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# Visible-light-enabled spirocyclization of alkynes leading to 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones†

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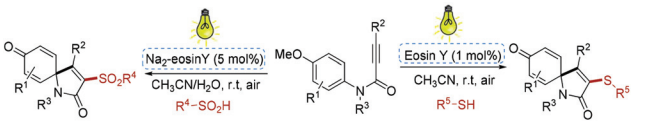
A mild and convenient visible-light-induced method has been developed for the construction of 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones through metal-free difunctionalization of alkynes with sulfinic acids or thiols at room temperature. The present protocol simply utilizes visible light as the safe and eco-friendly energy source, and inexpensive and non-toxic organic dyes (Eosin Y and $Na_2$-Eosin Y) as photocatalysts providing various sulfur-containing azaspiro[4,5]trienones in moderate to good yields.



Spirocycles are a class of key structural motifs frequently found in many natural products, and pharmacologically active compounds and materials.[1] Among the various spirocycles, azaspiro[4,5]trienones have spurred considerable interest in organic and medicinal chemistry because of their remarkable biological activities[2] and diverse synthetic applications in preparing complex molecular frameworks.[3] As a consequence, considerable research efforts have been dedicated to construct azaspiro[4,5]trienones and many useful synthetic methods have been thereby developed.[4,5] During the past several years, the difunctionalization of alkynes *via* electrophilic *ipso*-cyclization or cascade radical *ipso*-cyclization has been proved to be a highly attractive and efficient protocol for the synthesis of various functionalized azaspiro[4,5]trienones.[6–12] Through this strategy, some functionalities such as halogen,[7] carbonyl,[8] ether,[9] phosphoryl,[10] nitro,[11] and silyl[12] groups could be introduced into the azaspiro[4,5]trienone framework.

Sulfur-containing functionalities including sulfonyl and sulfenyl groups are extremely important in synthetic chemistry, pharmaceutical industry and materials science.[13] The importance of sulfur-containing groups has attracted great attention from synthetic chemists in the development of new methods for their incorporation into organic molecules.[14] Recently, Li,[15] Liang[16] and our group[17] independently reported the methods for the synthesis of sulfur-containing azaspiro[4,5]trienones *via* oxidative spirocyclization of alkynes with some thiolation agents. However, toxic metal reagents[15,16,17b] and hazardous oxidants such as stoichiometric amounts of peroxides[16,17a] and hypervalent iodine reagents[17a] are inevitably involved in these reaction systems, which led to the generation of a large volume of waste. Therefore, the development of simple, mild, safe, and especially, environmentally friendly methods to access sulfur-containing azaspiro[4,5]trienones is still highly desirable.

In recent years, photoredox catalysis enabled by green visible-light has emerged as a fascinating and powerful synthetic protocol to promote a wide range of synthetically useful organic transformations under mild conditions.[18] In this field, organic dyes are increasingly utilized as an attractive alternative to the transition-metal complexes in photoredox catalysis due to their advantages of being inexpensive, easily available and less toxic.[19] As a continuation of our interest in the construction of sulfur-containing molecules,[20] we describe herein a mild and convenient visible-light-enabled method for the synthesis of 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones *via* a metal-free organic dye catalyzed difunctionalization of alkynes with sulfinic acids or thiols in air (eqn (1)), in which the C–S, C–C, and C=O bonds were sequentially formed in this visible-light induced process.




(1)

Our initial investigation commenced with the visible-light-induced reaction of *N*-(*p*-methoxyaryl)propiolamide **1a** and 4-methylbenzenesulfinic acid **2a** in the presence of $Na_2$-Eosin

