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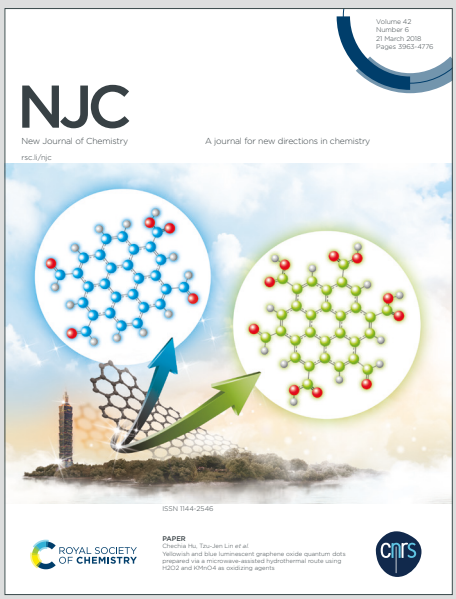

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ARTICLE

Metal-Free Annulative Hydrosulfonation of Propiolate Esters: Synthesis of 4-Sulfonates of Coumarins and Butenolides

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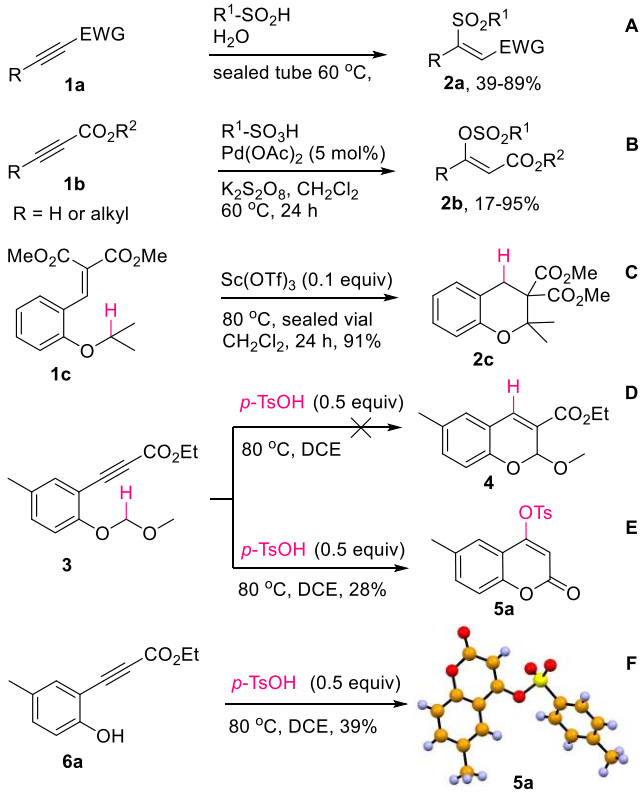
An efficient metal-free and cost-effective method for the synthesis of coumarin and butenolide 4-sulfonates (46 examples) has been developed. The reaction involves addition of sulfonic acids to ethyl propiolates followed by lactonization, resulting in direct formation of coumarin and butenolide 4-sulfonates. This methodology has been elaborated to Sonogashira and Suzuki coupling including the synthesis of rac-tolterodine.

Introduction

4-Substituted coumarins and butenolides are a family of biologically important molecules which possess interesting activities like antibacterial,[1] antifungal,[2] antioxidant,[3] antiviral,[4] antitumor,[5] hypotensive,[6] antiallergenic inflammation,[7] anti-HIV,[8] antiarrhythmic,[9] and central nervous system activities.[10] Sulfonate esters of coumarins are reported to inhibit NO and PGE2 productions in LPS-induced RAW 264.7 macrophages.[11] Metal-free hydrosulfonylation (C-S bond formation) of simple propiolate esters **1a** with sulfinic acid (R^1SO_2H) has been reported by He and co-workers (Scheme 1A).[12a] A Pd-catalyzed regio- and stereoselective hydrosulfonation (C-O bond formation) of propiolate esters **1b** was developed by Chuang et al. (Scheme 1B).[12b] Similarly, a recent report prepares 3-sulfonates from precursor 4-hydroxycoumarins.[13] Metal-free annulative hydrosulfonation of ethyl 3-(2-hydroxyaryl)propiolates and γ-aryl-γ-hydroxy-α,β-acetylenic esters is not developed to the best of our knowledge. This would provide coumarin 4-sulfonates and butenolide 4-sulfonates directly, involving cyclization.

Acid-catalyzed cascade rearrangements provide an opportunity for the formation of several bonds in a single step and these reactions are usually highly atom economic. Sames et al. have extensively studied acid-catalyzed 1,5-hydride transfer cyclizations.[14] In their work, alkyl ether **1c** led with a hydride transfer to the pendant enone using $Sc(OTf)_3$ as the catalyst to an active alkenyl-oxocarbenium ion that triggered cyclization by the in-situ formed enolate leading to pyran **2c** (Scheme 1C). We believed that a methylene group of MOM ether would also provide an active hydride for 1,5-shift in compound **3** to the Michael acceptor alkynoate intramolecularly followed by in-situ enolate cyclization to give **4** (Scheme 1D). Various Lewis acids including $Sc(OTf)_3$ failed to deliver the desired product **4**. However, when Brønsted acid *p*-TsOH was used as the catalyst, the annulative hydrosulfonated product **5a** (C-O bond formation, Scheme 1E) was formed. Product **5a** was characterized by ^1H and ^{13}C NMR and HRMS data. Further, the structure was unambiguously confirmed by single crystal XRD[15] (Scheme 1). This is an interesting metal-free annulative hydrosulfonation. The reaction involves MOM ether deprotection, hydrosulfonation and cyclization. The same



Scheme 1. Hydrosulfonation and Hydride Transfer Cyclization.

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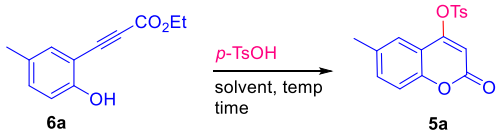
reaction on free phenol **6a** also delivered compound **5a** with better yield (Scheme 1F). While 4-sulfonates of coumarins are usually prepared by sulfonation of 4-hydroxycoumarins,[16] this direct method is promising as the sulfonates are precursors for various coupling reactions, providing an avenue for product diversification. We chose to study the scope and limitations of this reaction and the results are reported in this paper.

Results and discussion

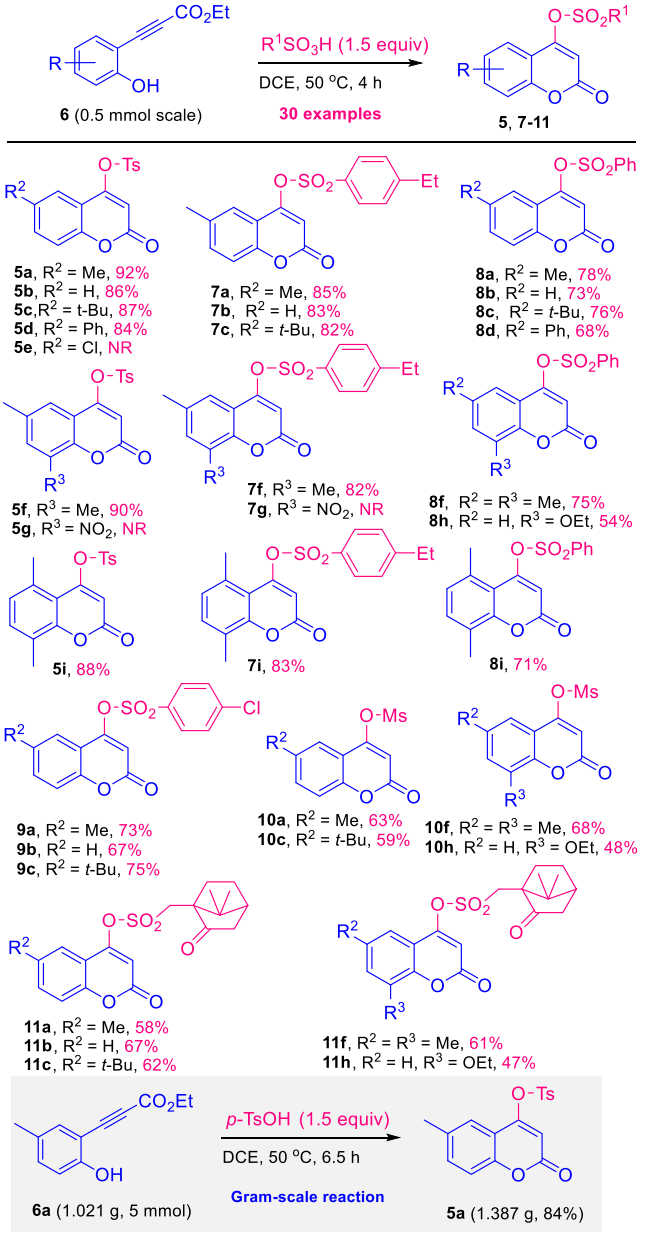
We chose compound **6a** for the optimization of reaction conditions using *p*-TsOH as hydrosulfonating agent. The starting ethyl 3-(2-hydroxyaryl)propiolates **6** were prepared by following Yamamoto's procedure.[17] In 1,2-dichloroethane (DCE) solvent, we varied the equivalence of *p*-TsOH from 0.5 to 2.0 equiv at room temperature, but it did not give reasonable yields of **5a** (Table 1, entries 1-4). The reaction worked well at both 50 °C and 80 °C (Table 1, entries 5-12). We found 1.5 equiv of *p*-TsOH was optimum at 50 °C, the reaction being complete in 4 h yielding **5a** in 92% yield (entry 7). Change in solvent was screened (entries 13-21) to indicate DCE to be the best solvent, although CH_2Cl_2 could also give the product in 73% yield (entry 13). In EtOAc, THF and Et_2O the reaction did not proceed and the starting material was recovered (entries 17-19). Non polar solvents like benzene and toluene gave the desired product in moderate yields (entries 20-21). Thus, the optimum conditions were found to be as in entry 7, i.e. in DCE at 50 °C with 1.5 equiv of *p*-TsOH. With the optimized conditions, the scope and limitations of the metal-free annulative hydrosulfonation of various ethyl 3-(2-hydroxyaryl)propiolates were investigated. As shown in Scheme 2, various ethyl 3-(2-hydroxyaryl)propiolates provided the corresponding coumarin 4-tosylates **5a-d,f** and **5i** in good to excellent yields (84-92%). Electron densities on the aryl ring of ethyl 3-(2-hydroxyaryl)propiolates governed the progress of the reaction. Electron withdrawing group on aryl part of the substrate ester terminated the reaction. Thus, ethyl 3-(4-chloro-2-hydroxyphenyl)propiolate **6e** and the nitro compound **6g** did

Table 1. Screening of Reaction Conditions[a]



Entry	Solvent	*p*-TsOH (equiv)	Temp. (°C)	Time (h)	Yield **5a** (%)[b]
1	DCE	0.5	rt	12	9
2	DCE	1.0	rt	12	15
3	DCE	1.5	rt	12	16
4	DCE	2.0	rt	12	19
5	DCE	0.5	50	12	35
6	DCE	1.0	50	6	69
7	DCE	1.5	50	4	92
8	DCE	2.0	50	4	93
9	DCE	0.5	80	4	39
10	DCE	1.0	80	4	72
11	DCE	1.5	80	4	86
12	DCE	2.0	80	4	90
13	CH_2Cl_2	1.5	45	6	73
14	DMF	1.5	50	6	26
15	DMSO	1.5	50	6	32
16	CH_3CN	1.5	50	6	36
17	EtOAc	1.5	50	12	0[c]
18	THF	1.5	50	12	0[c]
19	Et_2O	1.5	reflux	12	0[c]
20	Benzene	1.5	50	5	59
21	Toluene	1.5	50	5	54

[a]All reaction are done on 0.5 mmol of **6a** in 3 mL of solvent. [b]Isolated yields. [c]Starting material fully recovered.



