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Unified approach to synthesize diverse heterocyclics: a metal-free visible-light-promoted cyclization reaction to acquire sulfonylated spiro-trienones, coumarins and their derivatives†

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Herein, a visible-light-promoted 9-thioxanthone-catalyzed cascade cyclization reaction to synthesize sulfonylated spiro-trienones, coumarins and their derivatives in yields of up to 98% under mild irradiation reaction conditions is reported. Furthermore, extensive studies, including gram-scale, radical capture, isotope and DFT experiments, were performed to gain insights into the possible reaction mechanism.

Spiro[4.5]trienones and coumarins are recognized as important heterocyclic skeletons of biologically active molecules,¹ and they widely exist in many natural products (1 and 2, Fig. 1) and pharmaceutical agents (3 and 4, Fig. 1). Therefore, the synthesis of spiro[4.5]trienone compounds with strong structural diversities and potential bioactivities has always been desired in the field of organic synthesis and has drawn much attention from scientists. Consequently, some protocols have been devoted to the development of novel and efficient ways for the preparation of spiro[4.5]trienones.² Generally, spiro[4.5]trienone structures are constructed *via* the oxidative spiro-cyclization of phenol derivatives,³ electrophilic *ipso*-cyclization,⁴ transition-metal-mediated intramolecular nucleophilic *ipso*-cyclization,⁵ and radical-coupling *ipso*-cyclization.⁶ Notably, various substituent groups have been successfully introduced into spiro[4.5]trienone compounds *via* alkylation,⁷ alkenylation,⁸ amination,⁹ halogenation,¹⁰ siliconization,¹¹ phosphorylation,¹² nitrication,¹³ acylation,¹⁴ sulfuration,¹⁵ selenization,¹⁶ telurination,¹⁷ and germylation.¹⁸ In parallel, sulfone compounds are a class of important organic molecules, many of which have been found to exhibit unique pharmacological activities.¹⁹ Most importantly, they also serve as the key building blocks in many

organic transformations.²⁰ Furthermore, the introduction of sulfonyl groups into drug molecules may significantly enhance their biological activities.²¹ As a result, it is of great significance to develop methods to introduce a sulfonyl group into spiro[4.5]trienone skeletons. Electrophilic cyclization of heteroatom-containing alkynes with a neighboring aromatic or heteroaromatic ring, such as *N*-arylalkynamides, provides a useful strategy to develop annulated heterocycles. Several sulfonyl radical precursors, such as sulfonyl chloride,²² sulfonyl hydrazide,²³ sulfonic acid,²⁴ DABSO²⁵ and metabisulfite salt,²⁶ have been investigated to synthesize spiro[4.5]trienones. In 2018, Zhou and Liu²² reported the visible-light-induced radical sulfonylation and *ipso*-cyclization of *N*-substituted propiolamides with sulfonyl chloride using 2 mol% eosin Y as the photocatalyst and Na₂CO₃ as the base in a mixture of CH₃CN and H₂O. Wang and Wei²³ described the I₂O₅-mediated direct oxidative spirocyclization of *N*-arylpropiolamides with sulfonylhydrazides, leading to 3-sulfonylated azaspiro[4.5]trienones. Wang and Wei²⁴ also established a method for the synthesis of various 3-sulfonyl and 3-sulfenyl azaspiro[4.5]trienones from *N*-(*p*-methoxyaryl)-propiolamides and sulfonic acids using Na₂eosin Y in CH₃CN/H₂O. Tang^{25a} in 2019 and Volla^{25b} in 2020 independently developed a visible-light-promoted one-pot synthesis of sulfonylated spiro[4.5]trienones from anilines and diaryliodonium salts *via* SO₂ insertion under transition-metal-free conditions. In 2023, Zhao²⁶ developed a protocol to access sulfonylated spiro[4.5]trienones *via* SO₂ insertion by the visible-light-induced cyanoalkylsulfonylation/*ipso*-cyclization of *N*-arylpropiolamide with cyclobutanone oxime esters and Na₂S₂O₅ in the presence of the eosin Y disodium salt in CH₃CN. As part of our continued interest in the synthesis of sulfonylated 2-oxindole frameworks,²⁷ herein, we report a visible-light-

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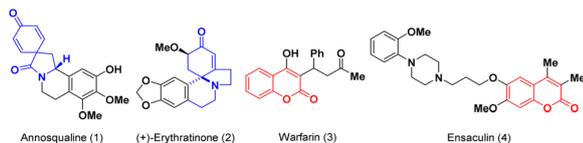


Fig. 1 Representative natural products and biologically active pharmaceuticals containing spiro-trienone frameworks.