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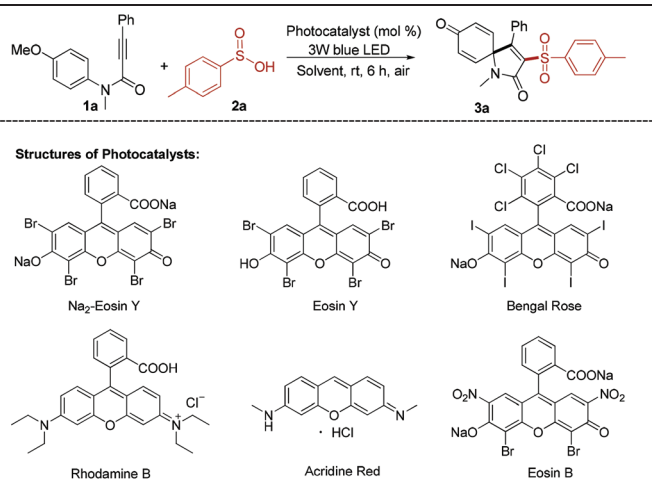
Y (10 mol%). The reaction was conducted by exposure to air in the acetone/$H_2O$ (v/v = 1/1) mixed solvent under irradiation with 3 W blue LED lamps. To our delight, the sulfonylation-*ipso*-cyclization reaction gave the desired 3-sulfonyl azaspiro[4,5]trienone **3a** in 34% yield after 6 h at room temperature (Table 1, entry 1). Encouraged by this result, we examined alternative mixed solvents in attempting to improve the yield (Table 1, entries 2–10). Fortunately, the yield was improved to 57% when the reaction was performed in $CH_3CN/H_2O$ (v/v = 1/1) (Table 1, entry 9), which might be caused by the good solubility of $Na_2$-Eosin Y in the mixed solvent of MeCN and $H_2O$. The reaction efficiency was relatively lower in sole $CH_3CN$ or $H_2O$ (Table 1, entries 11 and 12). Furthermore, the reaction afforded the desired product **3a** in good yield (76%) by decreasing the amount of $Na_2$-Eosin Y to 5 mol% (Table 1, entries 13–15). Next, a series of organic dyes such as Eosin Y, Bengal Rose, Rhodamine B, Acridine Red and Eosin B were examined (Table 1, entries 16–20). Among the above catalysts screened, $Na_2$-Eosin Y still demonstrated the highest catalytic activity (Table 1, entries 13 and 16–20). Notably, this spirocyclization reaction did not occur without a photocatalyst or visible-light irradiation (Table 1, entries 21 and 22).

After determining the optimal reaction conditions, the substrate scope in this visible-light-mediated sulfonylation-*ipso*-cyclization was investigated (Table 2). The reaction could proceed well by using diverse arylsulfinic acids to afford the desired products (**3a–3f**) in good yields. As we expected, alkylsulfinic acid such as trifluoromethanesulfinic acid was also compatible with this reaction, but affording the desired

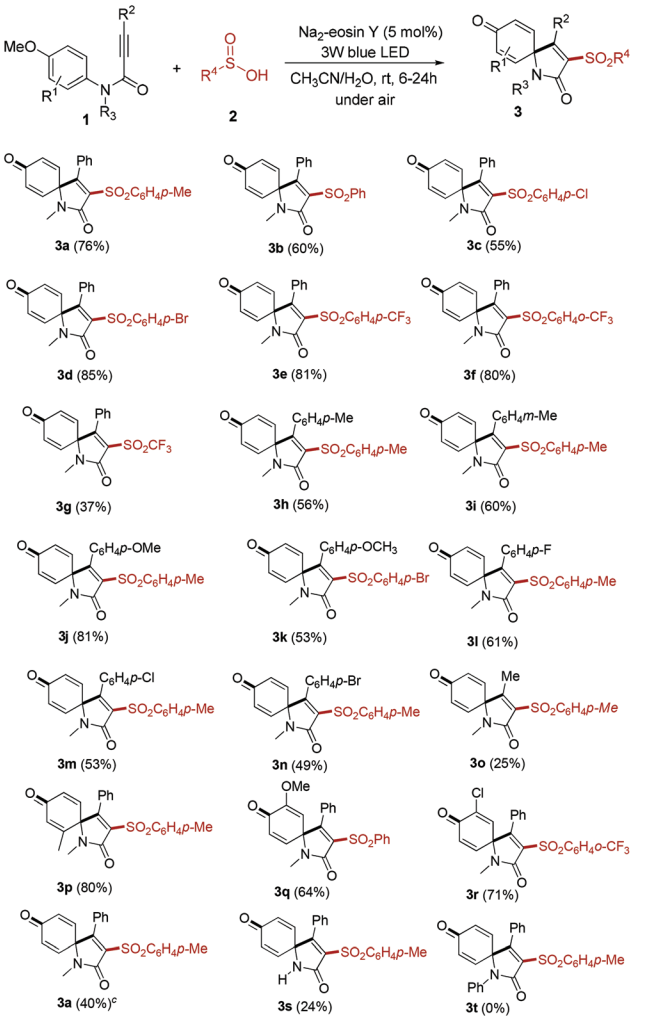
**Table 1** Optimization of the reaction conditions[a]




