

Article

# Photoinduced Photocatalyst-Free Cascade Cyclization of Alkynes with Sodium Sulfinates for the Synthesis of Benzothiophenes and Thioflavones

Hongqiang Dong <sup>1,\*</sup>, Chunli Chen <sup>1</sup>, Jinlei Zhao <sup>2,3</sup>, Yigang Ji <sup>4,\*</sup> and Wenchao Yang <sup>5</sup>

- <sup>1</sup> The Open Research Fund of the National and Local Joint Engineering Laboratory of High Efficiency and Superior-Quality Cultivation and Fruit Deep Processing Technology of Characteristic Fruit Trees in South Xinjiang, College of Agriculture, Tarim University, Alaer 843300, China; chenchunli1111@163.com
- <sup>2</sup> National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass, Nanjing Forestry University, Nanjing 210037, China; hhuzhjl@163.com
- <sup>3</sup> Jiangsu Surveying and Design Institute of Water Resources Co., Ltd., Yangzhou 225127, China
- <sup>4</sup> Jiangsu Key Laboratory of Biofunctional Molecules, Department of Life Sciences and Chemistry, Jiangsu Second Normal University, Nanjing 210013, China
- <sup>5</sup> Guangling College and School of Plant Protection, Yangzhou University, Yangzhou 225009, China
- \* Correspondence: dhqzky@163.com (H.D.); ygjnba@126.com (Y.J.)

**Abstract:** The subject of this investigation is a new method for the construction of sulfonylated heterocycles which overcomes the limitations of classical approaches using a cheap feedstock sulfonylating agent, especially under photocatalyst- and metal-free conditions.

**Keywords:** sulfonylation; sodium sulfinates; radical; cyclization; alkynes



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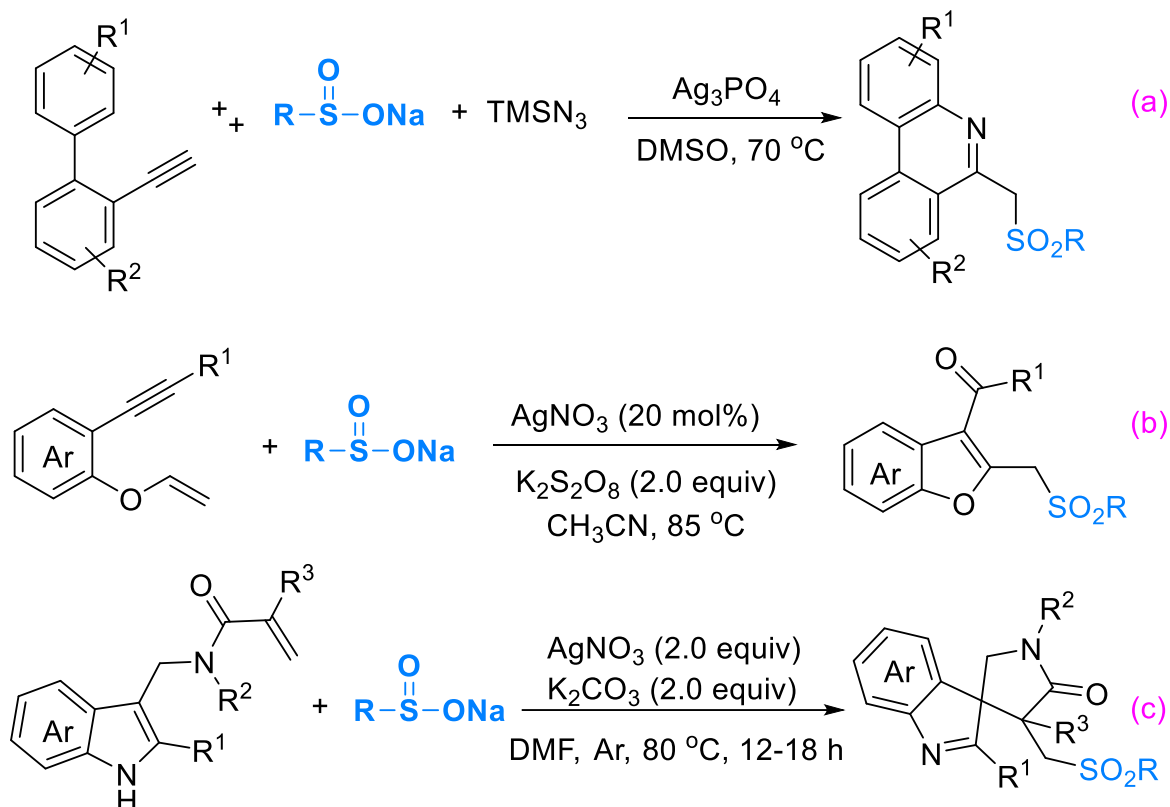
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## 1. Introduction

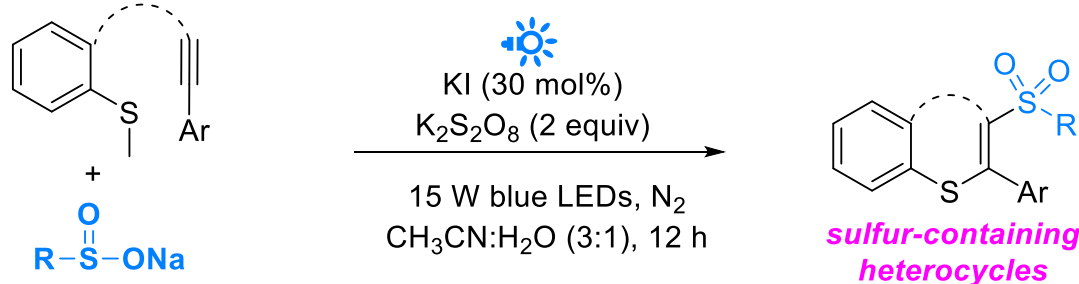
Sulfonylated heterocycles are important motifs found in many natural products, agrochemicals, and pharmaceuticals, with special physiological and biological activities [1–24]. Generally, the oxidation of thioethers is the most popular approach to access sulfones [25,26]. However, in many cases, strong oxidation conditions are not applicable to all functional groups. As a result, developing the efficient and mild synthesis of value-added sulfonylated heterocycles has played a significant role in advancing heterocyclic chemistry, as well as accelerating the discovery of novel agrochemicals [27–37]. Sodium sulfinates, as a common and stable sulfonation raw material, are widely applied in the construction of organic sulfones, including the cascade reaction, direct C–H functionalization, and oxidative coupling, etc., [38–41]. Among these protocols, radical cascade cyclization of C–C unsaturated bonds has provided a powerful tool for the collection of sulfonylated heterocycles by introducing two different functional groups on the both ends of the alkynes or alkenes in one step [42–48]. From the point of synthetic chemistry, these radical cascade reactions can be very convenient and efficient to realize direct conversion from relatively inexpensive C–C unsaturated bonds to high-value-added, complex molecular scaffolds with abundant bioactivities. For example, Bi and co-workers realized a silver-catalyzed cascade cyclization of alkynes with sodium sulfinates for the synthesis of 6-methyl sulfonylated phenanthridines, where mechanistic studies indicate the transformation should proceed through an iminyl radical intermediate (Scheme 1a) [42]. Soon afterward, Wu and Jiang's groups independently utilized sodium sulfinates and 1,6-enynes to achieve the sulfonylated benzofurans' synthesis by using an AgNO<sub>3</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system (Scheme 1b) [43]. Very recently, another radical cascade spiro-cyclization of alkenes with sodium sulfinates for the direct synthesis of sulfonylated spiro[indole-3,3'-pyrrolidines] was reported by Wang's group (Scheme 1c) [44]. Although significant progress has clearly been made in recent years, most of the traditional transformations usually depend on transition-metal

catalysts or harsh reaction conditions. As a result, the development of a practical and green protocol to realize the radical cyclization of alkynes is still an attractive topic.

### Selected reactions using sodium sulfinates as sulfonylation reagents



### (d): A new photochemical strategy for sulfur-containing heterocycles (this work)



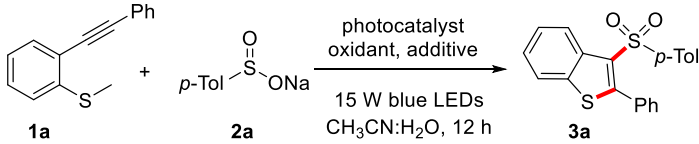
**Scheme 1.** Selected reactions using sodium sulfinates as sulfonylation reagents (a–c) and our work (d).

