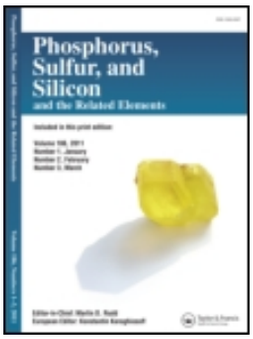

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SYNTHESIS OF A NEW CLASS OF SULFONE-LINKED 3-([1,2,3]-THIADIAZOL-4-YL)-CHROMEN-2-ONES

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A new class of 3-[5-(phenylsulfonyl)1,2,3-thiadizol-4-yl)-2H-chromen-2-ones (5) has been prepared from 3-(2-(phenylsulfonyl)-2H-chromen-2-ones (4).

Keywords β-Keto sulfones; 3-2(bromo acetyl) coumarin; hydrazones; thiadiazole; thionyl chloride

INTRODUCTION

The development of simple, facile, and efficient methods for the synthesis of five-membered heterocycles is one of the major challenges in organic synthesis. Among five-membered heterocycles, thiadazoles, oxadiazoles, and trizoles have gained importance because of their intrinsic biological activities, and because they constitute the structural features of many bioactive compounds. In fact, some of them have also emerged as potential drugs.[1–5] The molecules having a substituted thiadiazole act as an intermediate for the therapeutically useful antibiotic cefazolin.[6]

The prominence of 2*H*-chromen-2-ones in natural products and biologically active molecules[7–16] has promoted considerable efforts toward their synthesis. As a "privileged" scaffold, 2*H*-chromen-2-ones show interesting biological properties, especially for their anti-HIV and antibiotic activities.[17–25] For example, novobiocin is a 2*H*-chromen-2-one–derived antibiotic used as a competitive inhibitor of the bacterial ATP binding gyrase B subunit, blocking the negative supercoiling of relaxed DNA.[17,20] Lamellarin is utilized as a selective inhibitor of HIV-I integrase.[25] The discovery of promising lead antivirus 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.

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Our interest is in the development of novel heterocyclic systems at the three position of 2*H*-chromen-2-ones. In continuation of our earlier work on the synthesis of heterocyclic systems derived from coumarin, in this article we report the synthesis of a new class of 5-phenylsulfonyl-2*H*-coumarinyl 1,2,3-thiadiazoles exploiting ketomethylene functionality in 3-(2-benzenesulfonylacetyl)-chromen-2-ones.

RESULTS AND DISCUSSION

The synthetic method involves the condensation of 3-(2-bromoacetyl) coumarins prepared from the appropriate 3-acetylcoumarins, with sodiumaryl sulfinates to obtain 3-[2-(phenylsulfonyl)acetyl-2*H*-chromen-2-ones **(3)**.[26] These, in reaction with semicarbazide hydrochloride, afforded the expected semicabazones **(4).** Upon cyclization with thionylchloride, thiadiazoles **(5)** were furnished.

The IR spectra of **4a** displayed bands in the region 3284–3469 ($CONH_2$ and NHCO) and 1713 cm^{-1} (C═O of lactone), 1446 cm^{-1} (C═N), apart from the bands at 1314 and 1147 cm^{-1} (SO_2). The ^1H NMR spectrum of **4a** displayed a characteristic singlet for the methylene proton at δ 4.96. The C_4 proton of coumarin appeared as a singlet as 7.8. The NH proton was observed at δ 9.9. In the mass spectrum of **4a**, a molecular ion was recorded at m/z 385. The IR spectra of **5a** displayed bands in the region 1331 and 1152 cm^{-1} (SO_2), 1446 (N═N) cm^{-1}. The ^1H NMR spectrum of **5a** displayed a singlet 8.14 (C_4 of coumarin), and the remaining protons were observed in the expected region. In the mass spectrum of **5a**, the molecular ion was recorded at m/z 370.The newly synthesized compounds have been characterized by their analytical and spectral data (Scheme 1).

