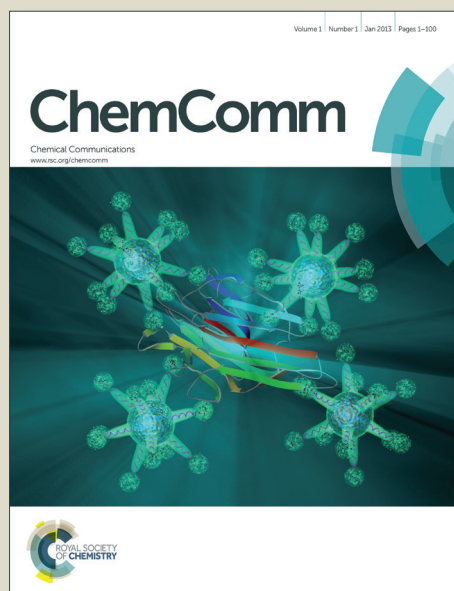


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COMMUNICATION

Visible-light initiated oxidative cyclization of phenyl propiolates with sulfinic acids to coumarin derivatives under metal-free conditions

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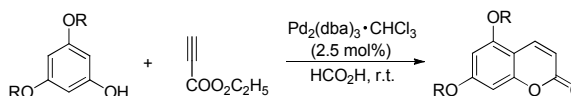
DOI: 10.1039/b000000x

A visible-light initiated oxidative cyclization of phenyl propiolates with sulfinic acids has been developed. The arylsulfonylation of alkyne was performed at room temperature under metal-free conditions to generate coumarin derivatives with wide functional group tolerance, good yields and high regio-selectivity.

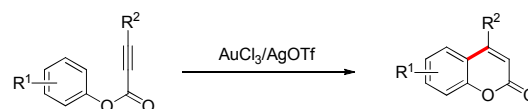
The coumarin skeleton has been widely found in the structure of natural products, pharmaceuticals and biologically active molecules as anti-HIV, anti-cancer, anti-psoriasis, anti-inflammatory, anti-depressant and anti-diabetic and it has attracted considerable attention of chemists towards their synthesis.^{1,2} Especially in the last decades, preparation of coumarins has turned into one of the most significant and fundamental missions in organic synthesis, and many routes have been established.³ As we known, Pechmann condensation has proven to be one of the most attractive methods.⁴ Recently, transition-metal-catalyzed synthesis of coumarin derivatives has become the useful strategies. The selected elegant examples, Trost employed a Pd-catalyzed addition reactions of propargylic esters with phenols to coumarins (Scheme 1a).⁵ Then, Shi and He reported a gold(III)-catalyzed intermolecular addition of arenes to alkynes within aryl alkynoates to various coumarins (Scheme 1b).⁶ Very recently, Alper described a novel synthesis of coumarins through Pd-catalyzed oxidative cyclocarbonylation of unsaturated compounds with CO (Scheme 1c).⁷ Most recently, we also developed a Ru-catalyzed reactions for the synthesis of 2,3-disubstituted coumarins involving decarboxylative annulations of α -keto acids with internal alkynes.⁸ In addition, other metal-catalyzed methods for the direct construction of coumarins have also been proven attractive.⁹ However, the above transformations suffer from the requirement of toxic metal, ligand or additive, extremely limiting their applications in pharmaceutical industry. Therefore, exploring more convenient, straightforward and green method for their synthesis is highly desirable.

Visible-light induced organic transformation has emerged as one of the most flourishing and attractive research area for its intrinsic characteristics of sustainability and green chemistry in recent years.¹⁰ Although ruthenium, iridium or copper complexes as photoredox catalysts have been well demonstrated for C–C, C–hetero bonds coupling under visible-light irradiation,¹¹ organic dyes compared with metal-based photoredox catalysts show splendid superiorities, cheapness and non-toxicity. The organic dyes including Eosin Y, Fluorescein, Rose Bengal and Eosin B in visible-light-promoted organic transformations have proven to be efficient, ecological and economical.¹² Nevertheless, it should be noted that the formation of coumarin and its derivatives has not been reported through a visible-light initiation method up to date.

