


Cite this: *RSC Adv.*, 2025, 15, 23633

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

Xin Sun,<sup>✉</sup> Si-Yu Li,<sup>‡</sup> Su-Yue Chen,<sup>‡</sup> Cheng-Cheng Zhang,<sup>‡</sup> Jia Li,<sup>a</sup> Bin Zhang,<sup>a</sup> Xiang-Fei Zhang,<sup>a</sup> Jianghong Dong,<sup>✉</sup> Wen-Ke Bai,<sup>c</sup> Xin-Qi Hao,<sup>✉</sup> Qi-Jie Xu,<sup>\*a</sup> Bin Wu<sup>✉</sup> and Miao Yu<sup>\*a</sup>

Received 20th May 2025  
Accepted 23rd June 2025

DOI: 10.1039/d5ra03553h

rsc.li/rsc-advances

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,<sup>1</sup> 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.<sup>2</sup> Generally, spiro[4.5]trienone structures are constructed *via* the oxidative spiro-cyclization of phenol derivatives,<sup>3</sup> electrophilic *ipso*-cyclization,<sup>4</sup> transition-metal-mediated intramolecular nucleophilic *ipso*-cyclization,<sup>5</sup> and radical-coupling *ipso*-cyclization.<sup>6</sup> Notably, various substituent groups have been successfully introduced into spiro[4.5]trienone compounds *via* alkylation,<sup>7</sup> alkenylation,<sup>8</sup> amination,<sup>9</sup> halogenation,<sup>10</sup> siliconization,<sup>11</sup> phosphorylation,<sup>12</sup> nitrification,<sup>13</sup> acylation,<sup>14</sup> sulfuration,<sup>15</sup> selenization,<sup>16</sup> telurination,<sup>17</sup> and germylation.<sup>18</sup> In parallel, sulfone compounds are a class of important organic molecules, many of which have been found to exhibit unique pharmacological activities.<sup>19</sup> Most importantly, they also serve as the key building blocks in many

organic transformations.<sup>20</sup> Furthermore, the introduction of sulfonyl groups into drug molecules may significantly enhance their biological activities.<sup>21</sup> 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 hetero-aromatic ring, such as *N*-arylalkynamides, provides a useful strategy to develop annulated heterocycles. Several sulfonyl radical precursors, such as sulfonyl chloride,<sup>22</sup> sulfonyl hydrazide,<sup>23</sup> sulfonic acid,<sup>24</sup> DABSO<sup>25</sup> and metabisulfite salt,<sup>26</sup> have been investigated to synthesize spiro[4.5]trienones. In 2018, Zhou and Liu<sup>22</sup> 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 Na<sub>2</sub>CO<sub>3</sub> as the base in a mixture of CH<sub>3</sub>CN and H<sub>2</sub>O. Wang and Wei<sup>23</sup> described the I<sub>2</sub>O<sub>5</sub>-mediated direct oxidative spirocyclization of *N*-arylpropiolamides with sulfonylhydrazides, leading to 3-sulfonylated azaspiro[4.5]trienones. Wang and Wei<sup>24</sup> 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 Na<sub>2</sub>-eosin Y in CH<sub>3</sub>CN/H<sub>2</sub>O. Tang<sup>25a</sup> in 2019 and Volla<sup>25b</sup> in 2020 independently developed a visible-light-promoted one-pot synthesis of sulfonylated spiro[4.5]trienones from anilines and diaryliodonium salts *via* SO<sub>2</sub> insertion under transition-metal-free conditions. In 2023, Zhao<sup>26</sup> developed a protocol to access sulfonylated spiro[4.5]trienones *via* SO<sub>2</sub> insertion by the visible-light-induced cyanoalkylsulfonylation/*ipso*-cyclization of *N*-arylpropiolamide with cyclobutanone oxime esters and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> in the presence of the eosin Y disodium salt in CH<sub>3</sub>CN. As part of our continued interest in the synthesis of sulfonylated 2-oxindole frameworks,<sup>27</sup> herein, we report a visible-light-

<sup>a</sup>School of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian, 463000, China. E-mail: sunxin@bjmu.edu.cn; miaoy050666@126.com; qijie001@163.com

<sup>b</sup>School of Pharmaceutical Sciences, South-Central Minzu University, Wuhan 430074, China. E-mail: 2015084@mail.scuec.edu.cn

<sup>c</sup>Henan Wei Nuo Biotechnology Co., Ltd, Zhumadian 463000, China

<sup>d</sup>Green Catalysis Center and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5ra03553h>

‡ These authors contributed equally.



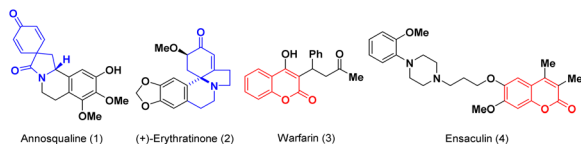


Fig. 1 Representative natural products and biologically active pharmaceuticals containing spiro-trienone frameworks.

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 CH<sub>3</sub>CN, DMF, and CH<sub>3</sub>OH, 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 K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.0 equiv.) under the irradiation of white light (Entries 1–3, Table 1). The yield increased up to 65% in CH<sub>3</sub>CN/H<sub>2</sub>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

results showed that PC-4 could afford the desired spiro[4.5]trienone product **6a** in 84% yield (Entries 9–12, Table 1). Besides K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (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 K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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<sub>3</sub> 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 CH<sub>3</sub>CN/H<sub>2</sub>O, CH<sub>3</sub>OH/H<sub>2</sub>O or dioxane/H<sub>2</sub>O 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 <sub>2</sub> O	(v/v)	PC	Oxidant	Yield(%) <sup>a</sup>
1	CH <sub>3</sub> OH	Neat	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	40
2	DMF	Neat	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	38
3	CH <sub>3</sub> CN	Neat	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	31
4	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	65
5	Dioxane/H <sub>2</sub> O	4/1	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50
6	CH <sub>3</sub> OH/H <sub>2</sub> O	4/1	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	27
7	DMF/H <sub>2</sub> O	4/1	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0
8	DMSO/H <sub>2</sub> O	4/1	PC-1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0
9	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-2	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	63
10	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-3	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	66
11	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	84
12	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-5	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	65
13	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	58
14	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	65
15 <sup>b</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	72
16 <sup>c</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	95
17 <sup>d</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	62
18	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	None	0
19 <sup>e</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0
20 <sup>f</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	None	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	85
21 <sup>g</sup>	CH <sub>3</sub> CN/H <sub>2</sub> O	4/1	PC-4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	90

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

Table 2 Control experiments of several selected substrates<sup>a</sup>

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

<sup>a</sup> Isolated yield. <sup>b</sup> The reaction was performed in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.0 equiv.) at room temperature. <sup>c</sup> The reaction was performed in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.0 equiv.) at 90 °C. <sup>d</sup> The reaction was performed in the presence of AgNO<sub>3</sub> (0.2 equiv.) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.0 equiv.) at room temperature. <sup>e</sup> The reaction was performed in the presence of AgNO<sub>3</sub> (0.2 equiv.) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.0 equiv.) at 90 °C.