Over the past few decades, visible-light-induced organic reactions have emerged as an essential tool to construct new chemical bonds, featuring mild reaction conditions such as metal-free, room temperature, and simple operation conditions [49–52]. In 2015, we reported an example of using sulfinic acids as sulfonation reagents to react with alkyne in the presence of TBHP under visible-light irradiation [10]. However, the sulfonation reagent in this work is prepared from sodium sulfonates, leading to increase reaction steps. With our continuing interest in sustainable and photochemical chemistry [53–58], herein we disclose a photo-induced radical cascade cyclization of alkynes with sodium sulfinates for the divergent synthesis of sulfonated benzothiophenes and thioflavones under metal- and photocatalyst-free conditions (Scheme 1d).

## 2. Results and Discussion

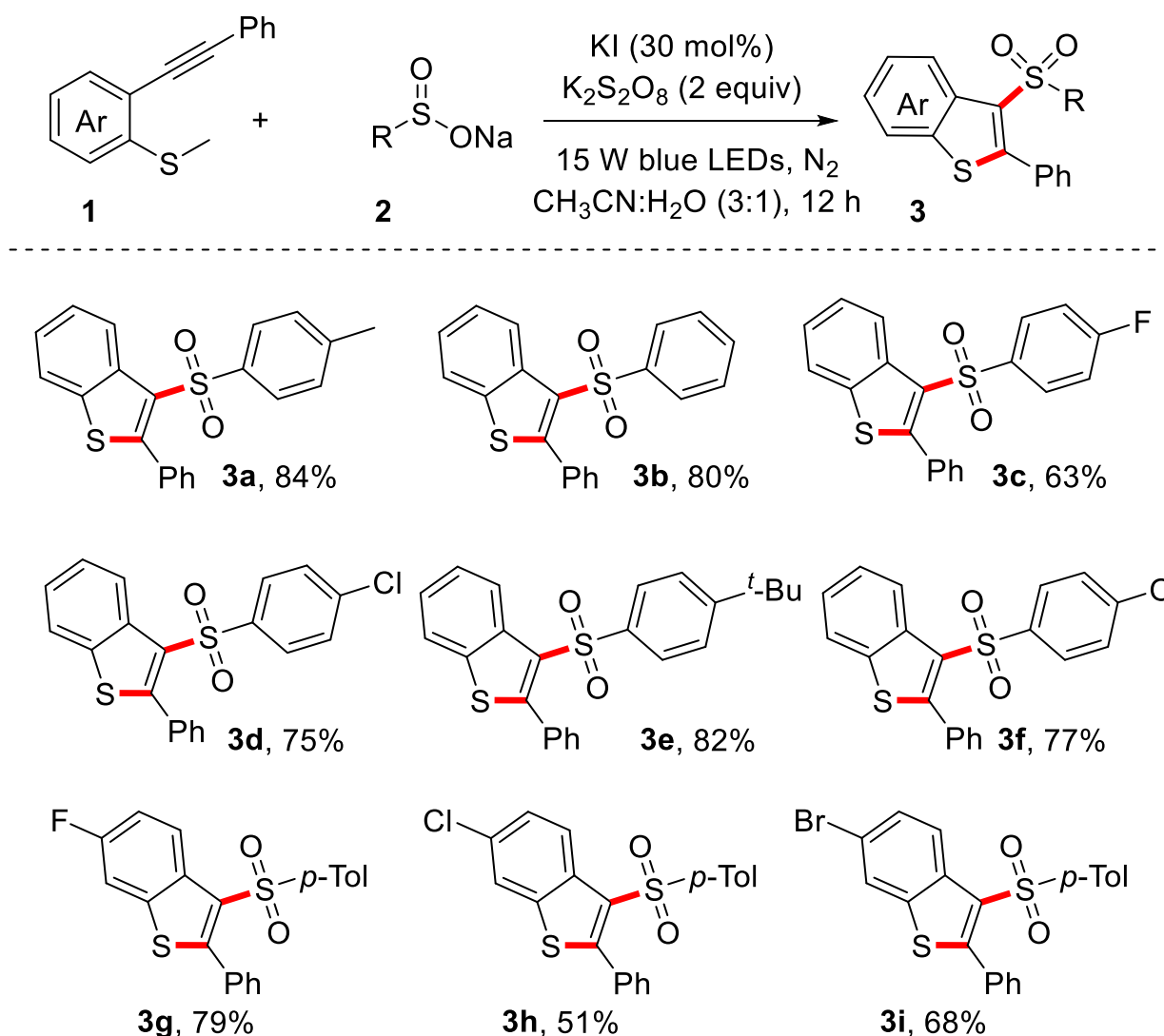
Given these considerations, we set out to study this photoinduced cascade cyclization reaction by the treatment of 4-methylbenzenesulfinate and 2-alkynylthioanisoles in the presence of 15-W blue LED. Thankfully, the desired product benzothiophene **3a** was obtained with 82% yield using  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  as a photocatalyst, KI as an additive, and  $\text{K}_2\text{S}_2\text{O}_8$  as an oxidant (Table 1, entry 1). After the evaluation of various additives such as NaI, NaBr, and KCl, KI was found to be the most effective to promote the reaction (Table 1, Entries 2–4). Then, other oxidants were further investigated, and the yields of the target products were lower than found using  $\text{K}_2\text{S}_2\text{O}_8$  (Table 1, Entries 5–8). We then examined the effect of other photocatalysts to this reaction, including 4CzIPN, 4CzIPN-*t*Bu and Mes-Acr<sup>+</sup>ClO<sub>4</sub> (Table 1, Entries 9–12). It was found that 4CzIPN, 4CzIPN-*t*Bu, and Mes-Acr<sup>+</sup>ClO<sub>4</sub> exhibited a lower catalytic activity than  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  and, to our surprise, the sulfonated benzothiophenes could be obtained with considerable yield in the absence of a photocatalyst. This result shows that a photocatalyst is not essential for this reaction system. Finally, no desired product was observed without the irradiation of 15-W blue LED.

**Table 1.** Optimization of the reaction conditions <sup>a</sup>.

				
Entry	Photocatalyst	Oxidant	Additive	Yield (%) <sup>b</sup>
1	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{K}_2\text{S}_2\text{O}_8$	KI	82
2	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{K}_2\text{S}_2\text{O}_8$	NaI	47
3	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{K}_2\text{S}_2\text{O}_8$	NaBr	29
4	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{K}_2\text{S}_2\text{O}_8$	KCl	35
5	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{Na}_2\text{S}_2\text{O}_8$	KI	67
6	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	$\text{O}_2$	KI	trace
7	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	DTBP	KI	15
8	$[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$	TBHP	KI	23
9	4CzIPN	$\text{K}_2\text{S}_2\text{O}_8$	KI	41
10	4CzIPN- <i>t</i> Bu	$\text{K}_2\text{S}_2\text{O}_8$	KI	47
11	Mes-Acr <sup>+</sup> ClO <sub>4</sub>	$\text{K}_2\text{S}_2\text{O}_8$	KI	65
12	–	$\text{K}_2\text{S}_2\text{O}_8$	KI	84
13	–	$\text{K}_2\text{S}_2\text{O}_8$	–	30
14	–	–	–	24