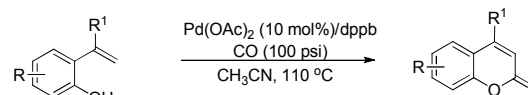
a: Trost's work: Palladium-catalyzed synthesis of coumarins



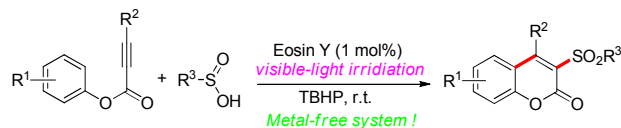
b: Shi and He's work: Au-(III)-catalyzed intermolecular addition of arenes to alkynes



c: Alper's work: Pd-catalyzed cyclocarbonylation of 2-vinylphenols



d: This work: Visible-light induced arylsulfonylation of alkynes

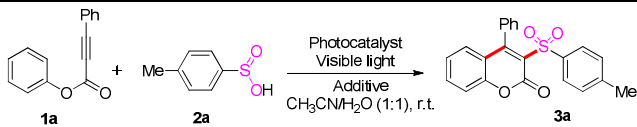


Scheme 1. Synthetic strategies for the coumarins synthesis

Arylsulfinic acids are versatile and readily available intermediates in organic synthesis.¹³ In recent years, many efforts have been devoted to develop sulfonylation reactions using sulfinic acids as sulfonylating agents for the construction of sulfone-containing molecules,¹⁴ including 3-sulfonylated coumarins,¹⁵ as materials, and pharmaceuticals.¹⁶ Herein, we report a novel visible-light induced Eosin Y catalyzed difunctionalization of alkynes with sulfinic acids via C–C and C–S bond formation for the synthesis of 3-sulfonylated coumarins at room temperature under metal-free conditions (Scheme 1d).

For the optimization of the reaction conditions, 3-phenylpropiolate (**1a**) and 4-methylbenzenesulfinic acid (**2a**) were chosen as the model substrates. Initially, the reaction was performed in the presence of 1.0 mol% Eosin Y as a photoredox catalyst, 1 equiv of *tert*-butyl hydroperoxide (TBHP) as an additive and CH₃CN–H₂O (1:1 v/v) as solvent at room temperature under the irradiation of 18 W fluorescent lamp for 12 h. To our delight, the desired coumarin (**3a**) was obtained in 71% isolated yield (Table 1, entry 1). When H₂O₂ was instead of TBHP, the model reaction generated the desired product **3a** in 42% yield (Table 1, entry 2). Other additives such as DTBP, DCP and PhI(OAc)₂ led to poor yield of **3a** (Table 1, entries 3–5). Changi-

Table 1. Optimization of the Reaction Conditions.^[a]

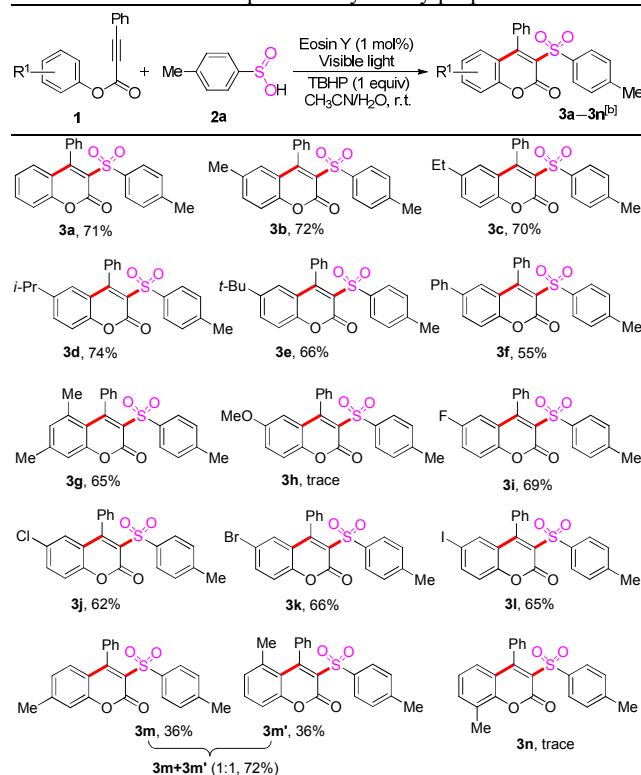
				
Entry	Light source	Catalyst	Additive	Yield(%) ^[b]
1	Light ^[c]	Eosin Y	TBHP	71
2	Light ^[c]	Eosin Y	H ₂ O ₂	42
3	Light ^[c]	Eosin Y	DTBP	15
4	Light ^[c]	Eosin Y	DCP	24
5	Light ^[c]	Eosin Y	PhI(OAc) ₂	N.R.
6	Light ^[c]	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O	TBHP	33
7	Light ^[c]	Acid Red 87	TBHP	16
8	Green LED ^[d]	Eosin Y	TBHP	41
9	Blue LED ^[e]	Eosin Y	TBHP	N.R.
10	—	Eosin Y	TBHP	N.R.
11	Light ^[c]	—	TBHP	N.R.
12	Light ^[c]	Eosin Y	—	N.R.