| Entry | Photocatalyst (mol%) | Solvent | Yield[b] (%) |
|---|---|---|---|
| 1 | $Na_2$-Eosin Y (10) | Acetone/$H_2O$ (1 : 1) | 34 |
| 2 | $Na_2$-Eosin Y (10) | EtOH/$H_2O$ (1 : 1) | Trace |
| 3 | $Na_2$-Eosin Y (10) | DCE/$H_2O$ (1 : 1) | 53 |
| 4 | $Na_2$-Eosin Y (10) | Toluene/$H_2O$ (1 : 1) | 25 |
| 5 | $Na_2$-Eosin Y (10) | THF/$H_2O$ (1 : 1) | 40 |
| 6 | $Na_2$-Eosin Y (10) | 1,4-Dioxane/$H_2O$ (1 : 1) | 30 |
| 7 | $Na_2$-Eosin Y (10) | DME/$H_2O$ (1 : 1) | 52 |
| 8 | $Na_2$-Eosin Y (10) | DMF/$H_2O$ (1 : 1) | 36 |
| 9 | $Na_2$-Eosin Y (10) | $CH_3CN/H_2O$ (1 : 1) | 57 |
| 10 | $Na_2$-Eosin Y (10) | $CH_3CN/H_2O$ (2 : 1) | 48 |
| 11 | $Na_2$-Eosin Y (10) | $CH_3CN$ | 46 |
| 12 | $Na_2$-Eosin Y (10) | $H_2O$ | 35 |
| **13** | **$Na_2$-Eosin Y (5)** | **$CH_3CN/H_2O$ (1 : 1)** | **76** |
| 14 | $Na_2$-Eosin Y (2) | $CH_3CN/H_2O$ (1 : 1) | 71 |
| 15 | $Na_2$-Eosin Y (1) | $CH_3CN/H_2O$ (1 : 1) | 66 |
| 16 | Eosin Y (5) | $CH_3CN/H_2O$ (1 : 1) | 41 |
| 17 | Bengal Rose (5) | $CH_3CN/H_2O$ (1 : 1) | 72 |
| 18 | Rhodamine B (5) | $CH_3CN/H_2O$ (1 : 1) | 68 |
| 19 | Acridine Red (5) | $CH_3CN/H_2O$ (1 : 1) | 31 |
| 20 | Eosin B (5) | $CH_3CN/H_2O$ (1 : 1) | 61 |
| 21 | — | $CH_3CN/H_2O$ (1 : 1) | 0 |
| 22 | $Na_2$-Eosin Y (5) | $CH_3CN/H_2O$ (1 : 1) | 0[c] |

[a] Reaction conditions: **1a** (0.125 mmol), **2a** (0.375 mmol), photocatalyst (1–10 mol%), solvent 2 mL, 3 W blue LED lamps, rt, air, 6 h. DME: 1,2-dimethoxyethane; DCE: 1,2-dichloroethane; THF: tetrahydrofuran. [b] Isolated yields based on **1a**. [c] Without visible-light irradiation.

**Table 2** Results for visible-light-induced difunctionalization of alkynes with sulfinic acids leading to 3-sulfonyl azaspiro[4,5]trienones[a,b]