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

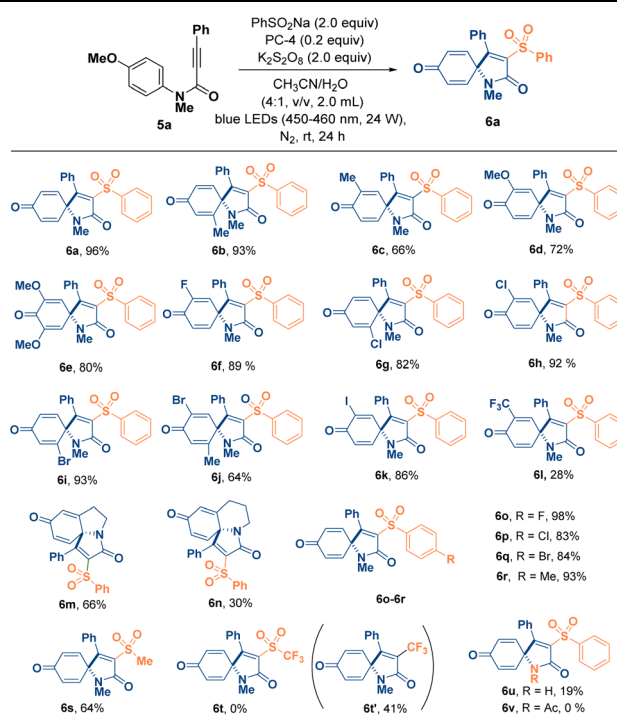
Entry	Solvent/H <sub>2</sub> O	Yield (%) <sup>a</sup>
1	CH <sub>3</sub> CN/H <sub>2</sub> O	0
2	CH <sub>3</sub> OH/H <sub>2</sub> O	0
3	Dioxane/H <sub>2</sub> O	0

<sup>a</sup> Isolated yield.

as a combination of **5a** (0.1 mmol), PhSO<sub>2</sub>Na (0.2 mmol), and 9-thioxanthone (0.02 mmol) in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (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

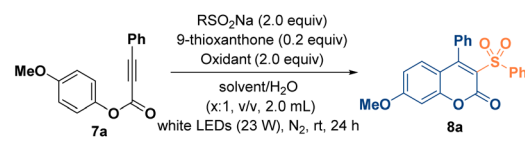
excellent yields. Substrates bearing electron-withdrawing groups, for example, –F (**6f**), –Cl (**6g** and **6h**), –Br (**6i** and **6j**), –I (**6k**), and –CF<sub>3</sub> (**6l**), also provided good product yields. To our delight, **5m** and **5n** afforded azaspiro[4.5]trienones **6m** and **6n** 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.<sup>28</sup> The increasing importance and widespread usage of coumarin derivatives have drawn attention to their synthetic methods,<sup>29</sup> among which metal-catalyzed and organocatalytic methods have proven to be the most effective. Several metal-catalyzed and/or organocatalytic synthetic strategies<sup>30</sup> 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 coumarin<sup>31</sup> scaffolds using aryl propiolates. Solvent screening results showed that in CH<sub>3</sub>CN/H<sub>2</sub>O (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<sup>a</sup>

<sup>a</sup> Reaction conditions: **5a** (0.1 mmol), PhSO<sub>2</sub>Na (0.2 mmol), PC-4 (0.02 mmol, 0.2 equiv.), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.2 mmol, 2.0 equiv.) in CH<sub>3</sub>CN/H<sub>2</sub>O (4 : 1, v/v, 2.0 mL) under the irradiation of blue LEDs in a nitrogen atmosphere; isolated yield.



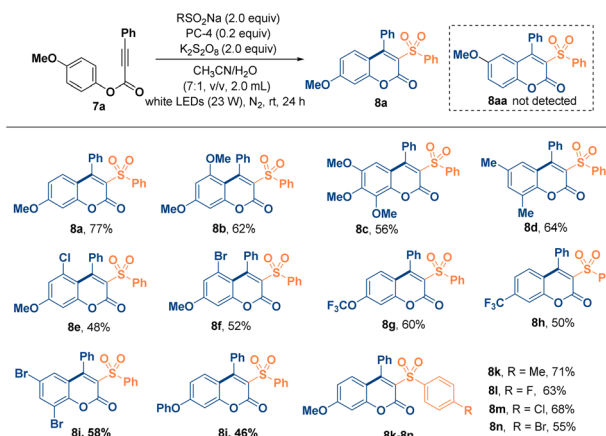
Table 5 Screening of the reaction conditions for coumarin **8a**


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

<sup>a</sup> Isolated yield. <sup>b</sup> The reaction was performed in the dark.

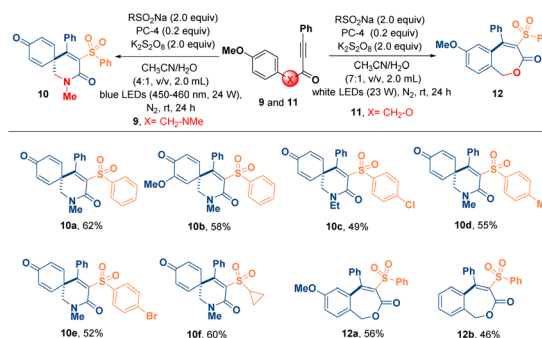
Table 5) produced lower product yields, and other solvent systems gave similar results (Entries 7–12, Table 5). Alteration of PCs (Entries 13 and 14, Table 5) or oxidants (Entries 15 and 17, Table 5) resulted in lower yields. The yield of **8a** decreased dramatically when the reaction was performed 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 K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

(Entry 19, Table 5). Therefore, the optimal reaction conditions were quickly established as a combination of substrate **7a** (0.1 mmol, 1.0 equiv.), PhSO<sub>2</sub>Na (0.2 mmol, 2.0 equiv.), 9-thioxanthone (0.02 mmol, 0.2 equiv.) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.2 mmol, 2.0 equiv.) in CH<sub>3</sub>CN/H<sub>2</sub>O (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<sup>a</sup>

<sup>a</sup> Reaction conditions: **5a** (0.1 mmol), PhSO<sub>2</sub>Na (0.2 mmol), PC-4 (0.02 mmol, 0.2 equiv.), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.2 mmol, 2.0 equiv.) in CH<sub>3</sub>CN/H<sub>2</sub>O (7 : 1, v/v, 2.0 mL) under the irradiation of white LEDs in a nitrogen atmosphere; isolated yield.