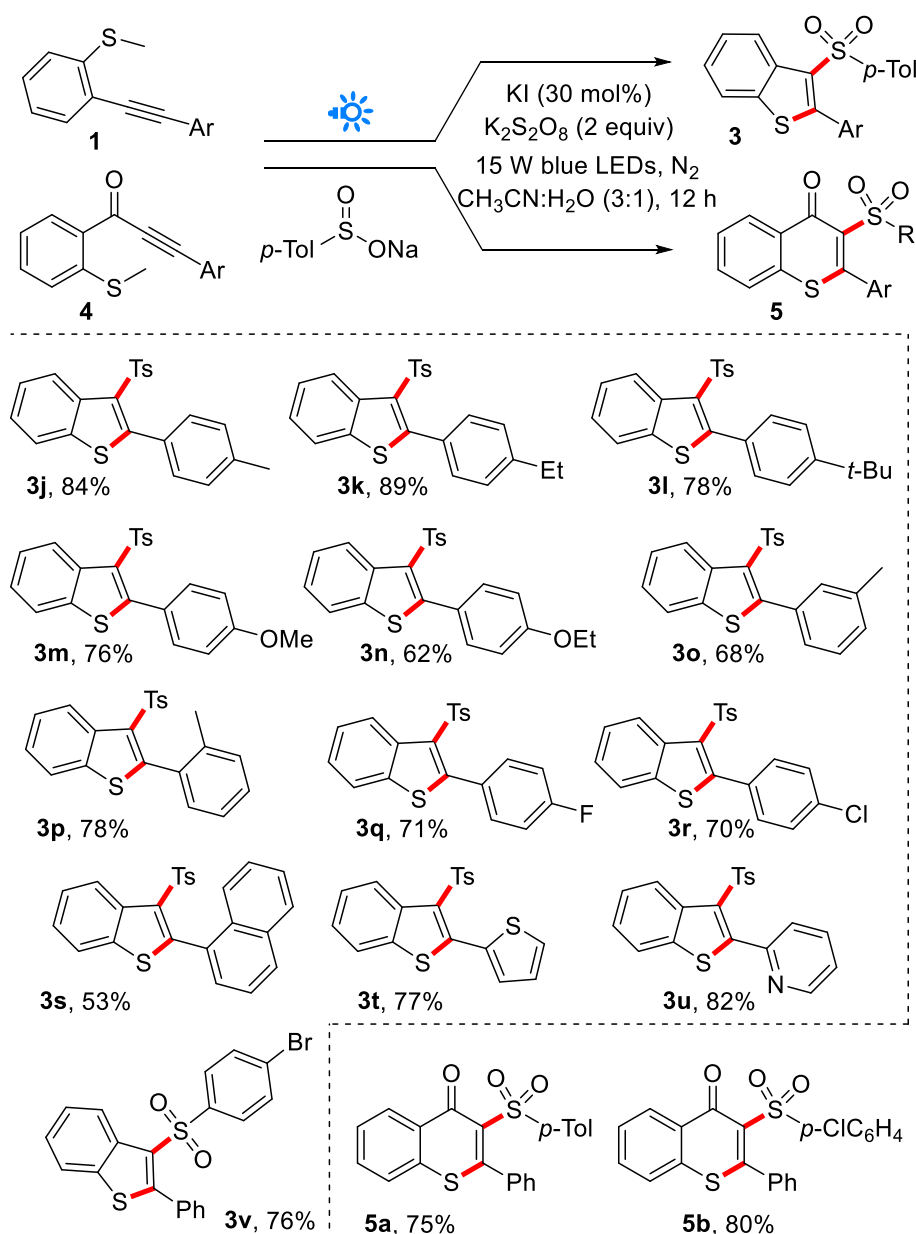
Reaction conditions: <sup>a</sup> **1a** (0.20 mmol), **2a** (0.4 mmol), photocatalyst (1 mol%), additive (30 mol%), oxidant (2 equiv),  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3:1, 2.0 mL),  $\text{N}_2$ , 15-W blue LED at room temperature for 12 h; <sup>b</sup> isolated yield of the product based on **1**, reaction progress is monitored through TLC.

After the standard reaction condition was optimized, we tested a variety of sodium sulfonates to explore the reaction scope, and the results are summarized in Scheme 2. The sodium sulfonates with electron-donating and electron-withdrawing groups on the phenyl ring proceeded through this reaction smoothly. For example, sodium sulfonates containing a halogen group (F or Cl) were all favorable, affording the corresponding products with 63% and 75% yields. In addition, sodium sulfonates containing OMe or OEt were also suitable substrates. As shown in Scheme 2, when sodium sulfonates containing a substituent group on the Ar ring were employed for this transformation, 51–79% yields of the products (**3g–3i**) were obtained.



**Scheme 2.** Substrate scope of sodium sulfonates: **1** (0.20 mmol), sodium sulfonates (**2**, 2.0 equiv), KI (30 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O (3:1, 2.0 mL), N<sub>2</sub>, 15-W blue LED at room temperature for 12 h; isolated yield of the product based on **1**, reaction progress is monitored through TLC.

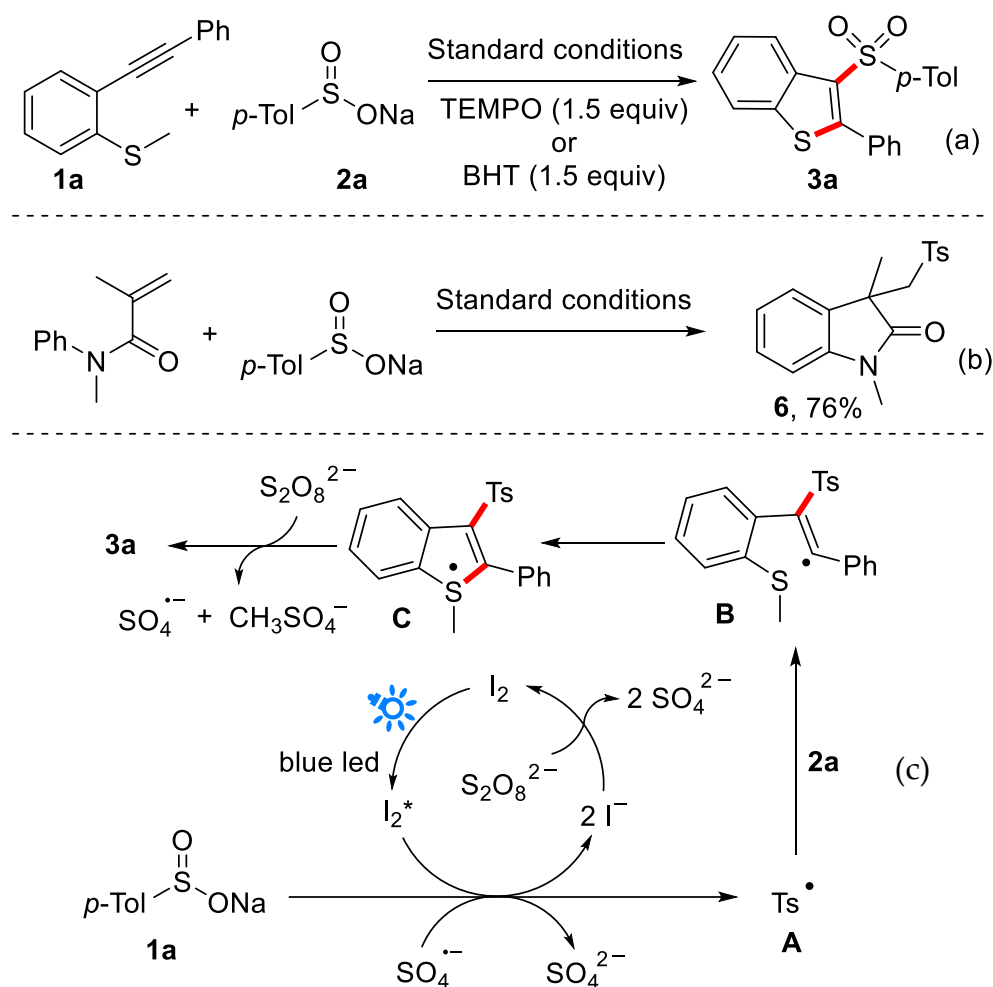
In order to further prove the practicability and efficiency of the photochemical approach, we further expand the substrate scope on 2-alkynylthioanisoles. As shown in Scheme 3, a variety of substituted 2-alkynylthioanisoles could react with 4-methylbenzenesulfonate to produce the corresponding sulfonated benzothiophenes (**3j–3u**) with 53–89% yields. The 2-alkynylthioanisoles bearing strong electron-donating groups on the Ar ring were compatible, affording the corresponding products (**3m** and **3n**) with 76% and 62% yields. Moreover, substrates possessing a heteroaromatic ring, such as pyridine and thiophene, could also undergo the reaction smoothly, generating the corresponding products with reasonable yields (**3t** and **3u**). There is no doubt that the bromine-substituted sodium sulfonate could be successfully transformed into the corresponding product **3v**, which will allow further complex molecule synthesis via cross-coupling reactions. We next examined the alkynes systems to evaluate their applicability to this transformation, synthesizing and applying aryl ynones as cascade substrates to provide sulfonated thioflavones (**5a–5b**) with good yields.



**Scheme 3.** Substrate scope of 2-alkynylthioanisoles: Unless otherwise noted, all reactions were performed with **1** (0.20 mmol), sodium sulfonates (**2**, 2.0 equiv), KI (30 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O (3:1, 2.0 mL), N<sub>2</sub>, 15-W blue LED at room temperature for 12 h; isolated yield of the product based on **1**, reaction progress is monitored through TLC.

