aromatic ring, such as methoxy (**1b**), methyl (**1c**), fluoro (**1d**), chloro (**1e**), and bromo (**1f**) groups, were compatible with this photocatalytic strategy, furnishing corresponding products **3b–3f** in 62–74% yields. Overall, neither the electron-withdrawing groups nor electron-donating groups had a particularly significant impact on this photochemical process. Additionally, the steric effect of the substituent at the ortho- or meta-position of the arene ring was briefly investigated. Representative functional groups such as Me, MeO, and Cl at the ortho-position were accommodated, and the target (*E*)-β-aminovinyl sulfones were generated with moderate yields (**3i–3k**). Unfortunately, when we used internal allenamide **1l** as the substrate, the

reaction did not proceed, demonstrating that a terminal allenyl is crucial for this transformation. Next, a brief survey of the possible structural variations of sodium sulfonates **2** was conducted by combining allenamide **1a** as model components. As shown in Scheme 2b, a series of sodium arylsulfonates were engaged in this photocatalytic process to form the desired (*E*)-β-aminovinyl sulfones (**3m–3v**). All tested sodium arylsulfonates **2m–2v**, whether electronically rich (e.g. methoxy and *tert*-butyl) or poor (e.g. fluoro, chloro, bromo, and trifluoromethyl) groups were attached to the aromatic ring, could be converted to the corresponding products **3m–3v** in 53–85% yields. It is worth noting that in sodium sulfinate, the ortho or meta-substituents of arene ring seem to behave less positively when undergoing photochemical processes, resulting in a lower yield of (*E*)-β-aminovinyl sulfone (**3s–3u**, 32–36%). We speculate that this may be due to the large steric resistance of the ortho-substituent, which affects reaction progress. Additionally, heterocyclic sodium sulfinate **2v** was also compatible with this transformation in an acceptable yield. To our delight, aliphatic sodium sulfinate starting materials such as sodium methylsulfinate (**2w**) and sodium ethylsulfinate (**2x**) also successfully provided the desired products **3w** and **3x** in moderate yields.

To achieve regio- and stereoselective hydrosulfonylation of allenamides for synthesizing (*E*)-β-amidovinyl sulfones under benzoic acid conditions, we conducted additional investigation into the photocatalytic process of varied allenamides with sodium sulfonates (Scheme 3). Substrates **1** exhibited good tolerance for functional substituents, including methyl, methoxyl, fluoro, chloro, and bromo, located on the aromatic ring of allenamides, resulting in the delivery of the corresponding *E*-amidovinyl sulfones **4a–4k** with yields ranging from 55% to 86%. Subsequently, various alkyl substituents were introduced onto the nitrogen atom of allenamides to enhance their synthetic versatility, including benzyl (Bn), *n*-pentyl and methyl (Me) groups. The resulting products (**4n–4r**) were obtained in yields ranging from 60% to 70%. It is noteworthy that the internal allenamides (**1s** and **1t**) underwent successful conversion to their respective products in acidic conditions. Furthermore, when allenamide is substituted with *p*-toluenesulfonamide, it can also readily undergo the reaction, although precise control of its stereoselectivity remains elusive (**4u**). In addition, various sodium arylsulfinate salts and sodium aliphatic sulfinate salts with **1a** were converted to the corresponding (*E*)-β-amidovinyl sulfones in moderate to good yields (**4v–4ah**).

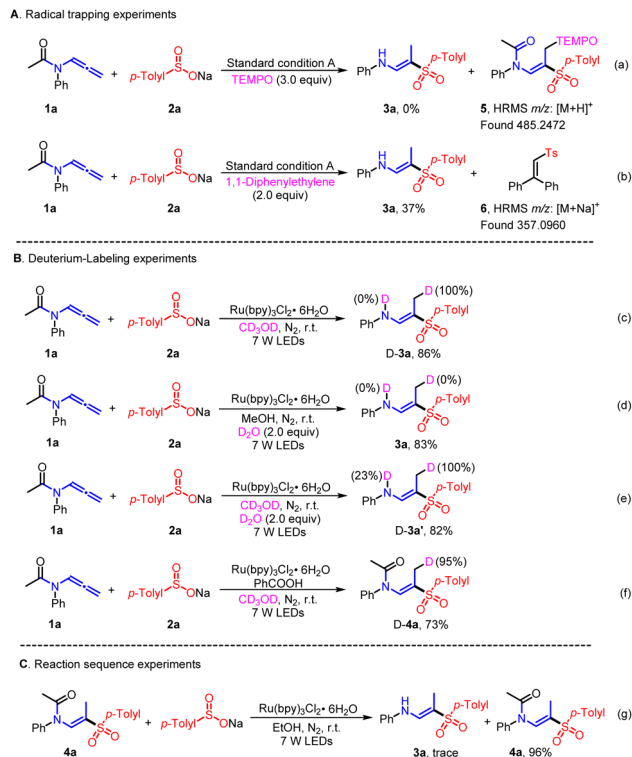
To clarify the working mechanisms, several verification experiments were implemented. Initially, an “on/off” visible light exposure experiment was carried out to highlight the significance of continuous visible light exposure for the effective and managed synthesis of (*E*)-β-aminovinyl sulfones or (*E*)-β-amidovinyl sulfones (Scheme S1†). Subsequently, radical inhibition and intermediate trapping experiments were performed in the presence of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) or 1,1-diphenylethylene (Scheme 4A). Upon adding 3.0 equivalents of TEMPO, it was observed that the reaction process was completely inhibited, and TEMPO adducts **5** were successfully identified through high-resolution mass