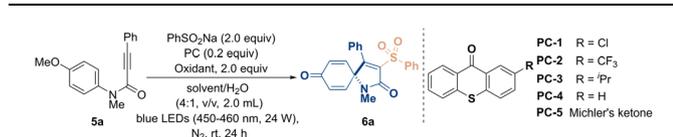
promoted cascade cyclization reaction to synthesize sulfonated spiro-trienones, coumarins and their derivatives.

Herein, a metal-free visible-light-promoted dearomatization *ipso*-cyclization reaction to synthesize spiro[5.5]trienones is reported. The study was initiated with the screening of the reaction solvent. As shown in Table 1, when the reaction was performed in CH₃CN, DMF, and CH₃OH, spiro[4.5]trienone product **6a** could be isolated in 31–40% yields in the presence of 9-thioxanthone derivative PC-1 (0.2 equiv.) and K₂S₂O₈ (2.0 equiv.) under the irradiation of white light (Entries 1–3, Table 1). The yield increased up to 65% in CH₃CN/H₂O (Entry 4, Table 1). The situation changed under different systems of mixed solvents (Entries 5–8, Table 1). Next, the investigation of photocatalysts was carried out. Several thioxanthone derivatives photocatalyst were subjected to the reaction conditions, and the

results showed that PC-4 could afford the desired spiro[4.5]trienone product **6a** in 84% yield (Entries 9–12, Table 1). Besides K₂S₂O₈, Na₂S₂O₈ and (NH₄)₂S₂O₈ (Entry 14, Table 1) could also produce **6a** in 58% and 65% yields, respectively (Entries 13 and 14, Table 1).

Further optimization of various light sources indicated that blue light was the best choice, whereas green and purple lights were relatively less effective (Entries 15–17, Table 1). Control experiments showed that oxidative (Entry 18, Table 1) and nitrogen atmospheres (Entry 19, Table 1) were necessary for the conversion. Notably, spiro[4.5]trienone **6a** could still be generated in 85 and 90% yields in the absence of the photosensitizer (Entry 20, Table 1) or in the dark (Entry 21, Table 1), respectively. In this case, several substrates were selected to verify that photo-irradiation was crucial to the reaction. The yields of spiro[4.5]trienones decreased dramatically when the reactions were carried out under oxidative conditions with only K₂S₂O₈ at room temperature. Even at 90 °C, **6d**, **6h** and **6i** could only produce much lower product yields compared to the standard reaction conditions. When AgNO₃ was introduced as the catalyst at room temperature, **6b**, **6d**, **6f** and **6h** could be isolated in only 24–43% product yields. By increasing the reaction temperature to 90 °C, the yield of **6d** increased to 64% (Table 2). Except for the selected template substrate **5a**, all of the other substrates in Table 2 could only produce much lower yields of the corresponding products at room temperature. These results explicitly indicated that visible light was very important for this transition-metal-free cyclization transformation to obtain elevated reaction yields at room temperature in a nitrogen atmosphere. Additionally, substrate **5a'** did not produce any product in CH₃CN/H₂O, CH₃OH/H₂O or dioxane/H₂O under the standard reaction conditions, demonstrating that a methoxy (–OMe) group at the *para*-position of phenyl was essential for the conversion (Table 3). Therefore, the optimal reaction conditions were established