In order to elucidate the reaction mechanism of this reaction, a free-radical inhibition experiment was conducted, in which stoichiometric amounts of radical scavengers were added and the reaction was fully suppressed (Scheme 4a). In addition, a well-known free radical acceptor *N*-arylacrylamide, which was widely used in radical tandem reactions, was applied instead of 2-alkynylthioanisoles to give sulfonated oxindole at a 76% yield (Scheme 4b). These results indicated that the free radical process may be involved in this transformation. A plausible reaction mechanism is outlined in Scheme 4 based on the above observations and previous reports [59]. Initially, I<sub>2</sub> is generated from KI by the oxidation of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, which would then transfer to the excited state I<sub>2</sub><sup>\*</sup> with the irradiation of 15-W blue LEDs. Subsequently, the reaction between I<sub>2</sub><sup>\*</sup>, SO<sub>4</sub><sup>•−</sup>, and 4-methylbenzenesulfinate produces a sulfonyl radical, followed by the radical addition of the sulfonyl radical with alkyne in **1a** to give a vinyl radical intermediate. After that, the addition of a vinyl radical

to the sulfur atom produces the intermediate C. Finally, the corresponding cascade product **3a** is obtained via oxidation and demethylation.



**Scheme 4.** The controlled experiments (a,b) and proposed mechanism (c).

### 3. Materials and Methods

#### 3.1. General Information

All reactions were carried out under a nitrogen atmosphere.  $^1\text{H}$  NMR  $^{13}\text{C}$  NMR, and  $^{19}\text{F}$  NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/151 MHz/565 NMR) in  $\text{CDCl}_3$  as solvent and recorded in ppm relative to the internal tetramethylsilane standard.  $^1\text{H}$  NMR data are reported as follows:  $\delta$ , chemical shift; coupling constants ( $J$  are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet). The 15-W blue LED was purchased from [https://item.taobao.com/item.htm?id=524749100016&ali\\_refid=a3\\_430673\\_1006:1121803562:N:FxDVklsg3f08W8u%2BfdnZUtGvFtTT9lsR:af40c0c0536da02c91473a14c4e25edc&ali\\_trackid=1\\_af40c0c0536da02c91473a14c4e25edc&spm=a2e0b.20350158.31919782.21&mt=](https://item.taobao.com/item.htm?id=524749100016&ali_refid=a3_430673_1006:1121803562:N:FxDVklsg3f08W8u%2BfdnZUtGvFtTT9lsR:af40c0c0536da02c91473a14c4e25edc&ali_trackid=1_af40c0c0536da02c91473a14c4e25edc&spm=a2e0b.20350158.31919782.21&mt=) (accessed on 15 May 2023). Due to the fact that the target compound is known, mass spectrometry analysis for compound characterization was not conducted in the article.

#### 3.2. Preparation of the Starting Materials

The 2-alkynylthioanisoles (**1a**) derivatives were prepared according to the reported method [56,60]. The solvents and oxidants including DMF, THF,  $\text{K}_2\text{S}_2\text{O}_8$ , DTBP, etc., were purchased from commercial suppliers including Bidepharm (Shanghai, China); functionalized anilines, photocatalysts, and functionalized aryl sulfonyl chlorides were purchased

from Energy Chemical (Shanghai, China); petroleum ether and ethyl acetate were purchased from Shanghai Chemical Company (Shanghai, China). All solvents were dried and freshly distilled in N<sub>2</sub> prior to use. Products were purified by flash chromatography on a 200–300 mesh silica gel.

### 3.3. General Procedure for the Synthesis of **3a**

A dry 15-mL tube was charged with 2-alkynylthioanisole (**1a**, 0.20 mmol), sodium sulfinates (**2a**, 0.40 mmol), CH<sub>3</sub>CN:H<sub>2</sub>O (3:1, 2 mL), KI (30 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 equiv), and a magnetic stir bar. Then, the mixture was reacted under a 15-W blue LED light at room temperature and a nitrogen atmosphere for 12 hours. After the reaction, the mixture was concentrated to obtain the crude product, and the crude product was further purified by rapid chromatography (silica gel, petroleum ether (PE)/ethyl acetate (EA) = 30/1 to 15/1) to obtain the required product **3a**. The <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra of the products can be found in the Supplementary Materials.

**Product 3a: 2-phenyl-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3a** as a white solid (58 mg, 84% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.62 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.52–7.48 (m, 1H), 7.47–7.43 (m, 1H), 7.43–7.37 (m, 5H), 7.10 (d, J = 8.1 Hz, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 152.5, 143.9, 139.4, 138.2, 136.1, 131.7, 130.5, 130.3, 129.5, 129.4, 127.6, 127.0, 125.9, 125.6, 124.6, 121.8, 21.5.

**Product 3b: 2-phenyl-3-(phenylsulfonyl)benzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford the **3b** as a white solid (56 mg, 80% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.64 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.4, 1.1 Hz, 2H), 7.55–7.51 (m, 1H), 7.48–7.43 (m, 3H), 7.43–7.39 (m, 4H), 7.33 (t, J = 7.9 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 152.9, 142.3, 138.1, 136.2, 132.9, 131.6, 130.5, 130.0, 129.5, 128.7, 127.7, 126.9, 126.0, 125.6, 124.6, 121.7.

**Product 3c: 3-((4-fluorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3c** as a yellow solid (46 mg, 63% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.65 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64–7.59 (m, 2H), 7.56–7.51 (m, 1H), 7.49–7.43 (m, 2H), 7.42–7.38 (m, 4H), 7.01–6.94 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 166.0, 164.3, 152.8, 138.3 (d, J = 3.1 Hz), 138.1, 136.0, 131.4, 130.5, 130.0, 129.8, 129.7 (d, J = 22.7 Hz), 126.9 (d, J = 252.1 Hz), 125.7, 124.5, 121.8, 115.9 (d, J = 22.8 Hz).

**Product 3d: 3-((4-chlorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3d** as a yellow solid (57 mg, 75% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.63 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 8.9 Hz, 3H), 7.50–7.44 (m, 2H), 7.43–7.38 (m, 4H), 7.28 (d, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 153.1, 140.7, 139.5, 138.1, 136.0, 131.4, 130.5, 129.7, 129.6, 129.0, 128.4, 127.7, 126.1, 125.7, 124.5, 121.8.

**Product 3e: 3-((4-(tert-butyl)phenyl)sulfonyl)-2-phenylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3e** as a white solid (66 mg, 82% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.65 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.55–7.52 (m, 1H), 7.47–7.43 (m, 2H), 7.43–7.38 (m, 4H), 7.33 (d, J = 8.6 Hz, 2H), 1.26 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 156.7, 152.4, 139.2, 138.1, 136.2, 131.7, 130.4, 129.4, 127.6, 126.9, 125.9, 125.7, 125.5, 124.7, 121.7, 35.1, 31.0.

**Product 3f: 3-((4-methoxyphenyl)sulfonyl)-2-phenylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–7/1) to afford **3f** as a white solid (58 mg, 77% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.56 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 9.0 Hz, 2H), 7.47–7.43 (m, 1H), 7.41–7.38 (m, 1H), 7.37–7.33 (m, 5H), 6.74–6.69 (m, 2H), 3.71 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 162.1, 151.0, 137.1, 135.0, 133.0, 130.7, 129.7, 129.4, 128.3, 128.2, 126.6, 124.8, 124.5, 123.6, 120.7, 112.9, 54.5.



**Product 3g: 6-fluoro-2-phenyl-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3g** as a brown solid (60 mg, 79% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (dd,  $J$  = 9.2, 5.1 Hz, 1H), 7.50 (d,  $J$  = 8.3 Hz, 2H), 7.48–7.44 (m, 2H), 7.41–7.38 (m, 4H), 7.29–7.24 (m, 1H), 7.12 (d,  $J$  = 8.2 Hz, 2H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.8 (d,  $J$  = 247.7 Hz), 152.0 (d,  $J$  = 3.3 Hz), 144.0, 139.2 (d,  $J$  = 4.4 Hz), 139.1, 132.6, 131.3, 130.5, 130.1, 129.6, 129.4, 127.7, 127.0, 126.1 (d,  $J$  = 8.9 Hz), 114.9 (d,  $J$  = 23.9 Hz), 107.9 (d,  $J$  = 25.4 Hz), 21.5.