Scheme 2. Substrate Scope for Synthesis of Coumarin 4-Sulfonates and a Gram-Scale Reaction

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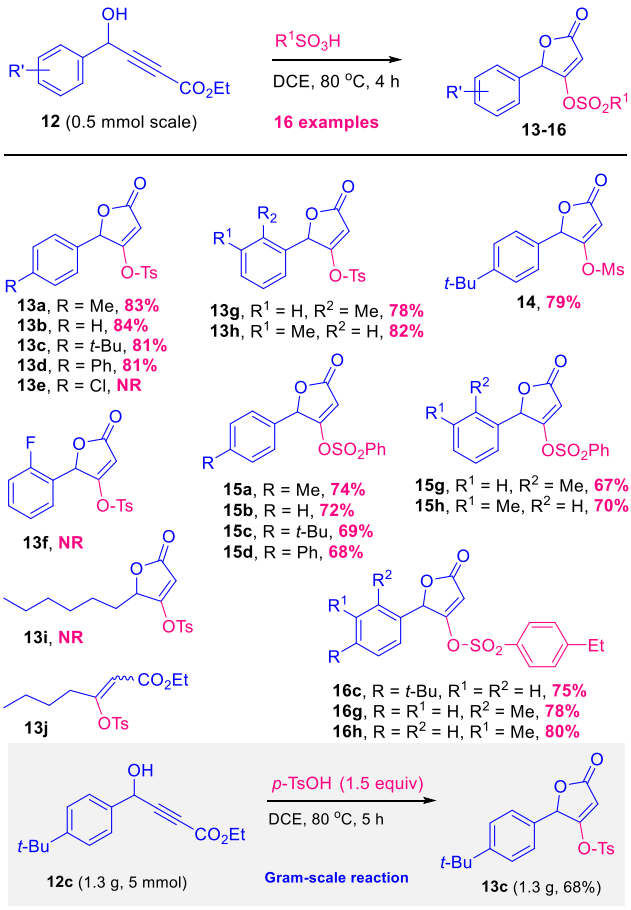
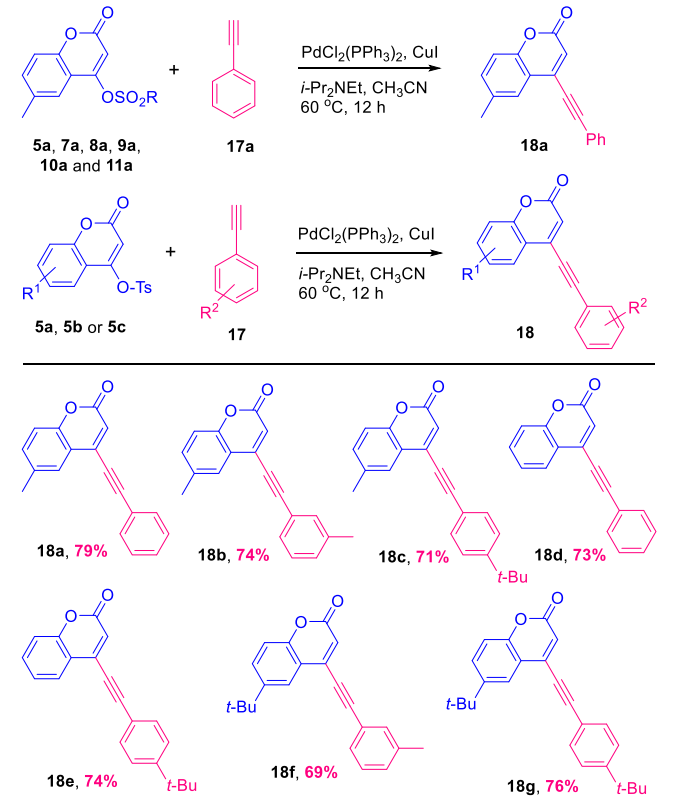
not yield the corresponding coumarin 4-sulfonate **5e** and **5g**. We also considered addition of various other sulfonic acids. *p*-Ethylbenzenesulfonic acid also gave good yields of coumarin 4-sulfonates **7a-c,f** and **7i** (82-85%). Here also the nitro compound **6g** did not yield **7g**. The use of benzenesulfonic acid ($PhSO_3H$) decreased the yields of sulfonates **8a-d**,**f**,**h** and **8i** marginally (54-78%). *p*-Chlorobenzenesulfonic acid addition gave moderate yields of **9a-c** (67-75%), while methanesulfonic acid (MsOH) addition on ethyl 3-(2-hydroxyaryl)propiolates gave moderate yields of the coumarin 4-mesylates **10a**,**c**,**f**,**h** (48-68%). Interestingly, camphorsulfonic acid (CSA) also reacted under these conditions to deliver the corresponding coumarin 4-camphorsulfonates **11a-c**,**f**,**h** in 47-67% yields (Scheme 2). Triflic acid did not participate in the hydrosulfonation reaction under various conditions including higher equivalence or temperature, and the starting material was unaffected. A reaction of **6a** at 5.0 mmol scale (1.021 g) delivered coumarin 4-tosylate **5a** in good yield of 84% (1.387 g), indicating the possibility for scale-up of this procedure.

The developed reaction was extended to the synthesis of 4-sulfonates of butenolides (Scheme 3). The substrate γ-aryl-γ-hydroxy-α,β-acetylenic esters **12** were prepared by addition of lithiated ethyl propiolate on aryl aldehydes. The reaction temperature of sulfonic acid addition had to be raised to 80 °C in these cases to get optimal yields. Addition of *p*-TsOH to **12a-d** provided the butenolide 4-tosylates **13a-d** in good yields of 81-84%. Substrates with slight electon withrawing Cl and F groups failed in this reaction to provide **13e** and **13f**. The ortho- and meta-methyl substituted products **13g** (78%) and **13h** (82%) were obtained in good yields. Aliphatic substrates **12i** and **12j** failed to deliver **13i** and **13j**. Probably these are not as activated as the aryl alkynoates. Thus the sulphonic acid addition to aliphatic substrates has been achieved under Pd-catalysis (Scheme 1B).[12b] MsOH could be added to **12c** to give **14** in 79% yield. Similarly, $PhSO_3H$ addition to **12a-d**, **12g** and **12h** furnished the butenolide 4-benzenesulfonates **15a-d**, **15g** and **15h** in 67-74% yields. Addition of 4-ethylbenzenesulfonic acid to **12c**, **12g** and **12h** provided the butenolide 4-sulfonate **16c**, **16g** and **16h** in 75-80% yields. A reaction of **12c** at 5.0 mmol scale (1.3 g) delivered butanolide 4-sulfonate **13c** in good yield of 68% (1.3 g), indicating the possibility for scale-up of this procedure.

Various coumarin 4-sulfonates were subjected to Sonogashira coupling[18] to choose the best sulfonate giving higher yield (Scheme 4). Tosylate **5a** gave the best yield of **18a** (79%) as compared to other sulfonates. *p*-Ethylbenzenesulfonate **7a**, benzenesulfonate **8a** and *p*-chlorobenzenesulfonate **9a** provided **18a** in 73%, 62% and 63% yields, respectively. Mesylate **10a** gave poor yield of **18a** (43%), whereas camphor sulfonate **11a** did not participate in this reaction and the starting materials decomposed. Considering the coumarin 4-tosylate to be the best coupling partner, **5a**, **5b** or **5c** were then subjected to Sonagashira coupling with different alkynes **17** to deliver 4-(arylethynyl)coumarins **18a-g** in good yields (69-79%, Scheme 4).

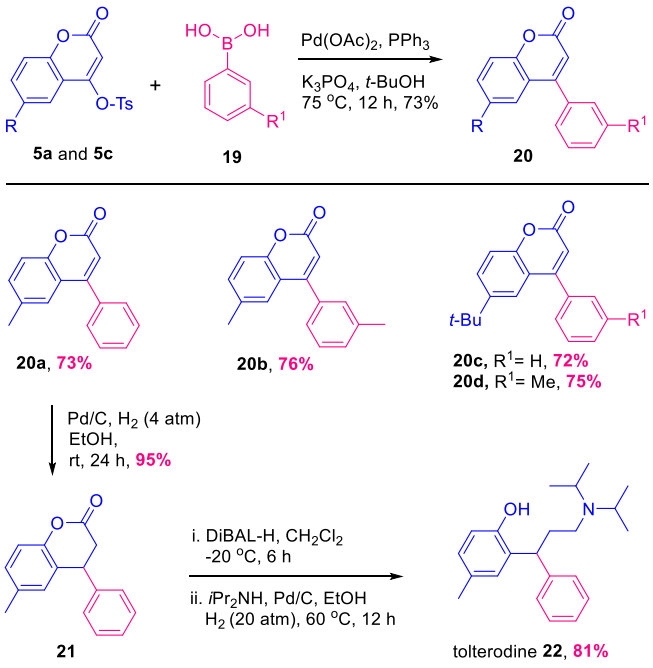


Scheme 3. Substrate Scope for Butenolide 4-Sulfonates.



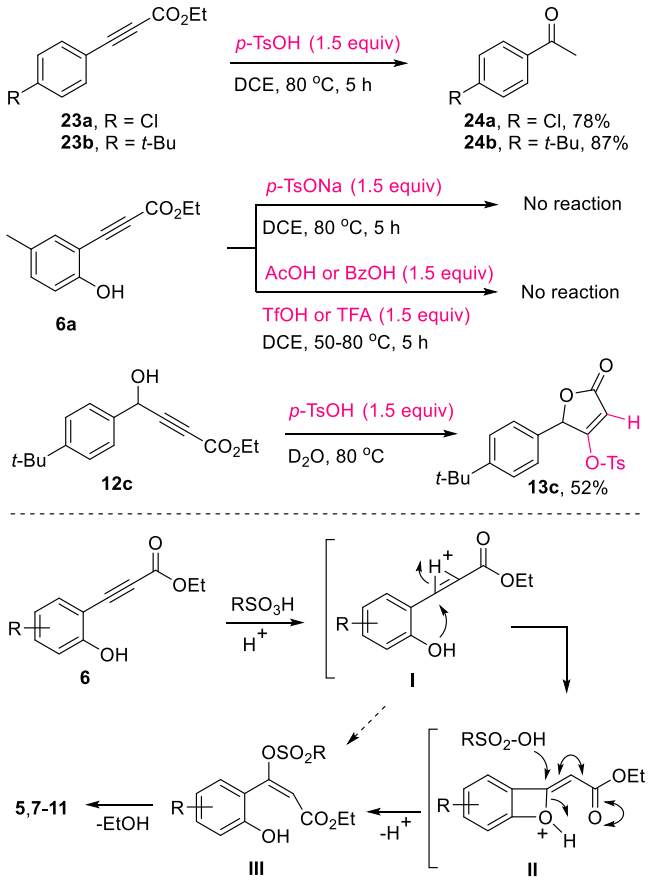
Scheme 4. Screening of Sulfonates for Sonogashira Reaction and Use of Coumarin 4-Tosylates for Synthesis of 4-(Arylethynyl)coumarins **18**.

Tosylates **5a** and **5c** were subjected to Suzuki coupling[19] with boronic acids **19** using $Pd(OAc)_2$ along with K_3PO_4 and PPh_3 in *t*-BuOH at 75 °C to furnish 4-arylcoumarins **20a-d** in 72-76% yields (Scheme 5). 4-Phenylcoumarin **20a** was transformed to tolterodine **22**, traded as Detrol or Detrusitol, an antimuscarinic drug[20] acting at the M2 and M3 subtypes of muscarinic receptors,[21] and it is used for the treatment of urinary incontinence. It selectively targets the bladder more than other areas of the body and hence is required in lower dosage. Therefore, it has fewer side effects in comparison to other drugs. Hydrogenation of **20a** using Pd/C in ethanol at 4 atm of H_2 at room temperature delivered dihydrocoumarin **21** in 95% yield. The subsequent DiBAL-H reduction to its corresponding lactol and further one-pot reductive amination gave tolterodine **22** in good yield (81% from **21**).



Scheme 5. Suzuki Coupling of Coumarin 4-Tosylates with Boronic Acids to 4-Arylcoumarins and Synthesis of *rac*-Tolterodine **22**.

We investigated further reactions to gain insight in the mechanism of the reaction (Scheme 6). We noted that sulfinic acid addition to propiolates in presence of water results in C-S bond formation (Scheme 1A) and involves protonation of the alkyne.[12a] In our case the reaction occurs with C-O bond formation in using the sulfonic acids. The reaction on compounds **23a** and **23b**, without the phenolic OH group resulted in the arylmethyl ketones **24a** and **24b** obtained in 78% and 87% yields, respectively. This unusual cleavage of 3-arylpropiolates via decarboxylative hydration of alkyne is known in the literature.[22] To check the hypothesis that the reaction involves acid catalysis and protonation is required, we carried out reaction with *p*-TsONa on **6a** in absence of water. The reaction failed to give **5a**. Other acids like AcOH, BzOH, TfOH or TFA also did not give addition products. The reaction of compound **12c** with *p*-TsOH in presence of D_2O gave **13c** with no significant deuterium incorporation at the α-position indicating that this proton originates from the sulfonic acid. Hence, similar to sulfinic acid addition,[12a] the protonation of alkyne in **6** gives the intermediate **I** that is possibly opened intramolecularly by the phenolic hydroxy group to give intermediate **II**.[23] Next, conjugate addition of the sulfonic acid and opening of the oxetane by the enolate results in the ester **III**. The latter cyclizes to the coumarin 4-sulfonates **5,7-11**. A similar mechanism is operative for butenolide 4-sulfonate formation. It is also probable that intermediate **I** may give directly **III** by reaction of the sulfonic acid on protonated alkyne.