Table 1 Screening of the reaction conditions for spiro[4.5]trienone **6a**



Entry	Solvent/H ₂ O	(v/v)	PC	Oxidant	Yield(%) ^a
1	CH ₃ OH	Neat	PC-1	K ₂ S ₂ O ₈	40
2	DMF	Neat	PC-1	K ₂ S ₂ O ₈	38
3	CH ₃ CN	Neat	PC-1	K ₂ S ₂ O ₈	31
4	CH ₃ CN/H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	65
5	Dioxane/H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	50
6	CH ₃ OH/H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	27
7	DMF/H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	0
8	DMSO/H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	0
9	CH ₃ CN/H ₂ O	4/1	PC-2	K ₂ S ₂ O ₈	63
10	CH ₃ CN/H ₂ O	4/1	PC-3	K ₂ S ₂ O ₈	66
11	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	84
12	CH ₃ CN/H ₂ O	4/1	PC-5	K ₂ S ₂ O ₈	65
13	CH ₃ CN/H ₂ O	4/1	PC-4	Na ₂ S ₂ O ₈	58
14	CH ₃ CN/H ₂ O	4/1	PC-4	(NH ₄) ₂ S ₂ O ₈	65
15 ^b	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	72
16 ^c	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	95
17 ^d	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	62
18	CH ₃ CN/H ₂ O	4/1	PC-4	None	0
19 ^e	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	0
20 ^f	CH ₃ CN/H ₂ O	4/1	None	K ₂ S ₂ O ₈	85
21 ^g	CH ₃ CN/H ₂ O	4/1	PC-4	K ₂ S ₂ O ₈	90

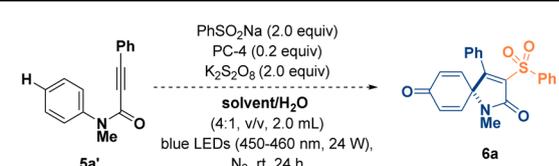
^a Isolated yield. ^b The reaction was performed in green light. ^c The reaction was performed in blue light. ^d The reaction was performed in purple light. ^e The reaction was performed in an air atmosphere. ^f The reaction was performed in the absence of photocatalyst. ^g The reaction was performed in the dark.

Table 2 Control experiments of several selected substrates^a

Entry	Sub	K ₂ S ₂ O ₈ ^b	K ₂ S ₂ O ₈ ^c	AgNO ₃ , K ₂ S ₂ O ₈ ^d	AgNO ₃ , K ₂ S ₂ O ₈ ^e
1	6d	28%	71%	43%	—
2	6d	7%	16%	24%	64%
3	6f	6%	69%	43%	—
4	6h	5%	38%	27%	—
5	6i	16%	30%	77%	—

^a Isolated yield. ^b The reaction was performed in the presence of K₂S₂O₈ (2.0 equiv.) at room temperature. ^c The reaction was performed in the presence of K₂S₂O₈ (2.0 equiv.) at 90 °C. ^d The reaction was performed in the presence of AgNO₃ (0.2 equiv.) and K₂S₂O₈ (2.0 equiv.) at room temperature. ^e The reaction was performed in the presence of AgNO₃ (0.2 equiv.) and K₂S₂O₈ (2.0 equiv.) at 90 °C.



Table 3 Control experiments of substrate **5a'** using various solvents


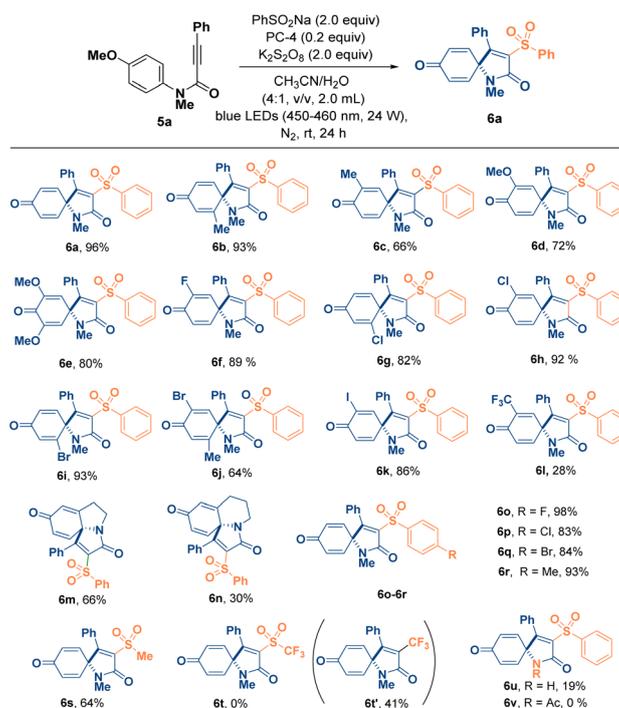
Entry	Solvent/H ₂ O	Yield (%) ^a
1	CH ₃ CN/H ₂ O	0
2	CH ₃ OH/H ₂ O	0
3	Dioxane/H ₂ O	0

