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Visible-Light-Induced Radical Cascade Cyclizations of 1,7-Enynes with Sulfinic Acids: Direct Access to Sulfonated Chromanes and Sulfonated Tetrahydroquinolines under Metal-Free Conditions

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Abstract: A visible-light-induced strategy to access sulfonated chromanes and sulfonated 1,2,3,4-tetrahydroquinolines *via* a radical cascade cyclization of 1-(arylethynyl)-2-(vinyloxy)benzenes and *N*-allyl-2-(arylethynyl)anilines with aromatic and aliphatic sulfinic acids has been developed. In the presence of TBHP (7.5 mol%) as an oxidant and Eosin Y (3.0 mol%) as a photocatalyst, the reactions undergo smoothly to afford the corresponding products in good yields at room temperature under metal-free conditions. This transformation features low loading of TBHP, mild reaction conditions, simple operation, broad functional-group tolerance, and good yields of products.

Key words: 1,7-enynes; chromanes; tetrahydroquinolines; visible-light photocatalysis; Eosin Y; sulfinic acids

Introduction

The free radical tandem cyclization is a powerful platform for the rapid construction of complicated carbocyclic and heterocyclic architectures in a chemoselective and atom-economical manner.[1] In the last two decades, the considerable attention in this field has focused on the radical addition and cascade cyclization, in which free radical species add to unsaturated chemical bonds, followed by an intramolecular cyclization to access cyclic frameworks.[2] 1,n-Enynes, including 1,5-enynes, 1,6-enynes, and 1,7-enynes are proven to be the excellent skeletons for the synthesis of cyclic compounds. The reactions are initiated by an addition of carbon-centered radicals,[3] oxygen-centered radicals,[4] nitrogen-centered radicals,[5] sulfur-centered radicals,[6] phosphorus-centered radicals,[7] or azide-centered radicals,[8] to the carbon-carbon multiple bond within substrates, and subsequently undergo the intramolecular radical cyclization. It should be noted that Tu's group reported sulfonyl radical-induced bicyclization of *O*-tethered 1,7- enynes with aryl sulfonhydrazides for accessing tetracyclic chromen-2-ones.[3e]

The sulfone-containing compounds have been frequently found in the natural products, pharmaceuticals and biologically active molecules, which are used for anti-HIV, anti-cancer, anti-psoriasis, anti-inflammatory and anti-depressant.[9] Representative medicinally interesting molecules containg sulfone unit, shown in Figure 1, are DPP-IV inhibitor,[10a] Eletriptan as 5-HT1-like agonists,[10b] Amisulfride as psychotropic agents,[10c] Dapsone as treatment adjunct

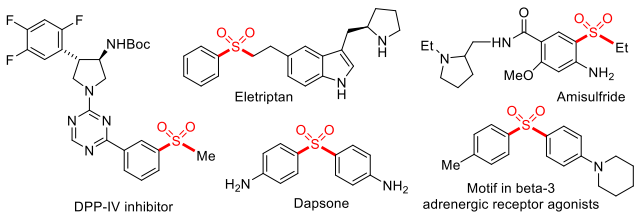

Figure 1. Representative medicines containg sulfone unit.

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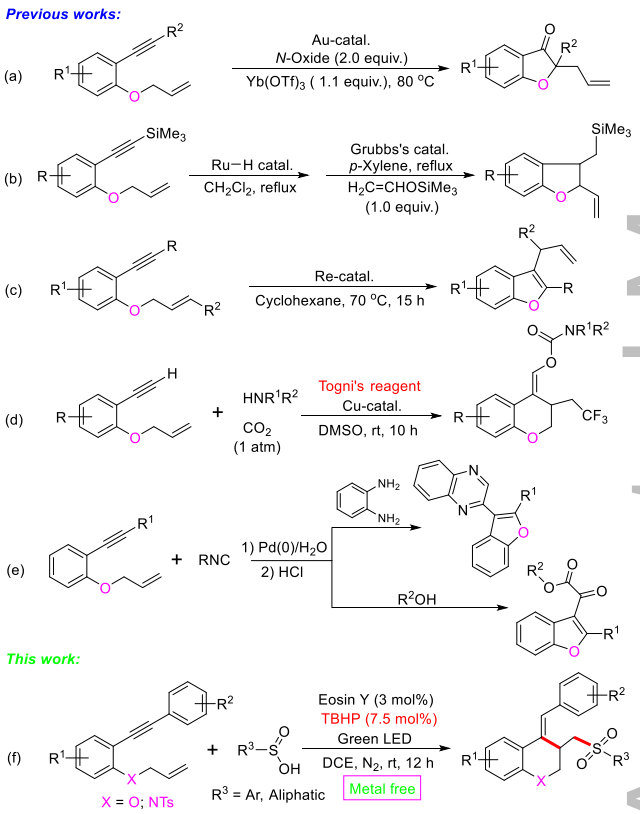
in ARDS,[10d] and motif in β-3 adrenergic receptor agonists.[10e] They have been also applied as the building blocks in organic synthesis.[11] Therefore, the synthesis of sulfones has gained considerable attention of chemists and one of the most classic method is based on the addition of sulfonyl radicals to alkenes and alkynes.[12] Comparing with sulphonyl halides as sulfonylation reagents, sulfinic acids and their salts are relatively stable and versatile intermediates in organic synthesis and the considerable efforts have been devoted to the synthesis of organic sulfones using aryl(alkyl)sulfinic acids (salts) as sulfonylation agents. As a result, the addition of sulfonyl radicals to carbon-carbon multiple bonds for the synthesis of functionalized sulfones have gained a variety of achievements in recent years.[13]

Recently, 1,7-enynes have been recognized as highly versatile substrates for the construction of functionalized benzofurans and benzopyrans with structural diversity and complexity via a radical induced tandem cyclization. For example, Tang and co-workers reported a Au-catalyzed synthesis of functionalized dihydrobenzofuran-3-ones from 1,7-enynes via a [2,3]-sigmatropic rearrangement of oxonium ylides in the presence of pyridine *N*-oxide (Scheme 1a).[14] In addition, Arisawa et al developed a Ru-hydride catalyzed cycloisomerization of aryl enol ether and silylalkynes to yield 2,3-disubstituted benzofurans by two steps. Under the catalysis of Ru-hydride, the aryl enol ether finished the migration of olefinic double bonds to complete cycloisomerization, followed by a Grubbs's catalysis to the desired products with vinyl and trimethylsilylmethyl groups on the 2- and 3-positions (Scheme 1b).[15] Recently, Zi's group described a Re(I)-catalyzed carboalkoxylation of 1,7-enynes for the preparation of C3-substituted benzofurans, in which Re plays an important role of a π acid catalyst to activate alkynes, followed by a charge-accelerated [3,3]-sigmatropic rearrangement (Scheme 1c).[16] It should be noted that Jiang reported an elegant work on a Cu-catalyzed cascade cyclization of 1,7-enynes with Togni's reagent, carbon dioxide, and amines, providing a direct and efficient route to a range of trifluoromethyl-substituted carbamates (Scheme 1d).[17a] In addition, Jiang also developed a Pd-catalyzed tandem intermolecular cyclization of 1-(allyloxy)-2-ethynylbenzenes with isocyanides and water, generating 2,3-difunctionalized benzofurans including 2-benzofurylquinoxalines, benzofuran-3-α-ketoesters and benzofuryl ynediones (Scheme 1e).[17b] It should be noted that Li, Guo and co-workers reported a metal-free oxidative 6-exo-dig cyclization of *N*- and *O*-tethered 1,7-enynes triggered by addition of sulfonyl radicals generated in situ from sulfinic acids, enabling the assembly of 3,4-dihydroquinolin-2(1*H*)-one and 2-chromanone skeletons.[18a] Moreover, the use of sulfinic acids in sulfonyl radical addition/cyclization of alkynes/enynes under visible light irradiation was also extensive investigated.[18b-d] However, most of these reported methods require stoichiometric amounts of an oxidant (typically TBHP) and often employ enynes containing Michael acceptor-type alkenes. Herein, we wish to report a visible-light-induced synthesis of sulfonated chromane derivatives via a radical cascade cyclization of 1-(arylethynyl)-2-(vinyloxy)benzenes and *N*-allyl-2-(arylethynyl)anilines having 1,7-enyne moiety with sulfinic acids using Eosin Y (3.0 mol%) as a photocatalyst in the presence of TBHP (7.5 mol%) as an oxidant, providing the corresponding products in good yields at room temperature under metal-free conditions (Scheme 1f). It provides a direct protocol for the synthesis of a diverse range of sulfonated chromanes and sulfonated 1,2,3,4-tetrahydroquinolines in an efficient way.



