JOC The Journal of Organic Chemistry

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Synthesis of 3-Sulfenylated Coumarins: BF_3·Et_2O-Mediated Electrophilic Cyclization of Aryl Alkynoates Using *N*-Sulfanylsuccinimides

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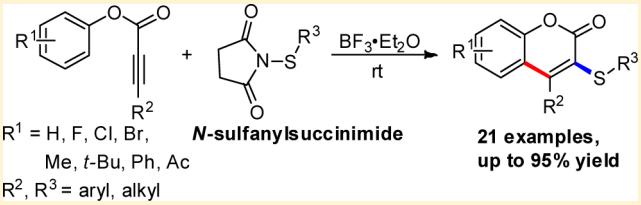
Supporting Information

ABSTRACT: A simple and efficient metal-free sulfenylation/cyclization of aryl alkynoates has been developed, obtaining various 3-sulfenylated coumarins in moderate to excellent yields. In the presence of BF_3·Et_2O, the stable and readily accessible *N*-sulfanylsuccinimides were employed as electrophiles to induce the 6-*endo*-*dig* electrophilic cyclization of alkynoates. The reaction using substrates bearing a methoxy group on the phenoxy ring proceeded in an exclusively distinct pathway via either *ipso* sulfenylcyclization or sulfenylation of the phenoxy ring depending on the different locations of the methoxy substituent. The resulting 3-sulfenylated coumarins can be readily transformed to 3-sulfinylated or 3-sulfonylated coumarins under different oxidation conditions.



INTRODUCTION

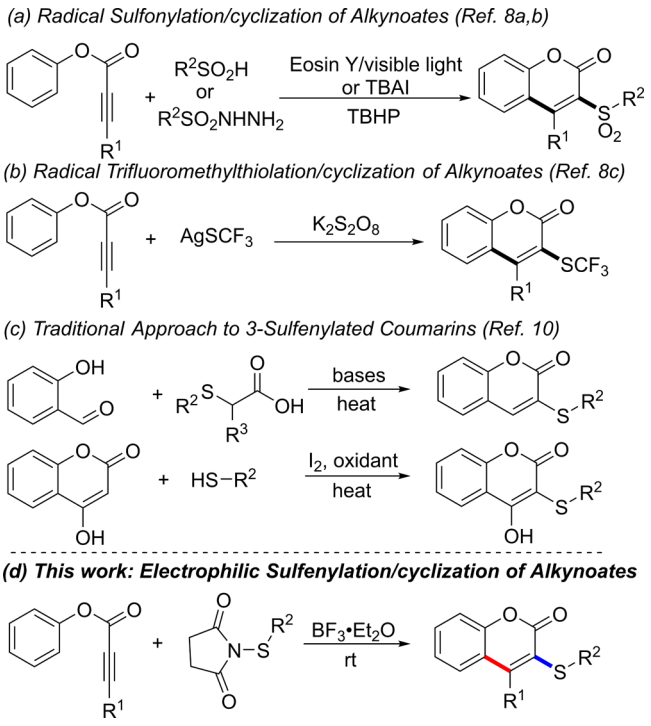
Electrophilic cyclization of alkynes has been considered to be one of the most powerful methods to form heteroatom- or carbon-tethered cycles efficiently in one step.[1] Among such reactions, electrophilic halocyclization of alkynes containing heteroatoms has been intensively studied because the resulting heterocycles can be transformed to more complex derivatives by the further conversion of a residual halogen atom. Various halo-substituted heterocycles, such as iodo-substituted spiro-[4.5]trienones,[2a,b] 3-iodo-2*H*-benzopyrans,[2c] 3-haloquinolones,[2d,e] and 3-halocoumarins,[2f] have been synthesized through intramolecular cyclization using I_2, ICl, Br_2, NXS, or other halo electrophile reagents.[2g,h] In addition, to access the desired organoselenium heterocycles, arylselenenyl chloride (ArSeCl) or diaryl diselenides (ArSeSeAr) have been applied to the electrophilic seleno-cyclization.[3] Despite these achievement being reported, the electrophilic cyclization of alkynes to directly access heterocyclic sulfides promoted by sulfur-containing electrophiles remains rare.[4] In the past few years, electrophilic sulfenylating reagents, such as *N*-thioanilides and *N*-thioamides, have been utilized to perform numerous sulfenylation reactions. For instance, Benati and co-workers developed a method for the synthesis of *β*-keto sulfides through BF_3·Et_2O-promoted sulfenylation of alkynes using nitrobenzenesulfenanilide as the sulfenylating reagent.[5] Very recently, the direct arylthiolation of (hetero)aromatic C−H bonds was also achieved with *N*-sulfanylsuccinimides as stable and readily accessible sulfenylating reagents.[6] The known examples included palladium-catalyzed C−H sulfenylation of unactivated arenes,[6a] TFA-promoted C−H sulfenylation of electron-rich arenes and C2 sulfenylation of nonprotected indoles,[6b,c] and Lewis acid catalyzed C−H arylthiolation of substituted phenols.[6d] Inspired by these elegant procedures, we speculate that the electrophilic cyclization of alkynes could be readily accessed using *N*-sulfanylsuccinimides as electrophiles.

As one of the most important heterocycles, the coumarin skeleton has been extensively found in a variety of natural products, biologically active molecules, and functional materials.[7] Particularly, the introduction of some functional groups at the C3 position of coumarins would improve the properties of coumarin-based molecules and enrich the library of coumarin-based compounds. Consequently, various 3-substituted coumarins have been successfully constructed from aryl alkynoates via radical cyclization in recent years.[8] For example, it was reported that 3-sulfonylated coumarins could be synthesized via oxidative radical sulfonylation/cyclization of phenyl propiolates with sulfonic acids or sulfonylhydrazides as sulfonylating reagents under metal-free conditions (Scheme 1a).[8a,b] Similarly, 3-trifluoromethylthiolated coumarins could also be successfully accessed through oxidative radical cascade cyclization of aryl alkynoates employing AgSCF as the radical source (Scheme 1b).[8c] The sulfenyl group functionalized at the C3 position of coumarins modifies the molecular reactivity and pharmacological properties, and the resulting 3-sulfenylated coumarins have shown important biological activities like hepatoprotective effects[9a] and estrogenic effects.[9b] In this context, particular emphasis has been put on the development of strategies to the

Received: September 15, 2016
Published: October 5, 2016

DOI: 10.1021/acs.joc.6b02271
J. Org. Chem. 2016, 81, 11297−11304

Scheme 1. Different Methods for the Synthesis of 3-Sulfur-Containing Coumarins



synthesis of 3-sulfenylated coumarins. Traditionally, 3-sulfenylated coumarins were prepared through esterification/intramolecular cyclization of mercaptoacetic acid derivatives with salicylaldehydes or cross-coupling reactions of 4-hydroxy coumarin with thiols (Scheme 1c);[10] however, these established methods often suffered from the use of high reaction temperature,[10a−c] excess amount of bases,[10a,b] or the pre-existing coumarin frameworks.[10d,e] Therefore, the development of a practical and efficient protocol by direct difunctionalization of readily available aryl alkynoates to access 3-sulfenylated coumarins is more convenient and highly desirable. As the continuous work on heterocycle syntheses under metal-free conditions,[11] we herein report a mild and efficient approach to 3-sulfenylated coumarins via electrophilic cyclization of aryl alkynoates with *N*-sulfanylsuccinimides mediated by $BF_3{\cdot}Et_2O$ (Scheme 1d).