^a Isolated yield.

as a combination of **5a** (0.1 mmol), PhSO₂Na (0.2 mmol), and 9-thioxanthone (0.02 mmol) in the presence of K₂S₂O₈ (0.2 mmol) under the irradiation of blue light and a nitrogen atmosphere. As shown in Table 4, with the optimized conditions in hand, we then investigated the scope and generality of this metal-free visible-light-promoted dearomative *ipso*-spirocyclization reaction with respect to various phenylacrylamides. Substrates bearing electron-donating groups, such as -Me (**6b** and **6c**) and the stronger electron-donating group -OMe (**6d** and **6e**), produced azaspiro[4.5]trienones in

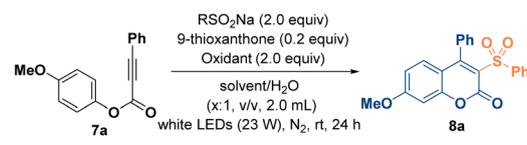
excellent yields. Substrates bearing electron-withdrawing groups, for example, -F (**6f**), -Cl (**6g** and **6h**), -Br (**6i** and **6j**), -I (**6k**), and -CF₃ (**6l**), also provided good product yields. To our delight, **5m** and **5n** afforded azaspiro[4.5]trienones **6m** and **6n** in 66% and 30% yields, respectively. Next, several similarly structured sulfonyl radicals were introduced in the reaction, which resulted in the formation of **6o-6s** in 64–98% yields. When sodium trifluoromethanesulfonate (Langlois reagent) was used as the sulfonyl donor, **6t'** was isolated in 41% yield instead of **6t**. The amide-protected free substrate **5u** only afforded **6u** in 19% yield. By contrast, *N*-acetyl substrate **5v** did not form product **6v**.

Coumarin is an important pharmaceutical structural motif and shows a broad spectrum of medicinal properties and biological activities.²⁸ The increasing importance and widespread usage of coumarin derivatives have drawn attention to their synthetic methods,²⁹ among which metal-catalyzed and organocatalytic methods have proven to be the most effective. Several metal-catalyzed and/or organocatalytic synthetic strategies³⁰ for coumarin have been investigated and reported in recent years. Therefore, after successfully introducing the sulfonyl radical onto spiro[4.5]trienones, we continued trying to expand the application scope of the proposed method to access more versatile sulfonyl-substituted coumarin³¹ scaffolds using aryl propiolates. Solvent screening results showed that in CH₃CN/H₂O (7/1, v/v, 2 mL, Entry 5, Table 5), **7a** could offer coumarin **8a** in 77% yield; other proportions (Entries 1–4 and 6,

Table 4 Substrate scope^a

^a Reaction conditions: **5a** (0.1 mmol), PhSO₂Na (0.2 mmol), PC-4 (0.02 mmol, 0.2 equiv.), and K₂S₂O₈ (0.2 mmol, 2.0 equiv.) in CH₃CN/H₂O (4 : 1, v/v, 2.0 mL) under the irradiation of blue LEDs in a nitrogen atmosphere; isolated yield.



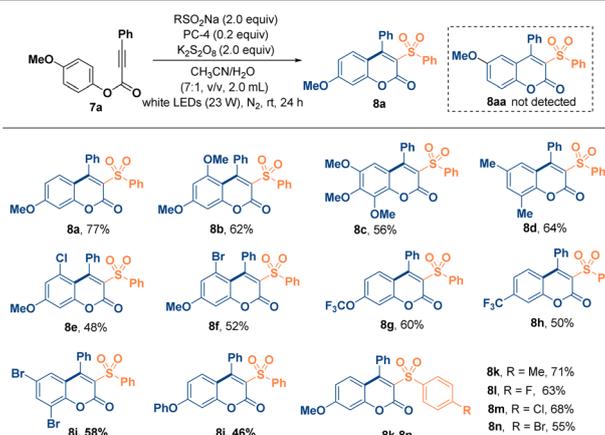
Table 5 Screening of the reaction conditions for coumarin **8a**