**Product 3h: 6-chloro-2-phenyl-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3h** as a white solid (40 mg, 51% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57 (d,  $J$  = 8.9 Hz, 1H), 7.78 (d,  $J$  = 1.9 Hz, 1H), 7.50–7.46 (m, 4H), 7.40 (d,  $J$  = 4.4 Hz, 4H), 7.12 (d,  $J$  = 8.2 Hz, 2H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 144.1, 139.1, 139.1, 134.6, 131.9, 131.2, 130.5, 130.3, 129.6, 129.4, 127.7, 127.0, 126.8, 125.6, 121.3, 21.5.

**Product 3i: 6-bromo-2-phenyl-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3i** as a yellow solid (60 mg, 68% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51 (d,  $J$  = 8.9 Hz, 1H), 7.94 (d,  $J$  = 1.8 Hz, 1H), 7.62 (dd,  $J$  = 8.9, 1.8 Hz, 1H), 7.48 (t,  $J$  = 7.0 Hz, 3H), 7.40 (d,  $J$  = 4.4 Hz, 4H), 7.12 (d,  $J$  = 8.2 Hz, 2H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 144.1, 139.4, 139.1, 135.0, 131.1, 130.5, 130.3, 129.7, 129.4, 129.4, 127.7, 127.0, 125.8, 124.2, 119.7, 21.5.

**Product 3j: 2-(*p*-tolyl)-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3j** as a white solid (63 mg, 84% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59 (d,  $J$  = 8.4 Hz, 1H), 7.76 (d,  $J$  = 8.0 Hz, 1H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.51–7.47 (m, 1H), 7.42–7.37 (m, 1H), 7.33 (d,  $J$  = 8.0 Hz, 2H), 7.21 (d,  $J$  = 7.9 Hz, 2H), 7.12 (d,  $J$  = 8.2 Hz, 2H), 2.43 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.0, 143.8, 139.6, 139.5, 138.1, 136.2, 130.4, 129.9, 129.4, 128.7, 128.4, 127.0, 125.8, 125.5, 124.5, 121.7, 21.5, 21.5.

**Product 3k: 2-(4-ethylphenyl)-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3k** as a white solid (69 mg, 89% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (d,  $J$  = 8.4 Hz, 1H), 7.74 (d,  $J$  = 8.1 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 2H), 7.50–7.46 (m, 1H), 7.40–7.36 (m, 1H), 7.34 (d,  $J$  = 8.1 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 7.09 (d,  $J$  = 8.2 Hz, 2H), 2.71 (q,  $J$  = 7.6 Hz, 2H), 2.29 (s, 3H), 1.29 (t,  $J$  = 7.6 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.9, 145.8, 143.8, 139.5, 138.1, 136.2, 130.5, 130.0, 129.4, 128.9, 127.2, 127.0, 125.8, 125.5, 124.6, 121.7, 28.8, 21.5, 15.4.

**Product 3l: 2-(4-(*tert*-butyl)phenyl)-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3l** as a white solid (65 mg, 78% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (d,  $J$  = 8.3 Hz, 1H), 7.78 (d,  $J$  = 8.0 Hz, 1H), 7.52–7.48 (m, 3H), 7.43–7.37 (m, 3H), 7.36–7.32 (m, 2H), 7.08 (d,  $J$  = 8.1 Hz, 2H), 2.31 (s, 3H), 1.38 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 152.6, 143.6, 139.4, 138.1, 136.3, 130.2, 130.0, 129.2, 128.6, 127.1, 125.8, 125.4, 124.6, 124.6, 121.7, 34.8, 31.3, 21.5.

**Product 3m: 2-(4-methoxyphenyl)-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–7/1) to afford **3m** as a white solid (59 mg, 76% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J$  = 8.4 Hz, 1H), 7.77 (d,  $J$  = 8.0 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 2H), 7.52–7.47 (m, 1H), 7.42–7.36 (m, 3H), 7.12 (d,  $J$  = 8.2 Hz, 2H), 6.93 (d,  $J$  = 8.7 Hz, 2H), 3.88 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.6, 152.8, 143.8, 139.5, 138.0, 136.3, 131.9, 129.8, 129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.1, 55.4, 21.5.

**Product 3n: 2-(4-ethoxyphenyl)-3-tosylbenzo[b]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–7/1) to afford **3n** as a white solid (50 mg, 62% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (d,  $J$  = 8.3 Hz, 1H), 7.77 (d,  $J$  = 8.0 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 2H), 7.52–7.47 (m, 1H), 7.42–7.38 (m, 1H), 7.38–7.34 (m, 2H), 7.12 (d,  $J$  = 8.1 Hz, 2H), 6.94–6.89 (m, 2H), 4.10 (q,  $J$  = 7.0 Hz, 2H), 2.32 (s,



3H), 1.46 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 153.0, 143.7, 139.6, 138.0, 136.3, 131.9, 129.7, 129.3, 126.9, 125.8, 125.4, 124.5, 123.5, 121.6, 113.6, 63.6, 21.5, 14.8.

**Product 3o: 2-(*m*-tolyl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3o** as a white solid (51 mg, 68% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (d,  $J = 8.4$  Hz, 1H), 7.79 (d,  $J = 8.1$  Hz, 1H), 7.55 (d,  $J = 8.3$  Hz, 2H), 7.54–7.50 (m, 1H), 7.45–7.40 (m, 1H), 7.29 (dd,  $J = 14.9, 7.5$  Hz, 2H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.17–7.11 (m, 3H), 2.38 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 143.8, 139.5, 138.1, 137.2, 136.2, 131.5, 131.0, 130.2, 130.1, 129.3, 127.5, 127.1, 125.8, 125.5, 124.6, 121.7, 21.5, 21.3.

**Product 3p: 2-(*o*-tolyl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3p** as a white solid (58 mg, 78% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66 (d,  $J = 8.3$  Hz, 1H), 7.81 (d,  $J = 8.1$  Hz, 1H), 7.54 (t,  $J = 8.4$  Hz, 3H), 7.47–7.42 (m, 1H), 7.37 (td,  $J = 7.6, 1.1$  Hz, 1H), 7.22 (dd,  $J = 14.7, 7.2$  Hz, 2H), 7.17–7.12 (m, 3H), 2.35 (s, 3H), 2.08 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.6, 144.0, 139.2, 138.5, 138.1, 135.8, 131.2, 131.0, 130.2, 129.8, 129.6, 129.4, 127.3, 125.8, 125.5, 124.9, 124.5, 121.8, 21.5, 20.2.

**Product 3q: 2-(4-fluorophenyl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3q** as a yellow solid (54 mg, 71% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (d,  $J = 8.4$  Hz, 1H), 7.80 (d,  $J = 8.1$  Hz, 1H), 7.53 (t,  $J = 8.0$  Hz, 3H), 7.43 (m,  $J = 8.6, 6.7, 1.4$  Hz, 3H), 7.15 (d,  $J = 8.2$  Hz, 2H), 7.10 (t,  $J = 8.6$  Hz, 2H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.7, 151.2, 144.0, 139.3, 138.0, 136.0, 132.4 (d,  $J = 8.4$  Hz), 130.6, 129.4, 127.6, 126.9, 126.0, 125.7, 124.6, 121.7, 114.8 (d,  $J = 21.9$  Hz), 21.5.

**Product 3r: 2-(4-chlorophenyl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 30/1–15/1) to afford **3r** as a yellow solid (55 mg, 70% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 8.4$  Hz, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.55 (t,  $J = 5.8$  Hz, 2H), 7.54–7.51 (m, 1H), 7.46–7.42 (m, 1H), 7.40–7.36 (m, 4H), 7.16 (d,  $J = 8.2$  Hz, 2H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.8, 144.1, 139.3, 138.1, 136.0, 135.8, 131.8, 130.7, 130.1, 129.5, 127.9, 127.0, 126.0, 125.8, 124.6, 121.7, 21.5.

**Product 3s: 2-(naphthalen-1-yl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–7/1) to afford **3s** as a yellow solid (43 mg, 53% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 8.4$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.54 (d,  $J = 8.3$  Hz, 2H), 7.51–7.46 (m, 1H), 7.38 (m,  $J = 8.7, 7.4, 1.6$  Hz, 3H), 7.11 (d,  $J = 8.2$  Hz, 2H), 6.94–6.90 (m, 2H), 3.86 (s, 3H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.6, 152.9, 143.8, 139.6, 138.0, 136.3, 131.9, 131.4, 130.4, 129.8, 129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.2, 55.4, 53.5, 31.4, 30.2, 21.5.