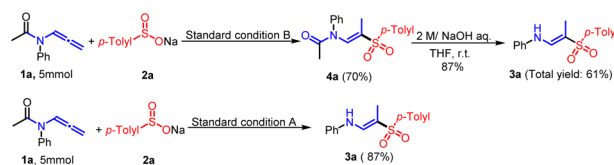


Scheme 3 Substrate scope of (*E*)- β -amidovinyl sulfones **4**. Reaction condition B: **1** (0.2 mmol), **2** (0.4 mmol), PhCOOH (0.4 mmol), Ru(bpy)₃Cl₂·6H₂O (3 mol%), EtOH (2 mL), under 7 W blue LEDs, at room temperature, N₂, 8 h.

spectrometry (HRMS), suggesting a possible radical pathway. Additionally, the vinyl-trapped product **6** was also detected and characterized through HRMS. To further elucidate the hydrogen atom source in this process, deuterium labeling experiments were conducted under standard conditions (Scheme 4B). The reaction of allenamide **1a** and sodium *p*-toluenesulfonate **2a** in the presence of CD₃OD led to the exclusive incorporation of deuterium in the methyl group of the resulting D-**3a**, while no deuterium was observed in the amino group (Scheme 4c). When D₂O was used in stoichiometric amounts, no deuterium was detected in the methyl group (Scheme 4d). However, when the same reaction was conducted in the presence of D₂O and CD₃OD, the resulting D-**3a'** showed 27% deuterium in the N-D group and 100% deuterium in the methyl group, indicating that the hydrogen on the methyl group originated from an alcohol solvent, while incidental traces of water acted as the resource of hydrogen in the medium to construct the N-H bond (Scheme 4e). The deuterium substitution experiment was likewise implemented on product D-**4a**, confirming that the solvent is the main source of the methyl hydrogen (Scheme 4f).



Scheme 4 Control experiments.

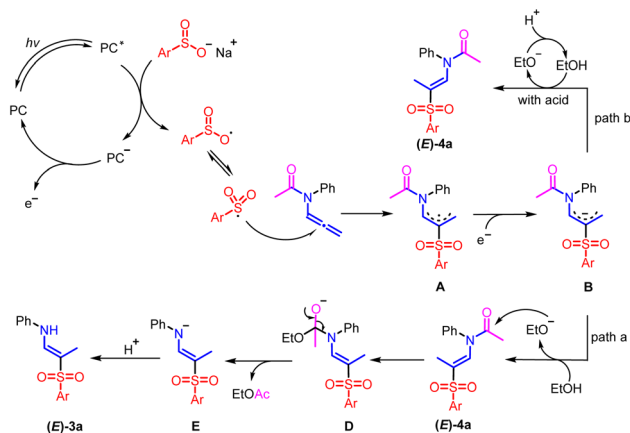


Scheme 5 Synthesis of **3a** and **4a** using gram scales.

Furthermore, the attempted synthesis of the (*E*)- β -aminovinyl sulfone under standard conditions using sodium *p*-toluenesulfonate resulted in the production of only trace amounts of the desired compound, suggesting that amide cleavage may not be initiated by an excess of sodium *p*-toluenesulfonate that may exist in the reaction system (Scheme 4g). To demonstrate the wider applicability of this method, an amplification reaction was conducted under the standard conditions, wherein hydrolysis of **4a** in the presence of 2 M aqueous sodium hydroxide solution in THF yielded **3a** in 87% yield. It was found that **3a** can be separated with a 61% total yield on a 5.0 mmol scale using a two-step reaction in condition B. However, using condition A, **3a** can be produced at an 87% yield in a one-step reaction (Scheme 5). These results indicate that this method has significant potential application value in the direct preparation of (*E*)- β -aminovinyl sulfone.

Based on the results presented above and in relevant literature,^{9,10,13} a plausible reaction mechanism for the photocatalytic regio- and stereoselective synthesis of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones is proposed in Scheme 6.





Scheme 6 Proposed pathway toward product **3a** and **4a**.

Initially, photoexcitation of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ with visible light generates $[\text{Ru}^{2+}]^*$, which is subsequently reductively quenched by free sulfinate to produce an Ru^+ ion and a sulfonyl radical. The sulfonyl radical then reacts with the allene moiety of **1a** to form a widely delocalized radical intermediate **A**, which is further reduced to an extensively delocalized carbanion **B** in the propagating step. There are two possible pathways for the transformation of intermediate **B**, which depend on the specific reaction conditions. In path a, intermediate **B** abstracts a proton from EtOH, generating (*E*)-**4a**, which undergoes intermolecular nucleophilic addition of the carbonyl group with ethoxy anion to yield intermediate **D**. Ultimately, proton transfer and selective C–N bond cleavage result in the formation of (*E*)- β -aminovinyl sulfone **3a**, along with a potential byproduct, EtOAc. In path b, intermediate **B** grabs hydrogen protons from the alcohol to produce (*E*)- β -amidovinyl sulfone **4a**. However, acid–base neutralization between the additive acid and the ethoxy anion inhibits subsequent reactions.

Conclusions

In summary, we have developed a photochemical hydro-sulfonylation method for the selective synthesis of (*E*)- β -aminovinyl sulfones and (*E*)- β -amidovinyl sulfones from readily available allenamides and sodium sulfinites. This reaction uses readily available and eco-friendly ethanol as a solvent, achieving significant chemical, regional, and stereoselectivity for the hydrosulfonylation of allenamide. Through the regulation of acid additions, selective cleavage of amide bonds can be achieved without the requirement of supplemental transition metal catalysts or stoichiometric quantities of bases. The photocatalytic methodology exhibited a wide range of substrates and enabled the synthesis of diverse (*E*)- β -aminovinyl sulfones. Its mild conditions and convenient operation underscore the method's advantages for constructing polyfunctionalized aminovinyl sulfone scaffolds, which offer promising applications.

Conflicts of interest

There are no conflicts to declare.

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