Scheme 1. The transformations of 1-(allyloxy)-2-(ethynyl)benzenes and *N*-allyl-2-(arylethynyl)anilines.

Results and Discussion

Initially, 1-(allyloxy)-2-(phenylethynyl)benzene (**1a**) and 4-methylbenzenesulfinic acid (**2a**) were selected as the model substrates for optimization of the reaction conditions and the results were listed in Table 1. When the model reaction of **1a** with **2a** was performed in the presence of Eosin Y (3.0 mol%) as a

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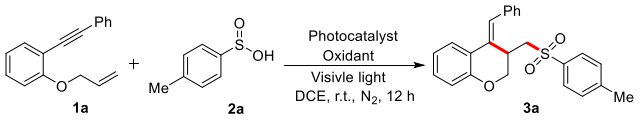
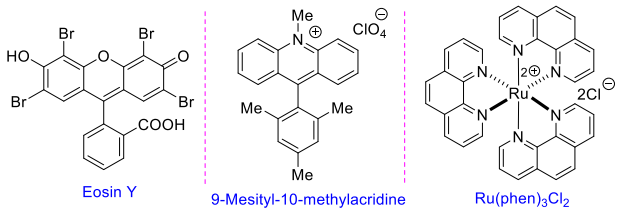
photoredox catalyst, *tert*-butyl hydroperoxide (TBHP, 1.0 equiv.) as an oxidant and DCE (1,2-dichloroethane) as solvent at room temperature under air atmosphere with irradiation of a green LED (530–535 nm, 3 W) for 12 h, to our delight, the reaction generated the corresponding product **3a** in 45% yield (Table 1, entry 1). An improved yield (66%) of **3a** was obtained when N_2 atmosphere was used instead of air atmosphere (Table 1, entry 2). When H_2O_2 was used as the oxidant instead of TBHP, the model reaction afforded the desired product **3a** in 27% yield (Table 1, entry 3). Other oxidants, such as $K_2S_2O_8$ and DTBP (di-*tert*-butyl peroxide) led to trace amount of **3a** only (Table 1, entries 4 and 5). For improvement of the desired product yield, $Ru(phen)_3Cl_2$ and Mes-Acr-Me$^+$ClO$_4^-$ (9-mesityl-10-methylacridine), as the photocatalysts were examined, providing no reactivity for the reaction (Table 1, entries 6 and 7). It is surprising that when the amount of TBHP decreased from 1.0 equiv. to 0.5 equiv., the yield of **3a** increased from 66% to 75% (Table 1, entry 8). Continuing to reduce the amount of TBHP to 25 mol% or even 7.5 mol%, the yield of **3a** was unchanged (Table 1, entries 9−11). In the absence of visible light or Eosin Y, the model reaction can not proceed to produce the target product **3a** (Table 1, entries 12 and 13). Furthermore, the desired product **3a** was obtained in 18% yield in the absence of TBHP (Table 1, entry 14). When the model reaction was irradiated under sunlight, **3a** was isolated in 62% yield (Table 1, entry 15). In addition, the effect of solvent on the reaction was also examined, and the results indicated that DCE is the best one amongst the tested solvents including EtOH, DMSO, THF, CH_2Cl_2, toluene, CH_3CN and H_2O.

Table 1. Optimization of the reaction conditions.[a]



Entry	Photocatalyst	Oxidant	Light source	Yield (%)[b]
1	Eosin Y	TBHP	Green LED	45[c]
2	Eosin Y	TBHP	Green LED	66
3	Eosin Y	H_2O_2	Green LED	27
4	Eosin Y	$K_2S_2O_8$	Green LED	Trace
5	Eosin Y	DTBP	Green LED	Trace
6	$Ru(phen)_3Cl_2$	TBHP	Blue LED	Trace
7	Mes-Acr$^+$ClO$_4^-$	TBHP	Blue LED	Trace
8	Eosin Y	TBHP	Green LED	75[d]
9	Eosin Y	TBHP	Green LED	75[e]
10	Eosin Y	TBHP	Green LED	75[f]
11	Eosin Y	TBHP	Green LED	75[g]
12	Eosin Y	TBHP	–	NR
13	–	TBHP	Green LED	NR
14	Eosin Y	–	Green LED	18
15	Eosin Y	TBHP	Sunlight	62



[a] *Reaction conditions:* 1-(allyloxy)-2-(phenylethynyl)benzene (**1a**, 0.10 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.15 mmol), photocatalyst (3.0 mol%), oxidant (0.10 mmol, 1.0 equiv.), DCE (3.0 mL) at room temperature under N_2 atmosphere with LED irradiation (3 W) for 12 h. NR = no reaction. Green LED (530–535 nm). Blue LED (450–455 nm).

[b] Isolated yield.

[c] Air atmosphere.

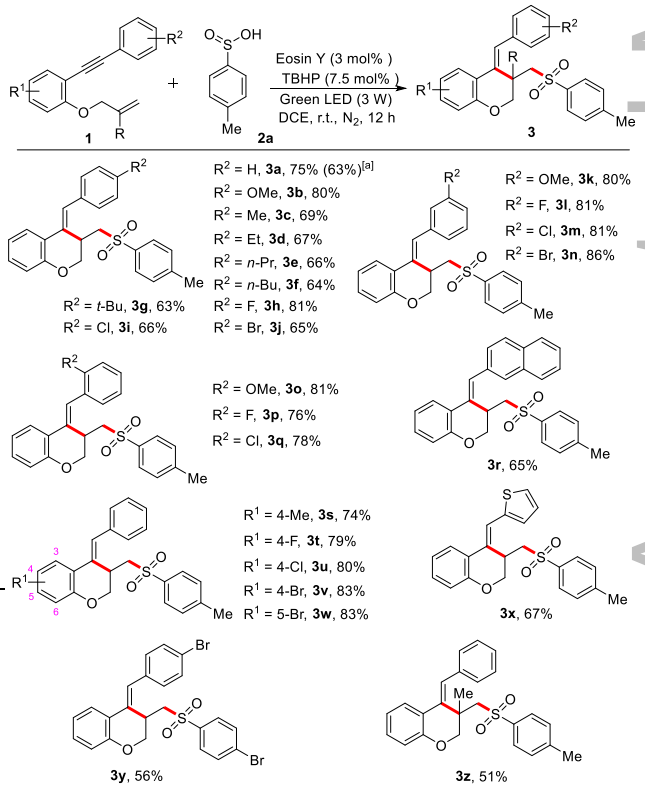
[d] TBHP (0.5 equiv.).

[e] TBHP (25 mol%).

[f] TBHP (15 mol%).

[g] TBHP (7.5 mol%).