Table 7 Substrate scope<sup>a</sup>

<sup>a</sup> Reaction conditions: **9** or **11** (0.1 mmol),  $\text{PhSO}_2\text{Na}$  (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 ynones<sup>32</sup> 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  $\text{PhSO}_2\text{Na}$  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,  $\text{H}_2\text{O}^{18}$  was introduced in the reaction mixture instead of  $\text{H}_2\text{O}$  (Fig. 4A). High-resolution mass spectrometry (HRMS) analysis showed that the oxygen atom of the product ketone carbonyl group was a mixture of  $\text{O}^{18}$  and  $\text{O}^{16}$ , indicating that the oxygen atom of the ketone originated from the original substrate  $-\text{OMe}$  group and reaction solvent ( $\text{H}_2\text{O}^{18}$ ) (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

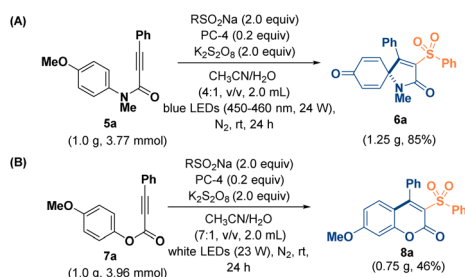


Fig. 2 Gram-scale experiments for the preparation of **6a** (A) and **8a** (B).

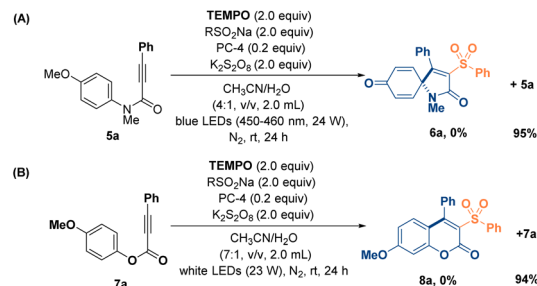


Fig. 3 Radical capture experiments for the preparation of **6a** (A) and **8a** (B).



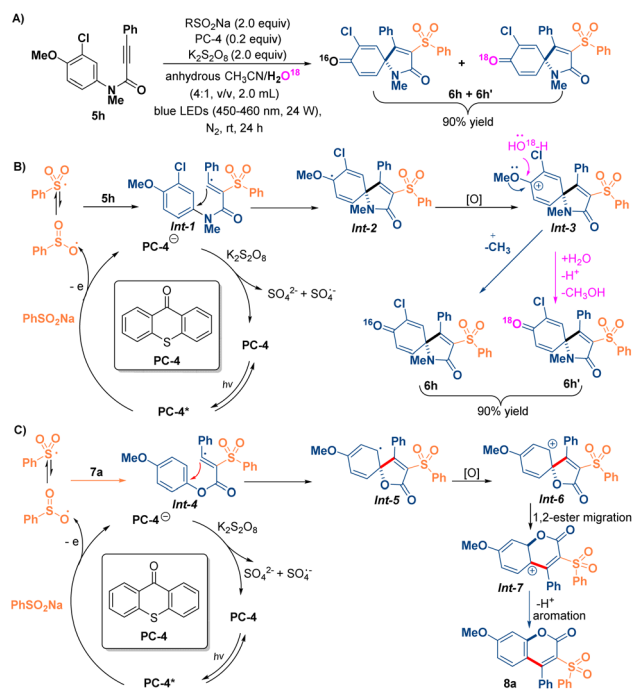


Fig. 4 Isotope experiment of 5h (A). Proposed reaction mechanism for 5h to 6h + 6h' (B) and proposed mechanism of the preparation of coumarin 8a (C).

photosensitizer 9-thioxanthone (PC-4). Then, a radical addition reaction with the  $\text{C}\equiv\text{C}$  bond occurred to afford intermediate **Int-1**, which subsequently produced intermediate **Int-2** via intramolecular radical addition. The demethylation<sup>24,26</sup> of **Int-3** afforded normal spiro[4.5]trienone **6h**. Meanwhile, a  $\text{H}_2\text{O}^{18}$  nucleophilic attack, followed by deprotonation and MeOH elimination<sup>25a</sup> reactions of intermediate **Int-3** afforded the spiro [4.5]trienone  $\text{O}^{18}$  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 migration<sup>33</sup> 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 **Int-4** is set as the zero point of the total electronic energy (unit in  $\text{kcal mol}^{-1}$ ). The zero point of the total electronic energy in brackets after double backslash is the ground state of corresponding intermediate (for example, **Int-6** and **8a**, 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 **Int-4** 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 **Int-4-c** to afford **Int-5**. Path 1 (Path 1: **Int-4**  $\rightarrow$  **Int-4-c**  $\rightarrow$  **Int-5**  $\rightarrow$  **Int-6**  $\rightarrow$  **Int-7**  $\rightarrow$  **8a**, dark line) is more favorable than Path 1-i (Path 1-i: **Int-4**  $\rightarrow$  **Int-4-c**  $\rightarrow$  **Int-5-i**  $\rightarrow$  **Int-6-i**  $\rightarrow$  **8aa**, red line) because the total electronic energy of **Int-5** is  $7.2 \text{ kcal mol}^{-1}$  lower than that of **Int-5-i**. The final product **8a** of the aromatic structure undergoes intramolecular 1,2-migration, whose energy is  $3.3 \text{ kcal mol}^{-1}$  lower than that of isomer **8aa**. This result indicated that the formation process of product **8a** was much more favorable than the formation process of isomer **8aa**.

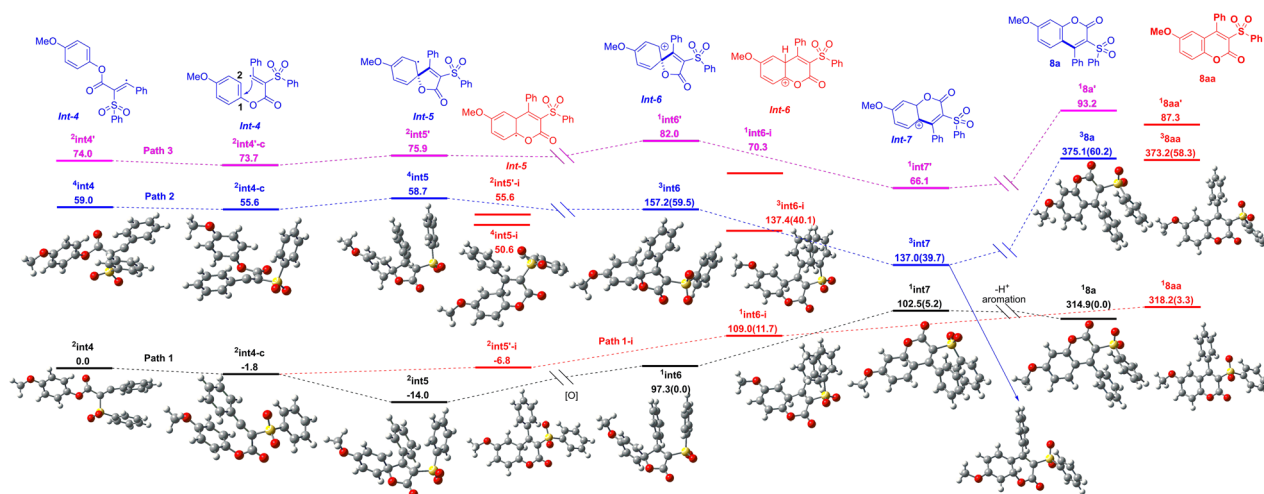


Fig. 5 DFT (M06-2X/6-311G(d)) computational studies of the formation of coumarin 8a.