Scheme 6. Mechanistic Investigations and Plausible Mechanism

Conclusions

In summary, we have developed an efficient metal-free annulative hydrosulfonation of ethyl propiolates. Various sulfonates have been synthesized through annulative hydrosulfonation reaction (46 examples). Different sulfonates have been screened for Sonogashira coupling reaction to find that the tosyl group works well. Some of the sulfonates were subjected to Suzuki coupling and the resultant 4-aryl coumarin **20a** has been elaborated to tolterodine **22**, an antimuscarinic drug.

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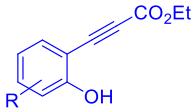
Experimental section

Solvents were dried by using standard procedures. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. ^1H NMR and ^{13}C NMR were recorded with a spectrometer operating at 400 or 500 and 100 or 125 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on the $CDCl_3$ peak at δ = 7.26 ppm for proton NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) for carbon NMR. IR spectra were obtained on an FT-IR spectrometer by evaporating compounds dissolved in $CHCl_3$ on CsCl pellets. HRMS (ESI-TOF) spectra were recorded using positive electrospray ionization by the TOF method.

General Procedure for Preparation of Ethyl 3-(2-Hydroxyphenyl)propiolates (6a-i). To a stirred solution of orthohydroxy arylaldehydes (5.0 mmol, 1.0 equiv) in THF (100 mL) was added portion wise NaH (240 mg of 60% emulsion in mineral oil, 6.0 mmol, 1.2 equiv) and stirred for 10 min. To this mixture, MOMCl (3.6 mL, 2.1 M solution in toluene, 7.5 mmol, 1.5 equiv) was added dropwise at 0 °C and the resulting mixture was then stirred at room temperature for 6 h. After completion of the reaction, which was monitored by TLC, the reaction was then quenched with sat. aqueous solution of NH_4Cl (20 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (2 × 30 mL). The combined organic layers were thoroughly washed with water (2 × 20 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated. The crude product was directly taken for next step.

A solution of carbon tetrabromide (3.32 g, 10 mmol, 2.0 equiv) in anhydrous CH_2Cl_2 (100 mL) was cooled to 0 °C and PPh_3 (5.25 g, 20 mmol, 4.0 equiv) was added to form an orange-reddish solution. The mixture was stirred at 0 °C for 15 min and the above aryl aldehyde dissolved in CH_2Cl_2 (10 mL) was added in one portion. After stirring for 1 h at 0 °C, the mixture was allowed to warm to room temperature for 4 h. To this, petroleum ether was added (100 mL) over 5 min at 0 °C and the precipitate obtained was filtered off through a pad of silica gel and the pad washed with petroleum ether/EtOAc (2 × 20 mL). The filtrate was concentrated to give the olefin dibromide.

To the solution of above olefin dibromide in anhydrous THF (100 mL) cooled to −78 °C was added *n*-BuLi (5.0 mL, 12.5 mmol, 2.5 M in hexanes) over a period of 30 min. The mixture was stirred at −78 °C for 1 h. Then ethyl chloroformate (0.814 g, 7.5 mmol) was added in one portion and the mixture was allowed to warm to room temperature and stirred for 3 h, and then quenched with sat. aqueous solution of NH_4Cl (20 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (2 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was then dissolved in THF (30 mL) and stirred at 0 °C with dropwise addition of HCl (10 mL, 6 M) and stirred for 3 h. The reaction mixture was then diluted with EtOAc (30 mL) and the organic layer was separated and the aqueous layer extracted with EtOAc (2 × 15 mL). The combined organic layers were thoroughly washed with water (2 × 20 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated. The residue was purified by silica-gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give the desired propiolate esters **6a-i** in good yields.



Ethyl 3-(2-hydroxy-5-methylphenyl)propiolate (6a). Yield = 541.2 mg, 53%, brown solid, M.p. 56–58 °C; IR ($CHCl_3$): ν_{max} = 3440, 2982, 2212, 1704, 1684, 1613, 1510, 1497, 1466, 1415, 1370, 1315, 1229, 1152, 1123, 1025, 909, 859, 820, 750, 732, 631 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 156.9, 154.1, 134.0, 133.3, 129.9, 115.6, 105.5, 86.8, 82.1, 62.3, 20.2, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{12}O_3Na$ 227.0679; Found 227.0682.

Ethyl 3-(2-hydroxyphenyl)propiolate (6b).[24] Yield = 485.0 mg, 51%, white solid, M.p. 44–46 °C; lit.[24] M.p. 44–46 °C; IR ($CHCl_3$): ν_{max} = 3390, 2983, 2928, 2209, 1705, 1686, 1604, 1486, 1450, 1371, 1307, 1216, 1190, 1156, 1103, 1020, 840, 765, 610 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.34 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 8.4 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 159.0, 154.3, 133.5, 133.0, 120.5, 115.9, 106.0, 86.7, 82.3, 62.4, 14.0 ppm. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{10}O_3Na$ 213.0522; Found 213.0525.

Ethyl 3-[5-(*tert*-butyl)-2-hydroxyphenyl]propiolate (6c). Yield = 554.2 mg, 45%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3345, 2965, 2211, 1708, 1677, 1607, 1507, 1464, 1412, 1370, 1319, 1264, 1225, 1206, 1185, 1137, 1100, 1020, 825, 750, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 156.7, 154.1, 143.5, 130.6, 130.0, 115.4, 105.2, 86.7, 82.4, 62.3, 34.1, 31.2, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_3Na$ 269.1148; Found 269.1152.

Ethyl 3-[4-hydroxy-(1,1'-biphenyl)-3-yl]propiolate (6d). Yield = 506.0 mg, 38%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3256, 2215, 1682, 1608, 1515, 1478, 1453, 1407, 1375, 1328, 1296, 1272, 1179, 1116, 1027, 898, 867, 820, 745, 698, 637, 599, 486 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.53–7.48 (m, 2H), 7.45–7.39 (m, 2H), 7.41–7.33 (m, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.33 (q, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.3, 154.0, 139.3, 134.0, 131.9, 131.7, 128.9, 127.3, 126.6, 116.3, 106.3, 87.1, 81.7, 62.4, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}O_3Na$ 289.0835; Found 289.0836.

Ethyl 3-(5-chloro-2-hydroxyphenyl)propiolate (6e). Yield = 370.7 mg, 33%, yellow solid, M.p. 88–90 °C; IR ($CHCl_3$): ν_{max} = 3207, 2979, 2214, 1700, 1667, 1595, 1495, 1468, 1409, 1371, 1316, 1286, 1123, 1182, 1114, 1085, 1016, 970, 908, 875, 858, 823, 749, 668, 631 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 2.3 Hz, 1H), 7.30 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 157.6, 153.8, 133.1, 132.4, 125.2,

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117.3, 107.4, 87.5, 80.1, 62.6, 14.0 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_9O_3ClNa$ 247.0135; Found 247.0136.

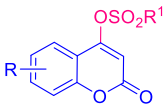
Ethyl 3-(2-hydroxy-3,5-dimethylphenyl)propiolate (6f). Yield = 523.8 mg, 48%, yellow semi solid; IR ($CHCl_3$): ν_{max} = 3457, 2983, 2925, 2864, 2207, 1707, 1478, 1369, 1335, 1244, 1223, 1158, 1051, 1014, 860, 782, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 1H), 7.03 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 155.0, 154.0, 135.4, 130.6, 129.4, 124.7, 104.9, 86.9, 82.3, 62.2, 20.2, 15.8, 14.0 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0837.

Ethyl 3-(2-hydroxy-5-methyl-3-nitrophenyl)propiolate (6g). Yield = 309 mg, 53%, yellow solid, M.p. 84–86 °C; IR ($CHCl_3$): ν_{max} = 3246, 2221, 1693, 1545, 1459, 1364, 1344, 1310, 1298, 1251, 1225, 1168, 1124, 1097, 1032, 941, 878, 853, 749, 699, 617. cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.87 (s, 1H), 7.97 (s, 1H), 7.63 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 154.7, 153.4, 142.8, 133.4, 129.9, 127.0, 111.7, 86.0, 79.2, 62.3, 20.0, 14.0 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{11}O_5NNa$ 272.0529; Found 272.0532.

Ethyl 3-(2-ethoxy-6-hydroxyphenyl)propiolate (6h). Yield = 363.1 mg, 31%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3451, 2981, 2215, 1704, 1584, 1486, 1467, 1396, 1369, 1307, 1278, 1231, 1198, 1069, 1027, 910, 780, 751, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.80 (t, *J* = 7.9 Hz, 1H), 4.30 (q, *J* = 7.3 Hz, 2H), 4.12 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 6.9 Hz, 3H), 1.35 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 154.2, 149.0, 145.8, 125.6, 119.9, 114.0, 106.0, 84.9, 82.2, 64.9, 62.0, 14.8, 14.1 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{14}O_4Na$ 257.0784; Found 257.0784.

Ethyl 3-(2-hydroxy-3,6-dimethylphenyl)propiolate (6i). Yield = 611.1 mg, 56%, yellow semi solid; IR ($CHCl_3$): ν_{max} = 3405, 2982, 2212, 1704, 1679, 1613, 1497, 1466, 1415, 1370, 1315, 1229, 1152, 1123, 1025, 909, 859, 820, 751, 697, 631 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.21 (s, 3H), 1.3 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$): δ = 157.1, 154.0, 140.3, 133.5, 121.7, 121.1, 105.7, 91.0, 80.8, 62.2, 20.4, 15.6, 14.1 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0839.

General Procedure for the Preparations of Coumarin 4-Sulfonates (5,7-11). To a solution of ethyl 3-(2-hydroxyaryl)propiolates **6** (0.5 mmol, 1.0 equiv) in DCE (5 mL) was added the sulfonic acid (0.75 mmol, 1.5 equiv) and the mixture stirred at 50 °C for 4 h. After completion of the reaction which was monitored by TLC, the reaction mixture was cooled and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1–4:1) as eluent to afford coumarin 4-sulfonates **5, 7-11** in 47–92% yields.



6-Methyl-2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (5a).[16e] Yield = 152.0 mg, 92%, white solid, M.p. 142–144 °C; lit.[16e] 149–151 °C; IR ($CHCl_3$): ν_{max} = 2925, 1733, 1631, 1579, 1491, 1427, 1391, 1365, 1316, 1276, 1200, 1170, 1090, 1062, 923, 861, 833, 817, 760, 745, 709, 666, 601, 572, 547 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.3 Hz, 2H), 7.46–7.30 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.25 (s, 1H), 2.47 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 161.0, 157.9, 151.7, 146.8, 134.4, 134.3, 131.7, 130.4, 128.5, 122.8, 116.7, 114.6, 103.5, 21.8, 20.8 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{15}O_5S$ 331.0635; Found 331.0632.

2-Oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (5b).[16e] Yield = 136 mg, 86%, white solid, M.p. 110–112 °C, lit.[16e] 110–111 °C; IR ($CHCl_3$): ν_{max} = 2969, 2935, 2874, 1735, 1627, 1607, 1570, 1488, 1453, 1373, 1325, 1274, 1191, 1176, 1127, 1067, 933, 875, 839, 793, 753, 714, 658, 601, 577, 541, 504 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.1 Hz, 2H), 7.63 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.57 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34–7.23 (m, 2H), 6.31 (s, 1H), 2.46 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.7, 157.8, 153.4, 146.9, 133.2, 131.6, 130.4, 128.4, 124.5, 123.1, 116.9, 114.9, 103.5, 21.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{12}O_5SNa$ 339.0298; Found 339.0295.

6-(tert-Butyl)-2-oxo-2*H*-chromen-4-yl-4-methylbenzenesulfonate (5c).[25] Yield = 162.0 mg, 87%, white solid, M.p. 176–178 °C, lit.[25] M.p. 177 °C; IR ($CHCl_3$): ν_{max} = 3101, 2965, 2871, 1738, 1630, 1606, 1576, 1491, 1426, 1388, 1371, 1357, 1315, 1285, 1263, 1205, 1178, 1143, 1111, 1092, 1061, 1018, 936, 908, 860, 843, 816, 765, 745, 679, 664, 599, 571, 549 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.30 (s, 1H), 2.44 (s, 3H), 1.27 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 161.0, 158.1, 151.5, 147.7, 146.7, 131.8, 130.9, 130.3, 128.3, 119.1, 116.5, 114.2, 104.3, 34.6, 31.1, 21.7 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{20}O_5SNa$ 395.0924; Found 395.0920.

