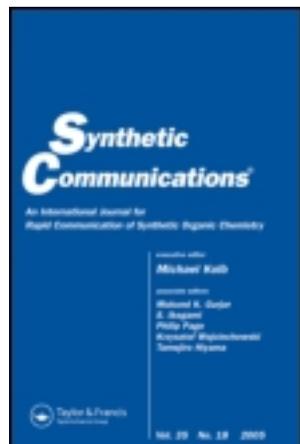


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## SIMPLE STRATEGY FOR SULFONYL ETHYNYLOGS OF COUMARINS

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### GRAPHICAL ABSTRACT



**Abstract** Synthesis of 3-(2-(phenylsulfonyl) ethynyl)-2H-chromen-2-one is described. Reaction of  $\beta$ -ketosulfones with semicarbazide hydrochloride in ethanol at reflux temperature gave the corresponding semicarbazones, which on oxidative cyclization with selenium dioxide resulted in the formation of the corresponding 1,2,3-selenodiazole derivatives. These on pyrolysis gave the titled compounds.

**Keywords** Alkynes;  $\beta$ -ketosulfones; 1,2,3-selenodiazoles; semicarbazones;  $\text{SeO}_2$

## INTRODUCTION

1,2,3-Selenodiazoles and their derivatives are well known and have attracted attention as versatile synthetic intermediates.<sup>[1,2]</sup> Substituted 1,2,3-selenodiazole and many of its derivatives have been prepared to date, and some of them show high antibacterial activity.<sup>[3–6]</sup> The antifungal activity of other substituted 1,2,3-selenodiazoles has also been determined.<sup>[6–8]</sup> It has been found that the introduction of a 1,2,3-selenodiazole ring to molecules of known biological activity changes their activities and in some cases leads to an increase in their biological activity.<sup>[9]</sup> 4-Methyl-1,2,3-selenodiazole-5-carboxamides inhibit tumor cell colony formation.<sup>[10,11]</sup> In the area of antibacterial therapeutics, resistance to currently available drugs is progressively limiting their utility in treating bacterial infections. This problem can be solved by discovering novel pharmaceutical drugs that inhibit novel targets. Advances in molecular microbiology and genomics have led to the identification of

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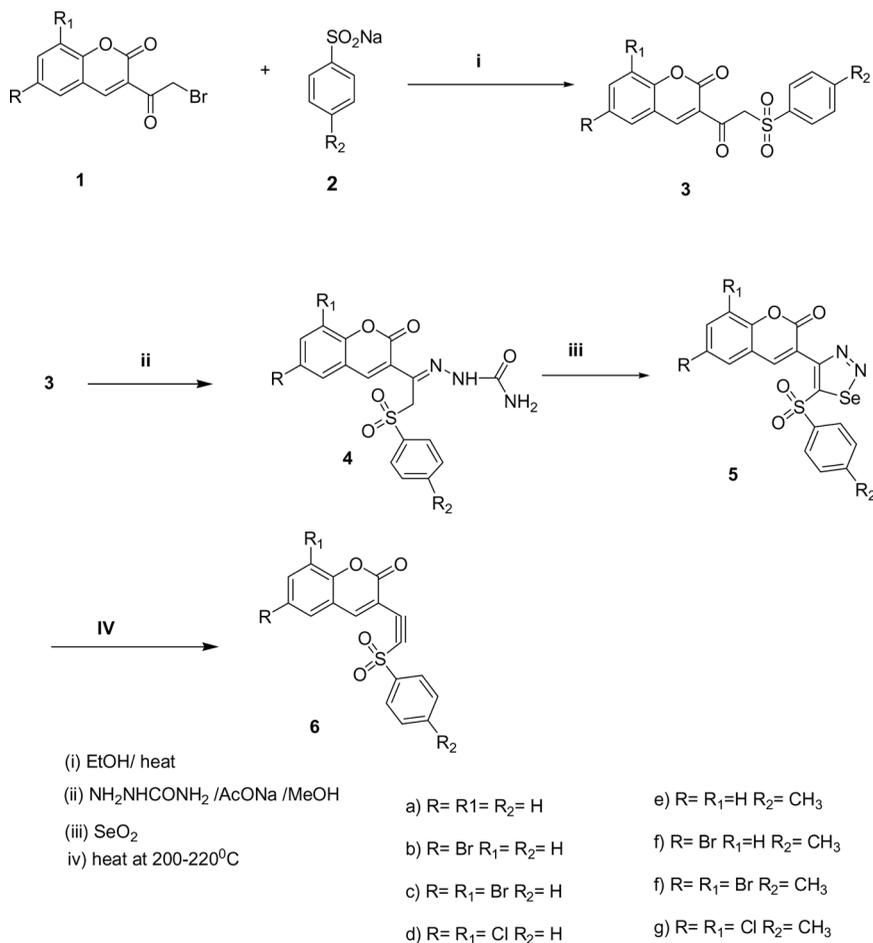
numerous bacterial genes that are encoding for novel proteins, which could potentially serve as novel targets for antibacterial compounds. Regulatory proteins such as the two-component histidine kinases, involved in bacterial signal transduction, have recently gained considerable attention as one such class of potential targets.<sup>[12]</sup>