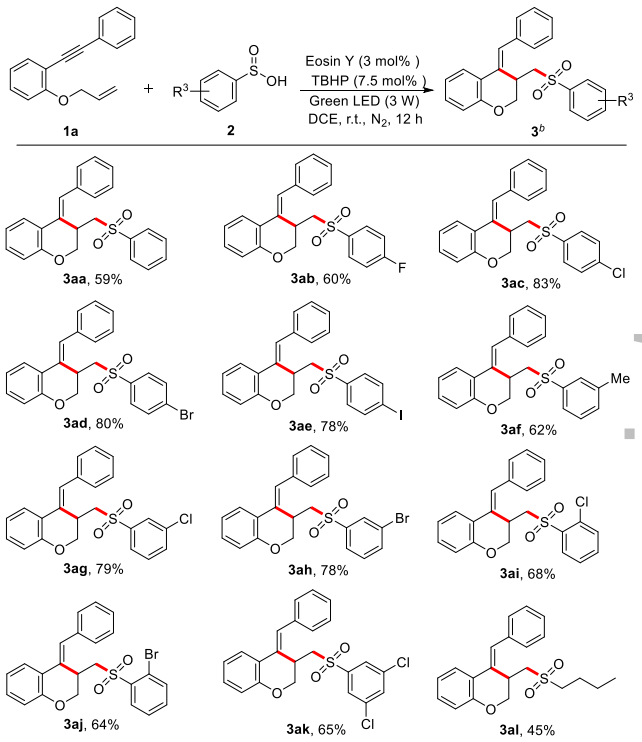
With the optimized conditions in hand, we next explored the scope of the oxidative radical cascade cyclization. The results are shown in Scheme 2. First, a variety of 1-(allyloxy)-2-(arylethynyl)benzene derivatives were examined under the standard conditions, indicating a broad tolerance of substituted groups on the aromatic rings. Unsubstituted **1** (**1a**) and substrates **1** with an electron-donating group (such as MeO, Me, Et, *n*-Pr, *n*-Bu and *t*-Bu) or an electron-withdrawing group (F and Br) at the *para*-position of the benzene rings in aromatic alkyne moiety (R^2), reacted with 4-methylbenzenesulfinic



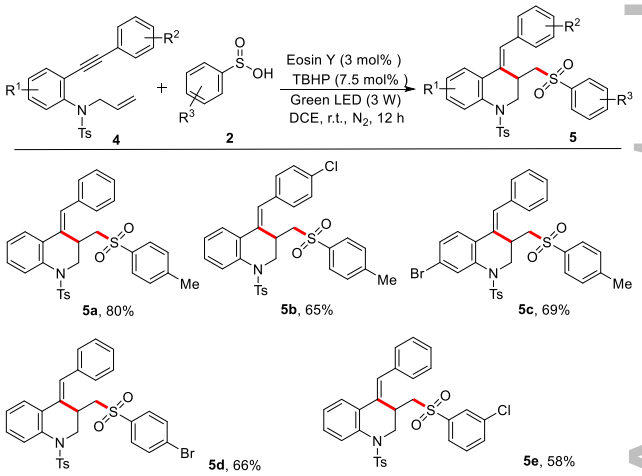
Scheme 2. The scope of substrates **1** [*Reaction conditions:* **1** (0.10 mmol), **2a** (0.15 mmol), Eosin Y (3.0 mol%), TBHP (7.5 mol%), and DCE (3.0 mL) at room temperature in N_2 atmosphere under green LED (530–535 nm, 3 W) irradiation for 12 h; isolated yield of the product; [a]isolated yield of product **3a** in 5 mmol scale].

acid (**2a**) smoothly to afford the corresponding products **3a**–**3j** in 63–81% yields. Furthermore, a gram-scale (up to 5.0 mmol scale) synthesis of **3a** was achieved in 63% isolated yield. Meanwhile, substrates **1** containing an electron-rich group (MeO) or an electron-withdrawing group (F, Cl and Br) on the *meta*- or *ortho*-position of phenylacetylene (R^2), underwent the tandem reaction with **2a** to generate the desired products **3k**–**3q** in 76–86% yields, neglecting steric effect. Furthermore, the reaction of **1**, which is introduced a 2-naphthylethynyl moiety, with **2a** led to the according product **3r** in 65% yield. On the other hand, a variety of substituted groups (R^1) on the aromatic rings were investigated. For the representative substituents (R^1), including electron-donating group (Me) and halogens (F, Cl and Br) on the aromatic rings, gave the anticipated products **3s**–**3w** in 74–83% yields. It should be noted that substrate **1** with a thienylethynyl group was used to react with **2a**, providing **3x** in an acceptable yield (67%). Product **3y** was obtained in 56% yield from the suitable substrates, and its stereochemistry was confirmed by single crystal X-ray diffraction analysis (see: Supporting Information),[19] leading to favorable *E*-isomer. Moreover, the influence of substitution on the alkene moiety was investigated using (*E*)-1-(but-2-en-1-yloxy)-2-(phenylethynyl)benzene (**1z**), generating the desired product **3z** in 51% yield. As an example of internal alkene on 1,7-enyne, 1-(cinnamyloxy)-2-(phenylethynyl)benzene reacted with **2a**, no desired product was obtained. However, alkyl-substituted alkynes, such as 1-(allyloxy)-2-(cyclopropylethynyl)benzene and 1-(allyloxy)-2-(hex-1-yn-1-yl)benzene were used as substrates to react with **2a** under the present reaction conditions, but failed.

Subsequently, a variety of sulfinic acids were examined under the standard reaction conditions and the results are summarized in Scheme 3. A range of arylsulfinic acids including hydrogen, an electron-withdrawing group (F, Cl, Br and I) or an electron-donating group (Me) on the aryl rings underwent the transformations well with **1a** to generate the corresponding products (**3aa**–**3aj**) in 59–83% yields. It should be noted that sterically hindered substituted arylsulfinic acids, including 2-chloro- and 2-bromobenzenesulfinic acids, are suitable substrates for the radical cascade cyclizations, thereby leading to the desired products **3ai** and **3aj** in 68% and 64% yield, respectively. Furthermore, disubstituted arylsulfinic acid, such as 3,5-dichlorobenzenesulfinic acid, was also a suitable sulfonylation reagent for this transformation, providing 65% yield of the product **3ak**. To our delight, when the scope of sulfinic acid was switched to an aliphatic analogue, the anticipant product **3al** was isolated in 45% yield by use of *n*-butylsulfinic acid as the sulfonylation reagent. Unfortunately, thiophene-2-sulfinic acid was attempted under the standard reaction conditions, and no desired product was obtained.



Scheme 3. Substrate scope of sulfinic acids **2** [*Reaction conditions:* **1a** (0.10 mmol), **2** (0.15 mmol), Eosin Y (3.0 mol%), TBHP (7.5 mol%), and DCE (3.0 mL) at room temperature in N atmosphere under green LED (530–535 nm, 3 W) irradiation for 12 h; isolated yield of the product].

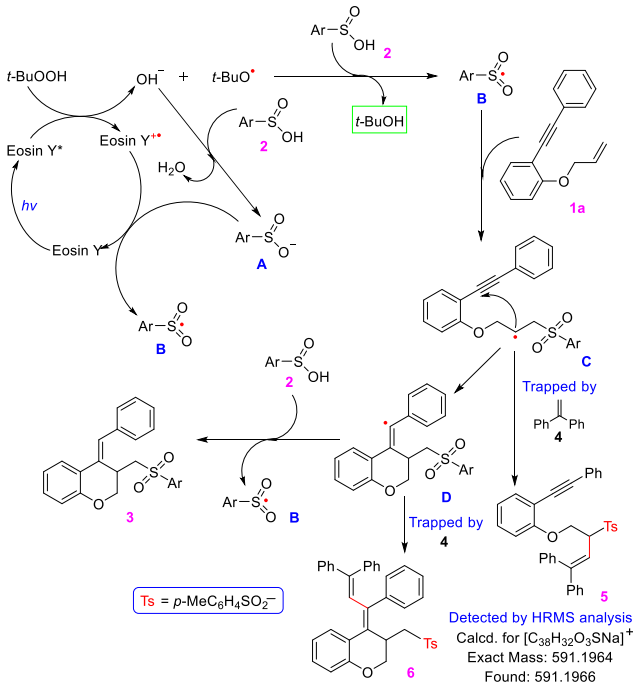


Scheme 4. The reactions of substrates **4** with sulfinic acids **2** [*Reaction conditions:* **4** (0.10 mmol), **2** (0.15 mmol), Eosin Y (3.0 mol%), TBHP (7.5 mol%), and DCE (3.0 mL) at room temperature in N_2 atmosphere under green LED (530–535 nm, 3 W) irradiation for 12 h; isolated yield of the product].