## 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.

## Acknowledgements

We are grateful to the Research Foundation for Doctoral of Huanghuai University (no. 12011942), National Scientific Research Project Cultivation Fund of Huanghuai University (No. 110719421001), Programs for Science and Technology Development of Henan Province (No. 232102310360, 212102310329, 242102310440 and 252102311232), the National Natural Science Foundation of China (No. U2004191), Graduate Education Reform Project of Henan Province (No. 2023SJGLX336Y and 2023SJGLX093Y) and the Key Scientific Research Projects of Universities in Henan Province (No. 23B150007 and 25B150032) for the support of this research.

## Notes and references

- 1 Y. L. Yang, F. R. Chang and Y. C. Wu, Annosqualine: A Novel Alkaloid from the Stems of *Annona Squamosa*, *Helv. Chim. Acta*, 2004, **87**, 1392–1399.
- 2 (a) A. J. S. Alves, N. G. Alves, M. I. L. Soares and T. M. V. D. Pinho e Melo, Strategies and Methodologies for the Construction of Spiro- $\gamma$ -lactams: An Update, *Org. Chem. Front.*, 2021, **8**, 3543–3593; (b) W. C. Yang, M.-M. Zhang and J.-G. Feng, Recent Advances in the Construction of Spiro Compounds *via* Radical Dearomatization, *Adv. Synth. Catal.*, 2020, **362**, 4446–4461; (c) R. J. Song and Y. X. Xie, Recent Advances in Oxidative *Ipso*-Annulation of *N*-Arylpropionamides, *Chin. J. Chem.*, 2017, **35**, 280–288; (d) C. R. Reddy, S. K. Prajapati, K. Warudikar, R. Ranjan and B. B. Rao, *Ipso*-Cyclization: An Emerging Tool for Multifunctional Spirocyclohexadienones, *Org. Biomol. Chem.*, 2017, **15**, 3130–3151.
- 3 (a) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma and Y. Kita, Versatile Hypervalent-iodine (III)-Catalyzed Oxidations with *m*-Chloroperbenzoic Acid as a Cooxidant, *Angew. Chem., Int. Ed.*, 2005, **44**, 6193–6196; (b) D. Magdziak, S. J. Meek and T. R. R. Pettus, Cyclohexadienone Ketals and Quinols: Four Building Blocks Potentially Useful for Enantioselective Synthesis, *Chem. Rev.*, 2004, **104**, 1383–1429.
- 4 (a) B. X. Tang, D. J. Tang, S. Tang, Q. F. Yu, Y. H. Zhang, Y. Liang, P. Zhong and J. H. Li, Selective Synthesis of Spiro [4,5]trienyl Acetates *via* an Intramolecular Electrophilic *Ipso*-Iodocyclization Process, *Org. Lett.*, 2008, **10**, 1063–1066; (b) Q. Yin and S. L. You, Intramolecular Alkene Electrophilic Bromination Initiated *Ipso*-Bromocyclization for the Synthesis of Functionalized Azaspirocyclohexadienones, *Org. Lett.*, 2012, **14**, 3526–3529; (c) D. Yugandhar, S. Kuriakose, J. B. Nanubolu and A. K. Srivastava, Synthesis of Alkaloid-Mimicking Tricyclic Skeletons by Diastereo- and Regioselective Ugi/*Ipso*-Cyclization/Aza-Michael Cascade Reaction in One-Pot, *Org. Lett.*, 2016, **18**, 1040–1043.
- 5 (a) A. H. Bansode, S. R. Shaikh, R. G. Gonnade and N. T. Patil, Intramolecular *Ipso*-Arylative Cyclization of Aryl-alkynoates and *N*-Arylpropionamides with Aryldiazonium Salts through Merged Gold/Visible Light Photoredox Catalysis, *Chem. Commun.*, 2017, **53**, 9081–9084; (b) S. Chiba, L. Zhang and J. Y. Lee, Copper-Catalyzed Synthesis of Azaspirocyclohexadienones from  $\alpha$ -Azido-*N*-arylamides under an Oxygen Atmosphere, *J. Am. Chem. Soc.*, 2010, **132**, 7266–7267; (c) T. Nemoto, Z. Zhao, T. Yokosaka, Y. Suzuki, R. Wu and Y. Hamada, Palladium-Catalyzed Intramolecular *Ipso*-Friedel–Crafts Alkylation of Phenols and Indoles: Rearomatization-Assisted Oxidative Addition, *Angew. Chem., Int. Ed.*, 2013, **52**, 2217–2220; (d) S. Rousseaux, J. García-Fortanet, M. A. Del Aguila Sanchez and S. L. Buchwald, Palladium (0)-Catalyzed Arylative Dearomatization of Phenols, *J. Am. Chem. Soc.*, 2011, **133**, 9282–9285; (e) Q. F. Wu, W. B. Liu, C. X. Zhuo, Z. Q. Rong, K. Y. Ye and S. L. You, Iridium-Catalyzed Intramolecular Asymmetric Allylic Dearomatization of Phenols, *Angew. Chem., Int. Ed.*, 2011, **50**, 4455–4458.
- 6 (a) D. P. Jin, P. Gao, D. Q. Chen, S. Chen, J. Wang, X. Y. Liu and Y. M. Liang, AgSCF<sub>3</sub>-Mediated Oxidative Trifluoromethylthiolation of Alkynes with Dearomatization to Synthesize SCF<sub>3</sub>-Substituted Spiro[4,5]trienones, *Org. Lett.*, 2016, **18**, 3486–3489; (b) D. Zheng, J. Y. Yu and J. Wu, Generation of Sulfonyl Radicals from Aryldiazonium Tetrafluoroborates and Sulfur Dioxide: The Synthesis of 3-Sulfonated Coumarins, *Angew. Chem., Int. Ed.*, 2016, **55**, 11925–11929.
- 7 (a) J.-W. Yuan, C.-X. Mou, Y. Zhang, W.-Y. Hu, L.-R. Yang, Y.-M. Xiao, P. Mao, S.-R. Zhang and L.-B. Qu, Transition-metal Catalyzed Oxidative Spirocyclization of *N*-aryl Alkynamides with Methylarenes under Microwave Irradiation, *Org. Biomol. Chem.*, 2021, **19**, 10348–10358; (b) M. Li, R.-J. Song and J.-H. Li, Nickel-Promoted Oxidative *Ipso*-Annulation of *N*-(*p*-Methoxyaryl)propionamides with  $\alpha$ -Carbonylalkyl Bromides, *Chin. J. Chem.*, 2017, **35**, 299–302; (c) S. Manna, P. K. S. Ashwathappa and K. R. Prabhu, Visible Light-Mediated-*Ipso*-Annulation of Activated Alkynes: Access to 3-Alkylated Spiro[4,5]trienones,