The long-standing but modest use of selenium reagents by organic synthetic chemists received new impetus because of the numerous organoselenium reagents, catalysts, and intermediates employed in synthesis. Nevertheless, their role in some synthetically useful reactions for preparation of nonselenium organic compounds is prominent and worthy of note. The reactions can be divided into two groups: (i) those that proceed through extrusion of the selenium in thermal or reductive conditions, or under treatment with a nucleophile (photochemical extrusion of the selenium is of minor importance for use in synthesis), and (ii) those in which selenium plays a role as oxygen-transfer agent. The ready thermal and photochemical decomposition of 1,2,3-selenadiazoles resulting in extrusion of nitrogen and selenium or nitrogen only has been exploited widely in synthesis for more than 30 years. Their thermolysis or decomposition with butyllithium gave the alkynes. More recently, thermolysis of 1,2,3-selenadiazoles fused them to carbocyclic rings.<sup>[13-15]</sup>

Novobiocin is a coumarin-derived antibiotic used as a competitive inhibitor of the bacterial ATP binding gyrase B subunit, blocking the negative supercoiling of relaxed DNA.<sup>[16-19]</sup> Lamellarin is utilized as a selective inhibitor of HIV-I integrase.<sup>[20]</sup> The discovery of promising lead antiviral compounds and their moderate activity warranted the development of efficient and rapid synthesis and evaluation of analogous structures in the search for better inhibitors. Thus, we initiated a program to develop efficient methods for the synthesis of diversified coumarin molecules, with the hope of finding more active hits or leads for our particular biological assays.

Our work on the synthesis of heterocyclic compounds containing sulfone-linked 1,2,3-thiadiazoles,  $\beta$ -ketosulfones, and heteryl styryl sulfones at the 3-position of coumarin<sup>[21-23]</sup> and our sustained interest in this field led us to develop a simple and elegant methodology for a new class of compounds, ethynesulfones, through a facile route. Literature search shows not only the compounds involving alkene and alkyne moieties but also chalone ethynylogs are relatively few.<sup>[24]</sup> One such method involves the Pd coupling reaction of vinyl halides with terminal alkynes and alkynyl metals. Moreover, the carbonyl activated enyne systems have also been obtained by the direct condensation of phenyl acetylenes with a stoichiometric amount of triethyl amine and dichlorobis(triphenyl phosphine)palladium and copper iodide as catalyst.<sup>[25]</sup> However, there have been no reports to date about ethynylogs of coumarins.

The synthetic scheme is based on the reactivity of the 1,2,3-selenadiazolyl ring, which on pyrolysis affords alkynes as major products. This paves the way for the synthesis of phenyl sulfonyl ethynylogs of coumarin derivatives. To achieve the targets species, 3-[2-(phenylsulfonyl)acetyl]-2*H*-chromen-2-ones<sup>[22]</sup> (**3**) have been chosen in which the  $\alpha$ -halo methylene group is exploited for developing a selenodiazole ring. The former on reaction with semicarbazide hydrochloride gave corresponding semicarbazones<sup>[21]</sup> (**4**), which on oxidative cyclization with selenium dioxide results in 3-(5-(phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2*H*-chromen-2-one (**5**). The reactivity of **5** has been assessed by pyrolysis, leading to the formation of 3-(2-(phenylsulfonyl)ethynyl)-2*H*-chromen-2-one (Scheme 1). The method described in the present



**Scheme 1.** Synthesis of 3-(2-(arylsulfonyl)ethynyl)-2H-chromen-2-ones.

instance is a facile route. Indeed, the sulfonyl ethylene analogs are valuable synthons in a number of organic reactions, and a study related to them is in progress.