To further extend the substrate scope, *N*-tethered enynes, such as *N*-allyl-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzene-sulfonamide, *N*-allyl-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)-4-met

hylbenzenesulfonamide and *N*-allyl-*N*-(5-bromo-2-(phenylethynyl)phenyl)-4-met hylbenzenesulfonamide were as used as substrates to react with 4-methylbenzenesulfinic acid, 4-bromobenzenesulfinic acid and 3-chlorobenzenesulfinic acid, providing the corresponding products **5a**–**5e** in 58–80% yields, as shown in Scheme 4.

To clarify the mechanism of this cascade cyclization, a radical-trapping reagent, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was added to the model reaction and it was completely inhibited, indicating that free-radical intermediates were involved in the reaction (ESI for details). Based on our observations and literature, a plausible mechanism is proposed in Scheme 5. Firstly, the excited-state Eosin Y* is formed under visible-light irradiation, which undergoes a reaction with TBHP via SET process to generate a hydroxide anion (HO^-) and *tert*-butyloxy radical (*t*-BuO$^\bullet$) along with the formation of Eosin Y$^{+\bullet}$. Then the obtained *t*-BuO$^\bullet$ abstracts a hydrogen from arylsulfinic acid (**2**) to generate the corresponding sulfonyl radical (**B**), which takes an addition to carbon-carbon double bond of **1a** to afford an alkyl radical (**C**), followed by an intramolecular radical cyclization with carbon-carbon triple bond of alkyne via a *6-exo-dig* cyclization, forming vinyl intermediate (**D**).[2b,6f] Finally, intermediate (**D**) gets a hydrogen from **2** to afford the desired product **3** along with the formation of **B** for next run. On the other hand, the generated Eosin Y$^{+\bullet}$ reacts with **A**, which is from the reaction of HO^- with arylsulfinic acid (**2**) to produce sulfonyl radical (**B**) for the repeat sulfonylation and the formation of Eosin Y to complete the photocatalyst cycle through a SET process. It should be noted that the key radical intermediates **C** and/or **D** could be trapped by 1,2-diphenylethene (**4**), providing adducts **5** and/or **6**, confirmed by HRMS analysis (ESI for details).



Scheme 5. The proposed mechanism.

Conclusion

In conclusion, we have developed a visible-light-induced strategy to access sulfonated chromanes and sulfonated 1,2,3,4-tetrahydroquinolines via radical cascade cyclization of 1-(arylethynyl)-2-(vinyloxy)benzenes and *N*-allyl-2-(arylethynyl)anilines with sulfinic acids under metal-free conditions. In the presence of TBHP (7.5 mol%) as an oxidant and Eosin Y (3.0 mol%) as a photocatalyst, the reactions undergo smoothly to afford the corresponding products in good yields under green LED irradiation and nitrogen atmosphere at room temperature. This transformation features low loading of TBHP, mild reaction conditions, simple operation, broad functional-group tolerance, and high efficiency. Its detailed reaction mechanism and further applications are underway in our laboratory.

Experimental Section

General Considerations

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 or a 600 MHz Bruker FT-NMR spectrometer (600/150 MHz or 400/100 MHz, respectively), and ^{19}F NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (565 MHz). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). All the solvents and commercially available reagents were purchased from commercial suppliers. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

Typical Procedure for the Synthesis of 3a

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 1-(allyloxy)-2-(phenylethynyl)benzene (**1a**, 0.10 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.15 mmol), Eosin Y (3.0 mol%), TBHP (7.5 mol%), and DCE (3.0 mL). The reaction vessel was exposed to green LED (530–535 nm, 3

W) irradiation at room temperature in N_2 atmosphere with stirring for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate) to give the desired product **3a** (29.4 mg, 75% yield).

Characterization data for the products

(*E*)-4-Benzylidene-3-(tosylmethyl)chromane (3a): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (29.4 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.32–7.28 (m, 4H), 7.26–7.23 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.92–6.88 (m, 3H), 4.76 (d, *J* = 11.4 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 3.80 (d, *J* = 10.8 Hz, 1H), 3.64–3.60 (m, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.7, 144.8, 136.8, 135.7, 132.4, 130.0, 129.5, 128.8, 128.5, 127.8, 127.2, 125.0, 123.2, 121.2, 121.1, 117.3, 67.0, 54.5, 29.8, 21.6. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{24}H_{22}NaO_3S]^+$: 413.1182, Found: 413.1184.

(*E*)-4-(4-Methoxybenzylidene)-3-(tosylmethyl)chroman (3b): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (33.8 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.92–6.85 (m, 5H), 4.75 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.86 (s, 1H), 3.84 (s, 3H), 3.64 (t, *J* = 12.6 Hz, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.9, 153.5, 144.9, 137.0, 130.8, 130.3, 130.0, 129.2, 128.3, 127.9, 124.9, 122.9, 121.5, 121.3, 117.3, 114.1, 67.1, 55.3, 54.5, 29.8, 21.6. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{25}H_{24}NaO_4S]^+$: 433.1288, Found: 433.1288.

(*E*)-4-(4-Methylbenzylidene)-3-(tosylmethyl)chroman (3c): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.0 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.18–7.09 (m, 5H), 6.92–6.87 (m, 3H), 4.76 (d, *J* = 11.4 Hz, 1H), 3.97 (d, *J* = 11.4 Hz, 1H), 3.81 (d, *J* = 11.4 Hz, 1H), 3.64–3.60 (m, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 144.7, 137.1, 136.9, 132.8, 131.7, 130.0, 129.3, 129.3, 128.8, 127.9, 124.9, 123.2, 121.3, 121.2, 117.3, 67.0, 54.5, 29.8, 21.6, 21.2. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{25}H_{24}NaO_3S]^+$: 427.1338, Found: 427.1339.

(*E*)-4-(4-Ethylbenzylidene)-3-(tosylmethyl)chroman (3d): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.1 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.19–7.13 (m, 5H), 6.92–6.88 (m, 3H), 4.77 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 3.85 (dd, J_1 = 1.2 Hz, J_2 = 10.8 Hz, 1H), 3.66–3.62 (m, 1H), 3.13 (d, *J* = 14.4 Hz, 1H), 2.66 (q, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 1.26 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 144.8, 143.5, 137.0, 133.1, 131.7, 130.0, 129.4, 128.9, 128.1, 128.0, 125.0, 123.2, 121.4, 121.3, 117.3, 67.0, 54.5, 29.9, 28.6, 21.6, 15.4. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{26}H_{26}NaO_3S]^+$: 441.1495, Found: 441.1497.

(*E*)-4-(4-(*n*-Propyl)benzylidene)-3-(tosylmethyl)chroma n (3e): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.7 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 7.8 Hz, 2H), 7.47 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.17–7.14 (m, 3H), 7.11–7.10 (m, 2H), 6.91–6.87 (m, 3H), 4.77 (dd, J_1 = 1.2 Hz, J_2 = 10.8 Hz, 1H), 3.97 (d, *J* = 11.4 Hz, 1H), 3.84 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 3.65–3.61 (m, 1H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 1.69–1.62 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 144.7, 141.9, 137.0, 133.1, 131.6, 130.0, 129.3, 128.8, 128.7, 127.9, 125.0, 123.2, 121.3, 121.2, 117.3, 66.9, 54.4, 37.7, 29.8, 24.3, 21.6, 13.8. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{27}H_{28}NaO_3S]^+$: 455.1651, Found: 455.1650.

(*E*)-4-(4-(*n*-Butyl)benzylidene)-3-(tosylmethyl)chroman (3f): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.6 mg, 64% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 7.8 Hz, 2H), 7.48 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.18–7.15 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.92–6.87 (m, 3H), 4.77 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.85 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 3.66–3.61 (m, 1H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 1.64–1.59 (m, 2H), 1.41–1.35 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ:153.6, 144.8, 142.2, 137.0, 133.0, 131.7, 130.0, 129.3, 128.8, 128.7, 127.9, 125.0, 123.2, 121.4, 121.2, 117.3, 67.0, 54.5, 35.3, 33.4, 29.8, 22.3, 21.6, 13.9. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{28}H_{30}NaO_3S]^+$: 469.1808, Found: 469.1806.