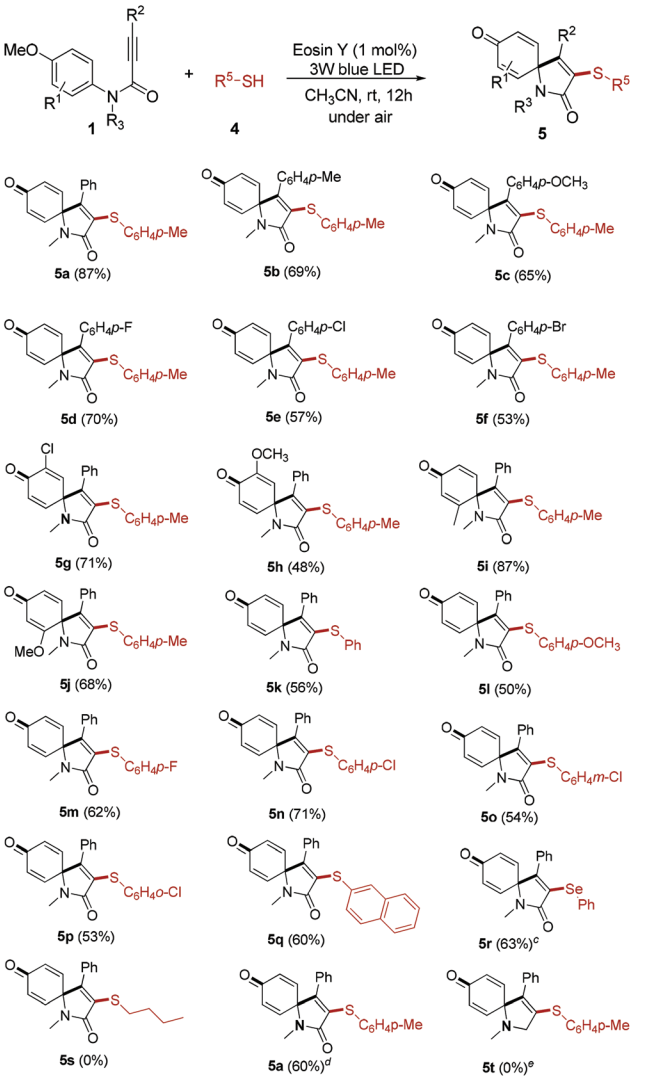



[a] Reaction conditions: **1** (0.125 mmol), **2** (0.375 mmol), $Na_2$-Eosin Y (5 mol%), $CH_3CN/H_2O$ (2 mL, $v_1/v_2$ = 1 : 1), 3 W blue LED lamps, rt, air, 6–24 h. [b] Isolated yields based on **1**. [c] *N*-Methyl-*N*,3-diphenylpropiolamide (0.125 mmol).

product **3g** in a relatively lower yield. Then the electronic nature of the substituents on the arylalkynyl ($R^2$) moiety was examined. The results indicated that the substrates with both electron-donating and electron-withdrawing groups were all tolerated in the process to give the corresponding products in moderate to good yields (**3h–3n**). The reaction of an alkyl-substituted alkyne such as *N*-(4-methoxyphenyl)-*N*-methylbut-2-ynamide with 4-methylbenzenesulfinic acid **2a** could proceed smoothly to afford the desired product **3o** in 25% yield. Next, the substitution effect of the *N*-aryl moiety was investigated. *N*-(*p*-Methoxyaryl)propiolamides with a Me, OMe, or Cl group at the *ortho* or *meta* position of an aniline were all suitable substrates, affording the corresponding 3-sulfonyl azaspiro[4,5]trienones in good yields (**3o–3q**). A non-substituted *N*-arylamide such as *N*-methyl-*N*,3-diphenylpropiolamide could also be used in the present reaction system, and the corresponding 3-sulfonyl product **3a** was obtained in 40% yield. It is worth mentioning that the amide with a N–H group could also be used in the present reaction system to afford product **3s**, albeit in low yield. In addition, changing the N–Me group to the N–Ph group failed to afford the desired product **3t**, which might be caused by the electronic effects.

Subsequently, we turned our attention to explore the reaction of sulfenylation-*ipso*-cyclization of *N*-(*p*-methoxyaryl)propiolamides with thiols. After an extensive screening of the reaction parameter for the model reaction between *N*-(*p*-methoxyaryl)propiolamide **1a** and 4-methylbenzenethiol **4a** (see ESI, Table S1†), the highest yield (87%) of the desired 3-sulfenyl azaspiro[4,5]trienone **5a** was obtained when the reaction was carried out using Eosin Y (1 mol%) as the photocatalyst in $CH_3CN$ under irradiation with 3 W blue LED lamps. Having the optimized reaction conditions in hand, the generality of this sulfenylation-*ipso*-cyclization was investigated by examining various *N*-(*p*-methoxyaryl)propiolamides and thiols. As shown in Table 3, *N*-(*p*-methoxyaryl)propiolamides with a series of substituents on the arylalkynyl ($R^2$) moiety and *N*-aryl moiety were found to be suitable for this reaction under the standard conditions, providing the corresponding products in moderate to good yields (**5a–5j**). Gratifyingly, a series of arylthiols with an electron-donating group or an electron-withdrawing group on the aromatic ring were suitable substrates, thus providing the corresponding products in moderate to good yields (**5k–5q**). Notably, when 1,2-diphenyldiselane was employed as the substrate, the reaction could also proceed smoothly to afford the 3-phenylselanyl-substituted azaspiro[4.5]trienone **5r** in 63% yield. Unfortunately, none of the desired products were obtained when aliphatic thiols were investigated in the present reaction system. It should be noted that a non-substituted *N*-arylamide such as *N*-methyl-*N*,3-diphenylpropiolamide would also lead to the formation of the 3-sulfenyl product **5a** in 60% yield. In addition, the carbonyl group in the substrate is essential for the present reaction. For example, none of the desired product **5t** was detected when propargylamine such as 4-methoxy-*N*-methyl-*N*-(3-phenylprop-2-ynyl)aniline was used in the present reaction system.