RESULTS AND DISCUSSION

Initially, the electrophilic cyclization of alkynoate **1a** was chosen as a model reaction by employing *N*-(*p*-tolylthio)succinimide (**3a**) in CH_2Cl_2 as the solvent (Table 1). In the absence of Lewis acid, there is no desired cyclization product detected (entry 1). In contrast, when the Lewis acid $BF_3{\cdot}Et_2O$ was added to this reaction, the electrophilic cyclization occurred and the yield of desired product **2a** could be improved with the increase of the amount of $BF_3{\cdot}Et_2O$ (entries 2−4). The best yield of **2a** (87%) was obtained when **1a** was treated with *N*-(*p*-tolylthio)succinimide in the presence of 1.5 equiv of $BF_3{\cdot}Et_2O$ in CH_2Cl_2 (entry 4). Other Lewis acids such as $FeCl_3$ or $AlCl_3$ led to a decrease in the yield of **2a** (entries 5 and 6). Furthermore, two Brønsted acids, trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TfOH), were also investigated for this transformation. No desired product was detected using TFA (entry 7), and the reaction promoted or catalyzed by the stronger one TfOH gave **2a** in lower yield (entries 8 and 9). The influence of different solvents was also evaluated, and the results revealed that CH_2Cl_2 was superior to the other solvents (entry 4 vs entries 10−14). In addition, various other electrophilic sulfenylating reagents were also investigated for this intramolecular cyclization (entries 15−17): only 14% yield of **2a** was produced by using disulfide **4**, while the use of thiosulfonate **5** gave no products at all; as for the sulfenyl chloride **6**, although the reaction proceeded smoothly, the yield of **2a** was inferior to that with the utilization of **3a**.

To test the general scope and limitations of the cyclization reaction, various aryl alkynoates and *N*-(arylthio)succinimides were subjected to the optimized conditions (Table 2). First, we examined the reaction scope of aryl 3-phenylpropiolates bearing different substituents reacting on the phenoxy ring with *N*-(*p*-tolylthio)succinimide (**3a**). Either moderate electron-donating groups (methyl and *tert*-butyl) or electron-withdrawing groups (fluoro, chloro, bromo, and acetyl groups) located at the *para*-position of aryl 3-phenylpropiolates did not significantly affect the reaction efficiency, resulting in the desired products in good to high yields (Table 2, **2b−g**). Substrates bearing bulky groups at the *ortho* position of the phenoxy ring did not hamper the cyclization reaction, giving the corresponding product in good to excellent yields (**2h−j**). Moreover, the structure of **2i** was unambiguously confirmed by X-ray crystal analysis (Figure 1). Another aromatic system, the naphthyl group was also well tolerated in this reaction and delivered the product **2k** in 81% yield. Next, we investigated the compatibility of substituents on the alkynyl moiety. Phenyl arylpropiolates with either electron-donating or electron-withdrawing groups were suitable for this transformation and converted to the desired products in moderate to good yields (**2l−n**). Alkylpropiolates such as methylpropiolate was also tested for this cyclization, and its product **2o** was obtained in 42% yield only. Additionally, the scope of sulfenylating reagent **3** with different arylthiol partners was also investigated. Similarly, *N*-(arylthio)succinimides with substituents on the arylthiol ring, regardless of the electron-withdrawing or electron-donating properties, were all suitable for this cyclization, and the desired products were produced in moderate to excellent yields (**2p−t**). Furthermore, by employing *N*-(ethylthio)succinimide as the sulfenylating reagent, the corresponding 3-sulfenylated coumarin **2u** was isolated in 35% yield.

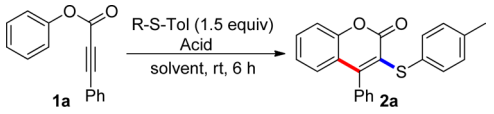
Interestingly, when the methoxy group (OMe) was introduced at the *para* position of the phenoxy ring, the desired 3-sulfenylated coumarin **2v** was not detected at all, and unexpected spiro[4.5]triene-2,8-dione **7**, generated via *ipso* sulfenylcyclization,[2a] was isolated as the sole product (Scheme 2, eq 1). Furthermore, alkynoate **1w** bearing two methoxy groups at both *meta* positions of the phenoxy moiety also failed to give the 6-*endo*-*dig* cyclization product, and the direct bisulfenylation of the phenoxy ring proceeded instead to afford **8** as the major product due to the strong electron-donating effect (Scheme 2, eq 2).[6b]

To elucidate the underlying reaction mechanism, two control experiments were performed as shown in Scheme 3. No reaction occurred when **1a** was performed under the standard conditions in the absence of **3a**. Moreover, 4-phenyl coumarin **9** was also prepared and treated with **3a** under standard conditions, while the desired product **3a** was not detected. These results indicated that coumarin **9** might not be the key intermediate in the present transformation.

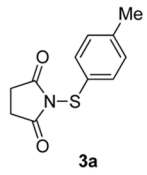
As shown in Scheme 4, a working mechanism for the synthesis of 3-sulfenylated coumarins using *N*-sulfanyl-

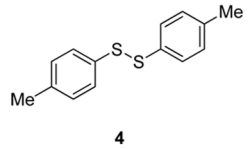
DOI: 10.1021/acs.joc.6b02271
J. Org. Chem. 2016, 81, 11297−11304

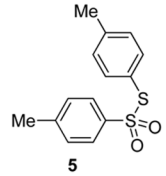
Table 1. Evaluation of Reaction Conditions[a]

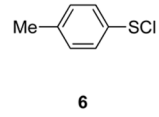


Entry	R-S-Tol	Acid (equiv)	Solvent	Yield (%)[b]
1	**3a**	0	CH_2Cl_2	0
2	**3a**	$BF_3{\cdot}Et_2O$ (0.5)	CH_2Cl_2	10
3	**3a**	$BF_3{\cdot}Et_2O$ (1.0)	CH_2Cl_2	61
4	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	CH_2Cl_2	87
5	**3a**	$FeCl_3$ (1.5)	CH_2Cl_2	82
6	**3a**	$AlCl_3$ (1.5)	CH_2Cl_2	58
7	**3a**	TFA (1.5)	CH_2Cl_2	0
8	**3a**	TfOH (1.5)	CH_2Cl_2	76
9	**3a**	TfOH (0.2)	CH_2Cl_2	52
10	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	DCE	76
11	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	$CHCl_3$	62
12	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	Toluene	67
13	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	CH_3CN	trace
14	**3a**	$BF_3{\cdot}Et_2O$ (1.5)	EtOAc	0
15	**4**	$BF_3{\cdot}Et_2O$ (1.5)	CH_2Cl_2	14
16	**5**	$BF_3{\cdot}Et_2O$ (1.5)	CH_2Cl_2	0
17	**6**	$BF_3{\cdot}Et_2O$ (1.5)	CH_2Cl_2	74









[a]The reaction was performed with **1a** (0.15 mmol) and sulfenyl reagent (0.225 mmol) in 1.5 mL of solvent. [b]Isolated yields.

succinimides was proposed based on the experimental results and earlier reports.[4−6] Initially, the treatment of **3a** with Lewis acid $BF_3{\cdot}Et_2O$ gave a thio cation **A**, which can react with the carbon−carbon triple bond of **1a** to form sulfonium intermediate **B**. Subsequent intramolecular nucleophilic attack of the phenoxy ring of alkynoates to the activated triple bond produced intermediate **C**, which underwent deprotonation to form the target product **2a**.