- Thiaspiro[4,5]-trienones and Azaspiro[4,5]-trienones, *Chem. Commun.*, 2020, **56**, 13165–13168; (d) P. P. Zeng, X. X. Huang, W. Tang and Z. W. Chen, Copper-Catalyzed Cascade Radical Cyclization of Alkynoates: Construction of Aryldifluoromethylated Coumarins, *Org. Biomol. Chem.*, 2021, **19**, 10223–10227; (e) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li and J.-H. Li, Copper-Catalyzed Oxidative *Ips*o-Carboalkylation of Activated Alkynes with Ethers Leading to 3-Etherified Azaspiro[4.5]trienones, *Org. Chem. Front.*, 2014, **1**, 484–489; (f) P. Chen, J.-H. Fan, W.-Q. Yu, B.-Q. Xiong, Y. Liu, K.-W. Tang and J. Xie, Alkylation/*Ips*o-Cyclization of Active Alkynes Leading to 3-Alkylated Aza- and Oxa-spiro[4,5]trienones, *J. Org. Chem.*, 2022, **87**, 5643–5659; (g) S. Manna and K. R. Prabhu, Visible-Light-Mediated Vicinal Difunctionalization of Activated Alkynes with Boronic Acids: Substrate-Controlled Rapid Access to 3-Alkylated Coumarins and Unsaturated Spirocycles, *Org. Lett.*, 2023, **25**, 810–815.
- 8 C. R. Reddy, D. H. Kolgave, U. Ajaykumar and R. Ramesha, Copper (II)-Catalyzed Oxidative *Ips*o-Annulation of *N*-Arylpropiolamides and Biaryl Ynones with 1,3-Diketones: Construction of Diketoalkyl Spirotrienones, *Org. Biomol. Chem.*, 2022, **20**, 6879–6889.
- 9 A. Mathuri, B. Pal, M. Pramanik and P. Mal, Chemodivergent Chalcogenation of Aryl Alkynoates or *N*-Arylpropynamides Using 9-Mesityl-10-Methylacridinium Perchlorate Photocatalyst, *J. Org. Chem.*, 2023, **88**, 10096–10110.
- 10 (a) Y.-C. Wang, J.-B. Liu, H. W. Zhou, P. Rojsitthisak, G. Y. S. Qiu and W. L. Xie, *Ortho*-Hydroxylative *Ips*o-Cyclization of *N*-arylpropiolamide, *J. Org. Chem.*, 2020, **85**, 1906–1914; (b) Y. Chen, F.-Y. Lu, R.-X. Li, Z. Guan and Y.-H. He, Visible-light-mediated Synthesis of Bromo-containing Azaspirotrienediones from *N*-phenylpropynamides, *Asian J. Org. Chem.*, 2021, **10**, 668–673; (c) X. X. Li, B. B. Zhang, B. Y. Zhao, X. F. Wang, L. Z. Xu and Y. F. Du, Synthesis of 3-Halogenated Quinolin-2-Ones from *N*-Arylpropynamides via Hypervalent Iodine (III) Mediated. Umpolung Process, *Adv. Synth. Catal.*, 2022, **364**, 1427–1433; (d) T. Liu, Y. M. Li, L. L. Jiang, J. A. Wang, K. Jin, R. Zhang and C. Y. Duan, Photo-Mediated Synthesis of Halogenated Spiro[4,5]trienones of *N*-Aryl Alkynamides with  $\text{PhI}(\text{OCOCF}_3)_2$  and  $\text{KBr/KCl}$ , *Org. Biomol. Chem.*, 2020, **18**, 1933–1939; (e) B. Pal, A. Mathuri, A. Manna and P. Mal,  $\text{CsPbBr}_3$  Perovskite Photocatalyst in Chemodivergent Functionalization of *N*-Methylalkanamides Using  $\text{CBr}_4$ , *Org. Lett.*, 2023, **25**, 4075–4079; (f) B.-X. Tang, Y.-H. Zhang, R.-J. Song, D.-J. Tang, G.-B. Deng, Z.-Q. Wang, Y.-X. Xie, Y.-Z. Xia and J.-H. Li, Intramolecular *Ips*o-Halocyclization of 4-(*p*-Unsubstituted-aryl)-1-alkynes Leading to Spiro[4,5]trienones: Scope, Application, and Mechanistic Investigations, *J. Org. Chem.*, 2012, **77**, 2837–2849; (g) K. Yu, X. Q. Kong, J. J. Yang, G. D. Li, B. Xu and Q. J. Chen, Electrochemical Oxidative Halogenation of *N*-Aryl Alkynamides for the Synthesis of Spiro[4.5]trienones, *J. Org. Chem.*, 2021, **86**, 917–928; (h) D. Yugandhar and A. K. Srivastava, Efficient Construction of Azaspiro[4.5]trienone Libraries via Tandem Ugi 4CC/Electrophilic *Ips*o-Iodocyclization in One-Pot, *ACS Comb. Sci.*, 2015, **17**, 474–481.