2-Oxo-6-phenyl-2*H*-chromen-4-yl 4-methylbenzenesulfonate (5d). Yield = 164.8 mg, 84%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3058, 2926, 1735, 1630, 1597, 1576, 1482, 1454, 1421, 1388, 1364, 1301, 1271, 1201, 1177, 1138, 1093, 1064, 936, 891, 819, 762, 743, 706, 665, 602, 584, 559, 547, 525, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.77 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.54–7.44 (m, 4H), 7.44–7.33 (m, 4H), 6.35 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.7, 157.9, 152.8, 147.0, 139.0, 138.0, 132.1, 131.7, 130.4, 129.0, 128.5, 128.0, 127.1, 121.3, 117.4, 115.2, 104.3, 21.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{16}O_5SNa$ 415.0611; Found 415.0611.

6,8-Dimethyl-2-oxo-2*H*-chromen-4-yl-4-methylbenzenesulfonate (5f). Yield = 155 mg, 90%, white solid, M.p. 140–144 °C; IR ($CHCl_3$): ν_{max} = 1734, 1630, 1593, 1470, 1377, 1371, 1201, 1167, 1129, 1088, 1005, 921, 845, 763, 749, 732, 669, 624, 580, 548 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.22 (s, 1H), 6.23 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.1, 158.2, 150.0, 146.8, 135.7, 133.8, 131.8, 130.3, 128.5, 126.1, 120.4, 114.4, 103.2,

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21.8, 20.8, 15.5 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0611.

5,8-Dimethyl-2-oxo-2*H*-chromen-4-yl-4-methylbenzenesulfonate (5i). Yield = 151.5 mg, 88%, white solid, M.p. 146–148 °C; IR ($CHCl_3$): ν_{max} = 2967, 1727, 1646, 1598, 1446, 1411, 1374, 1282, 1220, 1194, 1179, 1095, 1039, 1011, 971, 924, 876, 816, 695, 660, 566, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.27 (s, 1H), 2.53 (s, 3H), 2.46 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.6, 159.9, 153.0, 146.8, 133.7, 133.5, 132.0, 130.4, 128.4, 127.7, 124.4, 113.2, 102.4, 22.8, 21.7, 15.7 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0611.

6-Methyl-2-oxo-2*H*-chromen-4-yl 4-ethylbenzenesulfonate (7a). Yield = 146.4 mg, 85%, white solid, M.p. 96–98 °C; IR ($CHCl_3$): ν_{max} = 2972, 1732, 1631, 1578, 1491, 1425, 1388, 1365, 1317, 1276, 1203, 1169, 1131, 1062, 923, 833, 792, 744, 705, 659, 603, 573, 541 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.38–7.31 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 6.27 (s, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.26 (t, *J* = 8.1 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.0, 157.8, 152.8, 151.6, 134.4, 134.2, 131.8, 129.2, 128.5, 122.7, 116.6, 114.5, 103.5, 28.9, 20.8, 14.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0605.

2-Oxo-2*H*-chromen-4-yl 4-ethylbenzenesulfonate (7b). Yield = 137.1 mg, 83%, brown semi-solid; IR ($CHCl_3$): ν_{max} = 2969, 2932, 2874, 1732, 1626, 1608, 1569, 1490, 1452, 1372, 1327, 1274, 1197, 1176, 1132, 1067, 1032, 933, 875, 837, 790, 753, 719, 658, 602, 577, 546 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37–7.21 (m, 2H), 6.36 (s, 1H), 2.78 (q, *J* = 7.7 Hz, 2H), 1.30 (t, *J* = 7.8 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.8, 157.8, 153.4, 152.9, 133.2, 131.8, 129.2, 128.5, 124.5, 123.1, 116.9, 114.9, 103.6, 28.9, 14.8 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{15}O_5S$ 331.0635; Found 331.0632.

6-(*tert*-Butyl)-2-oxo-2*H*-chromen-4-yl-4-ethylbenzenesulfonate (7c). Yield = 158.5 mg, 82%, white semi solid; IR ($CHCl_3$): ν_{max} = 3101, 2967, 2871, 1735, 1630, 1597, 1577, 1491, 1461, 1427, 1390, 1371, 1354, 1315, 1263, 1208, 1178, 1143, 1111, 1093, 1060, 935, 909, 859, 842, 791, 762, 744, 720, 679, 658, 599, 550 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 1H), 6.32 (s, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (s, 9H), 1.24 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.0, 158.1, 152.7, 151.5, 147.7, 132.0, 130.9, 129.2, 128.4, 119.1, 116.5, 114.2, 104.4, 34.6, 31.1, 28.9, 14.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{22}O_5SNa$ 409.1080; Found 409.1077.

6,8-Dimethyl-2-oxo-2*H*-chromen-4-yl 4-ethylbenzenesulfonate (7f). Yield = 147 mg, 82%, white semi-solid; IR ($CHCl_3$): ν_{max} = 3106, 2970, 2928, 2877, 1732, 1631, 1596, 1578, 1491, 1413, 1391, 1366, 1317, 1276, 1202, 1169, 1131, 1093, 1061, 923, 859, 833, 792, 760, 745, 706, 681, 659, 618, 602, 573, 542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.25–7.19 (m, 2H), 6.25 (s, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.27 (t, *J* = 7.7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.2, 158.2, 152.7, 150.0, 135.7, 133.8, 131.9, 129.2, 128.6, 126.1, 120.4, 114.4, 103.3, 29.0, 20.8, 15.5, 14.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{18}O_5SNa$ 381.0767; Found 381.0769.

5,8-Dimethyl-2-oxo-2*H*-chromen-4-yl 4-ethylbenzenesulfonate (7i). Yield = 148.6 mg, 83%, white solid; M.p. 152–154 °C; IR ($CHCl_3$): ν_{max} = 1732, 1630, 1593, 1377, 1201, 1167, 1129, 1088, 1005, 975, 921, 845, 814, 763, 734, 669, 580, 548 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.27 (s, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.50 (s, 3H), 2.30 (s, 3H), 1.25 (t, *J* = 7.7 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.5, 159.7, 152.8, 152.7, 133.5, 133.4, 132.0, 129.1, 128.4, 127.6, 124.2, 113.0, 102.2, 28.8, 22.7, 15.6, 14.6 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{18}O_5SNa$ 381.0767; Found 381.0769.

6-Methyl-2-oxo-2*H*-chromen-4-yl benzenesulfonate (8a).[16g] Yield = 123.4 mg, 78%, white solid, M.p. 140–142 °C, lit.[16g] M.p. 139–141 °C; IR ($CHCl_3$): ν_{max} = 3127, 1730, 1629, 1578, 1450, 1425, 1382, 1364, 1316, 1203, 1168, 1063, 935, 922, 860, 820, 776, 759, 748, 684, 606, 586, 566 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 8.02 (d, *J* = 8.2Hz, 2H), 7.74 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.64–7.59 (m, 2H), 7.40–7.39 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.27 (s, 1H), 2.36 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): *δ* = 160.9, 157.8, 151.7, 135.3, 134.8, 134.5, 134.3, 129.8, 128.4, 122.7, 116.7, 114.5, 103.8, 20.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{12}O_5SNa$ 339.0298; Found 339.0299.

2-Oxo-2*H*-chromen-4-yl benzenesulfonate, (8b).[16g] Yield = 110.3 mg, 73%, white solid, M.p. 116–120 °C, lit.[16g] M.p. 118–120 °C; IR ($CHCl_3$): ν_{max} = 3075, 1736, 1625, 1606, 1567, 1450, 1386, 1373, 1278, 1177, 1128, 1092, 1071, 1031, 936, 910, 877, 855, 767, 720, 683, 606, 588, 568, 538 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.3 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.66–7.59 (m, 3H), 7.59–7.55 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29–7.24 (m, 1H), 6.33 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.7, 157.7, 153.5, 135.4, 134.8, 133.3, 129.8, 128.4, 124.5, 123.1, 117.0, 114.9, 103.9 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{10}O_5SNa$ 325.0141; Found 325.0143.

6-(*tert*-Butyl)-2-oxo-2*H*-chromen-4-yl benzenesulfonate (8c). Yield = 136.2 mg, 76%, brown semi solid; IR ($CHCl_3$): ν_{max} = 2967, 2905, 1736, 1630, 1577, 1449, 1427, 1393, 1372, 1315, 1263, 1203, 1185, 1143, 1092, 1060, 935, 909, 863, 843, 769, 722, 685, 603, 575, 550 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.1 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.62–7.55 (m, 3H), 7.46 (d, *J* = 1.4 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.32 (s, 1H), 1.25 (s, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.8, 157.9, 151.5, 147.7, 135.2, 134.8, 130.9, 129.7, 128.2, 119.0, 116.4, 114.1, 104.4, 34.5, 31.1 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{18}O_5SNa$ 381.0767; Found 381.0768.

2-Oxo-6-phenyl-2*H*-chromen-4-yl benzenesulfonate (8d). Yield = 128.7 mg, 68%, brown semi solid; IR ($CHCl_3$): ν_{max} = 2979, 2932, 1732, 1626, 1576, 1467, 1376, 1277, 1199, 1168, 1090, 1050, 985, 922, 911, 790, 758, 733, 666, 548 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.2 Hz, 2H), 7.90–7.69 (m, 3H),

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7.64–7.57 (m, 2H), 7.53–7.44 (m, 4H), 7.44–7.36 (m, 2H), 6.36 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.6, 157.8, 152.8, 139.0, 138.1, 135.4, 134.8, 132.2, 129.8, 129.0, 128.4, 128.0, 127.1, 121.2, 117.4, 115.1, 104.3 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{14}O_5SNa$ 401.0454; Found 401.0454.

6,8-Dimethyl-2-oxo-2*H*-chromen-4-yl benzenesulfonate (8f). Yield = 123.9 mg, 75%, brown solid, M.p. 116–118 °C; IR ($CHCl_3$): ν_{max} = 3116, 2924, 1726, 1631, 1591, 1478, 1449, 1424, 1369, 1316, 1239, 1201, 1166, 1128, 1088, 1005, 972, 945, 923, 860, 830, 767, 750, 685, 663, 646, 626, 586, 560 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.1 Hz, 2H), 7.74 (t, *J* = 7.1 Hz, 1H), 7.64–7.58 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.25 (s, 1H), 2.37 (s, 3H), 2.31 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.0, 158.1, 150.0, 135.8, 135.3, 134.9, 133.8, 129.7, 128.4, 126.2, 120.3, 114.3, 103.5, 20.8, 15.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{14}O_5SK$ 369.0194; Found 369.0189.

8-Ethoxy-2-oxo-2*H*-chromen-4-yl benzenesulfonate (8h). Yield = 93.5 mg, 54%, brown semi solid; IR ($CHCl_3$): ν_{max} = 2983, 1733, 1629, 1577, 1466, 1451, 1376, 1277, 1201, 1166, 1090, 1048, 982, 924, 912, 758, 734, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.73 (td, *J* = 7.0, 1.3 Hz, 1H), 7.64–7.57 (m, 2H), 7.19–7.14 (m, 2H), 7.12–7.07 (d, *J* = 8.6 Hz, 1H), 6.34 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.4, 158.0, 146.7, 143.6, 135.3, 134.8, 129.8, 128.4, 124.4, 116.2, 115.8, 114.1, 104.1, 65.1, 14.7 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}O_6SNa$ 369.0403; Found 369.0403.

5,8-Dimethyl-2-oxo-2*H*-chromen-4-yl benzenesulfonate (8i). Yield = 117.3 mg, 71%, white solid, M.p. 124–126 °C; IR ($CHCl_3$): ν_{max} = 3127, 1727, 1629, 1578, 1451, 1423, 1382, 1316, 1203, 1168, 1129, 1093, 1063, 1003, 935, 860, 820, 776, 758, 680, 606, 586, 566, 541 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 8.0, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* =7.6 Hz, 1H) 6.28 (s, 1H), 2.53 (s, 3H), 2.36 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.6, 159.8, 153.0, 135.3, 135.1, 133.8, 133.5, 129.8, 128.4, 127.7, 124.5, 113.2, 102.7, 22.8, 15.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{14}O_5SK$ 369.0194; Found 369.0189.