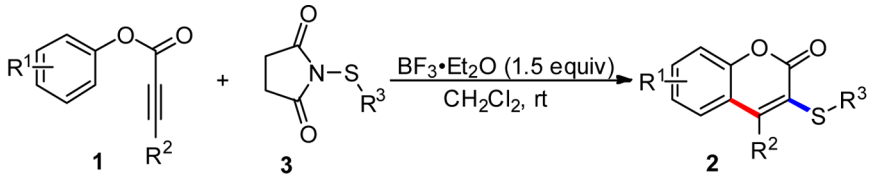
Both sulfinyl and sulfonyl groups are versatile functionalities, which have been found various applications in organic synthesis and medicinal chemistry.[12] To access the 3-sulfinylated and 3-sulfonated coumarins, we extended our study on the further conversion of **2a**. As shown in Scheme 5, sulfoxide **10** was exclusively obtained in 75% yield by employing the oxidation combination of KBr and (diacetoxyiodo)benzene (PIDA) (Scheme 5, eq 1), whereas sulfone **11** was produced as the sole product in almost quantitative yield by using *meta*-chloroperbenzoic acid (*m*-CPBA) as the oxidant (Scheme 5, eq 2). Therefore, the developed method for the synthesis of 3-sulfenylated coumarins would also provide a readily and reliably alternative access to the corresponding 3-sulfinylated and 3-sulfonylated derivatives.

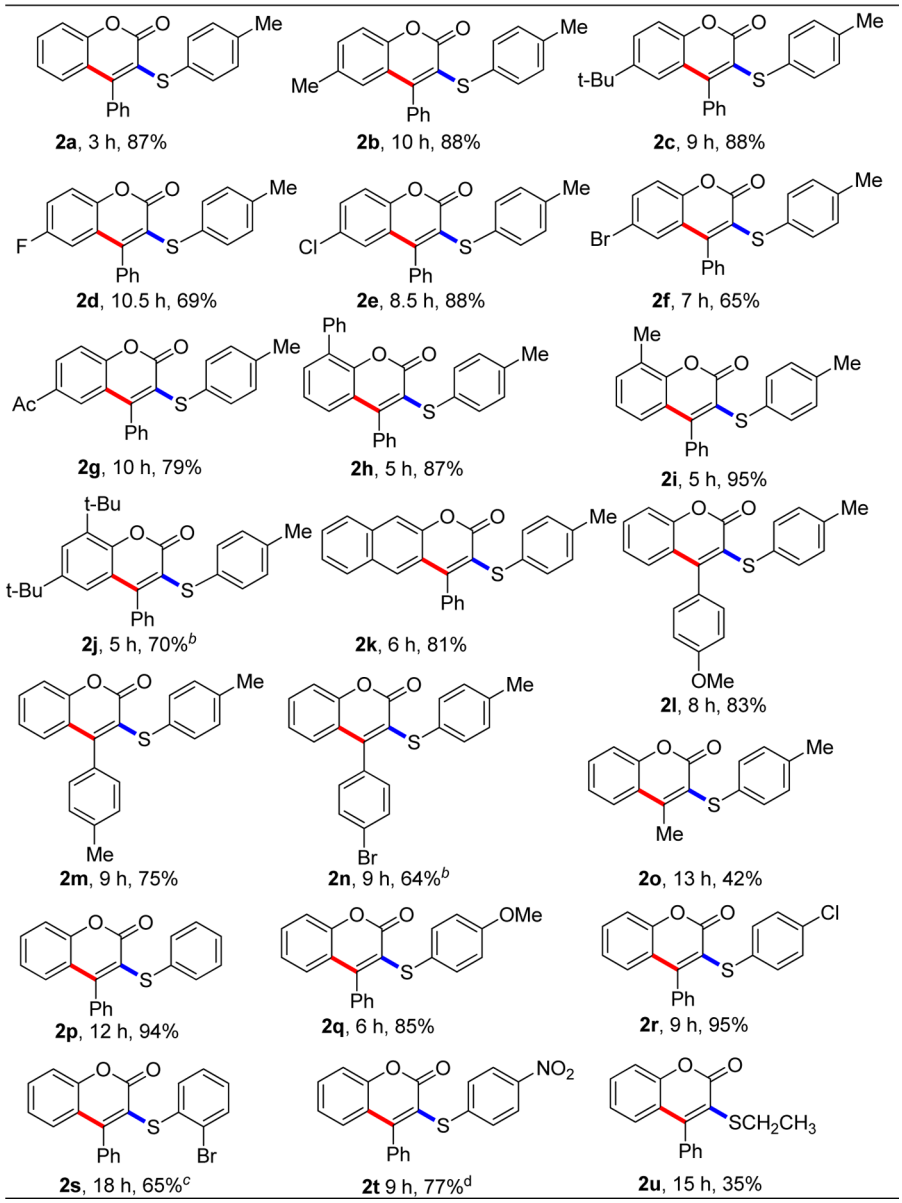
CONCLUSION

In summary, we have developed a simple and practical approach to 3-sulfenylated coumarins via electrophilic cyclization of aryl alkynoates. In the presence of $BF_3{\cdot}Et_2O$, *N*-sulfanylsuccinimides were utilized as electrophiles to induce the cyclization and introduce the sulfenyl group at the C3 position

DOI: 10.1021/acs.joc.6b02271
J. Org. Chem. 2016, 81, 11297−11304

Table 2. Electrophilic Cyclization of Alkynoates with *N*-Sulfanylsuccinimides: Scope and Limitations[a]





[a]Reaction conditions: **1** (0.15 mmol), **3** (0.225 mmol), $BF_3{\cdot}Et_2O$ (0.225 mmol), in CH_2Cl_2 (1.5 mL), at room temperature. [b]**3a** (0.375 mmol) and $BF_3{\cdot}Et_2O$ (0.3 mmol) were used. [c]$BF_3{\cdot}Et_2O$ (0.3 mmol) was used. [d]The reaction was performed in DCE (1.5 mL) at reflux.

of coumarins. A series of 3-sulfenylated coumarins were efficiently prepared in one step from the corresponding aryl alkynoates under mild and metal-free conditions. Besides, the methoxy substituent on the phenoxy ring of aryl 3-phenylpropiolate favored the formation of either 3-sulfenylspirotrienone product or sulfenylated arene product depending on different locations of the methoxy group. Furthermore, the selectively oxidative conversions of 3-*p*-tolylthio coumarin were achieved under different oxidations. Environmentally friendly conditions, broad substrate scope, high reaction efficiency, as well as successfully selective oxidation made this strategy highly valuable for the synthesis of sulfur-containing coumarins.

