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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 nitrification,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-sulphenyl azaspiro[4.5]trienones from *N*-(*p*-methoxyaryl)-propiolamides and sulfinic acids using Na₂-eosin 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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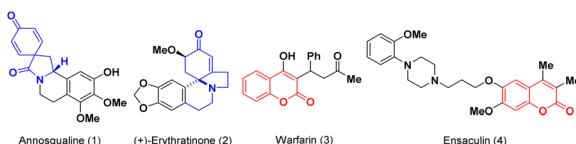
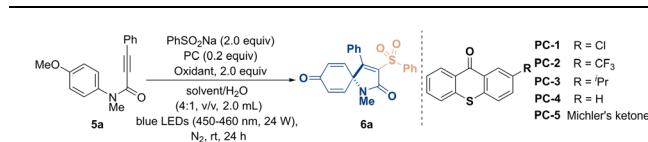


Fig. 1 Representative natural products and biologically active pharmaceuticals containing spiro-trienone frameworks.

promoted cascade cyclization reaction to synthesize sulfonylated 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 CH_3CN , DMF, and CH_3OH , 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 $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv.) under the irradiation of white light (Entries 1–3, Table 1). The yield increased up to 65% in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (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

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



Entry	Solvent/ H_2O	(v/v)	PC	Oxidant	Yield(%) ^a
1	CH_3OH	Neat	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	40
2	DMF	Neat	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	38
3	CH_3CN	Neat	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	31
4	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	65
5	Dioxane/ H_2O	4/1	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	50
6	$\text{CH}_3\text{OH}/\text{H}_2\text{O}$	4/1	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	27
7	DMF/ H_2O	4/1	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	0
8	DMSO/ H_2O	4/1	PC-1	$\text{K}_2\text{S}_2\text{O}_8$	0
9	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-2	$\text{K}_2\text{S}_2\text{O}_8$	63
10	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-3	$\text{K}_2\text{S}_2\text{O}_8$	66
11	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	84
12	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-5	$\text{K}_2\text{S}_2\text{O}_8$	65
13	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{Na}_2\text{S}_2\text{O}_8$	58
14	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	65
15 ^b	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	72
16 ^c	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	95
17 ^d	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	62
18	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	None	0
19 ^e	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	0
20 ^f	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	None	$\text{K}_2\text{S}_2\text{O}_8$	85
21 ^g	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	4/1	PC-4	$\text{K}_2\text{S}_2\text{O}_8$	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.

results showed that **PC-4** could afford the desired spiro[4.5]trienone product **6a** in 84% yield (Entries 9–12, Table 1). Besides $\text{K}_2\text{S}_2\text{O}_8$, $\text{Na}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (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 $\text{K}_2\text{S}_2\text{O}_8$ 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 AgNO_3 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 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ or dioxane/ H_2O 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 2 Control experiments of several selected substrates^a

Entry	Sub	$\text{K}_2\text{S}_2\text{O}_8$ ^b	$\text{K}_2\text{S}_2\text{O}_8$ ^c	AgNO_3 , $\text{K}_2\text{S}_2\text{O}_8$ ^d	AgNO_3 , $\text{K}_2\text{S}_2\text{O}_8$ ^e
1	6b	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 $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv.) at room temperature. ^c The reaction was performed in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv.) at 90 °C. ^d The reaction was performed in the presence of AgNO_3 (0.2 equiv.) and $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv.) at room temperature. ^e The reaction was performed in the presence of AgNO_3 (0.2 equiv.) and $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv.) at 90 °C.