6-Methyl-2-oxo-2*H*-chromen-4-yl 4-chlorobenzenesulfonate (9a). Yield = 128.0 mg, 73%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3108, 2970, 2932, 2874, 1732, 1631, 1578, 1491, 1422, 1366, 1317, 1276, 1203, 1170, 1132, 1093, 1061, 923, 861, 833, 791, 760, 744, 706, 659, 602, 573, 543 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.32 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.29 (s, 1H), 2.36 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.7, 157.6, 151.6, 142.3, 134.6, 134.5, 133.1, 130.1, 129.8, 122.5, 116.8, 114.3, 103.8, 20.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{11}O_5ClSNa$ 372.9908; Found 372.9907.

2-Oxo-2*H*-chromen-4-yl 4-chlorobenzenesulfonate (9b). Yield = 112.8 mg, 67%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3088, 1733, 1628, 1608, 1576, 1398, 1373, 1274, 1192, 1176, 1088, 1064, 934, 876, 832, 768, 751, 714, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.63–7.55 (m, 4H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.35 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.5, 157.6, 153.5, 142.4, 133.4, 133.1, 130.2, 129.8, 124.6, 123.0, 117.1, 114.7, 103.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_9ClO_5SNa$ 358.9751; Found 358.9750.

6-(*tert*-Butyl)-2-oxo-2*H*-chromen-4-yl-4-chlorobenzenesulfonate (9c). Yield = 147.3 mg, 75%, white solid, M.p. 94–96 °C; IR ($CHCl_3$): ν_{max} = 3097, 2964, 2908, 2874, 1735, 1630, 1606, 1576, 1491, 1476, 1424, 1399, 1372, 1357, 1315, 1285, 1263, 1205, 1185, 1143, 1111, 1093, 1059, 1014, 936, 909, 863, 842, 799, 771, 744, 720, 678, 628, 550 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 2H), 7.60 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.58–7.47 (m, 2H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.33 (s, 1H), 1.28 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.8, 157.8, 151.6, 147.9, 142.3, 133.3, 131.1, 130.1, 129.7, 118.9, 116.6, 114.0, 104.7, 34.6, 31.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{17}O_5ClSNa$ 415.0377; Found 415.0376.

6-Methyl-2-oxo-2*H*-chromen-4-yl methanesulfonate (10a).[16g] Yield = 80.1 mg, 63%, white solid, M.p. 118–120 °C, lit.[16g] M.p. 121–122 °C; IR ($CHCl_3$): ν_{max} = 3033, 1725, 1630, 1576, 1425, 1375, 1360, 1195, 1171, 1063, 898, 944, 923, 893, 829, 794, 739, 602, 561, 529 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.42 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.50 (s, 1H), 3.39 (s, 3H), 2.43 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.7, 157.2, 151.7, 134.7, 134.6, 122.5, 116.9, 114.3, 103.2, 39.1, 20.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{10}O_5SNa$ 277.0141; Found 277.0145.

6-(*tert*-Butyl)-2-oxo-2*H*-chromen-4-yl methanesulfonate (10c). Yield = 87.4 mg, 59%, brown semi solid; IR ($CHCl_3$): ν_{max} = 3023, 2965, 2871, 1731, 1629, 1606, 1577, 1491, 1426, 1372, 1334, 1315, 1264, 1205, 1178, 1144, 1112, 1066, 972, 939, 911, 845, 791, 740, 717, 675, 590, 521 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.64 (m, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 6.51 (s, 1H), 3.39 (s, 3H), 1.36 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.8, 157.6, 151.7, 148.1, 131.3, 118.9, 116.8, 113.9, 103.2, 39.1, 34.7, 31.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_5SNa$ 319.0611; Found 319.0610.

6,8-Dimethyl-2-oxo-2*H*-chromen-4-yl methanesulfonate (10f). Yield = 91.2 mg, 68%, brown solid, M.p. 134–138 °C; IR ($CHCl_3$): ν_{max} = 3024, 1711, 1629, 1593, 1476, 1427, 1363, 1339, 1196, 1159, 1126, 1011, 972, 943, 920, 855, 834, 796, 766, 707, 646, 572, 504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H), 7.28 (s, 1H), 6.48 (s, 1H), 3.37 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.9, 157.6, 150.1, 136.0, 134.0, 126.4, 120.0, 114.0, 102.9, 39.0, 20.8, 15.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{12}O_5SNa$ 291.0298; Found 291.0301.

8-Ethoxy-2-oxo-2*H*-chromen-4-yl methanesulfonate (10h). Yield = 68.2 mg, 48%, brown semi solid; IR ($CHCl_3$): ν_{max} = 2922, 1725, 1623, 1576, 1468, 1382, 1352, 1285, 1237, 1206, 1168, 1143, 1046, 993, 970, 927, 882, 828, 794, 758, 737, 623, 507 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.27 (t, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.57 (s, 1H), 4.21 (q, *J* = 8.2 Hz, 2H), 3.39 (s, 3H), 1.53 (t, *J* = 8.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.2, 157.4, 146.9, 143.7, 124.6, 116.3, 115.5, 113.9, 103.8, 65.2, 39.1, 14.7 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{12}O_6SNa$ 307.0247; Found 307.0246.

6-Methyl-2-oxo-2*H*-chromen-4-yl (7,7-dimethyl-2-oxobicyclo [2.2.1]heptan-1-yl) methanesulfonate (11a). Yield = 113.2 mg, 58%, white solid, M.p. 128–130 °C; IR ($CHCl_3$): ν_{max} = 2966, 1749, 1726, 1629, 1578, 1491, 1424, 1365, 1317, 1200, 1183, 1163, 1068, 1056, 924, 835, 794, 742, 607, 526, 496 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 3.99 (d, *J* = 14.7 Hz, 1H), 3.38 (d, *J* = 14.8 Hz, 1H), 2.54–2.40 (m, 5H), 2.19 (t, *J* = 4.6 Hz, 1H), 2.16–2.07 (m, 1H), 2.01 (d, *J* = 18.5Hz, 1H), 1.82–1.73 (m, 1H), 1.54–1.47 (m, 1H), 1.17 (s, 3H), 0.94 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 213.5, 160.9, 157.4, 151.7, 134.6, 134.4, 122.7, 116.8, 114.4, 102.8, 58.2, 49.7, 48.1, 42.8, 42.4, 26.8, 25.2, 20.9, 19.74, 19.7 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{20}H_{22}O_6SNa$ 413.1029; Found 413.1031.

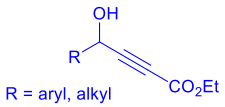
2-Oxo-2*H*-chromen-4-yl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (11b). Yield = 126.1 mg, 67%, white solid, M.p. 134–136 °C; IR ($CHCl_3$): ν_{max} = 2961, 1734, 1627, 1606, 1571, 1453, 1375, 1274, 1173, 1128, 1073, 935, 877, 790, 764, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.40–7.30 (m, 2H), 6.60 (s, 1H), 3.98 (d, *J* = 15.1 Hz, 1H), 3.37 (d, *J* = 15.1 Hz, 1H), 2.55–2.36 (m, 2H), 2.18 (t, *J* = 4.6 Hz, 1H), 2.16–2.05 (m, 1H), 2.00 (d, *J* = 18.8 Hz, 1H), 1.81–1.73 (m, 1H), 1.55–1.46 (m, 1H), 1.15 (s, 3H), 0.93 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 213.4, 160.7, 157.3, 153.5, 133.3, 124.6, 123.1, 117.0, 114.8, 103.0, 58.2, 49.8, 48.2, 42.8, 42.3, 26.8, 25.2, 19.7, 19.65 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{19}H_{20}O_6SNa$ 399.0873; Found 399.0878.

6-(*tert*-Butyl)-2-oxo-2*H*-chromen-4-yl-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl) methanesulfonate (11c). Yield = 134.1 mg, 62%, white solid, M.p. 70–72 °C; IR ($CHCl_3$): ν_{max} = 2964, 1746, 1628, 1606, 1577, 1491, 1425, 1372, 1316, 1265, 1219, 1173, 1143, 1111, 1064, 1027, 937, 912, 845, 798, 762, 718, 680, 611, 560, 523 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 2.1 Hz, 1H), 7.65 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.59 (s, 1H), 3.99 (d, *J* = 15.6 Hz, 1H), 3.36 (d, *J* = 15.3 Hz, 1H), 2.56–2.40 (m, 2H), 2.19 (t, *J* = 4.6 Hz, 1H), 2.16–2.06 (m, 1H), 2.00 (d, *J* = 19.6 Hz, 1H), 1.83–1.74 (m, 1H), 1.54–1.46 (m, 1H), 1.36 (s, 9H), 1.16 (s, 3H), 0.93 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 213.3, 161.0, 157.7, 151.6, 147.9, 131.0, 119.2, 116.6, 114.1, 102.8, 58.1, 49.7, 48.2, 42.8, 42.4, 34.7, 31.3, 26.8, 25.2, 19.7, 19.66 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{23}H_{28}O_6SNa$ 455.1499; Found 455.1497.

6,8-Dimethyl-2-oxo-2*H*-chromen-4-yl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl) methanesulfonate (11f). Yield = 123.4mg, 61%, brown semi solid; IR ($CHCl_3$); ν_{max} = 2961, 1747, 1728, 1631, 1592, 1474, 1426, 1388, 1373, 1324, 1199, 1161, 1129, 1054, 1007, 972, 921, 858, 831, 793, 671, 575 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (s, 1H), 7.28 (s, 1H), 6.58 (s, 1H), 3.97 (d, *J* = 14.9 Hz, 1H), 3.36 (d, *J* = 14.9 Hz, 1H), 2.55–2.41 (m, 5H), 2.40 (s, 3H), 2.19 (t, *J* = 4.5 Hz, 1H), 2.16–2.06 (m, 1H), 2.00 (d, *J* = 18.6Hz, 1H), 1.82–1.72 (m, 1H), 1.55–1.46 (m, 1H), 1.17 (s, 3H), 0.94 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 213.5, 160.1, 157.8, 150.1, 135.8, 134.0, 126.3, 120.3, 114.2, 102.5, 58.2, 49.6, 48.1, 42.9, 42.4, 26.9, 25.2, 20.9, 19.8, 19.7, 15.5 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{24}O_6SNa$ 427.1186; Found 427.1189.

8-Ethoxy-2-oxo-2*H*-chromen-4-yl (7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl) methanesulfonate (11h). Yield = 98.8 mg, 47%, white solid, M.p. 102–106 °C; IR ($CHCl_3$): ν_{max} = 2974, 1745, 1731, 1626, 1576, 1466, 1377, 1277, 1198, 1167, 1049, 984, 926, 885, 791, 754, 734, 629, 501 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.61 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 14.9 Hz, 1H), 3.36 (d, *J* = 14.9 Hz, 1H), 2.54–2.39 (m, 2H), 2.18 (t, *J* = 4.4 Hz, 1H), 2.16–2.05 (m, 1H), 2.00 (d, *J* = 18.8 Hz, 1H), 1.81–1.72 (m, 1H), 1.54–1.45 (m, 4H), 1.16 (s, 3H), 0.93 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 213.4, 160.4, 157.5, 146.8, 143.7, 124.5, 116.3, 115.7, 114.1, 103.2, 65.2, 58.2, 49.7, 48.1, 42.9, 42.4, 26.9, 25.2, 19.8, 19.7, 14.7 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{24}O_7SNa$ 443.1135; Found 443.1134.

General Procedure for Synthesis of Alcohols (12a-i). To a stirred solution of ethyl propiolate (245 mg, 2.5 mmol) at −78 °C in anhydrous THF (10 mL) was added *n*-BuLi (1.72 mL, 2.75 mmol, 1.1 equiv, 1.6M in THF) and the mixture allowed to stir for 30 min. To this mixture was added the aryl/alkyl aldehyde (2.75 mmol, 1.1 equiv) in anhydrous THF (2 mL) dropwise at same temperature and reaction was allowed to stir for 1 h. The reaction mixture was then warmed to 0 °C and stirred for additional 2 h and then quenched with saturated aq. solution of NH_4Cl. The solution was extracted with EtOAc (2 × 15 mL) and the combined organic layers were thoroughly washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give the propiolate esters **12a-i** in good yields.



Ethyl 4-hydroxy-4-(*p*-tolyl)but-2-ynoate (12a).[26] Yield = 409.2 mg, 75%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3397, 2983, 2235, 1713, 1612, 1513, 1466, 1368, 1279, 1192, 1114, 1073, 1017, 858, 817, 753, 656, 564 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.39 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.51 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* = 153.4, 138.8, 135.7, 129.4, 126.6, 86.4, 77.7, 64.0, 62.2, 21.1, 13.9 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0835.