EXPERIMENTAL SECTION

General. ^1H NMR spectra were recorded at 600 or 400 MHz and ^{13}C NMR spectra were measured at 150 or 100 MHz using NMR spectrometers with $CDCl_3$ as the solvent. Chemical shifts (δ) were measured in ppm and referenced to the deuterated chloroform (^1H: δ = 7.26 ppm, ^{13}C: δ = 77.00 ppm). High-resolution mass spectrometry (HRMS) was performed on a TOF-Q spectrometer instrument with an ESI source. IR spectra were recorded on an FT-IR spectrometer in

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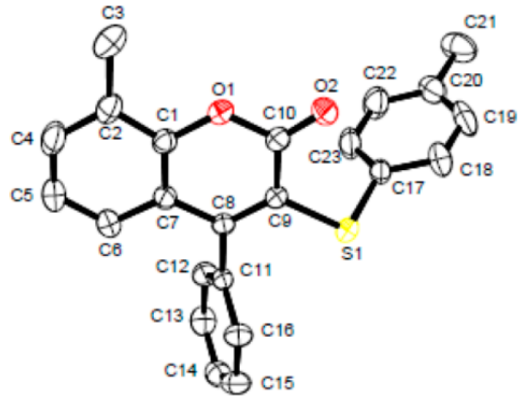
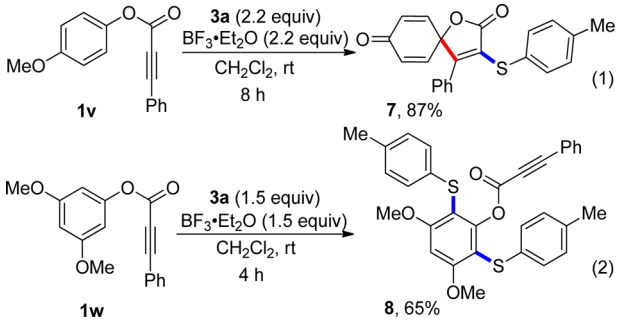
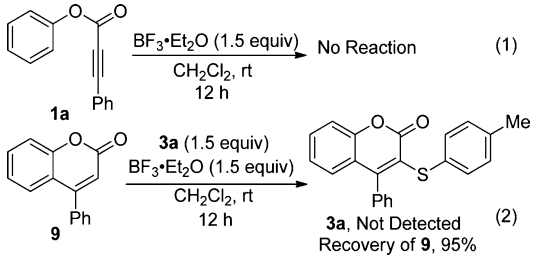


Figure 1. ORTEP drawing of **2i**; thermal ellipsoids at a 30% probability level.

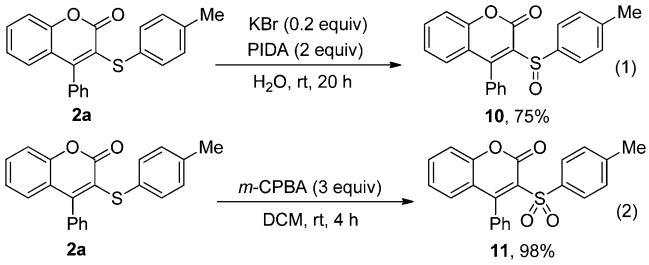
Scheme 2. Unexpected Transformations by Using Substrates with Methoxy Groups on Phenoxy Ring



Scheme 3. Control Experiments



Scheme 5. Further Oxidation of 2a

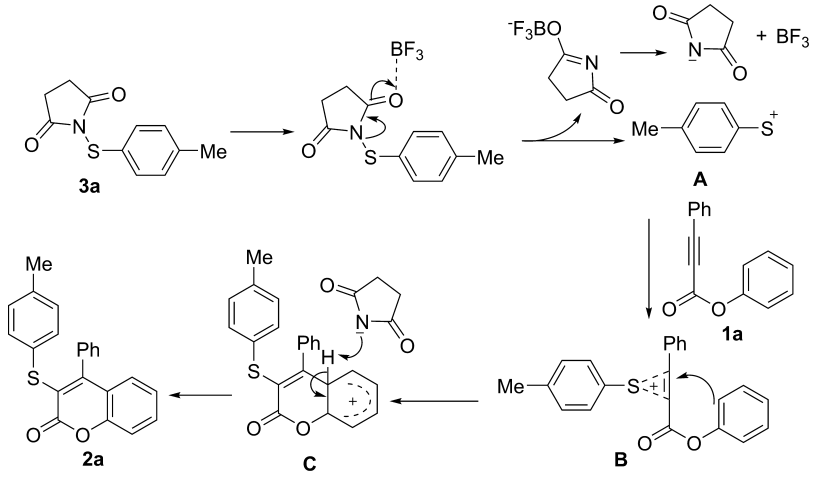


KBr pellets. Melting points were measured with an RD-II type melting point apparatus. X-ray structural analysis was obtained with an X-ray single-crystal diffractometer. Aryl alkynoates (**1a–w**) are all known compounds and identified by the comparison of their NMR spectra with reported data in the literature. Unless otherwise noted, reagents obtained from commercial sources were directly used without further purification; all solvents were obtained from commercial sources and were purified according to standard procedures. Petroleum ether (PE), where used, has the boiling point range of 60–90 °C. Column chromatography was performed on silica gel (200–300 mesh) by using ester acetate and petroleum ether as eluent.

Preparation of Aryl Alkynoates.[13] To a solution of the respective phenol (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added 3-phenylpropiolic acid (5.0 mmol, 1.0 equiv) at 0 °C; then a mixture of EDC (5.0 mmol, 1.0 equiv) and DMAP (2.0 mmol, 0.4 equiv) in CH_2Cl_2 (10 mL) was added dropwise. The mixture was stirred at 0 °C for 1 h, and then at room temperature for 12 h. The resulting reaction mixture was extracted by EtOAc (3 × 10 mL) and dried over anhydrous Na_2SO_4. After the organic layer was removed under vacuo, crude products were purified by column chromatography (Eluent: PE/EtOAc = 95/5).

Preparation of *N*-Sulfanylsuccinimides.[6c] To a solution of thiol (5.0 mmol, 1.0 equiv) and Et_3N (0.5 mmol, 0.1 equiv) in CH_2Cl_2 (10 mL) was added sulfuryl chloride (5.0 mmol, 1.0 equiv) dropwise at 0 °C. After stirring for 30 min, the reaction mixture was stirred for another 2 h at room temperature and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of succinimide (5.0 mmol, 1.0 equiv) and Et_3N (6.5 mmol, 1.3 equiv) in CH_2Cl_2 (8 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was diluted with H_2O (20 mL), extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (Eluent: PE/EtOAc = 80/10) on silica gel.

Scheme 4. Proposed Mechanism for the Synthesis of 3-Sulfenylated Coumarins



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1-(p-Tolylthio)pyrrolidine-2,5-dione (**3a**).[6c] Yield: 45%; white solid; mp 114−116 °C; TLC, R_f = 0.32 (PE:EtOAc = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.0 Hz), 2.78 (s, 4H), 2.33 (s, 3H).