(*E*)-4-(4-(*tert*-Butyl)benzylidene)-3-(tosylmethyl)chrom an (3g): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.3 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.37–7.33 (m, 4H), 7.24–7.22 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.92–6.87 (m, 3H), 4.78 (d, *J* = 11.4 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.90 (d, *J* = 11.4 Hz, 1H), 3.67–3.63 (m, 1H), 2.47 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 150.4, 144.8, 137.1, 132.8, 131.7, 130.0, 129.4, 128.8, 128.0, 125.6, 125.0, 123.1, 121.4, 121.2, 117.3, 67.0, 54.4, 34.6, 31.2, 29.8, 21.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{28}H_{30}NaO_3S]^+$: 469.1808, Found: 469.1806.

(*E*)-4-(4-Fluorobenzylidene)-3-(tosylmethyl)chroman (3h): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (33.1 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.21–7.17 (m, 3H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.93–6.88 (m, 3H), 4.75 (d, *J* = 11.4 Hz, 1H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.70 (d, *J* = 10.8 Hz, 1H), 3.64–3.60 (m, 1H), 3.04 (d, *J* = 11.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 161.8 (d, *J* = 246.5 Hz), 153.6, 144.9, 136.6, 132.5, 131.8

(d, *J* = 3.2 Hz), 130.5 (d, *J* = 7.8 Hz), 130.0, 129.6, 127.8, 124.9, 122.0, 121.3, 120.9, 117.4, 115.5 (d, *J* = 21.2 Hz), 67.0, 54.4, 29.7, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -113.91. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}FNaO_3S]^+$: 431.1088, Found: 431.1091.

(*E*)-4-(4-Chlorobenzylidene)-3-(tosylmethyl)chroman (3i): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.2 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.8 Hz, 2H), 7.47 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.25–7.23 (m, 2H), 7.19 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.93–6.88 (m, 2H), 6.86 (s, 1H), 4.76 (dd, J_1 = 1.8 Hz, J_2 = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.69–3.60 (m, 2H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.7, 145.0, 136.6, 134.2, 133.2, 133.0, 130.1, 130.0, 129.8, 128.7, 127.9, 125.0, 121.8, 121.3, 120.8, 117.4, 67.0, 54.4, 29.8, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}ClNaO_3S]^+$: 477.0792, Found: 477.0794.

(*E*)-4-(4-Bromobenzylidene)-3-(tosylmethyl)chroman (3j): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (30.6 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.19 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.93–6.88 (m, 2H), 6.83 (s, 1H), 4.76 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 3.97 (d, *J* = 11.4 Hz, 1H), 3.66–3.59 (m, 2H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.7, 145.0, 136.5, 134.6, 133.2, 131.6, 130.3, 130.0, 129.8, 127.8, 124.9, 121.8, 121.3, 121.2, 120.7, 117.4, 66.9, 54.3, 29.8, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}BrNaO_3S]^+$: 491.0287, Found: 491.0287.

(*E*)-4-(3-Methoxybenzylidene)-3-(tosylmethyl)chroman (3k): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (33.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.0 Hz, 2H), 7.49 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22–7.16 (m, 2H), 6.93–6.81 (m, 6H), 4.75 (dd, J_1 = 2.0 Hz, J_2 = 11.2 Hz, 1H), 4.01 (d, *J* = 11.6 Hz, 1H), 3.87–3.85 (m, 4H), 3.64–3.57 (m, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 153.7, 144.7, 137.1, 136.9, 132.7, 130.0, 129.6, 127.8, 125.0, 123.2, 121.3, 121.1, 121.1, 117.4, 114.2, 113.3, 67.1, 55.3, 54.6, 29.9, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{25}H_{24}NaO_4S]^+$: 443.1288, Found: 443.1289.

(*E*)-4-(3-Fluorobenzylidene)-3-(tosylmethyl)chroman (3l): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (33.1 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.27–7.23 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.95–6.86 (m, 5H), 4.76 (dd, J_1 = 1.2 Hz, J_2 = 11.4 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.74–3.73 (m, 1H), 3.62–3.58 (m, 1H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 162.7 (d, *J* = 244.8 Hz), 153.7, 144.8, 137.9 (d, *J* = 7.7 Hz), 136.5, 133.6, 130.0 (d, *J* = 8.6 Hz), 129.9, 129.8, 127.7, 124.9, 124.4 (d, *J* = 2.4 Hz), 121.8 (d, *J* = 1.8 Hz), 121.3, 120.6, 117.4, 115.6 (d, *J* = 21.3 Hz), 114.0 (d, *J* = 21.2 Hz), 66.9, 54.4, 29.7, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -112.31. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}FNaO_3S]^+$: 431.1088, Found: 431.1086.

(*E*)-4-(3-Chlorobenzylidene)-3-(tosylmethyl)chroman (3m): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (34.5 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.32–7.28 (m, 3H), 7.25–7.13 (m, 4H), 6.94–6.86 (m, 3H), 4.75 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 4.01 (d, *J* = 11.2 Hz, 1H), 3.75 (dd, J_1 = 1.6 Hz, J_2 = 10.8 Hz, 1H), 3.63–3.57 (m, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 144.8, 137.6, 136.7, 134.5, 133.8, 130.0, 129.9, 129.8, 128.9, 127.7, 127.3, 126.8, 124.9, 121.6, 121.3, 120.6, 117.5, 67.1, 54.6, 29.7, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}ClNaO_3S]^+$: 447.0792, Found: 447.0790.

(*E*)-4-(3-Bromobenzylidene)-3-(tosylmethyl)chroman (3n): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (40.5 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.20–7.16 (m, 3H), 6.93–6.88 (m, 2H), 6.85 (s, 1H), 4.74 (d, *J* = 11.4 Hz, 1H), 4.00 (d, *J* = 10.8 Hz, 1H), 3.76–3.74 (m, 1H), 3.62–3.58 (m, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.8, 144.8, 137.9, 136.7, 133.8, 131.8, 130.2, 130.0, 130.0, 129.9, 127.7, 127.2, 124.9, 122.7, 121.5, 121.3, 120.6, 117.5, 67.1, 54.5, 29.7, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}BrNaO_3S]^+$: 491.0287, Found: 491.0287.

(*E*)-4-(2-Methoxybenzylidene)-3-(tosylmethyl)chroman (3o): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (34.1 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.29–7.24 (m, 3H), 7.17–7.16 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 6.91–6.84 (m, 4H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.01 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 2H), 3.08 (d, *J* =8.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.2, 153.6, 144.6, 136.9, 132.5, 129.9, 129.5, 129.3, 128.7, 127.8, 125.2, 124.7, 121.4, 121.2, 120.4, 119.1, 117.2, 110.6, 67.2, 55.4, 54.7, 30.3, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{25}H_{24}NaO_4S]^+$: 433.1288, Found: 433.1286.

(*E*)-4-(2-Fluorobenzylidene)-3-(tosylmethyl)chroman (3p): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (31.0 mg, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.25–7.17 (m, 3H), 7.06 (td, J_1 = 1.2 Hz, J_2 = 8.1 Hz, 1H), 7.00 (td, J_1 = 1.2 Hz, J_2 = 9.6 Hz, 1H), 6.93–6.88 (m, 3H), 4.76 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 4.02 (d, *J* = 11.4 Hz, 1H), 3.59–3.53 (m, 2H), 3.06 (d, *J* = 13.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.1 (d, *J* = 245.9 Hz), 153.7, 144.6, 136.6, 134.7, 130.1

(d, *J* = 2.3 Hz), 129.9, 129.8, 129.0 (d, *J* = 8.3 Hz), 127.7, 125.1, 124.0 (d, *J* = 3.3 Hz), 123.5 (d, *J* = 14.1 Hz), 121.2, 120.7, 117.3, 115.6 (t, *J* = 2.0 Hz), 115.4, 67.1, 54.4, 30.2, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -114.00. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}FNaO_4S]^+$: 431.1088, Found: 431.1087.