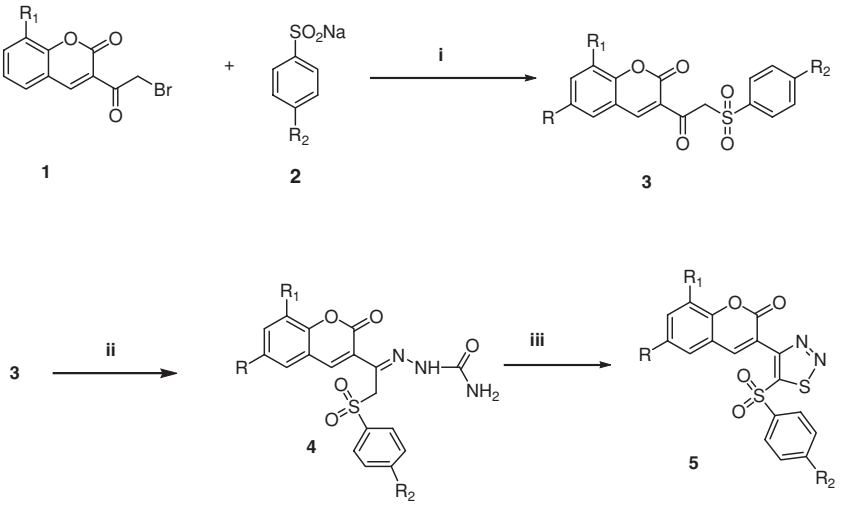
EXPERIMENTAL

All the reagents and solvents were pure, were purchased from commercial sources, and were used with out further purification unless otherwise stated. 3-(2-Bromoacetyl) coumarins[27,28] were prepared by the procedure in the literature. Melting points were determined in open capillaries with a Cintex melting point apparatus, Mumbai, India, and were uncorrected. CHNS analysis was done by a Carlo Erba EA 1108 automatic elemental analyzer. The purity of the compounds was checked by TLC plates (E. Merck, Mumbai, India), and IR spectra (KBr) were recorded on a BrukerWM-4(X) spectrometer (577 model). ^1H NMR spectra were recorded on a Bruker WM-300 spectrometer in δ ppm using TMS as internal standard. The NH and NH_2 protons were exchanged with D_2O. Mass spectra (EI-MS) were determined on a Perkin Elmer (SCIEX API-2000, ESI) at 12.5 eV.

(1Z)-1-(1-(2-Oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethylidene)semicarbazide (4)

A mixture of 3-(2-(phenylsulfonyl)acetyl)-2H-chromen-2-one (1 mmol), semicarbazide hydrochloride (1.2 mmol), and sodium acetate (1 mmol) in methanol was refluxed for 4–6 h on a steam bath and cooled. The reaction mixture was concentrated, cooled, and poured on to crushed ice. The solid was collected by filtration, dried, and recrystallized from ethanol. All other compounds were prepared similarly.

(1Z)-1-(1-(2-Oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethylidene)semicarbazide (4a). Yield 96%, mp 208–210°C. IR (KBr, γ_{max} cm^{-1}): 1147, 1314 (SO_2), 1446



(i) EtOH/ heat
(ii) $NH_2NHCONH_2$ /AcONa /MeOH
(iii) $SOCl_2$, heat

a) R= R1= R_2= H
b) R= Br R_1= R_2= H
c) R= R_1= Br R_2= H
d) R= Cl R_1= R_2= H
e) R= R_1= Cl R_2= H
f) 7,8 benzo R_2= H
g) R= R_1=H R_2= CH_3
h) R= Br R_1=H R_2= CH_3
i) R= R_1= Br R_2= CH_3
j) R= Cl R_1=H R_2= CH_3
k) R= R_1= Cl R_2= CH_3
l) 7,8 benzo R_2= CH_3

Scheme 1

(C═N), 1699 (NHCO), 1713 (C═O of lactone), 3284 ($CONH_2$), 3469 (NHCO), ^{1}H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.96 (s, 2H CH_2), 7.13–7.39 (m, 9H, Ar—H and NH_2), 7.69–7.75 (m, 3H, Ar—H and C_4 of coumarin), 9.89 (br, s, NH). EI-MS 386 $(M+H)^+$. Anal. Calcd. for $C_{18}H_{15}N_3O_5S$: C, 56.10; H, 3.92; N, 10.90. Found: C, 56.00; H, 3.90; N, 10.84%.

(1Z)-1-(1-(6-Bromo-2-oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethylidene) semicarbazide (4b). Yield 92%, mp 224–226°C. IR (KBr, γ_{max} cm^{-1}): 1148, 1318 (SO_2), 1447 (C═N), 1692 (NHCO), 1716 (C═O of lactone), 3200 ($CONH_2$), 3333 (NHCO), ^{1}H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.60 (s, 2H CH_2), 7.0–7.40 (m, 7H, Ar—H and NH_2), 7.50–7.70 (m, 3H, Ar—H), 8.30 (s, 1H, C_4 of coumarin), 9.30 (br, s, NH) Anal. Calcd. for $C_{18}H_{14}BrN_3O_5S$: C, 46.56; H, 3.04; N, 9.05. Found: C, 46.60; H, 3.00; N, 9.10%.