## EXPERIMENTAL

All the reagents and solvents were pure, purchased from commercial sources, and used without further purification unless otherwise stated. 3-(2-Bromoacetyl) coumarins<sup>[26,27]</sup> are prepared by literature procedures. Melting points were determined in open capillaries with a Cintex melting-point apparatus (Mumbai, India) and were uncorrected. CHNS analysis was done on a Carlo Erba EA 1108 automatic elemental analyzer. The purity of the compounds was checked by thin-layer chromatographic (TLC) plates (E. Merck, Mumbai, India), and infrared (IR) spectra (KBr) were recorded on a Bruker WM-4(X) spectrometer (577 model).  $^1\text{H}$  NMR spectra were recorded on a Bruker WM-300 spectrometer in  $\delta$  ppm using tetramethylsilane

(TMS) as internal standard. Mass spectra (EI-MS) were determined on a Perkin-Elmer (SCIEX API-2000, ESI) instrument at 12.5 eV.

### **3-(5-(Phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one: General Procedure**

Semicarbazone **4** (0.001 mol) was dissolved in acetic acid, and selenium dioxide (0.001 mol) was added. Then the reaction mixture was heated at reflux temperature for more than 6 h. The reaction was followed by TLC until completion. After cooling, the selenium metal deposited was filtered, and the reaction mixture was poured into ice-cold water and neutralized with saturated sodium carbonate. The solid separated was filtered, washed with water, dried, and purified by column chromatography (silica gel 60–120 mesh, hexane–ethylacetate, 9:1).

### **Spectral Data of 5a–h**

**3-(5-(Phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5a).** Yellow solid, yield 92%, mp 198–200 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1150, 1320 (SO<sub>2</sub>), 1420 (N=N), 1610 (C=C), 1710 (C=O of lactone); <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.90–6.95 (m, 2H, Ar-H), 7.22–7.40 (m, 5H, Ar-H), 7.55–7.61 (m, 2H, Ar-H), 8.15 (s, 1H, C<sub>4</sub> of coumarin proton). EI-MS 419 (M + H)<sup>+</sup>. Anal. calcd. for C<sub>17</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 48.93; H, 2.42; N, 6.71; S, 7.68. Found: C, 48.90; H, 2.47; N, 6.74; S, 7.71%.

**6-Bromo-3-(5-(phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5b).** Yellow solid, yield 87%, mp 208–210 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1170, 1330 (SO<sub>2</sub>), 1440 (N=N), 1610 (C=C), 1730 (C=O of lactone). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.36–7.40 (m, 3H, Ar-H), 7.53–7.55 (m, 2H, Ar-H), 7.84–7.86 (m, 3H, Ar-H), 8.12 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>17</sub>H<sub>9</sub>BrN<sub>2</sub>O<sub>4</sub>SSe: C, 41.15; H, 1.83; N, 5.65; S, 6.46. Found: C, 41.18; H, 1.87; N, 5.69; S, 6.49%.

**6,8-Dibromo-3-(5-(phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5c).** Yellow solid, yield 78%, mp 228–230 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1150, 1315 (SO<sub>2</sub>), 1460 (N=N), 1612 (C=C), 1715 (C=O of lactone). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.38–7.97 (m, 7H, Ar-H), 8.12 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>17</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 35.50; H, 1.40; N, 4.87; S, 5.58. Found: C, 35.58; H, 1.44; N, 4.91; S, 5.60%.

**6,8-Dichloro-3-(5-(phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5d).** Yellow solid, yield 83%, mp 188–190 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1150, 1350 (SO<sub>2</sub>), 1430 (N=N), 1612 (C=C), 1720 (C=O of lactone). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.15–7.55 (m, 7H, Ar-H), 8.50 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>17</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 42.00; H, 1.66; N, 5.76; S, 6.60. Found: C, 42.10; H, 1.70; N, 5.79; S, 6.64%.

**3-(5-Tosyl-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5e).** Yellow solid, yield 91%, mp 192–194 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1150, 1340 (SO<sub>2</sub>), 1430 (N=N), 1620 (C=C), 1720 (C=O of lactone). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 2.35 (s, 3H, CH<sub>3</sub>), 7.52–7.70 (m, 4H, Ar-H), 7.80–8.10 (m, 4H, Ar-H), 8.5 (s, 1H, C<sub>4</sub> of coumarin proton). EI-MS 433 (M + H)<sup>+</sup>. Anal. calcd. for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 50.12; H, 2.80; N, 6.49; S, 7.43. Found: C, 50.16; H, 2.84; N, 6.52; S, 7.46%.