**Product 3t: 2-(thiophen-2-yl)-3-tosylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **3t** as a yellow solid (56 mg, 77% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.67 (d,  $J = 8.4$  Hz, 1H), 7.77 (d,  $J = 8.1$  Hz, 1H), 7.59 (d,  $J = 8.3$  Hz, 2H), 7.53–7.49 (m, 3H), 7.44–7.40 (m, 1H), 7.17–7.11 (m, 3H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6, 143.9, 139.1, 138.2, 136.5, 132.2, 131.0, 130.7, 129.4, 129.3, 127.4, 126.9, 126.0, 125.8, 124.8, 121.5, 21.5.

**Product 3u: 2-(3-tosylbenzo[*b*]thiophen-2-yl)pyridine.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **3u** as a white solid (59 mg, 82% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.71–8.68 (m, 1H), 8.45 (d,  $J = 8.3$  Hz, 1H), 7.85–7.79 (m, 5H), 7.51–7.46 (m, 1H), 7.43–7.40 (m, 1H), 7.40–7.37 (m, 1H), 7.20 (d,  $J = 8.2$  Hz, 2H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.1, 150.8, 149.0, 144.0, 138.9, 138.6, 135.8, 135.6, 130.3, 129.6, 127.3, 126.9, 125.9, 125.9, 124.5, 123.9, 122.0, 21.5.

**Product 3v: 3-((4-bromophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **3v** as a white solid (65 mg, 76% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.62 (d,

J = 6 Hz, 1H), 7.81 (d, J = 6 Hz, 1H), 7.55–7.53 (m, 1H), 7.48–7.43 (m, 6H), 7.42–7.39 (m, 4H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 153.1, 141.2, 138.1, 136.0, 132.7, 132.0, 131.4, 130.5, 129.7, 128.5, 128.1, 127.7, 126.1, 125.7, 124.5, 121.8.

**Product 5a: 2-phenyl-3-tosyl-4H-thiochromen-4-one.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **5a** as a white solid (58 mg, 75% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.20 (d, J = 7.9 Hz, 1H), 7.84–7.73 (m, 2H), 7.61–7.54 (m, 1H), 7.52–7.34 (m, 7H), 7.19 (d, J = 7.7 Hz, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 175.9, 162.4, 144.0, 138.9, 135.7, 134.9, 132.8, 132.5, 131.6, 130.1, 128.9, 128.7, 128.5, 128.0, 127.9, 125.3, 21.3.

**Product 5b: 3-((4-chlorophenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **5b** as a yellow solid (66 mg, 80% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.28 (dd, J = 8.1, 1.0 Hz, 1H), 7.91–7.86 (m, 2H), 7.58 (td, J = 8.0, 1.4 Hz, 1H), 7.50–7.42 (m, 7H), 7.38–7.34 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 176.0, 163.2, 140.2, 139.6, 135.7, 134.5, 132.7, 132.6, 131.6, 130.5, 130.3, 129.2, 128.9, 128.7, 128.2, 128.1, 125.3.

**Product 6: 1,3-dimethyl-3-(tosylmethyl)indolin-2-one.** The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt: 15/1–5/1) to afford **6** as a white solid (50 mg, 76% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.38–7.37 (m, 2H), 7.30–7.27 (m, 1H), 7.16 (d, J = 6 Hz, 2H), 7.07 (d, J = 6 Hz, 1H), 6.93–6.90 (m, 1H), 6.84 (d, J = 6 Hz, 1H), 3.85 (d, J = 12 Hz, 1H), 3.67 (d, J = 18 Hz, 1H), 3.16 (s, 3H), 2.39 (s, 3H), 1.38 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 177.6, 144.3, 143.2, 137.0, 129.6, 129.5, 128.5, 127.8, 124.1, 122.4, 108.3, 61.9, 45.6, 26.5, 25.5, 21.5.

#### 4. Conclusions

In summary, we have reported a straightforward strategy for the synthesis of sulfonated benzothiophenes and thioflavones from 2-alkynylthioanisoles and sodium sulfonates via visible-light-induced cascade cyclization reaction under metal- and photocatalyst-free conditions. This approach features good functional group tolerance, simple operation, and mild conditions. The further synthetic application of this strategy is underway in our laboratory.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28114436/s1>. References [61–64] are cited in the supplementary materials.

**Author Contributions:** H.D. and C.C. performed the experiments, and J.Z. analyzed the data. Y.J. and W.Y. conceived the concept, and the manuscript was written through contributions of all authors. All authors have read and agreed to the published version of the manuscript.

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#### References

- Xie, L.-Y.; Peng, S.; Liu, F.; Chen, G.-R.; Xia, W.; Yu, X.; Li, W.-F.; Cao, Z.; He, W.-M. Metal-free deoxygenative sulfonylation of quinoline N-oxides with sodium sulfonates via a dual radical coupling process. *Org. Chem. Front.* **2018**, *5*, 2604–2609. [CrossRef]
- Sun, K.; Shi, Z.; Liu, Z.; Luan, B.; Zhu, J.; Xue, Y. Synthesis of (E)-β-Selenovinyl Sulfones through a Multicomponent Regio- and Stereospecific Selenosulfonation of Alkynes with Insertion of Sulfur Dioxide. *Org. Lett.* **2018**, *20*, 6687–6690. [CrossRef] [PubMed]