Entry	Solvent/H ₂ O	(v/v)	PC	Oxidant	Yield ^a (%)
1	CH ₃ CN	Neat	9-Thioxanthone	K ₂ S ₂ O ₈	Trace
2	CH ₃ CN/H ₂ O	1 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	50
3	CH ₃ CN/H ₂ O	3 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	63
4	CH ₃ CN/H ₂ O	5 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	60
5	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	77
6	CH ₃ CN/H ₂ O	9 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	49
7	CH ₃ OH/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	28
8	Dioxane/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	59
9	DCE/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	0
10	PhCF ₃ /H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	Trace
11	DMF/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	0
12	DMSO/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	29
13	CH ₃ CN/H ₂ O	7 : 1	Eosin disodium	K ₂ S ₂ O ₈	28
14	CH ₃ CN/H ₂ O	7 : 1	Solvent red 72	K ₂ S ₂ O ₈	29
15	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	Na ₂ S ₂ O ₈	31
16	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	Ce(NH ₄) ₂ (NO ₃) ₆	22
17	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	(NH ₄) ₂ S ₂ O ₈	Trace
18	CH ₃ CN/H ₂ O	7 : 1	None	K ₂ S ₂ O ₈	28
19	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	None	0
20 ^b	CH ₃ CN/H ₂ O	7 : 1	9-Thioxanthone	K ₂ S ₂ O ₈	26

^a Isolated yield. ^b The reaction was performed in the dark.

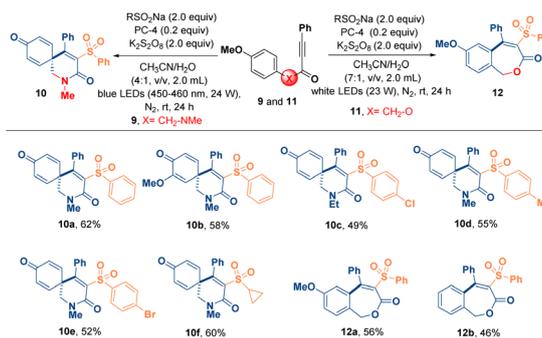
Table 5) produced lower product yields, and other solvent systems gave similar results (Entries 7–12, Table 5). Alteration of PCs (Entries 13 and 14, Table 5) or oxidants (Entries 15 and 17, Table 5) resulted in lower yields. The yield of **8a** decreased dramatically when the reaction was performed in the absence of 9-thioxanthone (Entry 18, Table 5) or visible light (Entry 20, Table 5). No product could be detected in the absence of K₂S₂O₈

(Entry 19, Table 5). Therefore, the optimal reaction conditions were quickly established as a combination of substrate **7a** (0.1 mmol, 1.0 equiv.), PhSO₂Na (0.2 mmol, 2.0 equiv.), 9-thioxanthone (0.02 mmol, 0.2 equiv.) and K₂S₂O₈ (0.2 mmol, 2.0 equiv.) in CH₃CN/H₂O (7/1, v/v, 2.0 mL) under irradiation with a 23 W white LED in a nitrogen atmosphere (for details, see ESI Table S4 and Page S20†). As shown in Table 6, aryl propiolates

Table 6 Substrate scope^a

^a Reaction conditions: **5a** (0.1 mmol), PhSO₂Na (0.2 mmol), PC-4 (0.02 mmol, 0.2 equiv.), and K₂S₂O₈ (0.2 mmol, 2.0 equiv.) in CH₃CN/H₂O (7 : 1, v/v, 2.0 mL) under the irradiation of white LEDs in a nitrogen atmosphere; isolated yield.



Table 7 Substrate scope^a

^a Reaction conditions: **9** or **11** (0.1 mmol), PhSO_2Na (0.2 mmol), PC-4 (0.02 mmol, 0.2 equiv.), and $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol, 2.0 equiv.) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4 : 1 or 7 : 1, v/v, 2.0 mL) under the irradiation of blue or white LEDs in a nitrogen atmosphere; isolated yield.

with strong electron-donating substituents were efficient under the reaction conditions to afford coumarins in 56–77% yields (**8a–8d**). Notably, an intermediate product of **8b** and **8b'** was also isolated in 17% yield (for details, see the ESI, Pages S22 and S23[†]). Substrates with electron-donating and -withdrawing groups substituted simultaneously afforded the corresponding coumarin products (**8e** and **8f**) in moderate yields, respectively. The annulation of substrates with the electron-poor group produced the desired coumarins (**8g–8j**) in 46–60% yields.