1-(Phenylthio)pyrrolidine-2,5-dione (**3b**).[6c] Yield: 43%; white solid; mp 116−118 °C; TLC, R_f = 0.30 (PE:EtOAc = 7:3); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.64−7.61 (m, 2H), 7.37−7.31 (m, 3H), 2.82 (s, 4H).

1-((4-Methoxyphenyl)thio)pyrrolidine-2,5-dione (**3c**).[6c] Yield: 50%; white solid; mp 103−105 °C; TLC, R_f = 0.43 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, 2H, J = 8.8 Hz), 6.85 (d, 2H, J = 8.8 Hz), 3.80 (s, 3H), 2.76 (s, 4H).

1-((4-Chlorophenyl)thio)pyrrolidine-2,5-dione (**3d**).[6a] Yield: 46%; white solid; mp 142−144 °C; TLC, R_f = 0.32 (PE:EtOAc = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, 2H, J = 8.4 Hz), 7.31(d, 2H, J = 8.4 Hz), 2.82 (s, 4H).

1-((2-Bromophenyl)thio)pyrrolidine-2,5-dione (**3e**).[6a] Yield: 47%; white solid; mp 128−130 °C; TLC, R_f = 0.39 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.52 (dd, 1H, J = 8.4, 1.2 Hz), 7.24 (t, 1H, J = 7.8 Hz),7.09 (td, 1H, J = 7.8, 1.2 Hz), 6.80 (dd,1H, J = 7.8, 1.2 Hz), 2.98 (s, 4H).

1-((4-Nitrophenyl)thio)pyrrolidine-2,5-dione (**3f**).[6c] Yield: 42%; white solid; mp 148−150 °C; TLC, R_f = 0.38 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.18 (d, 2H, J = 9.0 Hz), 7.44 (d, 2H, J = 9.0 Hz), 2.97 (s, 4H).

1-(Ethylthio)pyrrolidine-2,5-dione (**3g**).[6c] Yield: 38%; brown oil; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.88 (q, 2H, J = 7.2 Hz), 2.84 (s, 4H), 1.22 (t, 3H, J = 7.2 Hz).

Typical Procedure for the Synthesis of 3-Sulfenylated Coumarins. To a solution of aryl alkynoates (0.15 mmol, 1.0 equiv) and *N*-sulfanylsuccinimides (0.225 mmol, 1.5 equiv) in CH_2Cl_2 (1.5 mL) was added $BF_3{\cdot}Et_2O$ (0.225 mmol, 1.5 equiv) dropwise at room temperature. The reaction mixture was continuously stirred until the starting material was consumed. The resulting mixture was then diluted with H_2O, extracted with EtOAc (3 × 10 mL), and dried over anhydrous Na_2SO_4. After the organic solvent was removed under reduced pressure, the crude product was purified by flash chromatography (Eluent: PE/EtOAc = 95:5).

4-Phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2a**). Yield: 45 mg (87%); time: 3 h; yellow solid; mp 117−119 °C; TLC, R_f = 0.40 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54−7.46 (m, 4H), 7.37 (d, 1H, J = 8.4 Hz), 7.27−7.23 (m, 2H), 7.16 (t, 1H, J = 7.2 Hz), 7.16 (d, 2H, J = 8.0 Hz), 7.08 (dd, 1H, J = 8.0, 1.2 Hz), 7.01 (d, 2H, J = 8.0 Hz), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 158.2, 153.2, 136.8, 134.9, 132.0, 131.0, 129.9, 129.7, 128.9, 128.5, 128.3, 128.0, 124.2, 122.3, 120.5, 116.7, 21.0; IR (neat) 3071, 3021, 2924, 1726, 1589, 1489, 1339, 1173, 1119, 993, 804, 754, 704 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{17}O_2S$ $[M + H]^+$: 345.0944, found: 345.0950.

6-Methyl-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2b**). Yield: 47 mg (88%); time: 10 h; yellow solid; mp 134−136 °C; TLC, R_f = 0.40 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.52−7.48 (m, 3H), 7.33 (dd, 1H, J = 8.4, 1.8 Hz), 7.28 (d, 1H, J = 8.4 Hz), 7.26−7.23 (m, 2H), 7.11 (d, 2H, J = 7.8 Hz), 7.01 (d, 2H, J = 7.8 Hz), 6.84 (d, 1H, J = 1.8 Hz), 2.27 (d, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 159.4, 158.3, 151.5, 136.8, 135.2, 134.0, 133.0, 131.3, 130.0, 129.7, 128.9, 128.5, 128.4, 127.7, 122.4, 120.3, 116.6, 21.0, 20.9; IR (neat) 3023, 2920, 1726, 1537, 1491, 1252, 1180, 1132, 1003, 816, 700 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{19}O_2S$ $[M + H]^+$: 359.1100, found: 359.1107.

6-(tert-Butyl)-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2c**). Yield: 55 mg (88%); time: 9 h; yellow solid; mp 158−160 °C; TLC, R_f = 0.43 (PE:EtOAc = 8:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (dd, 1H, J = 8.8, 2.0 Hz), 7.52−7.48 (m, 3H), 7.32 (d, 1H, J = 8.4 Hz), 7.29−7.24 (m, 2H), 7.10 (d, 2H, J = 8.0 Hz), 7.05 (d, 1H, J = 2.4 Hz), 7.00 (d, 2H, J = 8.0 Hz), 2.27 (s, 3H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 158.9, 151.4, 147.3, 136.7, 135.0, 131.4, 129.72, 129.69, 129.6, 129.0, 128.4, 124.3, 121.9, 119.8, 116.3, 34.5, 31.2, 21.0; IR (neat) 3023, 2957, 2868, 1732, 1537, 1493, 1385, 1134, 1003, 804 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{26}H_{25}O_2S$ $[M + H]^+$: 401.1570, found: 401.1578.

6-Fluoro-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2d**). Yield: 37.5 mg (69%); time: 10.5 h; yellow solid; mp 122−124 °C; TLC, R_f = 0.40 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54−7.49 (m, 3H), 7.35 (dd, 1H, J = 9.2, 4.4 Hz), 7.26−7.20 (m, 3H), 7.12 (d, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 8.0 Hz), 6.77 (dd, 1H, J = 8.8, 3.2 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.8, 158.6 (d, J = 242.5 Hz), 156.7 (d, J = 2.8 Hz), 149.3 (d, J = 1.9 Hz), 137.2, 134.4, 130.5, 130.3, 129.8, 129.2, 128.7, 128.3, 124.1, 121.4 (d, J = 8.5 Hz), 119.3 (d, J = 24.5 Hz), 118.3 (d, J = 8.4 Hz), 113.4 (d, J = 25.1 Hz), 21.1; IR (neat) 3063, 2922, 2855, 1719, 1541, 1493, 1422, 1256, 1132, 997, 810, 700 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{16}FO_2S$ $[M + H]^+$: 363.0850, found: 363.0849.