(*E*)-4-(2-Chlorobenzylidene)-3-(tosylmethyl)chroman (3q): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (33.2 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.26–7.25 (m, 2H), 7.23–7.16 (m, 4H), 6.96–6.89 (m, 3H), 4.73 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 4.04 (d, *J* = 11.2 Hz, 1H), 3.61–3.55 (m, 1H), 3.46 (dd, J_1 = 1.6 Hz, J_2 = 10.8 Hz, 1H), 3.00 (d, *J* = 14.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 144.6, 136.4, 134.2, 134.0, 133.9, 130.1, 129.9, 129.5, 128.5, 127.7, 126.7, 125.1, 121.3, 120.4, 121.2, 117.4, 67.1, 54.6, 30.1, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}ClNaO_3S]^+$: 447.0792, Found: 447.0792.

(*E*)-4-(Naphthalen-2-ylmethylene)-3-(tosylmethyl)chroman (3r): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.6 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.82–7.74 (m, 4H), 7.57–7.47 (m, 3H), 7.36 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.23–7.17 (m, 3H), 7.08 (s, 1H), 6.96–6.89 (m, 2H), 4.73-4.71 (m, 1H), 4.03–4.00 (m, 2H), 3.71–3.64 (m, 1H), 3.18 (d, *J* = 14.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 144.8, 136.9, 133.5, 133.1, 132.8, 132.4, 129.9, 129.6, 128.4, 128.1, 127.9, 127.7, 127.4, 127.1, 126.4, 126.3, 125.0, 123.1, 121.3, 121.2, 117.4, 67.2, 54.6, 29.9, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{28}H_{24}NaO_3S]^+$: 463.1338, Found: 463.1338.

(*E*)-4-Benzylidene-6-methyl-3-(tosylmethyl)chroman (3s): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (30.1 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.0 Hz, 2H), 7.32–7.23 (m, 8H), 6.99 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.91 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.72 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 3.96 (d, *J* = 11.2 Hz, 1H), 3.78 dd, J_1 = 2.0 Hz, J_2 = 11.2 Hz, 1H), 3.65-3.59 (m, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 144.7, 136.8, 135.8, 132.6, 130.4, 130.4, 130.0, 128.8, 128.5, 127.8, 127.1, 125.0, 122.9, 120.7, 117.1, 67.0, 54.5, 29.8, 21.6, 20.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{24}NaO_3S]^+$: 427.1338, Found: 427.1338.

(*E*)-4-Benzylidene-6-fluoro-3-(tosylmethyl)chroman (3t): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (32.4 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.4 Hz, 2H), 7.34–7.23 (m, 7H), 7.17 (dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz, 1H), 6.91–6.82 (m, 3H), 4.76 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 3.96 (d, *J* = 11.2 Hz, 1H), 3.81–3.78 (m, 1H), 3.63–3.57 (m, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4 (d, *J* = 237.3 Hz), 149.8 (d, *J* = 1.6 Hz), 144.9, 136.7, 135.3, 131.7 (d, *J* = 2.0 Hz), 130.0, 128.9, 128.6, 127.8, 127.5, 124.3, 122.0 (d, *J* = 7.5 Hz), 118.5 (d, *J* = 8.3 Hz), 116.5 (d, *J* = 23.7 Hz), 110.5 (d, *J* = 23.9 Hz), 67.1, 54.4, 29.6, 21.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ: -122.32. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}FNaO_4S]^+$: 431.1088, Found: 431.1088.

(*E*)-4-Benzylidene-6-chloro-3-(tosylmethyl)chroman (3u): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (34.2 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.2 Hz, 2H), 7.33–7.29 (m, 5H), 7.27–7.23 (m, 3H), 7.05 (s, 1H), 7.03–7.02 (m, 1H), 6.90 (s, 1H), 4.77 (d, *J* = 10.8 Hz, 1H), 3.97 (d, *J* = 11.4 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 1H), 3.55 (t, *J* = 12.6, 1H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.1, 144.9, 136.7, 135.4, 131.5, 130.0, 128.8, 128.6, 127.8, 127.4, 126.2, 124.5, 123.7, 122.5, 120.3, 120.3, 67.2, 54.4, 29.6, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}ClNaO_3S]^+$: 447.0792, Found: 447.0790.

(*E*)-4-Benzylidene-6-bromo-3-(tosylmethyl)chroman (3v): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (39.1 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.8 Hz, 2H), 7.57 (s, 1H), 7.33–7.23 (m, 8H), 6.88 (s, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 3.96 (d, *J* = 11.4 Hz, 1H), 3.80 (d, *J* = 10.8 Hz, 1H), 3.55 (t, *J* = 12.6 Hz, 1H), 3.09 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.6, 144.9, 136.7, 135.2, 132.1, 131.2, 130.0, 128.8, 128.6, 127.8, 127.5, 124.5, 123.1, 119.1, 113.6, 67.2, 54.3, 29.5, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}BrNaO_3S]^+$: 491.0287, Found: 491.0289.

(*E*)-4-Benzylidene-7-bromo-3-(tosylmethyl)chroman (3w): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (39.0 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.8 Hz, 2H), 7.43 (s, 1H), 7.33–7.23 (m, 7H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 3.96 (d, *J* = 11.4 Hz, 1H), 3.79 (d, *J* = 10.8 Hz, 1H), 3.56 (t, *J* = 12.6 Hz, 1H), 3.09 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.1, 144.9, 136.7, 135.2, 131.3, 130.0, 129.3, 128.8, 128.6, 127.8, 127.5, 126.3, 124.5, 124.4, 122.6, 118.7, 67.2, 54.3, 29.5, 21.6. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{24}H_{21}BrNaO_3S]^+$: 491.0287, Found: 491.0286.

(*E*)-4-(Thiophen-2-ylmethylene)-3-(tosylmethyl)chroman (3x): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (26.6 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (s, 1H), 7.16–7.15 (m, 1H), 7.13 (s, 1H), 7.07 (s, 1H), 7.03–7.03 (m, 1H), 6.91–6.90 (m, 2H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.05 (t, *J* = 12.0 Hz, 2H), 3.56 (t, *J* = 12.9 Hz, 1H), 3.05 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.9, 144.8, 138.9, 137.1, 129.9, 129.7, 129.4, 128.1, 127.9, 127.7, 126.2, 124.3, 121.3, 120.7, 117.7, 115.2, 66.4, 53.9, 30.6, 21.5. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{22}H_{20}NaO_3S_2]^+$: 419.0746, Found: 419.0746.

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(*E*)-4-(4-bromobenzylidene)-3-(((4-bromophenyl)sulfonyl)methyl)chromane (3y): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (30.0 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.48–7.45 (m, 3H), 7.21 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.94 (td, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 6.89 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 6.85 (s, 1H), 4.73 (dd, J_1 = 1.8 Hz, J_2 = 11.4 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.74 (d, J_1 = 1.8 Hz, J_2 = 10.8 Hz, 1H), 3.64–3.60 (m, 1H), 3.05 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.7, 138.6, 134.6, 133.0, 132.8, 131.8, 130.4, 129.9, 129.4, 125.0, 122.1, 121.5, 121.5, 120.7, 117.5, 67.1, 54.5, 29.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{18}Br_2NaO_3S]^+$: 554.9236, Found: 554.9238.

(*E*)-4-Benzylidene-3-methyl-3-(tosylmethyl)chromane (3z): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (20.8 mg, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.4 Hz, 2H), 7.23–7.17 (m, 7H), 7.01 (td, J_1 = 1.8 Hz, J_2 = 7.2 Hz, 1H), 6.74 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 6.51 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 6.46 (s, 1H), 6.35 (td, J_1 = 0.6 Hz, J_2 = 7.8 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 3.92 (d, *J* = 11.4 Hz, 1H), 3.43 (d, *J* = 15.0 Hz, 1H), 3.23 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.4, 144.2, 137.7, 137.4, 135.1, 130.2, 129.5, 129.4, 128.9, 128.3, 127.8, 126.9, 123.8, 119.5, 118.0, 116.3, 74.9, 59.6, 36.5, 21.5, 19.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{25}H_{24}NaO_3S]^+$: 427.1338, Found: 427.1339.