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

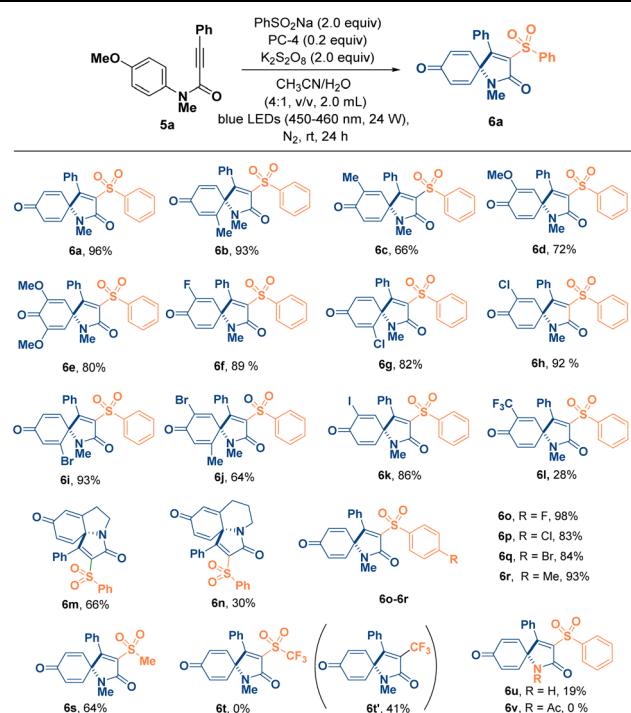
Entry	Solvent/H ₂ O	Yield (%) ^a	Reaction conditions:	
			PhSO ₂ Na (2.0 equiv)	PC-4 (0.2 equiv)
1	CH ₃ CN/H ₂ O	0	K ₂ S ₂ O ₈ (2.0 equiv)	
2	CH ₃ OH/H ₂ O	0		
3	Dioxane/H ₂ O	0		

^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 phenyl-acrylamides. 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 trifluoromethanesulfinate (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.



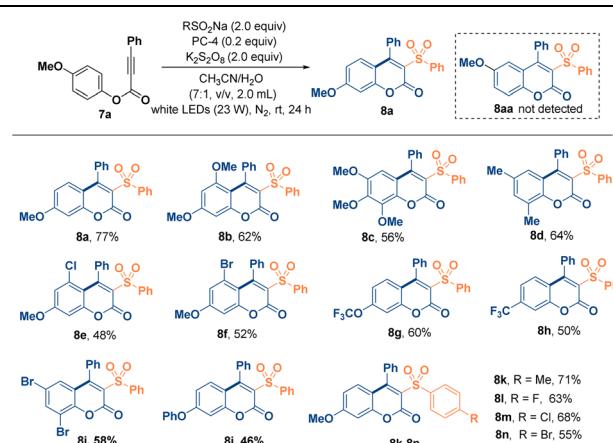
Table 5 Screening of the reaction conditions for coumarin 8a

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.

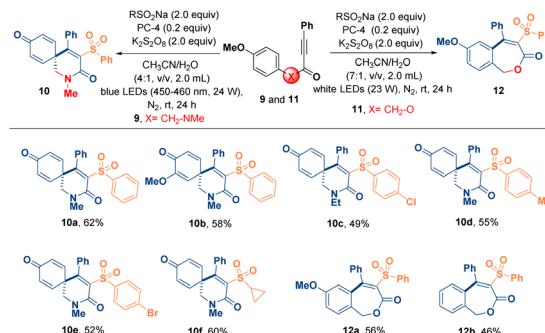
Table 5) produced lower product yields, and other solvent systems gave similar results (Entries 7–12, Table 5). Alteration of PCs (Entries 13 and 14, Table 5) or oxidants (Entries 15 and 17, Table 5) resulted in lower yields. The yield of 8a decreased dramatically when the reaction was performed in the 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), 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 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, –CF₃, –OCF₃ and –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 yrones³² 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

methoxybenzyl-3-phenylpropiolate **11** was subjected to the same conditions, 7-methoxy-5-phenyl-4-(phenylsulfonyl)benzo [c]oxepin-3(1H)-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 PhSO₂Na 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, H₂O¹⁸ was introduced in the reaction mixture instead of H₂O (Fig. 4A). High-resolution mass spectrometry (HRMS) analysis showed that the oxygen atom of the product ketone carbonyl group was a mixture of O¹⁸ and O¹⁶, indicating that the oxygen atom of the ketone originated from the original substrate –¹⁶OMe group and reaction solvent (H₂O¹⁸) (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

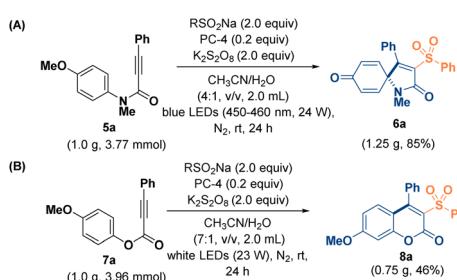


Fig. 2 Gram-scale experiments for the preparation of **6a** (A) and **8a** (B).