**Table 3** Results for visible-light-induced difunctionalization of alkynes with thiols leading to 3-sulfenyl azaspiro[4,5]trienones[a,b]

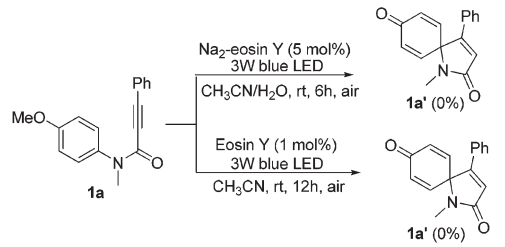



[a] Reaction conditions: **1** (0.125 mmol), **4** (0.25 mmol), Eosin Y (1 mol%), $CH_3CN$ (2 mL), 3 W blue LED lamps, rt, air, 12 h. [b] Isolated yields based on **1**. [c] Diphenyl diselenide (0.4 mmol). [d] *N*-Methyl-*N*,3-diphenylpropiolamide (0.125 mmol). [e] 4-Methoxy-*N*-methyl-*N*-(3-phenylprop-2-ynyl)aniline (0.125 mmol).

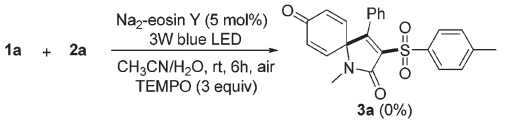
To understand the possible reaction mechanism, the following control experiments were carried out. When *N*-(*p*-methoxyaryl)propiolamide **1a** was added independently under the standard conditions, none of the azaspiro[4,5]trienone **1a′** was detected (eqn (2)), indicating that azaspiro[4,5]trienone **1a′** might not be the key intermediate in the present reaction system. Furthermore, the sulfonylation/sulfenylation-*ipso*-cyclization reaction was completely inhibited by the addition of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), and a TEMPO-trapped thiyl radical complex (*p*-MePhS–TEMPO) was detected by LC-MS analysis (see the ESI†), suggesting that a radical reaction pathway should be involved in this transformation (eqn (3) and (4)). The radical reaction pathway was further con-

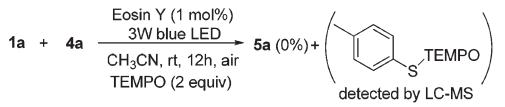
firmed by electron spin resonance (ESR) spectroscopy (see the ESI†). In addition, when the reaction of *N*-(*p*-methoxyaryl)propiolamide **1a** with 1,2-diphenyldisulfide was carried out under standard conditions, the desired 3-sulfenyl product was obtained in 55% yield, indicating that the disulfide might be involved in this reaction system (eqn (5)).



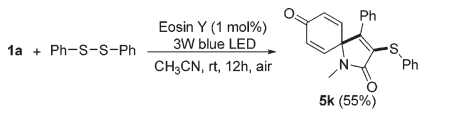

(2)




(3)




(4)




(5)

On/off visible-light irradiation experiments were performed to certify the effect of photoirradiation. The results demonstrated that the continuous irradiation of visible-light is essential for this reaction (Fig. 1).

Moreover, a number of fluorescence quenching (Stern–Volmer) experiments were also conducted to elucidate an energy transfer process between a photocatalyst and sulfinic acid **2a** or thiol **4a**. As shown in Fig. 2 and 3, the emission intensity of the excited photocatalyst was dramatically decreased along with the increasing of the concentration of **2a** or **4a**. In contrast, such an effect was not observed when *N*-(*p*-methoxyaryl)propiolamide **1a** was added dependently (see the ESI†). The above results strongly indicated that the photocatalyst should participate in single-electron transfer with sulfinic acid **2** or thiol **4** under the standard reaction conditions.