- 11 (a) F. Chen, Y. Zheng, H. Yang, Q.-Y. Yang, L.-Y. Wu and N. N. Zhou, Iron-Catalyzed Silylation and Spirocyclization of Biaryl-Ynones: A Radical Cascade Process toward Silylated Spiro[5.5]trienones, *Adv. Synth. Catal.*, 2022, **364**, 1537–1542; (b) P. Gao, W. W. Zhang and Z. C. Zhang, Copper-Catalyzed Oxidative *Ips*o-Annulation of Activated Alkynes with Silanes: An Approach to 3-Silyl Azaspiro[4,5]trienones, *Org. Lett.*, 2016, **18**, 5820–5823.
- 12 (a) F. Zeng, X. Chen, K. Sun, H. Zhu, X. Yuan, Y. Liu, L. Qu, Y. Zhao and B. Yu, Visible-Light-Induced Metal-Free Cascade Cyclization of *N*-arylpropiolamides to 3-Phosphorylated, Trifluoromethylated and Thiocyanated azaspiro[4.5]trienones, *Org. Chem. Front.*, 2021, **8**, 760–766; (b) L.-J. Wang, A.-Q. Wang, Y. Xia, X.-X. Wu, X.-Y. Liu and Y.-M. Liang, Silver-Catalyzed Carbon-Phosphorus Functionalization of *N*-(*p*-Methoxyaryl) Propiolamides Coupled with Dearomatization: Access to Phosphorylated Aza-Decenones, *Chem. Commun.*, 2014, **50**, 13998–14001.
- 13 D. Xia, L.-Y. Shen, Y. C. Zhang and W.-C. Yang, Radical Spirocyclization of Biaryl Ynones for the Construction of  $\text{NO}_2$ -Containing Spiro[5.5]trienones, *New J. Chem.*, 2022, **46**, 20061–20064.
- 14 (a) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu and J.-H. Li, J. Metal-Free Oxidative *Ips*o-Carboacylation of Alkynes: Synthesis of 3-Acylspiro[4,5]trienones from *N*-Arylpropiolamides and Aldehydes, *J. Org. Chem.*, 2014, **79**, 4582–4589; (b) C. R. Reddy, U. A. Kumar, A. D. Patil and R. Ramesh, *Ips*o-Cyclization of Unactivated Biaryl Ynones Leading to Thio-Functionalized Spirocyclic Enones, *Org. Biomol. Chem.*, 2023, **21**, 6379–6388; (c) C. M. Volla, A. M. Nair, A. H. Shinde and S. Kumar, Metal-free Spirocyclization of *N*-Arylpropiolamides with Glyoxylic Acids: Access to Complex Azaspiro-fused Tricycles, *Chem. Commun.*, 2020, **56**, 12367–12370; (d) C. R. Reddy, D. H. Kolgave, M. Subbarao, M. Aila and S. K. Prajapati, Ag-Catalyzed Oxidative *Ips*o-Cyclization via Decarboxylative Acylation/Alkylation: Access to 3-Acyl/Alkyl-spiro[4.5]trienones, *Org. Lett.*, 2020, **22**, 5342–5346; (e) V. J. Roy, N. Dagar, S. Choudhury and S. R. Roy, Unified Approach to Diverse Heterocyclic Synthesis: Organo-Photocatalyzed Carboacylation of Alkenes and Alkynes from Feedstock Aldehydes and Alcohols, *J. Org. Chem.*, 2023, **88**, 15374–15388; (f) P. Chen, J. Xie, Z. Chen, B.-Q. Xiong, Y. Liu, C.-A. Yang and K.-W. Tang, Visible-Light-Mediated Nitrogen-Centered Radical Strategy: Preparation of 3-Acylated Spiro[4,5]trienones, *Adv. Synth. Catal.*, 2021, **363**, 1–8; (g) Y. Liu, Q.-L. Wang, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, Visible-Light-Mediated *Ips*o-Carboacylation of Alkynes: Synthesis of 3-Acylspiro[4,5]trienones from *N*-(*p*-methoxyaryl) propiolamides and Acyl Chlorides, *J. Org. Chem.*, 2018, **83**, 2210–2218.
- 15 (a) X. X. Li, Y. X. Wang, Y. X. Ouyang, Z. Y. Yu, B. B. Zhang, J. R. Zhang, H. F. Shi, H. Zuillhof and Y. F. Du, Unexpected