**6-Bromo-3-(5-tosyl-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5f).**

Yellow solid, yield 82%, mp 200–202 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1130, 1355 (SO<sub>2</sub>), 1480 (N=N), 1616 (C=C), 1726 (C=O of lactone). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 2.40 (s, 3H, CH<sub>3</sub>), 7.36–7.41 (m, 5H, Ar-H), 7.65–7.83 (m, 2H, Ar-H), 8.11 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>18</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>4</sub>SSe: C, 42.37; H, 2.17; N, 5.49; S, 6.28. Found: C, 42.32; H, 2.19; N, 5.52; S, 6.32%.

**6,8-Dibromo-3-(5-tosyl-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5g).**

Yellow solid, yield 75%, mp 221–223 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1150, 1365 (SO<sub>2</sub>), 1425 (N=N), 1605 (C=C), 1715 (C=O of lactone); <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm) 2.44 (s, 3H, CH<sub>3</sub>), 7.36–7.41 (m, 4H, Ar-H), 7.63–7.72 (m, 2H, Ar-H), 8.11 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>18</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 36.70; H, 1.71; N, 4.76; S, 5.44. Found: C, 36.74; H, 1.76; N, 4.79; S, 5.49%.

**6,8-Dichloro-3-(5-tosyl-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one (5h).**

Yellow solid, yield 79%, mp 205–207 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm) 2.40 (s, 3H, CH<sub>3</sub>), 7.70–7.90 (m, 6H, Ar-H), 8.35 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>18</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SSe: C, 43.22; H, 2.02; N, 5.60; S, 6.41. Found: C, 43.25; H, 2.00; N, 5.63; S, 6.44%.

**3-(2-(Phenylsulfonyl)ethynyl)-2H-chromen-2-one: General Procedure**

3-(5-(Phenylsulfonyl)-1,2,3-selenadiazol-4-yl)-2H-chromen-2-one 4 (0.001 mol) was heated for 15 min above its melting point. After completion of the reaction, as monitored by TLC, the reaction mass was poured into water, stirred for 10 min, filtered, and dried. The crude product was purified by column chromatography (ethyl acetate/hexane, 1:9). All the other compounds were prepared similarly.

**Spectral Data of 6a–h**

**3-(2-(Phenylsulfonyl)ethynyl)-2H-chromen-2-one (6a).** Red solid, yield 90%, mp 180–182 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1156, 1346 (SO<sub>2</sub>), 1746 (C=O of lactone), 2210 (C≡C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.25–7.40 (m, 2H, Ar-H), 7.50–7.60 (m, 2H, Ar-H), 7.63–7.80 (m, 5H, Ar-H), 8.61 (s, 1H, C<sub>4</sub> of coumarin proton). EI-MS 311 (M + H)<sup>+</sup>. Anal. calcd. for C<sub>17</sub>H<sub>10</sub>O<sub>4</sub>S: C, 65.80; H, 3.25; S, 10.33. Found: C, 65.83; H, 3.27; S, 10.35%.

**6-Bromo-3-(2-(phenylsulfonyl)ethynyl)-2H-chromen-2-one (6b).** Red solid, yield 85%, mp 168–170 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1152, 1331 (SO<sub>2</sub>), 1723 (C=O of lactone), 2192 (C≡C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.25–7.60 (m, 8H, Ar-H), 8.55 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>17</sub>H<sub>9</sub>BrO<sub>4</sub>S: C, 52.46; H, 2.33; S, 8.24. Found: C, 52.49; H, 2.35; S, 8.27%.

**6,8-Dibromo-3-(2-(phenylsulfonyl)ethynyl)-2H-chromen-2-one (6c).**

Red solid, yield 79%, mp 208–210 °C. IR (KBr,  $\gamma_{\max}$  cm<sup>-1</sup>): 1156, 1324 (SO<sub>2</sub>), 1725 (C=O of lactone), 2270 (C≡C). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.25–8.10 (m, 7H, Ar-H), 8.56 (s, 1H, C<sub>4</sub> of coumarin proton). Anal. calcd. for C<sub>17</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>4</sub>S: C, 43.62; H, 1.72; S, 6.85. Found: C, 43.65; H, 1.75; S, 6.87%.