^[a] Reaction conditions: phenyl 3-phenylpropionate (**1a**, 0.30 mmol), 4-methylbenzenesulfonic acid (**2a**, 0.60 mmol), photocatalyst (1.0 mol%), additive (1.0 equiv), CH₃CN/H₂O (1:1, 1.5 mL) at room temperature under air for 12 h. ^[b] Isolated yields. ^[c] Fluorescent lamp (18 W) was used. ^[d] Green LED (530–535 nm) was used. ^[e] Blue LED (450–455 nm) was used. N.R. = no reaction.

ng photoredox catalyst from Eosin Y to [Ru(bpy)₃]Cl₂·6H₂O or Acid Red 87 could not make better contribution to this transformation (Table 1, entries 6 and 7). As shown in Table 1, the application of green LED got lower yield of **3a**, but blue LED failed (Table 1, entries 8 and 9). It is important to note that visible light, catalyst and additive are essential in the reaction (Table 1, entries 10–12).

With the optimized conditions in hand, we next explored the scope of the oxidative coupling reaction. The results are shown in Scheme 2. Some representative substituents, including electron-donating groups, electron-withdrawing groups and halogens, were introduced into phenyl ring of phenyl propiolates (**1**), and which were evaluated under standard reaction conditions, respectively. The arylsulfonylations of phenyl propiolates (**1**) without substituent group and containing electron-donating groups, such as Me, Et, *i*-Pr, *t*-Bu and Ph on the *para*-position of phenyl rings with 4-methylbenzenesulfonic acid (**2a**) generated the corresponding compounds (**3a–3f**) in moderate to good yields (55–74%). It should be noted that substrate **1** with a strong electron-donating substituent (MeO) on the benzene ring could be reacted with **2a**, providing trace amount of the desired product **3h**. Meanwhile, substrate **1** with 3,5-dimethyl groups on phenyl ring underwent the tandem reaction to afford the coumarin **3g** in acceptable yield (65%). Moreover, halogens (F, Cl, Br and I) attached on the substrate **1** could be well tolerated, giving the desired products (**3i–3l**) in 62–69% yields. The reaction of substrate **1** with a methyl group on the *meta*-position of phenyl ring reacted and **2a**, providing two isomers **3m** and **3m'** in a ratio of 1:1 with 72% total yield. However, a significant steric effect was observed during the reaction of **1** with a methyl group on the *ortho*-position of phenyl ring and **2a**, and trace amount of **3n** was found.

On the other hand, a variety of arylsulfonic acids were examined and the results are shown in Scheme 3. A number of substituted arylsulfonic acids containing both electron-withdrawi-

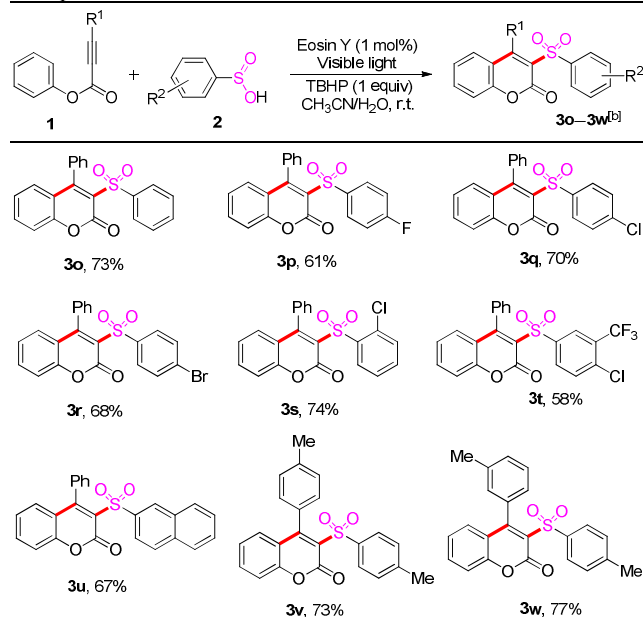
Scheme 2. Reaction Scope of Phenyl 3-Arylpropiolates.^[a]

^[a] Reaction conditions: **1** (0.30 mmol), **2** (0.60 mmol), Eosin Y (1 mol%), TBHP (0.30 mmol), CH₃CN/H₂O (1:1, 1.5 mL), 18 W fluorescent lamp, at room temperature for 12 h. ^[b] Isolated yields.

ng groups (F, Cl, Br and F₃C) and electron-donating groups (Me) underwent the transformation well to generate the corresponding arylsulfonylation products (**3a–3t**, **3v** and **3w**) in 58–77% yields. It also indicated that the reactions are well tolerated for the substituted groups on the benzene rings of R¹ (Scheme 3). The reaction of 3-phenylpropiolate (**1a**) with 2-naphathenesulfonic acid also afforded the anticipated product **3u** in 67% yield. When R¹ was used as alkyl-substitute (Me or *n*-C₅H₁₁) in the oxidative cyclization with **2a**, no desired product was found. These results indicated that alkyl-substitutes dramatically affect the reaction.