(*E*)-4-Benzylidene-3-((phenylsulfonyl)methyl)chroman (3aa): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (22.4 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91–7.89 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55–7.48 (m, 3H), 7.33–7.29 (m, 2H), 7.26–7.23 (m, 3H), 7.19 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 6.93–6.88 (m, 3H), 4.77 (dd, J_1 = 2.0 Hz, J_2 = 11.2 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.86 (dd, J_1 = 2.0 Hz, J_2 = 11.2 Hz, 1H), 3.67–3.61 (m, 1H), 3.12 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 139.8, 135.7, 133.8, 132.3, 129.5, 129.4, 128.8, 128.6, 127.3, 125.0, 123.3, 121.3, 121.1, 117.3, 67.1, 54.5, 29.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{20}NaO_3S]^+$: 339.1025, Found: 339.1023.

(*E*)-4-Benzylidene-3-(((4-fluorophenyl)sulfonyl)methyl)chroman (3ab): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (23.6 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.90–7.88 (m, 2H), 7.50 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29–7.24 (m, 3H), 7.21–7.18 (m, 3H), 6.95–6.89 (m, 3H), 4.77 (dd, J_1 = 1.8 Hz, J_2 = 10.8 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 3.82 (dd, J_1 = 1.8 Hz, J_2 = 10.8 Hz, 1H), 3.66-3.62 (m, 1H), 3.10 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.8 (d, *J* = 255.5 Hz), 153.7, 135.8, 135.7, 132.3, 130.7 (d, *J* = 9.6 Hz), 129.7, 128.8, 128.7, 127.4, 125.0, 123.4, 121.4, 121.1, 117.4, 116.7 (d, *J* = 22.8 Hz), 67.1, 54.8, 29.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -103.14. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}FNaO_3S]^+$: 417.0931, Found: 417.0930.

(*E*)-4-Benzylidene-3-(((4-chlorophenyl)sulfonyl)methyl)chroman (3ac): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (34.1 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.4 Hz, 2H), 7.49–7.45 (m, 3H), 7.31–7.27 (m, 3H), 7.20–7.17 (m, 3H), 6.93–6.88 (m, 3H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.01 (d, *J* = 11.4 Hz, 1H), 3.76 (d, *J* = 11.4 Hz, 1H), 3.62 (t, *J* = 12.6 Hz, 1H), 3.08 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 140.5, 138.0, 135.7, 132.2, 129.7, 129.6, 129.3, 128.7, 128.6, 127.3, 124.9, 123.3, 121.3, 120.9, 117.4, 67.0, 54.5, 29.8. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}ClNaO_3S]^+$: 433.0636, Found: 433.0639.

(*E*)-4-Benzylidene-3-(((4-bromophenyl)sulfonyl)methyl)chroman (3ad): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (36.6 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.31–7.27 (m, 3H), 7.20–7.17 (m, 3H), 6.94–6.88 (m, 3H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.01 (d, *J* = 11.4 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.64–3.60 (m, 1H), 3.07 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 138.6, 135.7, 132.7, 132.2, 129.6, 129.3, 129.2, 128.7, 128.6, 127.3, 124.9, 123.3, 121.4, 120.9, 117.4, 67.0, 54.5, 29.8. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}BrNaO_3S]^+$: 477.0130, Found: 477.1028.

(*E*)-4-Benzylidene-3-(((4-iodophenyl)sulfonyl)methyl)chroman (3ae): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (39.2 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.30–7.29 (m, 3H), 7.20–7.18 (m, 3H), 6.94–6.88 (m, 3H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.01 (d, *J* = 11.4 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 3.63–3.59 (m, 1H), 3.07 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 139.2, 138.6, 135.7, 132.2, 129.6, 129.1, 128.7, 128.6, 127.4, 124.9, 123.3, 121.4, 120.9, 117.4, 101.9, 67.0, 54.5, 29.8. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}INaO_3S]^+$: 524.9992, Found: 524.9995.

(*E*)-4-Benzylidene-3-((*m*-tolylsulfonyl)methyl)chroman (3af): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (24.3 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 7.6 Hz, 2H), 7.50-7.40 (m, 3H), 7.33–7.24 (m, 5H), 7.19 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 6.94–6.88 (m, 3H), 4.79 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 4.01 (d, *J* = 11.2 Hz, 1H), 3.86 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 3.67–3.60 (m, 1H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 139.7, 139.7, 135.7, 134.6, 132.4, 129.5, 129.3, 128.9, 128.6, 128.1, 127.3, 125.0, 124.9, 123.2, 121.3, 121.1, 117.3, 67.1, 54.4, 29.7, 21.3. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{24}H_{22}NaO_3S]^+$: 413.1182, Found: 413.1182.

(*E*)-4-Benzylidene-3-(((3-chlorophenyl)sulfonyl)methyl)chroman (3ag): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (32.6 mg, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.50–7.44 (m,

2H), 7.34–7.32 (m, 2H), 7.27–7.24 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.95–6.89 (m, 3H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 11.4 Hz, 1H), 3.83 (d, *J* = 10.8 Hz, 1H), 3.63 (t, *J* = 12.6 Hz, 1H), 3.11 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 141.4, 135.6, 135.6, 134.0, 132.1, 130.7, 129.6, 128.8, 128.6, 127.9, 127.4, 125.9, 124.9, 123.4, 121.4, 121.0, 117.4, 67.1, 54.5, 29.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}ClNaO_3S]^+$: 433.0636, Found: 433.0636.

(*E*)-4-Benzylidene-3-(((3-bromophenyl)sulfonyl)methyl) chroman (3ah): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (35.4 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.35–7.33 (m, 2H), 7.29–7.25 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.95–6.89 (m, 3H), 4.78 (d, *J* = 11.4 Hz, 1H), 4.04 (d, *J* = 11.4 Hz, 1H), 3.85 (d, *J* = 10.8 Hz, 1H), 3.64 (t, *J* = 12.3 Hz, 1H), 3.12 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 141.6, 136.9, 135.7, 132.2, 130.9, 130.7, 129.6, 128.8, 128.7, 127.5, 126.4, 125.0, 123.5, 123.4, 121.4, 121.0, 117.4, 67.1, 54.6, 29.7. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}BrNaO_3S]^+$: 477.0130, Found: 477.0128.

(*E*)-4-Benzylidene-3-(((2-chlorophenyl)sulfonyl)methyl) chroman (3ai): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (27.9 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.59–7.51 (m, 3H), 7.45 (td, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.31-7.28 (m, 1H), 7.21 (td, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 6.99–6.91 (m, 3H), 4.78 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 4.05 (d, *J* = 11.2 Hz, 1H), 3.95–3.82 (m, 2H), 3.55 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 137.2, 135.7, 134.7, 132.9, 132.3, 132.0, 131.5, 129.6, 128.9, 128.6, 127.5, 127.4, 125.0, 123.4, 121.3, 121.1, 117.4, 67.4, 52.5, 29.6. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}ClNaO_3S]^+$: 433.0636, Found: 433.0635.

(*E*)-4-Benzylidene-3-(((2-bromophenyl)sulfonyl)methyl) chroman (3aj): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.6 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.73 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.52–7.43 (m, 3H), 7.38–7.32 (m, 4H), 7.28–7.26 (m, 1H), 7.20 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.97–6.89 (m, 3H), 4.78 (dd, J_1 = 2.0 Hz, J_2 = 11.6 Hz, 1H), 4.04 (d, *J* = 11.2 Hz, 1H), 3.94–3.81 (m, 2H), 3.57 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 138.9, 135.7, 135.6, 134.8, 132.3, 131.8, 129.6, 129.0, 128.6, 128.1, 127.4, 125.1, 123.4, 121.3, 121.1, 121.1, 117.4, 67.4, 52.1, 29.6. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{19}BrNaO_3S]^+$: 477.0130, Found: 477.0130.