Based on the above results and previous reports,[6,10,21,22] a possible reaction mechanism is described in Scheme 1. As shown in path A, initially, $Na_2$-Eosin Y is photoexcited to form $Na_2$-Eosin Y* in the presence of blue LED light. Subsequently, a single electron transfer from sulfinic acid **2** to $Na_2$-Eosin Y* gives the radical cation **6** and $Na_2$-Eosin $Y^{\bullet-}$ radical anion. The oxidation of $Na_2$-Eosin $Y^{\bullet-}$ by dioxygen (air) affords the ground state $Na_2$-Eosin Y and $O_2^{\bullet-}$. Then, the radical cation **6** is deprotonated by $O_2^{\bullet-}$ leading to the oxygen-centered radical resonating with the sulfonyl radical **7**. The resulting sulfonyl radical interacts with **1** to produce the vinyl radical **8**. Next, the intramolecular spiro-cyclization of the vinyl radical with an aryl

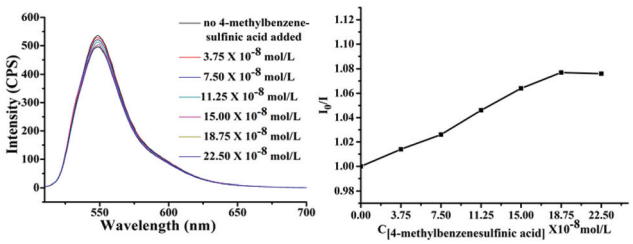



**Fig. 2** Quenching of $Na_2$-Eosin Y fluorescence emission in the presence of sulfinic acid **2a**. The excitation wavelength was fixed at 530 nm.

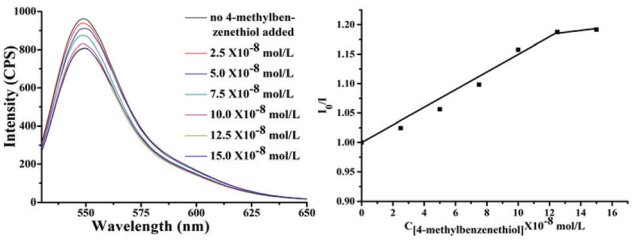
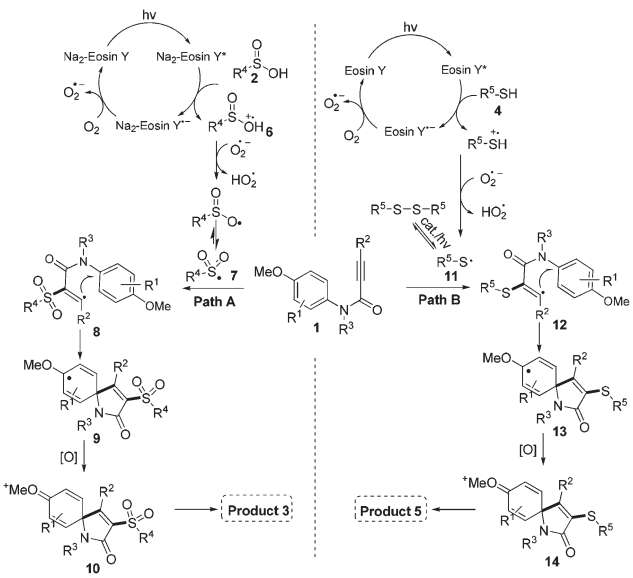
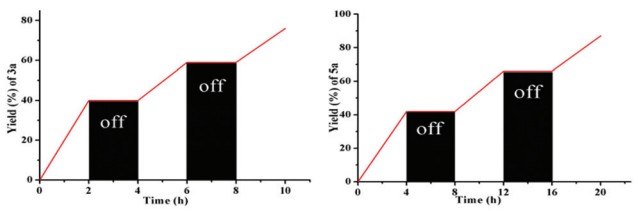



**Fig. 3** Quenching of Eosin Y fluorescence emission in the presence of **4a**. The excitation wavelength was fixed at 500 nm.




**Scheme 1** Proposed reaction mechanism.




**(A)** The reaction of **1a** and **2a** **(B)** The reaction of **1a** and **4a**

**Fig. 1** On/off experiments.

ring generates the radical intermediate **9**. Finally, **9** is oxidized to afford the corresponding oxygenium intermediate **10**, which is converted into the final 3-sulfonyl azaspiro[4,5]trienone **3**. A similar reaction pathway has been proposed for the synthesis of 3-sulfenyl azaspiro[4,5]trienone **5** (path B).

In conclusion, a simple and convenient visible-light-mediated strategy has been established for the synthesis of various 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones from *N*-(*p*-methoxyaryl)propiolamides and sulfinic acids or thiols at room temperature. This method achieves alkyne difunctionalization through a cascade radical addition and *ipso*-cyclization process. With advantages such as simple operation, mild conditions, eco-friendly energy source and oxidant, as well as inexpensive and non-toxic photocatalysts, this new synthetic method is expected to find wide applications in synthetic and medicinal chemistry.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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