3. Wang, L.; Zhang, M.; Zhang, Y.; Liu, Q.; Zhao, X.; Li, J.-S.; Luo, Z.; Wei, W. Metal-free visible-light-induced oxidative cyclization reaction of 1, 6-enynes and arylsulfonic acids leading to sulfonylated benzofurans. *Chin. Chem. Lett.* **2020**, *31*, 67–70. [\[CrossRef\]](#)
4. Li, G.-H.; Han, Q.-Q.; Sun, Y.-Y.; Chen, D.-M.; Wang, Z.-L.; Xu, X.-M.; Yu, X.-Y. Visible-light induced cascade radical cyclization of sulfonic acids and o-(allyloxy) arylaldehydes towards functionalized chroman-4-ones. *Chin. Chem. Lett.* **2020**, *31*, 3255–3258. [\[CrossRef\]](#)
5. Yang, W.C.; Feng, J.G.; Wu, L.; Zhang, Y.Q. Aliphatic Aldehydes: Novel Radical Alkylating Reagents. *Adv. Synth. Catal.* **2019**, *361*, 1700–1709. [\[CrossRef\]](#)
6. McReynolds, M.D.; Dougherty, J.M.; Hanson, P.R. Synthesis of phosphorus and sulfur heterocycles via ring-closing olefin metathesis. *Chem. Rev.* **2004**, *104*, 2239–2258. [\[CrossRef\]](#)
7. Liu, Q.; Lv, Y.; Liu, R.; Zhao, X.; Wang, J.; Wei, W. Catalyst-and additive-free selective sulfonylation/cyclization of 1, 6-enynes with arylazo sulfones leading to sulfonylated  $\gamma$ -butyrolactams. *Chin. Chem. Lett.* **2021**, *32*, 136–139. [\[CrossRef\]](#)
8. Xie, L.-Y.; Peng, S.; Tan, J.-X.; Sun, R.-X.; Yu, X.; Dai, N.-N.; Tang, Z.-L.; Xu, X.; He, W.-M. Waste-minimized protocol for the synthesis of sulfonylated N-heteroaromatics in water. *ACS Sustain. Chem. Eng.* **2018**, *6*, 16976–16981. [\[CrossRef\]](#)
9. Wang, Z.; Liu, Q.; Liu, R.; Ji, Z.; Li, Y.; Zhao, X.; Wei, W. Visible-light-initiated 4CzIPN catalyzed multi-component tandem reactions to assemble sulfonated quinoxalin-2 (1H)-ones. *Chin. Chem. Lett.* **2022**, *33*, 1479–1482. [\[CrossRef\]](#)
10. Yang, W.; Yang, S.; Li, P.; Wang, L. Visible-light initiated oxidative cyclization of phenyl propiolates with sulfonic acids to coumarin derivatives under metal-free conditions. *Chem. Commun.* **2015**, *51*, 7520–7523. [\[CrossRef\]](#)
11. Wang, N.; Saidharedy, P.; Jiang, X. Construction of sulfur-containing moieties in the total synthesis of natural products. *Nat. Prod. Rep.* **2020**, *37*, 246–275. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Devendar, P.; Yang, G.-F. Sulfur-containing agrochemicals. In *Sulfur Chemistry*; Springer: Berlin/Heidelberg, Germany, 2019; pp. 35–78.
13. Lu, Y.-H.; Zhang, Z.-T.; Wu, H.-Y.; Zhou, M.-H.; Song, H.-Y.; Ji, H.-T.; Jiang, J.; Chen, J.-Y.; He, W.-M. TBAI/H<sub>2</sub>O-cooperative electrocatalytic decarboxylation coupling-annulation of quinoxalin-2 (1H)-ones with N-arylglycines. *Chin. Chem. Lett.* **2022**, *34*, 108036. [\[CrossRef\]](#)
14. Zhu, C.; Cai, Y.; Jiang, H. Recent advances for the synthesis of chiral sulfones with the sulfone moiety directly connected to the chiral center. *Org. Chem. Front.* **2021**, *8*, 5574–5589. [\[CrossRef\]](#)
15. Yuxi, Z.; Ting, X.; Dong, X.; Wenchao, Y. Recent Advances in the Decarboxylative Fluoroalkylation of Fluoroalkyl Carboxylic Acids. *Chin. J. Org. Chem.* **2022**, *42*, 4067.
16. Wanwan, W.; Mingming, Z.; Wenchao, Y.; Xiaohu, Y. Research Progress in Radical Cascade Reaction Using Nitrogen Heterocycle in Indoles as Radical Acceptors. *Chin. J. Org. Chem.* **2022**, *42*, 75.
17. Li, D.; Yang, W. Copper-catalyzed regioselective alkylation of heteroarenes with functionalized alkyl halides. *Tetrahedron Lett.* **2019**, *60*, 1792–1795. [\[CrossRef\]](#)
18. Wei, W.; Cui, H.; Yang, D.; Yue, H.; He, C.; Zhang, Y.; Wang, H. Visible-light-enabled spirocyclization of alkynes leading to 3-sulfonyl and 3-sulfonyl azaspiro [4, 5] trienones. *Green Chem.* **2017**, *19*, 5608–5613. [\[CrossRef\]](#)
19. Yun, S.; Ting, X.; Dong, X.; Wenchao, Y. SCF3 Radical Initiated Cascade Reaction of Unsaturated Hydrocarbon. *Chin. J. Org. Chem.* **2022**, *42*, 2715.
20. Yang, W.C.; Zhang, M.M.; Feng, J.G. Recent advances in the construction of spiro compounds via radical dearomatization. *Adv. Synth. Catal.* **2020**, *362*, 4446–4461. [\[CrossRef\]](#)
21. Huang, M.-H.; Hao, W.-J.; Li, G.; Tu, S.-J.; Jiang, B. Recent advances in radical transformations of internal alkynes. *Chem. Commun.* **2018**, *54*, 10791–10811. [\[CrossRef\]](#)
22. Sun, K.; Wang, X.; Li, C.; Wang, H.; Li, L. Recent advances in tandem selenocyclization and tellurocyclization with alkenes and alkynes. *Org. Chem. Front.* **2020**, *7*, 3100–3119. [\[CrossRef\]](#)
23. Chen, J.-Y.; Huang, J.; Sun, K.; He, W.-M. Recent advances in transition-metal-free trifluoromethylation with Togni's reagents. *Org. Chem. Front.* **2022**, *9*, 1152–1164. [\[CrossRef\]](#)
24. Sun, K.; Lv, Q.-Y.; Chen, X.-L.; Qu, L.-B.; Yu, B. Recent advances in visible-light-mediated organic transformations in water. *Green Chem.* **2021**, *23*, 232–248. [\[CrossRef\]](#)
25. Liang, S.; Hofman, K.; Friedrich, M.; Keller, J.; Manolikakes, G. Recent progress and emerging technologies towards a sustainable synthesis of sulfones. *ChemSusChem* **2021**, *14*, 4878–4902. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Matavos-Aramyan, S.; Soukhakian, S.; Jazebizadeh, M.H. Selected methods for the synthesis of sulfoxides and sulfones with emphasis on oxidative protocols. *Phosphorus Sulfur Silicon Relat. Elem.* **2020**, *195*, 181–193. [\[CrossRef\]](#)
27. Zhu, J.; Yang, W.C.; Wang, X.d.; Wu, L. Photoredox Catalysis in C–S Bond Construction: Recent Progress in Photo-Catalyzed Formation of Sulfones and Sulfoxides. *Adv. Synth. Catal.* **2018**, *360*, 386–400. [\[CrossRef\]](#)
28. Dong, D.Q.; Chen, W.J.; Yang, Y.; Gao, X.; Wang, Z.L. Merrifield Resin Supported Ionic Liquids/Iodide as an Efficient and Recyclable Catalyst for the Synthesis of Benzimidazoles. *ChemistrySelect* **2019**, *4*, 2480–2483. [\[CrossRef\]](#)
29. Lv, Y.; Cui, H.; Meng, N.; Yue, H.; Wei, W. Recent advances in the application of sulfonic acids for the construction of sulfur-containing compounds. *Chin. Chem. Lett.* **2022**, *33*, 97–114. [\[CrossRef\]](#)
30. Wei, W.; Bao, P.; Yue, H.; Liu, S.; Wang, L.; Li, Y.; Yang, D. Visible-light-enabled construction of thiocarbamates from isocyanides, thiols, and water at room temperature. *Org. Lett.* **2018**, *20*, 5291–5295. [\[CrossRef\]](#)