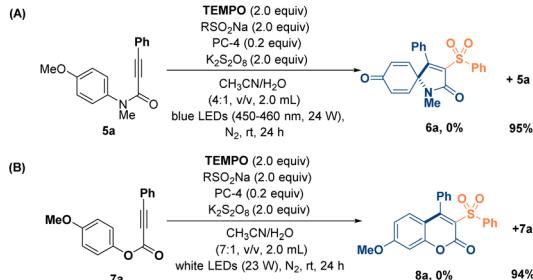


Fig. 3 Radical capture experiments for the preparation of **6a** (A) and **8a** (B).



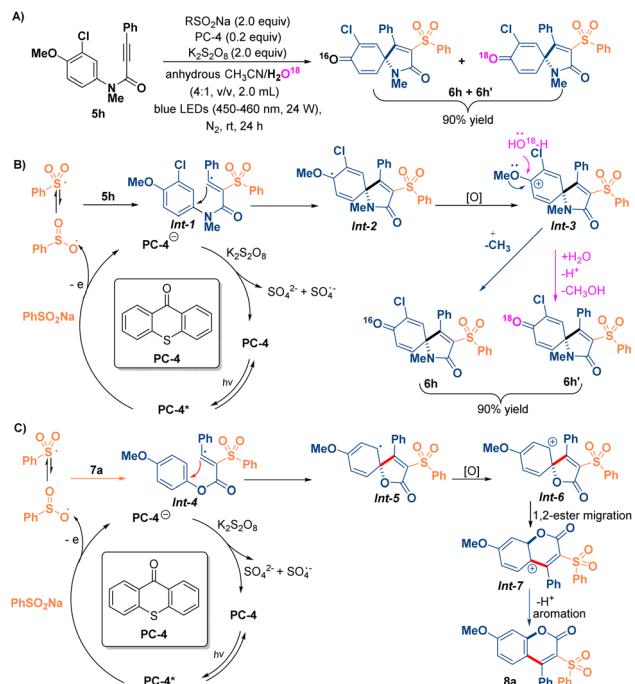


Fig. 4 Isotope experiment of **5h** (A). Proposed reaction mechanism for **5h** to **6h** + **6h'** (B) and proposed mechanism of the preparation of coumarin **8a** (C).

photosensitizer 9-thioxanthone (PC-4). Then, a radical addition reaction with the C≡C bond occurred to afford intermediate **Int-1**, which subsequently produced intermediate **Int-2** via intramolecular radical addition. The demethylation^{24,26} of **Int-3** afforded normal spiro[4.5]trienone **6h**. Meanwhile, a H₂O¹⁸ nucleophilic attack, followed by deprotonation and MeOH elimination^{25a} reactions of intermediate **Int-3** afforded the spiro[4.5]trienone O¹⁸ product **6h'**. As shown in Fig. 4C, similar to the

formation of **6a**, the benzenesulfonyl radical was first formed *via* the oxidation of the excited-state photosensitizer 9-thioxanthone (PC-4). Then, the benzenesulfonyl radical addition reaction with **7a** afforded intermediate **Int-4**, which subsequently afforded intermediate **Int-5** *via* intramolecular radical addition. The oxidation of **Int-5** afforded **Int-6**, followed by 1,2-ester migration³³ to afford **Int-6**, and the coumarin product **8a** finally formed *via* dehydrogenation aromatization.