6-Chloro-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2e**). Yield: 50 mg (88%); time: 8.5 h; yellow solid; mp 148−150 °C; TLC, R_f = 0.42 (PE:EtOAc = 8:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.50 (m, 3H), 7.45 (dd, 1H, J = 8.8, 2.4 Hz), 7.32 (d, 1H, J = 8.8 Hz), 7.26−7.22 (m, 2H), 7.12 (d, 2H, J = 8.0 Hz), 7.05−7.00 (m, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 156.4, 151.5, 137.2, 134.2, 131.8, 130.5, 130.3, 129.8, 129.7, 129.3, 128.7, 128.3, 127.1, 124.2, 121.6, 118.2, 21.0; IR (neat) 3057, 2916, 2855, 1726, 1532, 1179, 1125, 1001, 708 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{15}ClNaO_2S$ $[M + Na]^+$: 401.0373, found: 401.0367.

6-Bromo-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2f**). Yield: 42 mg (65%); time: 7 h; yellow solid; mp 156−158 °C; TLC, R_f = 0.48 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (dd, 1H, J = 8.8, 2.4 Hz), 7.54−7.50 (m, 3H), 7.26 (d, 1H, J = 4.0 Hz), 7.25−7.22 (m, 2H), 7.18 (d, 1H, J = 2.4 Hz), 7.11 (d, 2H, J = 8.4 Hz), 7.02 (d, 2H, J = 8.0 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 156.4, 152.0, 137.3, 134.6, 134.2, 130.5, 130.4, 129.8, 129.3, 128.8, 128.3, 124.2, 122.1, 118.5, 117.1, 21.1; IR (neat) 3057, 2918, 2855, 1722, 1530, 1489, 1400, 1265, 1179, 1128, 1003, 810, 706 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{16}BrO_2S$ $[M + H]^+$: 423.0049, found: 423.0054.

6-Acetyl-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2g**). Yield: 46 mg (79%); time: 10 h; yellow solid; mp 190−192 °C; TLC, R_f = 0.20 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (dd, 1H, J = 8.4, 2.0 Hz), 7.70 (d, 1H, J = 2.4 Hz), 7.56−7.52 (m, 3H), 7.43 (d, 1H, J = 8.8 Hz), 7.30−7.26 (m, 2H), 7.13 (d, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 8.0 Hz), 2.47(s, 3H), 2.28(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.0, 158.3, 157.3, 155.9, 137.3, 134.2, 133.4, 131.5, 130.41, 130.38, 129.8, 129.4, 128.75, 128.72, 128.4, 123.9, 120.4, 117.3, 26.4, 21.1; IR (neat) 3073, 3044, 2916, 1736, 1678, 1493, 1364, 1250, 1119, 1001, 959, 810, 718 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{24}H_{19}O_3S$ $[M + H]^+$: 387.1049, found: 387.1046.

4,8-Diphenyl-3-(p-tolylthio)-2H-chromen-2-one (**2h**). Yield: 55 mg (87%); time: 5 h; yellow oil; TLC, R_f = 0.48 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.62 (d, 2H, J = 7.8 Hz), 7.57 (dd, 1H, J = 7.2, 1.2 Hz), 7.53−7.50 (m, 3H), 7.47 (t, 2H, J = 7.2 Hz), 7.40 (t, 1H, J = 7.8 Hz), 7.29 (dd, 2H, J = 7.8, 2.4 Hz), 7.22 (t, 1H, J = 7.8 Hz), 7.14 (d, 2H, J = 7.8 Hz), 7.07 (dd, 1H, J = 8.4, 1.2 Hz), 7.00 (d, 2H, J = 8.4 Hz), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 158.1, 150.1, 137.0, 136.5, 135.6, 135.3, 133.2, 130.9, 130.4, 134.24, 130.18, 129.7, 129.6, 129.3, 128.9, 128.8, 128.54, 128.45, 128.4, 128.0, 127.6, 127.4, 124.1, 122.8, 121.0, 21.0; IR (neat) 2961, 2870, 1641, 1385, 1121, 636, 615 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{28}H_{21}O_2S$ $[M + H]^+$: 421.1257, found: 421.1258.

8-Methyl-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2i**). Yield: 51 mg (95%); time: 5 h; yellow solid; mp 110−112 °C; TLC, R_f = 0.44 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.45 (m, 3H), 7.37 (d, 1H, J = 7.2 Hz), 7.26−7.23 (m, 2H), 7.12 (d, 2H, J = 8.4 Hz), 7.06 (t, 1H, J = 7.6 Hz), 7.01 (d, 2H, J = 8.0 Hz), 6.91 (dd, 1H, J = 8.4, 1.2 Hz), 2.49 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 158.7, 151.6, 136.8, 135.3, 133.3, 131.2, 129.9, 129.6, 128.8, 128.4, 128.3, 126.2, 125.9, 123.7, 122.0, 120.3, 21.0, 15.6; IR (neat) 3067, 3032, 2920, 2861, 1730, 1543, 1491, 1341, 1080, 957, 800, 770, 704 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{19}O_2S$ $[M + H]^+$: 359.1100, found: 359.1104.

DOI: 10.1021/acs.joc.6b02271
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*6,8-Di-tert-butyl-4-phenyl-3-(p-tolylthio)-2H-chromen-2-one (**2j**).* Yield: 48 mg (70%); time: 5 h; yellow oil; TLC, R_f = 0.48 (PE:EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57 (dd, 1H, J = 2.4 Hz), 7.50−7.47 (m, 3H), 7.26−7.23 (m, 2H), 7.15 (d, 2H, J = 8.4 Hz), 7.01 (d, 2H, J = 7.8 Hz), 6.89 (d, 1H, J = 2.4 Hz), 2.27 (s, 3H), 1.54 (s, 9H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 158.9, 150.1, 146.2, 137.2, 136.8, 135.7, 131.3, 130.2, 129.6, 128.7, 128.34, 128.31, 127.3, 122.7, 121.3, 120.4, 35.2, 34.7, 31.2, 30.0, 21.0; IR (neat) 2961, 2870, 1641, 1572, 1385, 1121, 810, 615 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{30}H_{33}O_2S$ [M + H]$^+$: 457.2196, found: 457.2191.

*4-Phenyl-3-(p-tolylthio)-2H-benzo[g]chromen-2-one (**2k**).* Yield: 48 mg (81%); time: 6 h; yellow solid; mp 202−204 °C; TLC, R_f = 0.40 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00 (d, 1H, J = 9.0 Hz), 7.83 (d, 1H, J = 7.8 Hz), 7.57−7.50 (m, 4H), 7.38 (t, 1H, J = 7.8 Hz), 7.28 (dd, 2H, J = 7.8, 1.8 Hz), 7.13 (d, 2H, J = 7.8 Hz), 7.10 (t, 1H, J = 7.8 Hz), 7.03 (d, 2H, J = 7.8 Hz), 7.00 (d, 1H, J = 9.0 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.7, 158.4, 154.1, 139.1, 136.8, 134.4, 131.5, 131.48, 129.8, 129.7, 129.20, 129.15, 129.0, 128.1, 127.2, 125.6, 125.4, 123.0, 117.3, 114.0, 21.0; IR (neat) 3057, 2922, 2853, 1732, 1518, 1489, 1269, 1011, 990, 812, 696 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{26}H_{19}O_2S$ [M + H]$^+$: 395.1100, found: 395.1104.