Ethyl 4-hydroxy-4-phenylbut-2-ynoate (12b).[27] Yield = 377.8 mg, 74%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3440, 2983, 2238, 1713, 1495, 1456, 1369, 1304, 1246, 1191, 1069, 1019, 918, 862, 818, 753, 700, 665, 609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.52 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.43–7.34 (m, 3H), 5.57 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.41 (br s, 1H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): *δ* = 153.3, 138.5, 128.9, 128.8, 126.7, 86.1, 77.9, 64.3, 62.3, 13.9 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{12}O_3Na$ 227.0679; Found 227.0678.

Ethyl 4-(4-*tert*-butylphenyl)-4-hydroxybut-2-ynoate (12c).[28] Yield = 501.1 mg, 77%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3440, 2964, 2870, 2235, 1714, 1605, 1511, 1465, 1410, 1366, 1204, 1184, 1110, 1073, 1017, 839, 800, 752, 587 cm^{-1} ; ^1H NMR (400

MHz, $CDCl_3$): δ = 7.47–7.39 (m, 4H), 5.53 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.34–1.28 (m, 12H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 153.4, 152.0, 135.7, 126.4, 125.8, 86.3, 77.7, 64.0, 62.2, 34.6, 31.2, 13.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{13}H_{16}O_3K$ 295.1954; Found 295.1954.

Ethyl 4-([1,1'-biphenyl]-4-yl)-4-hydroxybut-2-ynoate (12d). Yield = 567.6 mg, 81%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3411, 2982, 2234, 1712, 1600, 1488, 1407, 1367, 1250, 1185, 1116, 1075, 1018, 857, 766, 752, 698, 660, 611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.55 (m, 6H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 5.62 (s, 1H), 4.26 (q, *J* =7.2 Hz, 2H), 2.95 (br s, 1H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 153.3, 141.7, 140.3, 137.5, 128.8, 127.5, 127.47, 127.1, 127.06, 86.2, 77.9, 63.9, 62.3, 13.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}O_3Na$ 303.0992; Found 303.0999.

Ethyl 4-(4-chlorophenyl)-4-hydroxybut-2-ynoate (12e). Yield = 465.4 mg, 78%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3453, 2983, 2867, 2236, 1689, 1589, 1490, 1401, 1369, 1343, 1253, 1195, 1170, 1092, 1014, 962, 836, 800, 753, 725, 627, 556, 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.44 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.53 (s, 1H), 4.24 (q, *J* =7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* = 153.2, 137.0, 134.7, 128.9, 128.0, 85.6, 78.0, 63.5, 62.4, 13.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{11}O_3NaCl$ 261.0289; Found 261.0284.

Ethyl 4-(2-fluorophenyl)-4-hydroxybut-2-ynoate (12f). Yield = 377.8 mg, 68%, pale green oil; IR ($CHCl_3$): ν_{max} = 3419, 2983, 2925, 2239, 1711, 1599, 1511, 1464, 1446, 1391, 1368, 1164, 1080, 1016, 981, 861, 803, 780, 752, 611, 508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* = 7.61 (t, *J* = 7.4 Hz, 1H), 7.36 (q, *J* = 7.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 9.4 Hz, 1H), 5.83 (s, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* = 161.2, 158.8, 153.2, 130.8 (d, *J* = 8 Hz), 128.4, 124.6, 115.8 (d, *J* = 20 Hz), 84.9, 77.7, 62.3, 58.8, 13.9 ppm; $^{19}F\{H\}$ NMR (471 MHz, $CDCl_3$): *δ* = –118.67 ppm. HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{11}FO_3Na$ 245.0584; Found 245.0583.

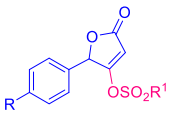
Ethyl 4-hydroxy-4-(*o*-tolyl)but-2-ynoate (12g). Yield = 371.0 mg, 68%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3393, 2983, 2358, 2233, 1710, 1605, 1490, 1463, 1367, 1252, 1176, 1114, 1095, 1072, 1015, 945, 858, 823, 787, 751, 725, 656, 612, 581, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.59 –7.57 (m, 1H), 7.27 –7.21 (m, 2H), 7.19 –7.17 (m, 1H), 5.67 (s, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.00 (br s, 1H, *OH*), 2.41 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$): *δ* = 153.4, 136.4, 135.8, 130.8, 128.8, 126.6, 126.3, 86.2, 77.6, 62.2, 61.9, 18.8, 13.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0835.

Ethyl 4-hydroxy-4-(*m*-tolyl)but-2-ynoate (12h). Yield = 431.0 mg, 79%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 3393, 2938, 2236, 1712, 1608, 1490, 1445, 1367, 1250, 1206, 1153, 1096, 1073, 1019, 907, 860, 794, 767, 752, 702, 665, 615 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.31 – 7.26 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 5.52 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.49 (br s, 1H, *OH*), 2.37 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$): *δ* = 153.4, 138.6, 138.5, 129.6, 128.7, 127.3, 123.7, 86.2, 77.8, 64.2, 62.2, 21.3, 13.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0835; Found 241.0829.

Ethyl 4-hydroxydec-2-ynoate (12i). Yield = 329.0 mg, 62%, colorless oil; IR ($CHCl_3$): ν_{max} = 3419, 2929, 2859, 2237, 1716, 1466, 1367, 1248, 1068, 1016, 964, 910, 860, 751, 726, 635 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* = 4.46 (t, *J* = 6.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.73 (brs, 1H), 1.76 – 1.70 (m, 2H), 1.44–1.41 (m, 2H), 1.30–1.26 (m, 9H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): *δ* = 153.6, 88.2, 76.3 62.1, 61.9, 36.8, 31.5, 28.7, 24.8, 22.5, 13.9, 13.87 ppm; HRMS (ESI–TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{20}O_3Na$ 235.1305; Found 235.1300.

Ethyl hept-2-ynoate (12j).[29] To a stirred solution of 1-hexyne (205 mg, 2.5 mmol) in anhydrous THF (8 mL) was added *n*-BuLi (1.7 mL, 2.73 mmol, 1.1 equiv, 1.6M in THF) at −78 °C and the mixture allowed to stir for 30 min. To this mixture was added ethyl chloroformate (2.75 mmol, 1.1 equiv) in anhydrous THF (2 mL) dropwise at same temperature and the mixture was allowed to stir for 1 h. The reaction mixture was then warmed to 0 °C and stirred for additional 1 h and then quenched with saturated aq. solution of NH_4Cl. The solution was extracted with EtOAc (2 × 15 mL) and the combined organic layers were thoroughly washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to give **12j**. Yield = 285.3 mg, 74%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 2923, 2854, 2359, 2339, 1677, 1599, 1451, 1321, 1287, 1271, 1209, 1178, 1130, 1031, 998, 928, 883, 864, 767, 719, 688, 667, 648, 539, 462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.19 (q, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.54 (m, 2H), 1.42 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ =153.8, 89.4, 73.1, 61.7, 29.5, 21.9, 18.3, 14.0, 13.4 ppm.

General Procedure for Synthesis of Butenolide 4-Sulfonates (13-16). To a solution of **12** (0.5 mmol, 1.0 equiv) in DCE (5 mL) was added sulfonic acid (0.75 mmol, 1.5 equiv) and the mixture stirred at 80 °C for 4 h. After completion of the reaction which was monitored by TLC, the reaction mixture was cooled and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1–4:1) as eluent to afford the 4-sulfonyl butenolides **13**-**16** in 69-84% yields.



5-Oxo-2-(*p*-tolyl)-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13a). Yield = 142.9 mg, 83%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 2925, 1785, 1653, 1388, 1294, 1192, 1178, 1109, 1089, 850, 819, 771, 674, 553 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.90 (d, *J* = 1.7 Hz, 1H), 2.48 (s, 3H), 2.37 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.6, 146.6, 139.9, 137.0, 135.0, 131.5, 130.3, 130.1, 129.7, 128.6, 126.8, 79.9, 21.8, 21.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0613.

5-Oxo-2-phenyl-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13b). Yield = 138.7 mg, 84%, yellow

semi-solid; IR ($CHCl_3$): ν_{max} = 2927, 2852, 2235, 1713, 1494, 1452, 1368, 1248, 1190, 1068, 1019, 918, 861, 818, 753, 699, 661, 608 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2H), 7.41–7.36 (m, 5H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.19–7.16 (m, 2H), 5.94 (d, *J* = 1.8 Hz, 1H), 2.47 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.5, 146.6, 137.0, 134.9, 133.4, 131.5, 130.1, 129.8, 129.1, 128.6, 126.8, 79.9, 21.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}O_5SNa$ 353.0454; Found 353.0452.

2-(4-*tert*-Butylphenyl)-5-oxo-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13c). Yield = 156.5 mg, 81%, pale yellow semisolid; IR ($CHCl_3$): ν_{max} = 2965, 1787, 1649, 1597, 1463, 1388, 1292, 1192, 1178, 1104, 1089, 1040, 952, 887, 837, 783, 752, 670, 596, 550 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.3 Hz, 2H), 7.43–7.36 (m, 4H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.92 (d, *J* = 1.7 Hz, 1H), 2.47 (s, 3H), 1.32 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.6, 153.2, 146.5, 137.0, 135.1, 131.6, 130.4, 130.1, 128.6, 126.7, 126.1, 79.8, 34.7, 31.2, 21.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_5SNa$ 409.1080; Found 409.1083.

2-([1,1'-Biphenyl]-4-yl)-5-oxo-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13d). Yield = 164.6 mg, 81%, pale yellow semisolid; IR ($CHCl_3$): ν_{max} = 2929, 2854, 1786, 1646, 1486, 1449, 1388, 1339, 1259, 1177, 1088, 1037, 919, 848, 816, 753, 698, 549 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.0 Hz, 2H), 7.63–7.50 (m, 5H), 7.46 (t, *J* = 7.1 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 4.8 Hz, 2H), 6.00 (s, 1H), 2.48 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.5, 146.6, 134.9, 134.8, 132.3, 131.5, 130.1, 129.8, 129.1, 128.9, 128.6, 127.8, 127.3, 127.1, 126.8, 79.9, 21.8, ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{18}O_5SNa$ 429.0767; Found 429.0768.

5-Oxo-2-(*o*-tolyl)-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13g). Yield = 134.3 mg, 78%, Pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 3106, 2931, 1784, 1709, 1650, 1596, 1463, 1386, 1289, 1249, 1202, 1177, 1104, 1088, 1044, 940, 885, 851, 818, 787, 736, 669, 595, 548 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31–7.26 (m, 2H), 7.22 (d *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 1.5 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.6, 146.6, 137.1, 136.6, 134.8, 131.7, 131.4, 131.1, 130.1 129.6, 128.5, 126.5, 126.2, 77.3, 21.8, 18.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0607.

5-Oxo-2-(*m*-tolyl)-2,5-dihydrofuran-3-yl-4-methylbenzenesulfonate (13h). Yield = 141.2 mg, 82%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 2920, 2861, 1786, 1649, 1596, 1492, 1454, 1387, 1290, 1206, 1179, 1104, 1088, 1041, 958, 912, 873, 829, 795, 734, 702, 669, 595, 595, 548 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29–7.19 (m, 3H), 6.98–6.96 (m,2H), 5.90 (d, *J* = 2.0 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.5, 146.6, 139.0, 136.9, 135.0, 133.3, 131.4, 130.5, 130.1, 129.0, 128.6, 127.3, 123.9, 79.9, 21.8, 21.3 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}O_5SNa$ 367.0611; Found 367.0616.

2-(4-*tert*-Butylphenyl)-5-oxo-2,5-dihydrofuran-3-yl-methanesulfonate (14). Yield = 122.6 mg, 79%, pale yellow semisolid; IR ($CHCl_3$): ν_{max} = 2965, 1783, 1650, 1415, 1380, 1334, 1291, 1271, 1203, 1178, 1103, 1040, 972, 857, 839, 816, 757, 522 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.9 Hz, 2H), 7.29–7.25 (m, 3H), 6.05 (s, 1H), 3.46 (s, 3H), 1.34 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 166.2, 153.3, 137.1, 137.0, 130.0, 126.8, 126.2, 80.2, 39.8, 34.8, 31.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_5SNa$ 333.0767; Found 333.0769.