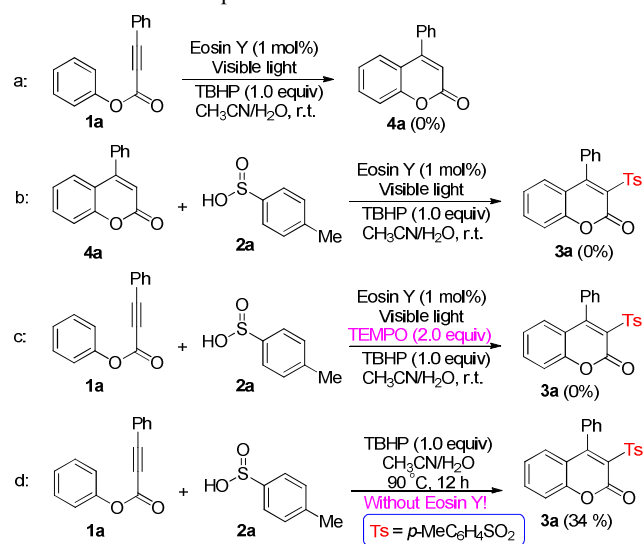
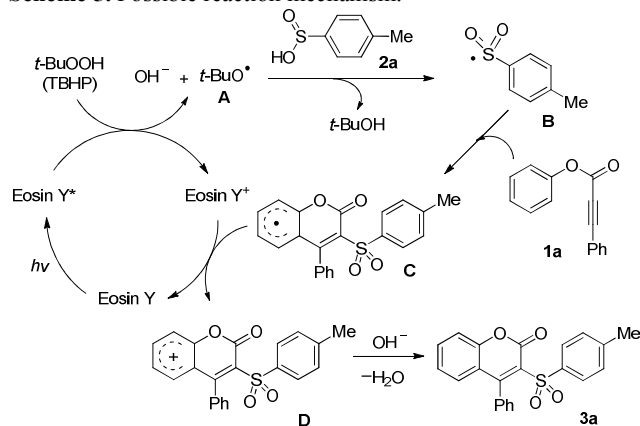
To gain more mechanistic insights of this reaction, we performed several control experiments as shown in Scheme 4. When phenyl 3-phenylpropiolate (**1a**) was carried out under the standard condition in the absence of **2a**, no **4a** was observed (Scheme 4a). In addition, the reaction **2a** with prepared **4a** could not transform into **3a** under the present conditions (Scheme 4b). When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a radical scavenger, was added to the system, the oxidative cyclization reaction was completely inhibited (Scheme 4c). In order to verify the *t*-BuO radical formation, we performed a control experiment involving in **1a**, **2a** and TBHP in MeCN/H₂O at 90 °C for 12 h without Eosin Y and visible light irradiation, providing the desired product **3a** in 34% yield (Scheme 4d). The result indicated that TBHP was readily split into *t*-BuO free radical to perform the reaction under heating conditions.

On the basis of above investigation and the literature,¹⁷ the reaction may involve a radical process, along with a sulfonyl radical addition to alkyne. Thus, a possible mechanism for this photoreaction is proposed in Scheme 5. Initially, a *t*-butoxyl radical (**A**) is produced by a SET from the reaction of excited state of Eosin Y* with *tert*-butyl hydroperoxide (TBHP). Then,

Scheme 3. The Scope of Arylsulfonic Acids and Substituent Group R¹ [a]

[a] Reaction conditions: **1** (0.30 mmol), **2** (0.60 mmol), Eosin Y (1 mol%), TBHP (0.30 mmol), CH₃CN/H₂O (1:1, 1.5 mL), 18 W fluorescent lamp, at room temperature for 12 h. [b] Isolated yields.

an abstraction of hydrogen radical from 4-methylbenzenesulfonic acid (**2a**) undergoes to give the corresponding sulfonyl radical (**B**) and *t*-BuOH. Addition of sulfonyl radical **B** to 3-phenylpropiolate (**1a**) delivers the radical intermediate **C**, which is further transformed into carbocation intermediate **D** through an oxidation of the radical species **C** by an Eosin Y⁺, a radical cation. Finally, species **D** is deprotonated, regenerating the aromatic system and affording the desired 3-sulfonated coumarin product **3a**.

Scheme 4. Control experiments.**Scheme 5.** Possible reaction mechanism.

In summary, we have developed an efficient and visible-light initiated, Eosin Y-catalyzed arylsulfonylation of alkynes with arylsulfonic acids, providing a novel and direct approach to the preparation of 3-sulfonated coumarins. The reactions generated the corresponding products in good yields through a tandem reaction process under metal-free conditions. Further application of this protocol and investigation of detail reaction mechanism are underway in our laboratory.

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