*4-(4-Methoxyphenyl)-3-(p-tolylthio)-2H-chromen-2-one (**2l**).* Yield: 46.6 mg (83%); time: 8 h; yellow oil; TLC, R_f = 0.36 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54−7.49 (m, 1H), 7.37 (d, 2H, J = 8.4 Hz), 7.22−7.17 (m, 4H), 7.12 (d, 2H, J = 8.0 Hz), 7.04−7.00 (m, 4H), 3.89 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1, 159.3, 158.2, 153.3, 136.8, 131.9, 131.3, 130.0, 129.7, 128.2, 127.1, 124.2, 122.3, 120.7, 116.8, 113.9, 55.3, 21.0; IR (neat) 2922, 1726, 1605, 1385, 1252, 1119, 754, 615 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{19}O_3S$ [M + H]$^+$: 375.1049, found: 375.1037.

*4-(p-Tolyl)-3-(p-tolylthio)-2H-chromen-2-one (**2m**).* Yield: 46.8 mg (87%); time: 9 h; yellow solid; mp 147−149 °C; TLC, R_f = 0.40 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (t, 1H, J = 7.6 Hz), 7.37 (d, 1H, J = 7.6 Hz), 7.31 (d, 2H, J = 7.6 Hz), 7.20−7.10 (m, 6H), 7.02 (d, 2H, J = 8.0 Hz), 2.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 158.6, 153.3, 139.0, 136.8, 132.0, 131.9, 131.2, 129.74, 129.69, 129.2, 128.4, 128.2, 124.2, 122.2, 120.6, 116.8, 21.4, 21.0; IR (neat) 3028, 2916, 2864, 1736, 1591, 1491, 1121, 993, 802, 766 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{23}H_{19}O_2S$ [M + H]$^+$: 359.1100, found: 359.1103.

*4-(4-Bromophenyl)-3-(p-tolylthio)-2H-chromen-2-one (**2n**).* Yield: 40.6 mg (64%); time: 9 h; yellow solid; mp 145−147 °C; TLC, R_f = 0.47 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, 2H, J = 8.4 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.39 (dd, 1H, J = 8.4, 0.8 Hz), 7.18 (t, 1H, J = 7.6 Hz), 7.14−7.08 (m, 4H), 7.06 (dd, 1H, J = 8.0, 1.2 Hz), 7.02 (d, 2H, J = 8.0 Hz), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 156.8, 153.2, 137.2, 133.7, 132.2, 131.8, 130.7, 130.10, 130.07, 129.8, 127.7, 124.4, 123.3, 122.9, 120.1, 116.9, 21.1; IR (neat) 3088, 2916, 2849, 1721, 1595, 1387, 1117, 995, 804, 762, 617 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{16}BrO_2S$ [M + H]$^+$: 423.0049, found: 423.0054.

*4-Methyl-3-(p-tolylthio)-2H-chromen-2-one (**2o**).* Yield: 18 mg (42%); time: 13 h; yellow solid; mp 78−80 °C; TLC, R_f = 0.47 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, 1H, J = 8.0 Hz), 7.56 (t, 1H, J = 7.6 Hz), 7.36−7.30 (m, 2H), 7.21 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 8.0 Hz), 2.77 (s, 3H), 2.29 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 156.4, 152.8, 136.7, 132.2, 131.3, 129.9, 129.2, 125.6, 124.4, 121.7, 120.2, 117.1, 21.0, 18.0; IR (neat) 3019, 2920, 2855, 1730, 1597, 1447, 1132, 1071, 978, 806, 748 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{15}O_2S$ [M + H]$^+$: 283.0787, found: 283.0783.

*4-Phenyl-3-(phenylthio)-2H-chromen-2-one (**2p**).* Yield: 46.6 mg (94%); time: 12 h; yellow solid; mp 148−150 °C; TLC, R_f = 0.47 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (t, 1H, J = 7.2 Hz), 7.50−7.46 (m, 3H), 7.39 (d, 1H, J = 7.8 Hz), 7.26−7.24 (m, 2H), 7.22−7.14 (m, 6H), 7.10 (dd, 1H, J = 7.8, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 158.9, 153.3, 134.9, 134.8, 132.2, 129.3, 129.0, 128.9, 128.5, 128.3, 128.1, 126.7, 124.3, 121.8, 120.4, 116.8; IR (neat) 3073, 2924, 2853, 1722, 1541, 1441, 1342, 1121, 990, 743 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{15}O_2S$ [M + H]$^+$: 331.0787, found: 331.0786.

*3-((4-Methoxyphenyl)thio)-4-phenyl-2H-chromen-2-one (**2q**).* Yield: 46 mg (85%); time: 6 h; yellow solid; mp 90−92 °C; TLC, R_f = 0.20 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54−7.48 (m, 4H), 7.37 (dd, 1H, J = 8.4, 0.8 Hz), 7.26−7.23 (m, 2H), 7.21 (d, 2H, J = 8.8 Hz), 7.16 (td, 1H, J = 7.2, 1.2 Hz), 7.07 (dd, 1H, J = 8.0, 1.2 Hz), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 159.3, 157.4, 153.2, 135.0, 133.1, 131.9, 128.9, 128.51, 128.48, 128.0, 124.7, 124.2, 123.4, 120.6, 116.7, 114.5, 55.3; IR (neat) 2924, 1719, 1385, 1117, 999, 758, 615 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{17}O_3S$ [M + H]$^+$: 361.0893, found: 361.0898.

*3-((4-Chlorophenyl)thio)-4-phenyl-2H-chromen-2-one (**2r**).* Yield: 52 mg (95%); time: 9 h; yellow solid; mp 118−120 °C; TLC, R_f = 0.44 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55 (t, 1H, J = 7.2 Hz), 7.52−7.49 (m, 3H), 7.40 (d, 1H, J = 8.4 Hz), 7.25−7.22 (m, 2H), 7.21−7.12 (m, 5H), 7.10 (dd, 1H, J = 8.4, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 159.0, 158.9, 153.4, 134.8, 133.4, 133.0, 132.3, 131.1, 129.2, 129.1, 128.6, 128.3, 128.2, 124.4, 121.7, 120.5, 116.9; IR (neat) 3075, 3048, 1724, 1539, 1474, 1342, 1175, 1092, 995, 814, 758 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{14}ClO_2S$ [M + H]$^+$: 365.0397, found: 365.0398.

*3-((2-Bromophenyl)thio)-4-phenyl-2H-chromen-2-one (**2s**).* Yield: 40 mg (65%); time: 18 h; pale yellow solid; mp 160−162 °C; TLC, R_f = 0.36 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.56 (t, 1H, J = 8.4 Hz), 7.48−7.44 (m, 4H), 7.42 (d, 1H, J = 7.8 Hz), 7.25−7.22 (m, 2H), 7.20 (t, 1H, J = 7.8 Hz), 7.16−7.11 (m, 2H), 7.06 (dd, 1H, J = 7.8, 1.8 Hz), 7.00 (t, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.9, 158.7, 153.5, 136.3, 134.6, 133.1, 132.3, 129.6, 129.2, 128.6, 128.10, 128.08, 127.6, 127.5, 124.4, 123.3, 121.1, 120.5, 116.9; IR (neat) 3055, 2924, 2853, 1724, 1603, 1445, 1342, 1121, 1001, 762, 743 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{14}BrO_2S$ [M + H]$^+$: 410.9872, found: 410.9869.