(*E*)-4-Benzylidene-3-(((3,5-dichlorophenyl)sulfonyl)met hyl)chroman (3ak): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (28.9 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (s, 2H), 7.59 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.30–7.27 (m, 1H), 7.26–7.25 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.97–6.90 (m, 3H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.07 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.64 (t, *J* = 12.6 Hz, 1H), 3.10 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.6, 142.6, 136.4, 135.7, 133.9, 132.0, 129.7, 128.7, 128.7, 127.6, 126.2, 124.9, 123.6, 121.5, 120.9, 117.5, 67.2, 54.7, 29.8. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{23}H_{18}Cl_2NaO_3S]^+$: 467.0246, Found: 467.0246.

(*E*)-4-Benzylidene-3-((*n*-butylsulfonyl)methyl)chroman (3al): Isolated by column chromatography (EtOAc/petroleum ether = 1:20); white solid (16.1 mg, 45% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.59 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.43–7.38 (m, 4H), 7.31–7.28 (m, 1H), 7.23–7.21 (m, 1H), 7.03 (s, 1H), 6.97 (td, J_1 = 1.2 Hz, J_2 = 8.1 Hz, 1H), 6.92 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 4.75 (dd, J_1 = 2.4 Hz, *J* = 11.4 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 1H), 3.93 (dd, J_1 = 2.4 Hz, J_2 = 10.8 Hz, 1H), 3.49–3.45 (m, 1H), 2.97 (dd, J_1 = 1.2 Hz, J_2 = 14.4 Hz, 1H), 2.88–2.84 (m, 2H), 1.77–1.72 (m, 2H), 1.43–1.37 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.8, 135.9, 132.5, 129.6, 129.0, 128.8, 127.5, 124.9, 123.3, 121.4, 121.1, 117.5, 67.5, 54.1, 51.0, 29.2, 23.8, 21.6, 13.5. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{21}H_{24}NaO_3S]^+$: 379.1338, Found: 379.1339.

(*E*)-4-Benzylidene-1-tosyl-3-(tosylmethyl)-1,2,3,4-tetrah ydroquinoline (5a): Isolated by column chromatography (EtOAc/petroleum ether = 1:15); white solid (43.4 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.68–7.66 (m, 3H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.32–7.25 (m, 6H), 7.14–7.10 (m, 3H), 7.07–7.06 (m, 2H), 6.54 (s, 1H), 4.16–4.13 (m, 1H), 4.08–4.05 (m, 1H), 3.97–3.93 (m, 1H), 3.15–3.05 (m, 2H), 2.45 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.8, 143.9, 136.7, 136.6, 136.4, 135.5, 133.6, 130.2, 130.0, 129.7, 128.7, 128.6, 127.9, 127.5, 127.4, 127.2, 125.8, 125.5, 123.3, 57.2, 50.0, 31.5, 21.6, 21.3. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{31}H_{29}NNaO_4S_2]^+$: 566.1430, Found: 566.1433.

(*E*)-4-(4-Chlorobenzylidene)-1-tosyl-3-(tosylmethyl)-1,2 ,3,4-tetrahydroquinoline (5b): Isolated by column chromatography (EtOAc/petroleum ether = 1:15); white solid (37.5 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 3H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.38–7.32 (m, 3H), 7.26–7.23 (m, 3H), 7.16–7.10 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 4.15–4.05 (m, 2H), 3.87 (d, *J* = 6.4 Hz, 1H), 3.19–3.13 (m, 1H), 2.99 (dd, J_1 = 2.4 Hz, J_2 = 14.4 Hz, 1H), 2.47 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0, 144.0, 136.6, 136.3, 134.6, 134.0, 133.3, 130.0, 129.9, 129.7, 129.5, 128.9, 128.7, 127.9, 127.2, 126.0, 125.8, 125.4, 123.0, 57.1, 49.9, 31.4, 21.6, 21.4. HRMS (ESI) ([M+Na]$^+$) Calcd. For $[C_{31}H_{28}ClNNaO_4S_2]^+$: 600.1040, Found: 600.1041.

(*E*)-4-Benzylidene-7-bromo-1-tosyl-3-(tosylmethyl)-1,2, 3,4-tetrahydroquinoline (5c): Isolated by column chromatography (EtOAc/petroleum ether = 1:15); white solid (43.1 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 1.6 Hz, 1H), 7.68–7.63 (m, 4H), 7.33–7.27 (m, 5H), 7.24–7.20 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, J_1 = 1.2 Hz, J_2 = 6.4 Hz, 2H), 6.57 (s, 1H), 4.20–4.15 (m,

1H), 4.01–3.94 (m, 2H), 3.16–3.02 (m, 2H), 2.45 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 144.3, 137.5, 136.4, 136.1, 135.2, 132.9, 130.0, 129.8, 128.7, 128.7, 128.3, 128.2, 127.9, 127.6, 127.6, 127.2, 127.1, 125.4, 121.1, 56.7, 49.8, 31.0, 21.6, 21.4. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{31}H_{28}BrNNaO_4S_2]^+$: 644.0535, Found: 644.0534.

(*E*)-4-Benzylidene-3-(((4-bromophenyl)sulfonyl)methyl) -1-tosyl-1,2,3,4-tetrahydroquinoline (5d): Isolated by column chromatography (EtOAc/petroleum ether = 1:15); white solid (40.1 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.68–7.60 (m, 7H), 7.40 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.33–7.28 (m, 3H), 7.27–7.25 (m, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 6.6 Hz, 2H), 6.63 (s, 1H), 4.17–4.14 (m, 1H), 4.08–4.05 (m, 1H), 3.93–3.92 (m, 1H), 3.21–3.17 (m, 1H), 3.06 (dd, J_1 = 3.0 Hz, J_2 = 15.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.1, 138.3, 136.7, 136.6, 135.6, 133.5, 132.7, 129.8, 129.5, 129.5, 129.2, 128.8, 128.7, 128.6, 127.6, 127.6, 127.2, 125.8, 125.4, 123.0, 57.0, 49.9, 31.3, 21.4. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{30}H_{26}BrNNaO_4S_2]^+$: 630.0379, Found: 630.0380.

(*E*)-4-Benzylidene-3-(((3-chlorophenyl)sulfonyl)methyl) -1-tosyl-1,2,3,4-tetrahydroquinoline (5e): Isolated by column chromatography (EtOAc/petroleum ether = 1:15); white solid (32.7 mg, 58% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.73 (t, J = 1.8 Hz, 1H), 7.69–7.66 (m, 2H), 7.63–7.61 (m, 3H), 7.47 (t, J = 8.4 Hz, 1H), 7.39 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.34–7.26 (m, 4H), 7.17–7.12 (m, 3H), 7.06 (d, J = 7.2 Hz, 2H), 6.62 (s, 1H), 4.15–4.08 (m, 2H), 4.00–3.96 (m, 1H), 3.20–3.16 (m, 1H), 3.07 (dd, J_1 = 2.4 Hz, J_2 = 14.4 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.1, 141.1, 136.7, 136.6, 135.6, 135.5, 134.0, 133.4, 130.7, 129.8, 129.7, 128.8, 128.7, 128.6, 128.0, 127.7, 127.2, 126.1, 125.8, 125.5, 123.2, 57.0, 50.0, 31.3, 21.4. HRMS (ESI) ($[M+Na]^+$) Calcd. For $[C_{30}H_{20}ClNNaO_4S_2]^+$: 586.0884 Found: 563.0882.

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[19] CCDC-2012271 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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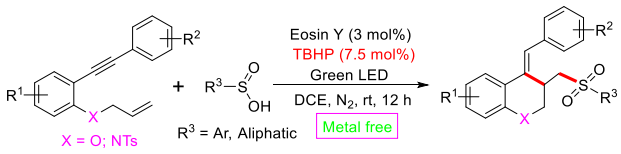
FULL PAPER

Visible-Light-Induced Radical Cascade Cyclizations of 1,7-Enynes with Sulfinic Acids: Direct Access to Sulfonated Chromanes and Sulfonated Tetrahydroquinolines under Metal-Free Conditions



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