5-Oxo-2-(*p*-tolyl)-2,5-dihydrofuran-3-yl-benzenesulfonate (15a). Yield = 122.2 mg, 74%, pale yellow semisolid; IR ($CHCl_3$): ν_{max} = 3098, 2922, 1785, 1649, 1516, 1450, 1389, 1299, 1209, 1188, 1105, 1089, 1040, 949, 887, 854, 817, 786, 749, 686, 607, 577, 510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.3 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H) 7.05 (d, *J* = 8.1 Hz, 2H), 5.92 (d, *J* = 1.8 Hz, 1H), 2.36 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.5, 140.0, 136.9, 135.2, 135.1, 134.6, 130.2, 129.8, 129.5, 128.5, 126.8, 79.9, 21.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}O_5SNa$ 353.054; Found 353.054.

5-Oxo-2-phenyl-2,5-dihydrofuran-3-yl benzenesulfonate (15b). Yield = 113.8 mg, 72%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 3108, 2925, 1784, 1649, 1586, 1449, 1388, 1290, 1212, 1188, 1103, 1090, 1041, 998, 953, 883, 846, 814, 785, 749, 699, 683, 646, 626, 602, 575, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.0 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 7.9 Hz, 1H), 7.65–7.55 (m, 2H), 7.45–7.33 (m, 3H), 7.25 (s, 1H), 7.22–7.13 (m, 2H), 5.96 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.4, 136.8, 135.2, 134.4, 133.3, 129.8, 129.5, 129.1, 128.5, 126.7, 79.8 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{12}O_5SNa$ 339.0298; Found 339.0296.

2-(4-*tert*-Butylphenyl)-5-oxo-2,5-dihydrofuran-3-yl benzenesulfonate (15c). Yield = 132.2 mg, 69%, pale yellow semisolid; IR ($CHCl_3$): ν_{max} = 2965, 1786, 1649, 1450, 1390, 1292, 1190, 1157, 1105, 1089, 1040, 954, 838, 815, 784, 752, 686, 590 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 2H), 7.41(d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 5.94 (s, 1H), 1.32 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 165.5, 153.2, 136.9, 135.1, 133.2, 129.5, 129.2, 128.5, 127.6, 126.6, 126.1, 79.8, 34.7, 31.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_5SNa$ 395.0924; Found 395.0923.

2-(Biphenyl-4-yl)-5-oxo-2,5-dihydrofuran-3-yl benzenesulfonate (15d). Yield = 133.4 mg, 68%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 2927, 1785, 1648, 1488, 1450, 1388, 1337, 1289, 1211, 1177, 1105, 1089, 1041, 1001, 950, 918, 884, 847, 816, 751, 717, 698, 685, 624, 602, 574, 504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06–7.97 (m, 2H), 7.78–7.70 (m, 1H), 7.65–7.53 (m, 5H), 7.50–7.43 (m, 2H), 7.42–7.35 (m, 2H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.24 (s, 1H), 7.20–7.14 (m, 1H), 6.0 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.4, 142.7, 139.9, 136.9, 135.2, 134.5, 132.1, 129.5, 129.1, 128.9, 128.5, 127.8, 127.2, 127.1, 126.7, 79.7 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{16}O_5SNa$ 415.0611; Found 415.0605.

5-Oxo-2-(*o*-tolyl)-2,5-dihydrofuran-3-yl-benzenesulfonate (15g). Yield = 110.7 mg, 67%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 3095, 2931, 1784, 1650, 1493, 1450, 1388, 1288, 1204, 1187, 1104, 1089, 1044, 940, 886, 851, 821, 789, 744, 718, 685, 659, 625, 603, 574 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.0 (d, *J*

= 7.6 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.0, 2H), 7.33–7.16 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 2.42 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.5, 137.1, 136.6, 135.2, 135.0, 134.6, 131.6, 131.1, 129.7, 129.5, 128.5, 126.6, 126.2, 18.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}O_5SNa$ 353.0454; Found 353.0457.

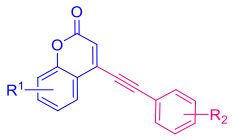
5-Oxo-2-(*m*-tolyl)-2,5-dihydrofuran-3-yl-benzenesulfonate (15h). Yield = 115.6 mg, 70%, pale yellow semi-solid; IR ($CHCl_3$): ν_{max} = 3095, 2919, 1786, 1649, 1608, 1450, 1388, 1290, 1208, 1187, 1105, 1089, 1042, 1000, 958, 912, 874, 830, 796, 740, 717, 685, 653, 604, 573 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.0 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.29–7.19 (m, 3H), 6.97 (d, *J* = 5.6 Hz, 2H), 5.91 (d, *J* = 1.6 Hz, 1H), 2.34 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.5, 139.0, 136.8, 135.2, 135.1, 134.5, 133.2, 130.5, 129.5, 129.0, 128.5, 127.2, 123.8, 79.9, 21.3 ppm; HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{14}O_5SK$ 369.0194; Found 369.0194.

2-(4-*tert*-Butylphenyl)-5-oxo-2,5-dihydrofuran-3-yl 4-ethylbenzenesulfonate (16c). Yield = 150.2 mg, 75%, White semi-solid; IR ($CHCl_3$): ν_{max} = 3142, 2962, 1774, 1652, 1593, 1391, 1283, 1212, 1180, 1124, 1112, 1090, 1046, 968, 912, 868, 836, 790, 753, 658, 593, 558, 533 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.3 Hz, 2H), 7.44–7.36 (m, 4H), 7.24 (s, 1H), 7.11 (d, *J* = 6.9 Hz, 2H), 5.92 (s, 1H), 2.77 (q, *J* = 7.5 Hz, 2H), 1.36–1.23 (m, 12H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.6, 153.2, 152.6, 137.0, 134.8, 131.7, 130.4, 129.0, 128.7, 126.7, 126.1, 79.8, 34.7, 31.2, 29.0, 14.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{24}O_5SNa$ 423.1237; Found 423.1232

5-Oxo-2-(*o*-tolyl)-2,5-dihydrofuran-3-yl 4-ethylbenzenesulfonate (16g). Yield = 139.8 mg, 78%, white semi-solid; IR ($CHCl_3$): ν_{max} = 2970, 2932, 1789, 1709, 1649, 1596, 1492, 1463, 1386, 1289, 1250, 1178, 1105, 1090, 1044, 940, 886, 852, 820, 793, 736, 665, 597, 550 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31–7.16 (m, 4H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.19 (d, *J* = 1.5 Hz, 1H), 2.76 (q, *J* = 7.5, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 165.6, 152.6, 137.1, 136.6, 134.5, 131.7, 131.5, 131.0, 129.6, 128.9, 128.6, 126.5, 126.2, 77.3, 28.9, 18.9, 14.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{18}O_5SNa$ 381.0767; Found 381.0771.

5-Oxo-2-(*m*-tolyl)-2,5-dihydrofuran-3-yl 4-ethylbenzenesulfonate (16h). Yield = 143.4 mg, 80%, white semi-solid; IR ($CHCl_3$): ν_{max} = 2969, 2931, 1786, 1649, 1596, 1490, 1457, 1386, 1289, 1209, 1178, 1105, 1089, 1042, 959, 912, 870, 830, 794, 701, 662, 597, 569 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27–7.19 (m, 3H), 6.98–6.96 (m, 1H), 6.19 (d, *J* = 1.5 Hz, 1H), 2.75 (q, *J* = 7.6, 2H), 2.35 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.6, 152.6, 139.0, 136.9, 134.8, 133.3, 131.6, 130.5, 129.0, 128.7, 127.3, 123.9, 79.9, 29.0, 21.3, 14.9 ppm; ; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{18}O_5SNa$ 381.0767; Found 381.0767.

Sonogashira Coupling Reaction for the Synthesis of 6-Methyl-4-(Phenylethynyl)-2*H*-Chromen-2-one (18a). To a solution of 4-sulfonyl coumarins (0.25 mmol), $PdCl_2(PPh_3)_2$ (17.6 mg, 10 mol %), CuI (4.8 mg, 10 mol %), *N,N*-(di-*iso*-propylethyl)amine (0.13 mL, 1.5 equiv) in MeCN (3 mL) was added phenylacetylene (38.3 mg, 0.375 mmol, 1.5 equiv). The reaction mixture was stirred 12 h at 60 °C. After completion of the reaction which was monitored by TLC, the reaction mixture was cooled, diluted with EtOAc (10 mL), and was then filtered through a short pad of Celite. The filtrate was concentrated under vacuum and the residue were purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as an eluent to afford **18a** (51.4 mg, 79% yield from **5a**; 47.5 mg, 73% from **7a**; 40.3 mg, 62% from **8a**; 41.0 mg, 63% from **9a**; 28.0 mg, 43% from **10a**, and **11a** did not gave any product), brown semi solid; IR ($CHCl_3$): ν_{max} = 2210, 1721, 1603, 1560, 1486, 1368, 1251, 1185, 933, 812, 756, 686, 536 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.52–7.41 (m, 3H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.61 (s, 1H), 2.46 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.5, 151.7, 137.2, 134.2, 133.3, 132.2, 130.1, 128.7, 126.4, 121.2, 118.4, 118.0, 116.8, 101.9, 82.9, 20.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{12}O_2Na$ 283.0730; Found 283.0729.



Compounds **18b-g** were prepared according to above procedure used for **18a**.

6-Methyl-4-(*m*-tolylethynyl)-2*H*-chromen-2-one (18b). Yield = 50.7 mg, 74%; white solid, M.p. 76 °C; IR ($CHCl_3$): ν_{max} = 2969, 2208, 1725, 1629, 1595, 1579, 1564, 1491, 1386, 1366, 1274, 1254, 1200, 1185, 1170, 1061, 933, 833, 757, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.51–7.43 (m, 2H), 7.41–7.21 (m, 4H), 6.60 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.5, 151.7, 138.5, 137.3, 134.2, 133.3, 132.7, 131.1, 129.3, 128.6, 126.4, 121.0, 118.3, 118.1, 116.8, 102.2, 82.6, 21.2, 21.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{14}O_2K$ 313.0625; Found 313.0622.

4-(4-*tert*-Butylphenylethynyl)-6-methyl-2*H*-chromen-2-one (18c). Yield = 56.2 mg, 71%, white semi solid; IR ($CHCl_3$): ν_{max} = 2963, 2867, 2210, 1726, 1617, 1598, 1561, 1507, 1421, 1365, 1270, 1251, 1182, 1108, 1039, 933, 859, 835, 819, 563 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 1.8, 8.3 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 6.59 (s, 1H), 2.45 (s, 3H), 1.35 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.5, 153.8, 151.7, 137.4, 134.1, 133.2, 132.0, 126.4, 125.7, 118.2, 118.1, 118.06, 116.7, 102.4, 82.5, 35.0, 31.1, 20.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{21}O_2$ 317.1536; Found 317.1539.

4-(Phenylethynyl)-2*H*-chromen-2-one (18d).[18b] Yield = 44.9 mg, 73%, colorless oil; IR ($CHCl_3$): ν_{max} = 2205, 1720, 1607, 1556, 1487, 1449, 1372, 1270, 1249, 1187, 934, 856, 768, 756, 685, 542 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.67–7.62 (m, 2H), 7.57 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50–7.41 (m, 3H), 7.38–7.33 (m, 2H), 6.63 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.2, 153.5, 137.2, 132.3, 132.2, 130.2, 128.7, 126.6, 124.4, 121.1, 118.3, 117.0, 102.1, 82.7 ppm; HRMS (ESI-

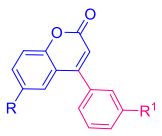
TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{10}O_2Na$ 269.0573; Found 269.0576.

4-(4-*tert*-Butylphenylethynyl)-2*H*-chromen-2-one (18e). Yield = 55.9 mg, 74%; brown semi solid; IR ($CHCl_3$): ν_{max} = 2964, 2207, 1724, 1604, 1557, 1449, 1373, 1323, 1270, 1249, 1181, 931, 861, 836, 768, 563 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.62–7.54 (m, 3H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.39–7.11 (m, 2H), 6.62 (s, 1H), 1.35 (s, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.3, 153.9, 153.6, 137.5, 132.2, 132.0, 126.7, 125.7, 124.4, 118.5, 118.1, 117.0, 102.7, 82.4, 35.0, 31.1 ppm HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{21}H_{18}O_2Na$ 325.1199; Found 325.1196.

6-(tert-Butyl)-4-(*m*-tolylethynyl)-2*H*-chromen-2-one (18f). Yield = 54.6 mg, 69%, white semi solid; IR ($CHCl_3$): ν_{max} = 2957, 2867, 2204, 1711, 1608, 1559, 1486, 1423, 1370, 1264, 1203, 1178, 1139, 1048, 937, 852, 828, 777, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.47–7.42 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.30–7.25 (m, 2H), 6.59 (s, 1H), 2.40 (s, 3H), 1.40 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.6, 151.5, 147.5, 138.5, 137.6, 132.7, 131.1, 129.9, 129.3, 128.6, 122.7, 121.0, 117.8, 117.6, 116.5, 102.5, 82.7, 34.6, 31.3, 21.2 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{22}H_{20}O_2Na$ 339.1356; Found 339.1353.