- Substituent Effects in Spiro-Compound Formation: Steering *N*-Aryl Propynamides and DMSO toward Site-Specific Sulfination in Quinolin-2-ones or Spiro[4,5]trienones, *J. Org. Chem.*, 2021, **86**, 9490–9502; (b) W.-C. Gao, T. Liu, Y.-F. Cheng, H.-H. Chang, X. Li, R. Zhou, A.-L. Wei and Y. Qiao,  $\text{AlCl}_3$ -Catalyzed Intramolecular Cyclization of *N*-Arylpropynamides with *N*-Sulfanylsuccinimides: Divergent Synthesis of 3-Sulphenyl Quinolin-2-ones and Azaspiro[4,5]trienones, *J. Org. Chem.*, 2017, **82**, 13459–13467; (c) L. Z. Xu, F. X. Sun, H. Zhao, H. F. Shi, Y. H. Wu, X. X. Li and Y. F. Du, Synthesis of Trifluoromethylthiolated Quinolinones via Trifluoromethanesulfanamide-Induced Electrophilic Intramolecular Cyclization of *N*-Arylpropynamides, *Adv. Synth. Catal.*, 2023, **365**, 3837–3842; (d) C. R. Reddy, U. Ajaykumar and D. H. Kolgave, Expedition Access to Spiro-Fused 2,5-Cyclohexadienones via Thio(seleno)cyanative *Ipso*-Cyclization, *J. Org. Chem.*, 2020, **85**, 15521–15531.
- 16 (a) A. Recchi, P. Rosa, D. F. Back and G. Zeni, Selenium-Promoted Electrophilic Cyclization of Arylpropiolamides: Synthesis of 3-Organoselenyl Spiro[4,5]trienones, *Org. Biomol. Chem.*, 2020, **18**, 3544–3551; (b) H. Sahoo, G. S. Grandhi, I. Ramakrishna and M. Baidya, Metal-free Switchable *ortho*/*Ipso*-Cyclization of *N*-aryl Alkynamides: Divergent Synthesis of 3-Selenyl Quinolin-2-ones and Azaspiro[4,5]trienones, *Org. Biomol. Chem.*, 2019, **17**, 10163–10166; (c) J. W. Hua, Z. Fang, M. Bian, T. Ma, M. Yang, J. Xu, C. K. Liu, W. He, N. Zhu, Z. Yang and K. Guo, Electrochemical Synthesis of Spiro[4.5]trienones through Radical-Initiated Dearomative Spirocyclization, *ChemSusChem*, 2020, **13**, 2053–2059; (d) H. Sahoo, A. Mandal, S. Dana and M. Baidya, Visible Light-Induced Synthetic Approach for Selenylative Spirocyclization of *N*-Aryl Alkynamides with Molecular Oxygen as Oxidant, *Adv. Synth. Catal.*, 2018, **360**, 1099–1103; (e) C. R. Reddy, M. Subbarao, D. H. Kolgave, U. Ajaykumar and P. P. Vinaya, Access to Diverse Seleno-Spirocyclohexadienones via Ag (II)-Catalyzed Selenylative *Ipso*-Annulation with Se and Boronic Acids, *ACS Omega*, 2022, **7**, 38045–38052; (f) J.-W. Yuan, Q. Chen, W.-T. Wu, J.-J. Zhao, L.-R. Yang, Y.-M. Xiao, P. Mao and L.-B. Qu, Selectfluor-mediated Construction of 3-Arylselenenyl and 3,4-Bisarylselenenyl spiro[4.5]trienones via Cascade Annulation of *N*-Phenylpropiolamides with Diselenides, *New J. Chem.*, 2022, **46**, 9451–9460.
- 17 G. Zeni, B. Godoi, C. K. Jurinic, A. L. Belladonna and R. F. Schumacher, Transition Metal-Free Synthesis of Carbo- and Heterocycles via Reaction of Alkynes with Organylchalcogenides, *Chem. Rec.*, 2021, **21**, 1–17.
- 18 Y. Y. Luo, L. Y. Lv and Z. P. Li, Light-Promoted Germylation of Aryl Propiolamides/Alkynoates: Synthesis of Ge-Containing Spiro[4.5]trienones and Vinylgermanes, *ChemCatChem*, 2023, e202300467.
- 19 (a) M. Tohnishi, H. Nakao, T. Furuya, A. Seo, H. Kodama, K. Tsubata, S. Fujioka, H. Kodama, T. Hirooka and T. N. Flubendiamide, a Novel Insecticide Highly Active against Lepidopterous Insect Pests, *J. Pestic. Sci.*, 2005, **30**, 354–360; (b) Y. Shen, C. A. Zifcsak, J. E. Shea, X. G. Lao, O. Boltt, X. F. Li, J. G. Lisko, J. P. Theroff, C. L. Scaife, M. A. Ator, B. A. Ruggeri, B. D. Dorsey and S. K. K. Design, Synthesis and Biological Evaluation of Sulfonyl Acrylonitriles as Novel Inhibitors of Cancer Metastasis and Spread, *J. Med. Chem.*, 2015, **58**, 1140–1158.
- 20 (a) C. Jia, D. Piao, T. Kitamura and Y. Fujiwara, New Method for Preparation of Coumarins and Quinolinones via Pd-Catalyzed Intramolecular Hydroarylation of C-C Triple Bonds, *J. Org. Chem.*, 2000, **65**, 7516–7522; (b) Z. Zhang, P. He, H. G. Du, J. X. Xu and P. F. Li, Sulfur-Mediated Electrophilic Cyclization of Aryl-Substituted Internal Alkynes, *J. Org. Chem.*, 2019, **84**, 4517–4524; (c) S. Mondal, D. Manna and G. Mughesh, Selenium-Mediated Dehalogenation of Halogenated Nucleosides and Its Relevance to the DNA Repair Pathway, *Angew. Chem., Int. Ed.*, 2015, **54**, 9298–9302; (d) C.-F. Lee, Y.-C. Liu and S. S. Badsara, Transition-Metal-Catalyzed C-S Bond Coupling Reaction, *Chem.-Asian J.*, 2014, **9**, 706–722; (e) Y. Li, M. Wang and X. Jiang, Controllable Sulfoxidation and Sulfenylation with Organic Thiosulfate Salts via Dual Electron- and Energy-Transfer Photocatalysis, *ACS Catal.*, 2017, **7**, 7587–7592; (f) M. Wang, Q. Fan and X. Jiang, Metal-Free Construction of Primary Sulfonamides through Three Diverse salts, *Green Chem.*, 2018, **20**, 5469–5473; (g) M. S. Iauciulis, S. Sapmaz, A. P. Pulis and D. J. Procter, Dual Vicinal Functionalisation of Heterocycles via An Interrupted Pummerer Coupling/[3,3]-Sigmatropic Rearrangement Cascade, *Chem. Sci.*, 2018, **9**, 754–759; (h) L. Smith, S. Coote, H. Sneddon and D. Procter, Beyond the Pummerer Reaction: Recent Developments in Thionium Ion Chemistry, *Angew. Chem., Int. Ed.*, 2010, **49**, 5832–5844; (i) N.-W. Liu, S. Liang and G. Manolikakes, Recent Advances in the Synthesis of Sulfones, *Synthesis*, 2016, **48**, 1939–1973; (j) K. M. Borys and Z. Ochal, Synthetic Approaches to Aryl Halomethyl Sulfones, *Curr. Org. Chem.*, 2016, **20**, 963–970; (k) G. B. Huang, X. Y. Li, J. R. Luo, Z. H. Luo and M. X. Tan, Recent Progress on Synthesis of Sulfur Compounds by Sodium Sulfinates, *Chin. J. Org. Chem.*, 2019, **39**, 617–624.
- 21 (a) P.-J. Zhu, Z.-Z. Yu, Y.-F. Lv, J.-L. Zhao, Y.-Y. Tong, Q.-D. You and Z.-Y. Jiang, Discovery of 3,5-Dimethyl-4-Sulfonyl-1H-Pyrrole-Based Myeloid Cell Leukemia 1 Inhibitors with High Affinity, Selectivity, and Oral Bioavailability, *J. Med. Chem.*, 2021, **64**, 11330–11353; (b) K. A. Scott and J. T. Njardarson, Analysis of US FDA-Approved Drugs Containing Sulfur Atoms, *Top. Curr. Chem.*, 2018, **376**, 1–34; (c) T. Nagase, T. Takahashi, T. Sasaki, A. Nagumo, K. Shimamura, Y. Miyamoto, H. Kitazawa, M. Kanesaka, R. Yoshimoto, K. Aragane, S. Tokita and N. Sato, Synthesis and Biological Evaluation of a Novel 3-Sulfonyl-8-azabicyclo[3.2.1]octane Class of Long Chain Fatty Acid Elongase 6 (ELOVL6) Inhibitors, *J. Med. Chem.*, 2009, **52**, 4111–4114; (d) R. Artschwager, D. J. Ward, S. Gannon, A. J. Brouwer, H. Langemheen, H. Kowalski and R. M. J. Liskamp, Potent and Highly Selective Inhibitors of the Proteasome Trypsin-like Site by