*3-((4-Nitrophenyl)thio)-4-phenyl-2H-chromen-2-one (**2t**).* Yield: 43 mg (77%); time: 9 h; pale yellow solid; mp 190−192 °C; TLC, R_f = 0.21 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, 2H, J = 8.8 Hz), 7.62 (t, 1H, J = 8.4 Hz), 7.53−7.49 (m, 3H), 7.46 (d, 1H, J = 8.4 Hz), 7.29−7.22 (m, 5H), 7.16 (dd, 1H, J = 8.0, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.4, 158.7, 153.6, 145.9, 145.0, 134.3, 133.2, 129.5, 128.7, 128.5, 127.9, 127.3, 124.7, 124.1, 120.1, 118.8, 117.1; IR (neat) 3090, 2916, 2849, 1721, 1576, 1508, 1337, 1123, 1094, 997, 853, 756, 702, 617 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{21}H_{14}NO_4S$ [M + H]$^+$: 376.0638, found: 376.0630.

*3-(Ethylthio)-4-phenyl-2H-chromen-2-one (**2u**).* Yield: 15 mg (35%); time: 15 h; yellow solid; mp 120−122 °C; TLC, R_f = 0.45 (PE:EtOAc = 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.46 (m, 4H), 7.38 (dd, 1H, J = 8.0, 1.2 Hz), 7.26−7.22 (m, 2H), 7.15 (t, 1H, J = 7.2 Hz), 7.02 (dd, 1H, J = 8.0, 1.2 Hz), 2.95 (q, 2H, J = 7.2 Hz), 1.13(t, 3H, J = 7.2 Hz) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 156.7, 152.8, 135.3, 131.4, 128.8, 128.53, 128.48, 127.6, 124.2, 122.4, 120.6, 116.6, 27.4, 15.0; IR (neat) 3059, 2920, 1717, 1638, 1385, 1119, 999, 760, 615 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{15}O_2S$ [M + H]$^+$: 283.0798, found: 283.0787.

*4-Phenyl-3-(p-tolylthio)-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**7**).* Yield: 47 mg (87%); time: 8 h; yellow solid; mp 143−145 °C; TLC, R_f = 0.28 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.34 (m, 1H), 7.33−7.27 (m, 4H), 7.23 (d, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 7.6 Hz), 6.65 (d, 2H, J = 10.0 Hz), 6.38 (d, 2H, J = 10.4 Hz), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 183.8, 168.4, 159.5, 142.75, 138.7, 132.2, 131.8, 130.5, 129.9, 129.2, 128.6, 127.9, 126.9, 126.2, 81.8, 21.1; IR (neat) 3041, 2918, 1776, 1672, 1491, 1209, 1117, 1001, 860, 808, 692 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{17}O_3S$ [M + H]$^+$: 361.0893, found: 361.0892.

*3,5-Dimethoxy-2,6-bis(p-tolylthio)phenyl 3-phenylpropiolate (**8**).* Yield: 51 mg (65%); time: 4 h; white solid; mp 147−149 °C; TLC, R_f = 0.30 (PE:EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, 2H, J = 8.4 Hz), 7.45 (t, 1H, J = 7.2 Hz), 7.37 (t, 2H, J = 7.2 Hz), 7.10 (d, 4H, J = 8.0 Hz), 7.00 (d, 4H, J = 8.0 Hz), 6.49 (s, 1H), 3.86 (s,

DOI: 10.1021/acs.joc.6b02271
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6H), 2.27 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8, 155.8, 151.4, 135.5, 133.3, 133.1, 130.8, 129.4, 128.5, 128.2, 119.5, 108.1, 94.4, 88.6, 80.2, 56.5, 21.0; IR (neat) 3078, 3017, 2918, 2851, 2224, 1724, 1586, 1491, 1219, 1153, 1103, 1015, 813, 758 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{31}H_{27}O_4S_2$ $[M + H]^+$: 527.1345, found: 527.1344.

Synthesis of 3-Sulfinylated Coumarin ***10***. To a stirred suspension of **3a** (0.15 mmol, 1 equiv) and KBr (0.03 mmol, 0.2 equiv) in H_2O (1.0 mL) was added PIDA (0.30 mmol, 2 equiv) at room temperature, and the resulting mixture was stirred vigorously for 20 h. Then, the mixture was extracted with EtOAc (3 × 10 mL), dried, and evaporated. The residue was purified by column chromatography (Eluent: PE/EtOAc = 70/30). Yield: 40.5 mg (75%); time: 20 h; pale yellow solid; mp 118−120 °C; TLC, R_f = 0.45 (PE:EtOAc = 3:2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.62−7.57 (m, 4H), 7.54 (d, 2H, J = 8.4 Hz), 7.52−7.49 (m, 1H), 7.36−7.33 (m, 2H), 7.26−7.24 (m, 2H), 7.21 (t, 1H, J = 8.4 Hz), 7.15 (dd, 1H, J = 8.4, 1.2 Hz), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.5, 154.6, 154.2, 141.1, 138.8, 133.8, 131.9, 129.8, 129.6, 129.5, 129.1, 128.9, 128.8, 128.49, 128.47, 125.0, 124.6, 119.8, 117.1, 21.3; IR (neat) 3063, 2920, 2859, 1742, 1721, 1593, 1543, 1346, 1248, 1036, 997, 756, 702 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{22}H_{17}O_3S$ $[M + H]^+$: 361.0893, found: 361.0899.

Synthesis of 3-Sulfonylated Coumarin ***11***.[8a] To a stirred solution of **3a** (0.15 mmol, 1 equiv) in CH_2Cl_2 (1.0 mL) was added *m*-CPBA (0.45 mmol, 3 equiv) at room temperature, and the resulting mixture was continuously stirred for another 4 h. Then, the mixture was diluted with H_2O (10 mL), extracted with EtOAc (3 × 10 mL), dried, and evaporated. The residue was purified by column chromatography (Eluent: PE/EtOAc = 90/10). Yield: 55 mg (98%); time: 5 h; white solid; mp 158−160 °C; TLC, R_f = 0.27 (PE:EtOAc = 8:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, 2H, J = 8.4 Hz), 7.64−7.56 (m, 4H), 7.37−7.32 (m, 3H), 7.29 (d, 2H, J = 8.0 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.01 (dd, 1H, J = 8.0, 1.2 Hz), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 155.6, 153.8, 144.7, 137.2, 134.5, 132.6, 129.9, 129.3, 129.2, 128.1, 127.4, 126.1, 124.8, 120.2, 116.7, 21.7.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02271.

Copies of NMR and IR spectra for all new compounds and crystallography of **2i** (PDF)

X-ray crystal data for **2i** (CIF)

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Notes

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■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of Shanxi Province (Grant No. 2015021037) and Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (STIP) (Grant No. 2015133).

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