**6,8-Dichloro-3-(2-(phenylsulfonyl)ethynyl)-2H-chromen-2-one (6d).** Red solid, yield 88%, mp 198–200 °C. IR (KBr,  $\gamma_{\max}$   $\text{cm}^{-1}$ ): 1179, 1367 ( $\text{SO}_2$ ), 1727 (C=O of lactone), 2275 ( $\text{C}\equiv\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 7.22–7.55(m, 7H, Ar-H), 8.55 (s, 1H,  $\text{C}_4$  of coumarin proton). Anal. calcd. for  $\text{C}_{17}\text{H}_8\text{Cl}_2\text{O}_4\text{S}$ : C, 53.84; H, 2.13; S, 8.46. Found: C, 53.87; H, 2.16; S, 8.49%.

**3-(2-Tosylethynyl)-2H-chromen-2-one (6e).** Red solid, yield 93%, mp 168–170 °C. IR (KBr,  $\gamma_{\max}$   $\text{cm}^{-1}$ ): 1150, 1331 ( $\text{SO}_2$ ), 1720 (C=O of lactone), 2232 ( $\text{C}\equiv\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 2.70 (s, 3H,  $\text{CH}_3$ ), 7.20–7.30 (m, 5H, Ar-H), 7.50–7.70 (m, 2H, Ar-H), 7.95–8.0 (m, 1H, Ar-H), 8.45 (s, 1H,  $\text{C}_4$  of coumarin proton). EI-MS 325 ( $\text{M} + \text{H}$ ) $^+$ . Anal. calcd. for  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{S}$ : C, 66.65; H, 3.73; S, 9.89. Found: C, 66.68; H, 3.71; S, 9.91%.

**6-Bromo-3-(2-tosylethynyl)-2H-chromen-2-one (6f).** Red solid, yield 88%, mp 180–182 °C. IR (KBr,  $\gamma_{\max}$   $\text{cm}^{-1}$ ): 1156, 1331 ( $\text{SO}_2$ ), 1726 (C=O of lactone), 2250 ( $\text{C}\equiv\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 2.28 (s, 3H,  $\text{CH}_3$ ), 7.50–7.60 (m, 2H, Ar-H), 7.62–7.80 (m, 4H, Ar-H), 8.05 (s, 1H, Ar-H), 8.55 (s, 1H,  $\text{C}_4$  of coumarin proton). Anal. calcd. for  $\text{C}_{18}\text{H}_{11}\text{BrO}_4\text{S}$ : C, 53.61; H, 2.75; S, 7.95. Found: C, 53.59; H, 2.73; S, 7.98%.

**6,8-Dibromo-3-(2-tosylethynyl)-2H-chromen-2-one (6g).** Red solid, yield 76%, mp 178–180 °C. IR (KBr,  $\gamma_{\max}$   $\text{cm}^{-1}$ ): 1135, 1350 ( $\text{SO}_2$ ), 1730 (C=O of lactone), 2215 ( $\text{C}\equiv\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 1.95 (s, 3H,  $\text{CH}_3$ ), 7.0–7.18 (m, 6H, Ar-H), 8.45 (s, 1H,  $\text{C}_4$  of coumarin proton). Anal. calcd. for  $\text{C}_{18}\text{H}_{10}\text{Br}_2\text{O}_4\text{S}$ : C, 44.84; H, 2.09; S, 6.65. Found: C, 44.87; H, 2.0; S, 6.61%.

**6,8-Dichloro-3-(2-tosylethynyl)-2H-chromen-2-one (6h).** Red solid, yield 80%, mp 188–190 °C. IR (KBr,  $\gamma_{\max}$   $\text{cm}^{-1}$ ): 1130, 1330 ( $\text{SO}_2$ ), 1725 (C=O of lactone), 2234 ( $\text{C}\equiv\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm) 2.65 (s, 3H,  $\text{CH}_3$ ), 7.25–7.40 (m, 2H, Ar-H), 7.60–7.75 (m, 4H, Ar-H), 8.50 (s, 1H,  $\text{C}_4$  of coumarin proton). Anal. calcd. for  $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{O}_4\text{S}$ : C, 54.98; H, 2.56; S, 8.15. Found: C, 54.94; H, 2.58; S, 8.19%.

## CONCLUSIONS

In conclusion, we have developed a simple, inexpensive, and efficient strategy for phenyl sulfonyl ethynyls of coumarins without using any catalyst.

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