On the other hand, different sodium sulfonate sources, such as halogens, $-\text{CF}_3$, $-\text{OCF}_3$ and $-\text{Oph}$ substituents, were used to synthesize coumarin products (**8k–8n**) with yields ranging from 55% to 71%. Similar to spiro[4.5]trienones, spiro[5.5]trienone skeletons are also widely found in natural products and pharmaceuticals. Consequently, the development of efficient methods for the construction of these privileged structures has also been an important task in organic synthesis. In a previous report, biaryl ynones³² were utilized to synthesize spiro[5.5]trienones. Therefore, we also hoped to extend the scope of this sulfonylated spiro-cyclization to spiro[5.5]trienones using this reaction method (Table 7). To our delight, various propargyl esters **9** afforded the corresponding spiro[5.5]trienone products **10a** and **10b** (62–58% yield) under the standard conditions. Several sulfonyl radicals introduced in the reaction could also produce spiro[5.5]trienones **10c–10f** in 49–60% yields, affording the desired spiro[5.5]trienones. Similarly, when 4-

methoxybenzyl-3-phenylpropiolate **11** was subjected to the same conditions, 7-methoxy-5-phenyl-4-(phenylsulfonyl)benzo[c]oxepin-3(1*H*)-ones (**12a** and **12b**) were successfully isolated in 46–56% yields. Even when the reactions were performed on the gram scale, cyclization involving the sulfonyl radical proceeded excellently to afford spiro[4.5]trienone product **6a** in 85% yield (Fig. 2A). Aryl propiolates formed coumarin **8a** with PhSO_2Na in 46% yield (Fig. 2B). The introduction of the radical scavenger reagent 2,2,6,6-tetramethylpiperidinyloxy (TEMPO; 2.0 equivalents) in the reaction mixture under the standard reaction conditions completely suppressed the conversions. Spiro[4.5]trienone product **6a** (Fig. 3A) and coumarin **10a** (Fig. 3B) were not detected, and the starting materials were recovered in 96% and 95% yields, respectively.

To gain a deep insight into the formation process of spiro[4.5]trienones, H_2O^{18} was introduced in the reaction mixture instead of H_2O (Fig. 4A). High-resolution mass spectrometry (HRMS) analysis showed that the oxygen atom of the product ketone carbonyl group was a mixture of O^{18} and O^{16} , indicating that the oxygen atom of the ketone originated from the original substrate $-\text{O}^{16}\text{Me}$ group and reaction solvent (H_2O^{18}) (also see ESI Fig. S5 and S6, Pages S8 and S9[†]). Therefore, a plausible mechanism for the reactions (Fig. 4B) was proposed based on the experimental results presented above. First, the benzene-sulfonyl radical was formed *via* the oxidation of the excited-state

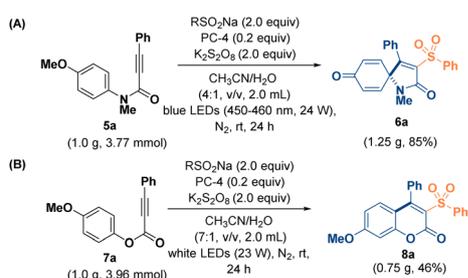


Fig. 2 Gram-scale experiments for the preparation of **6a** (A) and **8a** (B).

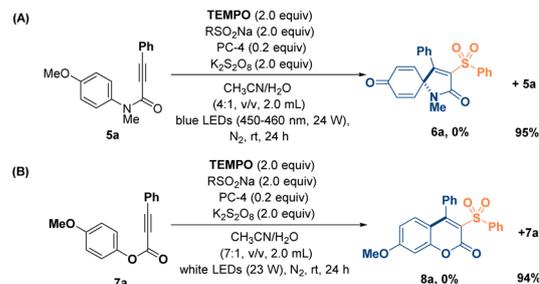


Fig. 3 Radical capture experiments for the preparation of **6a** (A) and **8a** (B).



Conclusions

In conclusion, a metal-free visible-light-promoted radical cascade cyclization reaction approach to access diverse heterocyclic spirotrienones, coumarins and their derivatives under mild irradiation conditions was reported. The results of radical scavenger and isotope experiments showed that the reaction involved radical addition, cyclization and deprotonation to afford the desired products. The mechanistic study of the synthesis of coumarins was also validated using the results of DFT calculations. Further study of the application of phenylsulfinyl radicals in organic synthesis is in progress in our laboratory.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

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