To confirm the proposed reaction process, density functional theory (DFT) calculations were also performed to gain additional insights into the reaction mechanism (Fig. 5). Two sequences (Paths 1 and 2) were compared using the Gaussian 16C 01 program with M06-2X/6-311G(d,p)). By taking the change in oxidation and dehydrogenation processes into consideration, the energy of intermediate **2Int4** is set as the zero point of the total electronic energy (unit in kcal mol⁻¹). The zero point of the total electronic energy in brackets after double backslash is the ground state of corresponding intermediate (for example, **1Int6** and **18a**, black line, Path 1). The higher spin multiplicity of the system are shown in the blue line (Path 2), and the corresponding excited states are shown in the pink line (Path 3). The change in the energy of isomer product **8aa** is shown in the red line (Path 1-i). The vinyl radical intermediate **2Int4** is generated *via* the addition of the benzenesulfinate radical to substrate **7a**. Then, the C atom radical of the vinyl attacks and bonds with the C1 atom in the bending structure of **2Int4-c** to afford **2Int5**. Path 1 (Path 1: **2Int4** → **2Int4-c** → **2Int5** → **1Int6** → **1Int7** → **18a**, dark line) is more favorable than Path 1-i (Path 1-i: **2Int4** → **2Int4-c** → **2Int5-I** → **1Int6-I** → **18aa**, red line) because the total electronic energy of **2Int5** is 7.2 kcal mol⁻¹ lower than that of **2Int5-I**. The final product **18a** of the aromatic structure undergoes intramolecular 1,2-migration, whose energy is 3.3 kcal mol⁻¹ lower than that of isomer **18aa**. This result indicated that the formation process of product **8a** was much more favorable than the formation process of isomer **8aa**.

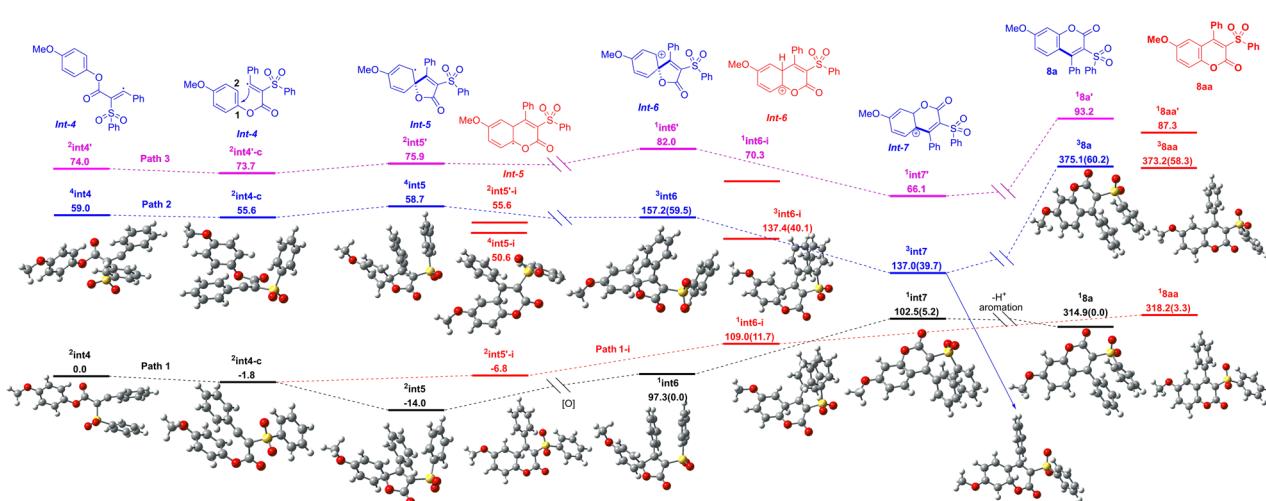


Fig. 5 DFT (M06-2X/6-311G(d)) computational studies of the formation of coumarin **8a**.



Conclusions

In conclusion, a metal-free visible-light-promoted radical cascade cyclization reaction approach to access diverse heterocyclic spiro-trienones, 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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