- Incorporation of Basic Side Chain Containing Amino Acid Derived Sulfonyl Fluorides, *J. Med. Chem.*, 2018, **61**, 5395–5411.
- 22 Y. Liu, Q.-L. Wang, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang, Y.-X. Gong, J. Liao and Q. Zhou, Visible-light-mediated *Ipso*-Carbosulfonylation of Alkynes: Synthesis of 3-Sulfonylspiro[4,5]trienones from Propiolamides and Sulfonyl Chlorides under Transition-metal-free Conditions, *Synlett*, 2018, **29**, 2396–2403.
  - 23 J. Wen, W. Wei, S. Xue, D. Yang, Y. Lou, C. Gao and H. Wang, Metal-free Oxidative Spirocyclization of Alkynes with Sulfonylhydrazides Leading to 3-Sulfonated Azaspiro[4,5]trienones, *J. Org. Chem.*, 2015, **80**, 4966–4972.
  - 24 W. Wei, H. H. Cui, D. S. Yang, H. L. Yue, C. L. He, Y. L. Zhang and H. Wang, Visible-light-enabled Spirocyclization of Alkynes Leading to 3-Sulfonyl and 3-Sulfenyl Azaspiro[4,5]trienones, *Green Chem.*, 2017, **19**, 5608–5613.
  - 25 (a) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, Visible-light Promoted One-pot Synthesis of Sulfonated Spiro[4,5]trienones from Propiolamides, Anilines and Sulfur Dioxide under Transition Metal-free Conditions, *Chem. Commun.*, 2019, **55**, 12212–12215; (b) A. M. Nair, I. Halder, S. Khan and C. M. R. Volla, Metal Free Sulfonylative Spirocyclization of Alkenyl and Alkynyl Amides *via* Insertion of Sulfur Dioxide, *Adv. Synth. Catal.*, 2020, **362**, 224.
  - 26 X. W. Shan, Y. Gao, Y. R. Lu, R. Huang, T. T. Sun, K. Lu and X. Zhao, Visible-light Promoted Cascade Cyanoalkylsulfonylation/*Ipso*-Cyclization of *N*-arylpropiolamides toward Sulfonated Spiro[4,5]trienones *via* SO<sub>2</sub> Insertion, *Org. Biomol. Chem.*, 2023, **21**, 4823–4832.
  - 27 X. Sun, J.-P. Zhu, Q.-C. Qiu, Y.-L. He, D.-R. Hu, X.-L. Li, G.-P. Lu, Y.-H. Yuan, X.-F. Zhang, X. B. Xu, M. Yu and B. Wu, Metal-Free Visible-Light-Driven Cascade Cyclization Reaction to Synthesize 2-Oxindoles *via* Benzoyl and Phenylsulfinyl Radicals with Acrylamide Derivatives, *Org. Biomol. Chem.*, 2022, **20**, 8042–8048.
  - 28 (a) F. G. Medina, J. G. Marrero, M. Macías-Alonso, M. C. González, I. Córdova-Guerrero, A. G. Teissier García and S. Osegueda-Robles, Coumarin Heterocyclic Derivatives: Chemical Synthesis and Biological Activity, *Nat. Prod. Rep.*, 2015, **32**, 1472–1507; (b) N. S. Reddy, M. R. Mallireddigari, S. Cosenza, K. Gumireddy, S. C. Bell, E. P. Reddy and M. V. R. Reddy, Synthesis of new coumarin 3-(*N*-aryl) sulfonamides and their anticancer activity, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 4093–4097.
  - 29 E. Calcio Gaudino, S. Tagliapietra, K. Martina, G. Palmisano and G. Cravotto, Recent Advances and Perspectives in the Synthesis of Bioactive Coumarins, *RSC Adv.*, 2016, **6**, 46394–46405.
  - 30 S. M. Farid, B. Seifinoferest, M. Gholamhosseini, B. Larijania and M. Mahdavi, Modern Metal-Catalyzed and Organocatalytic Methods for Synthesis of Coumarin Derivatives: a review, *Org. Biomol. Chem.*, 2022, **20**, 4846–4883.
  - 31 (a) W. Wei, J. W. Wen, D. S. Yang, M. Y. Guo, Y. Y. Wang, J. M. You and H. Wang, Direct and metal-free arylsulfonylation of alkynes with sulfonylhydrazides for the construction of 3-sulfonated coumarins, *Chem. Commun.*, 2015, **51**, 768–771; (b) D. Q. Zheng, J. Y. Yu and J. Wu, Generation of Sulfonyl Radicals from Aryldiazonium Tetrafluoroborates and Sulfur Dioxide: The Synthesis of 3-Sulfonated Coumarins, *Angew. Chem., Int. Ed.*, 2016, **55**, 11925–11929; (c) X. F. Wang, T. Liu, D. Q. Zheng, Q. Zhong and J. Wu, Synthesis of 3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl) coumarins through the reaction of 2-(allyloxy)anilines, sulfur dioxide, and aryl propiolates, *Org. Chem. Front.*, 2017, **4**, 2455–2458; (d) W. Q. Wu, Y. N. An, J. X. Li, S. R. Yang, Z. Z. Zhu and H. F. Jiang, Iodine-catalyzed cascade annulation of alkynes with sodium arylsulfonates: assembly of 3-sulfenylcoumarin and 3-sulfenylquinolinone derivatives, *Org. Chem. Front.*, 2017, **4**, 1751–1756; (e) Z. K. Chen, N.-W. Liu, M. Bolte, H. J. Ren and G. Manolikakes, Visible-light mediated 3-component synthesis of sulfonylated coumarins from sulfur dioxide, *Green Chem.*, 2018, **20**, 3059–3070.
  - 32 (a) Y. Li, L. J. Li, C. Y. Guo, Q. Q. Yan, H. X. Zhou, Y. Wang, Z.-Q. Liu and Z. J. Li, Nitro-Spirocyclization of Biaryl Ynones with *tert*-Butyl Nitrite: Access to NO<sub>2</sub>-Substituted Spiro[5.5]trienones, *J. Org. Chem.*, 2023, **88**, 4854–4862; (b) D. Xia and X.-F. Duan, Iron-Catalyzed Dearomatization of Biaryl Ynones with Aldehydes *via* Double C-H Functionalization in Eco-Benign Solvents: Highly Atom-Economical Synthesis of Acylated Spiro[5.5]trienones, *J. Org. Chem.*, 2021, **86**, 15263–15275; (c) Y. Zhang, C. C. Ma, J. Struwe, J. Feng, G. F. Zhu and L. Ackermann, Electrooxidative Dearomatization of Biaryls: Synthesis of Tri- and Difluoromethylated Spiro[5.5]trienones, *Chem. Sci.*, 2021, **12**, 10092–10096; (d) J. Wang, X.-X. Lu, R.-P. Yang, Z.-H. Xiang, B.-B. Zhang, S. J. Chao, L. X. Liu, Y. H. Yan and X. F. Shang, Synthesis of Spiro[5.5]trienones- and Spiro[4.5]trienones-Fused Selenocyanates *via* Electrophilic Selenocyanogen Cyclization and Dearomative Spirocyclization, *J. Org. Chem.*, 2022, **87**, 13089–13101; (e) C. R. Reddy and D. H. Kolgave, Electrochemical Selenylative Carbannulation of Biaryl Ynones to Seleno-Dibenzocycloheptenones/Spiro[5.5]Trienones, *J. Org. Chem.*, 2021, **86**, 17071–17081; (f) J.-N. Li, Z.-J. Li, L.-Y. Shen, P. H. Li, Y. C. Zhang and W.-C. Yang, Synthesis of Polychloromethylated and Halogenated Spiro[5.5]trienones *via* Dearomative Spirocyclization of Biaryl Ynones, *Org. Biomol. Chem.*, 2022, **20**, 6659–6666; (g) W.-C. Yang, M.-M. Zhang, Y. Sun, C.-Y. Chen and L. Wang, Electrochemical Trifluoromethylthiolation and Spirocyclization of Alkynes with AgSCF<sub>3</sub>: Access to SCF<sub>3</sub>-Containing Spiro[5.5]trienones, *Org. Lett.*, 2021, **23**, 6691–6696; (h) F.-S. He, L. J. Su, F. Y. Yu, Z. M. Tang and J. Wu, Construction of Sulfonated Spiro[5.5]trienones from Sulfur Dioxide *via* Iron-Catalyzed Dearomative Spirocyclization of Biaryls, *Org. Chem. Front.*, 2022, **9**, 1937–1942.
  - 33 S. Sau and P. Mal, 3-Nitro-Coumarin Synthesis *via* Nitrative Cyclization of Aryl Alkynoates Using *tert*-Butyl Nitrite, *Chem. Commun.*, 2021, **57**, 9228–9231.