31. Jiang, Y.Q.; Li, J.; Feng, Z.W.; Xu, G.Q.; Shi, X.; Ding, Q.J.; Li, W.; Ma, C.H.; Yu, B. Ethylene Glycol: A Green Solvent for Visible Light-Promoted Aerobic Transition Metal-Free Cascade Sulfonation/Cyclization Reaction. *Adv. Synth. Catal.* **2020**, *362*, 2609–2614. [\[CrossRef\]](#)
32. Dong, W.; Fang, Z.-Y.; Cao, T.-Y.; Cao, J.-H.; Zhao, Z.-Q.; Zhang, L.; Li, W.; Qi, L.; Wang, L.-J. Copper-catalyzed aminosulfonylation of O-homoallyl benzimidates with sodium sulfinates to access sulfonylated 1, 3-oxazines. *Org. Lett.* **2021**, *23*, 5809–5814. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Li, Y.; Miao, T.; Li, P.; Wang, L. Photo-driven synthesis of C6-polyfunctionalized phenanthridines from three-component reactions of isocyanides, alkynes, and sulfinic acids by electron donor–acceptor complex. *Org. Lett.* **2018**, *20*, 1735–1739. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Sun, K.; Chen, X.-L.; Zhang, Y.-L.; Li, K.; Huang, X.-Q.; Peng, Y.-Y.; Qu, L.-B.; Yu, B. Metal-free sulfonyl radical-initiated cascade cyclization to access sulfonated indolo [1, 2-a] quinolines. *Chem. Commun.* **2019**, *55*, 12615–12618. [\[CrossRef\]](#)
35. Meng, X.; Xu, H.; Cao, X.; Cai, X.-M.; Luo, J.; Wang, F.; Huang, S. Electrochemically enabled sulfonylation of alkynes with sodium sulfinates. *Org. Lett.* **2020**, *22*, 6827–6831. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Meng, X.-X.; Kang, Q.-Q.; Zhang, J.-Y.; Li, Q.; Wei, W.-T.; He, W.-M. Visible-light-initiated regioselective sulfonylation/cyclization of 1, 6-enynes under photocatalyst-and additive-free conditions. *Green Chem.* **2020**, *22*, 1388–1392. [\[CrossRef\]](#)
37. Xie, L.-Y.; Fang, T.-G.; Tan, J.-X.; Zhang, B.; Cao, Z.; Yang, L.-H.; He, W.-M. Visible-light-induced deoxygenative C2-sulfonylation of quinoline N-oxides with sulfinic acids. *Green Chem.* **2019**, *21*, 3858–3863. [\[CrossRef\]](#)
38. Wang, L.-J.; Chen, J.-M.; Dong, W.; Hou, C.-Y.; Pang, M.; Jin, W.-B.; Dong, F.-G.; Xu, Z.-D.; Li, W. Synthesis of Sulfonylated Lactams by Copper-Mediated Aminosulfonylation of 2-Vinylbenzamides with Sodium Sulfinates. *J. Org. Chem.* **2019**, *84*, 2330–2338. [\[CrossRef\]](#)
39. Wang, L.-J.; Chen, M.; Qi, L.; Xu, Z.; Li, W. Copper-mediated oxysulfonylation of alkenyl oximes with sodium sulfinates: A facile synthesis of isoxazolines featuring a sulfone substituent. *Chem. Commun.* **2017**, *53*, 2056–2059. [\[CrossRef\]](#)
40. Reddy, R.J.; Kumari, A.H. Synthesis and applications of sodium sulfinates (RSO<sub>2</sub>Na): A powerful building block for the synthesis of organosulfur compounds. *RSC Adv.* **2021**, *11*, 9130–9221. [\[CrossRef\]](#)
41. Ye, X.; Wu, X.; Guo, S.-r.; Huang, D.; Sun, X. Recent advances of sodium sulfinates in radical reactions. *Tetrahedron Lett.* **2021**, *81*, 153368. [\[CrossRef\]](#)
42. Tang, J.; Sivaguru, P.; Ning, Y.; Zaroni, G.; Bi, X. Silver-Catalyzed Tandem C≡C Bond Hydroazidation/Radical Addition/Cyclization of Biphenyl Acetylene: One-Pot Synthesis of 6-Methyl Sulfonylated Phenanthridines. *Org. Lett.* **2017**, *19*, 4026–4029. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Wu, W.; Yi, S.; Huang, W.; Luo, D.; Jiang, H. Ag-catalyzed oxidative cyclization reaction of 1, 6-enynes and sodium sulfinate: Access to sulfonylated benzofurans. *Org. Lett.* **2017**, *19*, 2825–2828. [\[CrossRef\]](#)
44. Dong, W.; Qi, L.; Song, J.-Y.; Chen, J.-M.; Guo, J.-X.; Shen, S.; Li, L.-J.; Li, W.; Wang, L.-J. Direct synthesis of sulfonylated spiro [indole-3, 3'-pyrrolidines] by silver-mediated sulfonylation of acrylamides coupled with indole dearomatization. *Org. Lett.* **2020**, *22*, 1830–1835. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Yang, D.; Yan, Q.; Zhu, E.; Lv, J.; He, W.-M. Carbon–sulfur bond formation via photochemical strategies: An efficient method for the synthesis of sulfur-containing compounds. *Chin. Chem. Lett.* **2022**, *33*, 1798–1816. [\[CrossRef\]](#)
46. Huo, J.; Geng, X.; Li, W.; Zhang, P.; Wang, L. A Traceless Heterocyclic Amine Mediator in Regioselectivity– Switchable Formal [1+ 2+ 2] Cycloaddition Reaction to 1, 3, 4-and 1, 4, 5-Trisubstituted Pyrazoles. *Org. Lett.* **2023**, *25*, 512–516. [\[CrossRef\]](#)
47. Wan, Q.; Hou, Z.-W.; Zhao, X.-R.; Xie, X.; Wang, L. Organoelectrophotocatalytic C–H Silylation of Heteroarenes. *Org. Lett.* **2023**, *25*, 1008–1013. [\[CrossRef\]](#)
48. Wang, Z.; Sun, Y.; Shen, L.-Y.; Yang, W.-C.; Meng, F.; Li, P. Photochemical and electrochemical strategies in C–F bond activation and functionalization. *Org. Chem. Front.* **2022**, *9*, 853–873. [\[CrossRef\]](#)
49. Romero, N.A.; Nicewicz, D.A. Organic photoredox catalysis. *Chem. Rev.* **2016**, *116*, 10075–10166. [\[CrossRef\]](#)
50. Yoon, T.P. Photochemical stereocontrol using tandem photoredox–chiral Lewis acid catalysis. *Acc. Chem. Res.* **2016**, *49*, 2307–2315. [\[CrossRef\]](#)
51. Prier, C.K.; Rankic, D.A.; MacMillan, D.W. Visible light photoredox catalysis with transition metal complexes: Applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322–5363. [\[CrossRef\]](#)
52. Wang, Z.; Wang, L.; Wang, Z.; Li, P.; Zhang, Y. A practical synthesis of  $\alpha$ -bromo/iodo/chloroketones from olefins under visible-light irradiation conditions. *Chin. Chem. Lett.* **2021**, *32*, 429–432. [\[CrossRef\]](#)
53. Yang, W.-C.; Zhang, M.-M.; Sun, Y.; Chen, C.-Y.; Wang, L. 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. [\[CrossRef\]](#)
54. Yang, W.-C.; Sun, Y.; Shen, L.-Y.; Xie, X.; Yu, B. Photoinduced cyclization of aryl ynones with 4-alkyl-DHPs for the divergent synthesis of indenones, thioflavones and spiro [5.5] trienones. *Mol. Catal.* **2023**, *535*, 112819. [\[CrossRef\]](#)
55. Yang, W.-C.; Shen, L.-Y.; Li, J.-N.; Feng, J.-G.; Li, P. Oxidative Cyclization of Aryl Ynones with NaNO<sub>2</sub> for the Divergent Synthesis of NO<sub>2</sub>-Containing Spiro [5.5] trienones, Indenones and Thioflavones. *Adv. Synth. Catal.* **2022**, *364*, 3651–3656. [\[CrossRef\]](#)
56. Zhang, M.-M.; Sun, Y.; Wang, W.-W.; Chen, K.-K.; Yang, W.-C.; Wang, L. Electrochemical synthesis of sulfonated benzothiophenes using 2-alkynylthioanisoles and sodium sulfinates. *Org. Biomol. Chem.* **2021**, *19*, 3844–3849. [\[CrossRef\]](#)

57. Zhang, M.M.; Shen, L.Y.; Dong, S.; Li, B.; Meng, F.; Si, W.J.; Yang, W.C. DTBP-Mediated Cascade Spirocyclization and Dearomatization of Biaryl Ynones: Facile Access to Spiro [5.5] trienones through C (sp<sup>3</sup>)–H Bond Functionalization. *Eur. J. Org. Chem.* **2021**, 2021, 4465–4468. [[CrossRef](#)]
58. Feng, J.; Chen, W.; Liu, Q.; Chen, Z.; Yang, J.; Yang, W. Development of abamectin-loaded nanoemulsion and its insecticidal activity and cytotoxicity. *Pest Manag. Sci.* **2020**, 76, 4192–4201. [[CrossRef](#)]
59. Liu, Y.; Lin, L.; Han, Y.; Liu, Y. Application of iodine and iodide in photocatalysis organic synthesis. *Chin. J. Org. Chem.* **2020**, 40, 4216. [[CrossRef](#)]
60. Yang, W.; Sun, Y.; Bao, X.; Zhang, S.; Shen, L. A general electron donor–acceptor complex enabled cascade cyclization of alkynes to access sulfur-containing heterocycle. *Green Chem.* **2023**, 25, 3111–3116. [[CrossRef](#)]
61. Xu, J.; Yu, X.; Yan, J.; Song, Q. Synthesis of 3-(arylsulfonyl) benzothiophenes and benzoselenophenes via TBHP-initiated radical cyclization of 2-alkynylthioanisoles or-selenoanisoles with sulfinic acids. *Org. Lett.* **2017**, 19, 6292–6295. [[CrossRef](#)]
62. Yan, J.; Xu, J.; Zhou, Y.; Chen, J.; Song, Q. A facile synthesis of diverse 5-arylated triazoles via a Cu-catalyzed oxidative interrupted click reaction with arylboronic acids in air. *Org. Chem. Front.* **2018**, 5, 1483–1487. [[CrossRef](#)]
63. Zhang, D.; Cai, J.; Du, J.; Wang, X.; He, W.; Yang, Z.; Liu, C.; Fang, Z.; Guo, K. Oxidant-and Catalyst-Free Synthesis of Sulfonated Benzothiophenes via Electrooxidative Tandem Cyclization. *J. Org. Chem.* **2021**, 86, 2593–2601. [[CrossRef](#)] [[PubMed](#)]
64. Liu, W.; Hu, Y.-Q.; Hong, X.-Y.; Li, G.-X.; Huang, X.-B.; Gao, W.-X.; Liu, M.-C.; Xia, Y.; Zhou, Y.-B.; Wu, H.-Y. Direct synthesis of 3-acylbenzothiophenes via the radical cyclization of 2-alkynylthioanisoles with  $\alpha$ -oxocarboxylic acids. *Chem. Commun.* **2018**, 54, 14148–14151. [[CrossRef](#)] [[PubMed](#)]

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