6-(*tert*-Butyl)-4-(4-tert-butylphenylethynyl)-2*H*-chromen-2-one (18g). Yield = 68.1 mg, 76%, white semi solid; IR ($CHCl_3$): ν_{max} = 2957, 2908, 2871, 2205, 1720, 1598, 1561, 1464, 1369, 1319, 1268, 1256, 1183, 1103, 1038, 941, 855, 839, 826, 753, 670, 568, 557 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 2.3 Hz, 1H), 7.64–7.54 (m, 3H), 7.50–7.45 (m, 2H), 7.28 (t, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 1.40 (s, 9H), 1.36 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.7, 153.9, 151.6, 147.5, 137.7, 132.0, 129.9, 125.8, 122.8, 118.2, 117.7, 117.65, 116.6, 102.7, 82.6, 35.0, 34.6, 31.3, 31.1 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{25}H_{26}O_2Na$ 381.1825; Found 381.1817.

Suzuki Coupling Reaction for the Synthesis of 4-Aryl-2*H*-Chromen-2-ones (20a-d). To a solution of 4-tosylcoumarins (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (5.6 mg, 5 mol %), PPh_3 (26.2 mg, 20 mol %), K_3PO_4 (318.2 mg, 3.0 equiv) in *t*-BuOH (3 mL) was added boronic acid (1.0 mmol, 2.0 equiv). The reaction mixture was stirred for 12 h at 75 °C. After completion of the reaction which was monitored by TLC, the reaction mixture was cooled, diluted with EtOAc (10 mL), and was then filtered through a short pad of Celite. The filtrate was then concentrated under vacuum and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as an eluent to give **20a-d** in good yields.



6-Methyl-4-phenyl-2*H*-chromen-2-one (20a).[30] Yield = 86.2 mg, 73%, white solid, M.p. 131–134 °C, lit.[30] M.p. 134.7–135.1 °C; IR ($CHCl_3$): ν_{max} = 2924, 1725, 1618, 1565, 1446, 1417, 1364, 1312, 1277, 1258, 1219, 1181, 1122, 1030, 940, 871, 819, 774, 701, 667, 587 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.50 (m, 3H), 7.47–7.41 (m, 2H), 7.35 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.25 (s, 1H), 6.34 (s, 1H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 161.0, 155.6, 152.3, 135.3, 133.8, 133.9, 129.6, 128.8, 128.4, 126.7, 118.6, 117.0, 115.1, 20.9 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{12}O_2$ 237.0910; Found 237.0903.

6-Methyl-4-(*m*-tolyl)-2*H*-chromen-2-one (20b). Yield = 95.1 mg, 76%, colorless oil; IR ($CHCl_3$): ν_{max} = 2923, 2859, 1731, 1618, 1566, 1485, 1420, 1363, 1314, 1277, 1255, 1194, 1176, 1121, 1042, 939, 868, 819, 794, 778, 756, 719, 700, 655, 593, 542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.27–7.21 (m, 3H), 6.33 (s, 1H), 2.45 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.0, 155.8, 152.3, 138.7, 135.3, 133.8, 132.8, 130.3, 128.9, 128.6, 126.7, 125.5, 118.7, 117.0, 115.0, 21.5, 20.9 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{14}O_2Na$ 273.0886; Found 273.0880.

6-(*tert*-Butyl)-4-phenyl-2*H*-chromen-2-one (20c).[30] Yield = 100.2 mg, 72%, white solid, M.p. 105–106 °C, lit.[30] M.p. 108.3–109 °C ; IR ($CHCl_3$): ν_{max} = 2963, 2867, 1732, 1615, 1567, 1487, 1464, 1369, 1313, 1263, 1200, 1178, 1128, 939, 867, 828, 790, 676, 580 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.57–7.52 (m, 3H), 7.50–7.45 (m, 3H), 7.35 (dd, *J* = 8.6 Hz, 1H), 6.36 (s, 1H), 1.26 (s, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 161.1, 155.9, 152.2, 147.2, 135.3, 129.7, 129.5, 128.8, 128.4, 123.1, 118.2, 116.8, 115.0, 34.6, 31.2 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{19}H_{19}O_2$ 279.1380; Found 279.1377.

6-(*tert*-Butyl)-4-(*m*-tolyl)-2*H*-chromen-2-one (20d). Yield = 109.6 mg, 75%, colorless oil; IR ($CHCl_3$): ν_{max} = 3064, 2963, 2911, 2874, 1727, 1615, 1567, 1489, 1447, 1418, 1370, 1313, 1263, 1185, 1129, 1029, 940, 869, 827, 773, 754, 731, 703, 641, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.31–7.24 (m, 2H), 6.35 (s, 1H), 2.45 (s, 3H), 1.27 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 161.1, 156.0, 152.1, 147.1, 138.6, 135.2, 130.4, 129.4, 129.1, 128.6, 125.5, 123.2, 118.2, 116.7, 114.7, 34.5, 31.2, 21.4 ppm; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{21}O_2$ 293.1536; Found 293.1540.

6-Methyl-4-phenylchroman-2-one (21).[31] To a solution of **20** (70 mg, 0.3 mmol) in EtOAc (6 mL) was added Pd/C (35 mg, 10% w/w) and the mixture stirred under 4 atm of H_2 for 24 h. After completion of reaction it was then filtered through Celite pad and the pad washed with EtOAc (10 mL). The filtrate was concentrated and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (19:1) as eluent to give **21** (67.9 mg, 95%) as white solid, M.p. = 84–86 °C, lit.[28] M.p. 81–84 °C; IR ($CHCl_3$): ν_{max} = 2924, 2851, 1770, 1610, 1587, 1514, 1487, 1455, 1344, 1280, 1222, 1177, 1138, 968, 920, 880, 823, 756, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 3H), 7.18–7.14 (m, 2H), 7.09 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.79 (s, 1H), 4.30 (t, *J* = 6.9 Hz, 1H), 3.10–2.96 (m, 2H), 2.26 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 167.8, 149.7, 140.5, 134.3, 129.3, 129.1, 128.6, 127.6, 127.5, 125.3, 116.9, 40.7, 37.1, 20.7 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{14}O_2Na$ 261.0886; Found 261.0886.

2-[(3-Diisopropylamino)-1-phenylpropyl]-4-methyl phenol, tolterodine (22).[16d] To a solution of 6-methyl-4-phenyl chroman-2-one **21** (60 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (4 mL) was added DIBAL-H (0.18 mL, 1.75 M in toluene, 0.6 mmol) dropwise under N_2 at −20 °C. After stirring for 6 h, the reaction was quenched with EtOAc (1 mL) and an aqueous solution of Rochelle salt was added. The mixture was stirred at room temperature for 1 h. The aqueous phase was extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. To a solution of the residue in EtOH (2 mL), placed in a glass cylinder in a stainless-steel autoclave, were added Pd/C (10 mg) and *i*Pr_2NH (30.4 mg, 0.6 mmol), and the autoclave was pressurized with H_2 (20 atm). The reaction mixture was stirred for 12 h at 60 °C and then the autoclave was cooled to room temperature and depressurized. The mixture was filtered through Celite pad and the pad washed with EtOAc (2 × 5 mL). The filtrate was concentrated and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (5:1) as eluent to give tolterodine **22** (65.9 g, 81%) as pale yellow oil. IR ($CHCl_3$): ν_{max} = 3294, 3027, 2967, 2942, 2877, 1601, 1508, 1494, 1454, 1388, 1361, 1253, 1164, 1114, 817, 734, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 4H), 7.23–7.20 (m, 1H), 6.89–6.81 (m, 2H), 6.54 (s, 1H), 4.50 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.26 (q, *J* = 7.1 Hz, 2H), 2.79–2.72 (m, 1H), 2.44–2.33 (m, 2H), 2.17–2.11 (m, 4H), 1.15 (d, *J* = 6.7 Hz, 6H), 1.09 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 153.1, 144.6, 132.2, 129.2, 128.6, 127.7, 126.1, 118.0, 48.2, 42.2, 39.4, 33.1, 20.7, 19.8, 19.4 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for calcd for $C_{22}H_{33}NO$ 326.2478; Found 326.2482.

Ethyl 3-(4-chlorophenyl)propiolate (23a). The title compound was prepared following literature procedure.[32] Pale yellow oil; IR ($CHCl_3$): ν_{max} = 2796, 2678, 2067, 1873, 1702, 1588, 1545, 1487, 1432, 1358, 1262, 1213, 1167, 1094, 1069, 1043, 1007, 821, 756, 697, 643, 606, 503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 153.8, 136.9, 134.1, 129.0, 118.0, 84.6, 81.4, 62.1, 14.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_9O_2NaCl$ 231.0183; Found 231.0183.

Ethyl 3-[4-(*tert*-butyl)phenyl]propiolate (23b). The title compound was prepared following literature procedure.[32] Pale yellow oil; IR ($CHCl_3$): ν_{max} = 2964, 2869, 2209, 1709, 1604, 1506, 1463, 1395, 1366, 1291, 1201, 1179, 1106, 1024, 948, 859, 837, 749, 670, 565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.31 (brs, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 154.2, 132.8, 125.5, 116.4, 86.5, 80.3, 61.9, 34.9, 31.0, 14.0 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_2Na$ 253.1199; Found 253.1194.

1-(4-Chlorophenyl)ethan-1-one (24a).[33] The title compound was obtained from **23a** (104.3 mg, 0.5 mmol) under similar reaction conditions as described for **13** to give **24a**. Yield = 60.3 mg, 78%, pale yellow oil; IR ($CHCl_3$): ν_{max} = 1735, 1690, 1590, 1488, 1424, 1396, 1357, 1259, 1198, 1127, 1095, 1014, 956, 907, 829, 763, 710, 624, 592, 524 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 196.9, 139.6, 135.4, 129.7, 128.9, 26.6 ppm.

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1-[4-(*tert*-Butyl)phenyl]ethan-1-one (24b).[33] The title compound was obtained from **23b** (115.2 mg, 0.5 mmol) under similar reaction conditions as described for **13** to give **24b**. Yield = 76.6 mg, 87%, colorless oil; IR ($CHCl_3$): ν_{max} = 2964, 2868, 1683, 1606, 1468, 1406, 1358, 1296, 1212, 1192, 1113, 1014, 957, 838, 734, 635, 599, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H), 1.33 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 197.8, 156.8, 134.5, 128.2, 125.4, 35.0, 31.0, 26.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{17}O$ 177.1274; Found 177.1276.

Conflicts of interest

There are no conflicts to declare.

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#These authors contributed equally

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Graphical Abstract

Metal-Free Annulative Hydrosulfonation of Propiolate Esters: Synthesis of 4-Sulfonates of Coumarins and Butenolides

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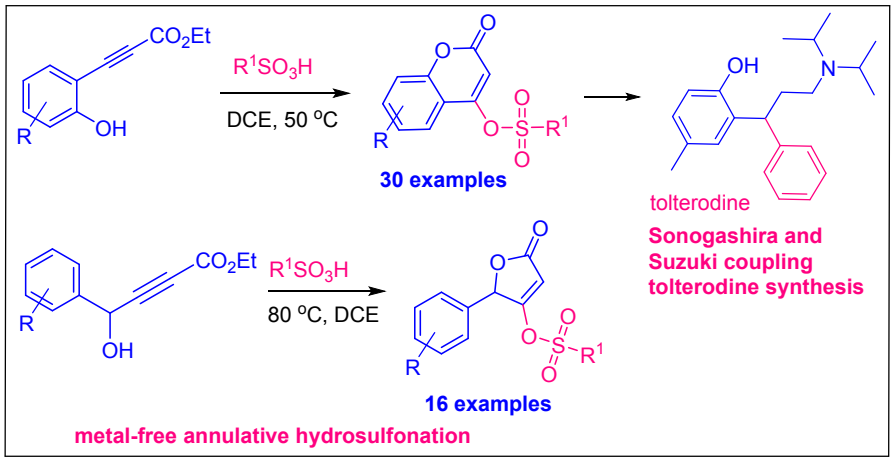

An efficient metal-free and cost-effective method for the synthesis of coumarin and butenolide 4-sulfonates has been developed involving addition of sulfonic acids to ethyl propiolates followed by lactonization.