(1Z)-1-(1-(6,8-Dibromo-2-oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethyli dene)semicarbazide (4c). Yield 89%, mp 232–234°C. IR (KBr, γ_{max} cm^{-1}): 1144, 1321 (SO_2), 1446 (C═N), 1688 (NHCO), 1726 (C═O of lactone), 3195 ($CONH_2$), 3454 (NHCO), ^{1}H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.80 (s, 2H CH_2), 7.0–7.60 (m, 9H, Ar—H and NH_2), 8.0 (s, 1H, C_4 of coumarin), 8.70 (br, s, NH). Anal. Calcd. for $C_{18}H_{13}Br_2N_3O_5S$: C, 39.80; H, 2.41; N, 7.74. Found: C, 39.83; H, 2.38; N, 7.71%.

(1Z)-1-(1-(6-Chloro-2-oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethylidene) semicarbazide (4d). Yield 93%, mp 226–228°C. IR (KBr, γ_{max} cm^{-1}): 1141, 1323 (SO_2), 1446 (C=N), 1702 (NHCO), 1725 (C=O of lactone), 3207 ($CONH_2$), 3452(NHCO), ^1H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.50 (s, 2H CH_2), 7.71–8.20 (m, 11H, Ar−H and NH_2), 8.60 (s, 1H, C_4 of coumarin), 9.22 (br, s, NH). Anal. Calcd. for $C_{18}H_{14}ClN_3O_5S$: C, 51.49; H, 3.36; N, 10.01. Found: C, 51.52; H, 3.33; N, 10.00%.

(1Z)-1-(1-(6,8-Dichloro-2-oxo-2H-chromen-3-yl)-2-(phenylsulfonyl)ethylidene)semicarbazide (4e). Yield 90%, mp 204–206°C. IR (KBr, γ_{max} cm^{-1}): 1142, 1323 (SO_2), 1446 (C=N), 1702 (NHCO), 1725 (C=O of lactone), 3205 ($CONH_2$), 3452 (NHCO), ^1H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.65 (s, 2H CH_2), 7.20–7.40 (m, 2H, Ar−H and NH_2), 7.61–7.73 (m, 7H, Ar−H), 8.40 (s, 1H, C_4 of coumarin), 9.12 (br, s, NH) Anal. Calcd. for $C_{18}H_{13}Cl_2N_3O_5S$: C, 47.59; H, 2.88; N,9.25. Found: C, 47.54; H, 2.83; N, 9.28%.

(1Z)-1-(1-(2-Oxo-2H-benzo[h]chromen-3-yl)-2-(phenylsulfonyl)ethylidene) semicarbazide (4f). Yield 85%, mp 210–213°C. IR (KBr, γ_{max} cm^{-1}): 1164, 1344 (SO_2), 1460 (C=N), 1683 (NHCO), 1720 (C=O of lactone), 3201 ($CONH_2$), 3404 (NHCO), ^1H NMR ($CDCl_3$+DMSO-d_6, δ ppm): 4.55 (s, 2H CH_2), 7.20–7.62 (m, 13H, Ar−H and NH_2), 8.05 (s, 1H, C_4 of coumarin), 8.9 (br, s, NH). Anal. Calcd. for $C_{22}H_{17}N_3O_5S$: C, 60.68; H, 3.93; N, 9.65. Found: C, 60.63; H, 3.90; N, 9.68%.

(1Z)-1-(1-(2-Oxo-2H-chromen-3-yl)-2-tosyl)ethylidene)semicarbazide (4g). Yellow solid, yield 94%, mp 238–240°C. IR (KBr, γ_{max} cm^{-1}): 1148, 1318 (SO_2),1455 (C=N), 1690 (NHCO), 1725 (C=O of lactone), 3316 ($CONH_2$), 3466 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.12 (s, 3H, CH_3), 5.16 (s, 2H CH_2), 6.65 (s, 2H,NH_2), 7.24–7.27 (m, 2H, Ar−H), 7.39–7.41 (m, 2H, Ar−H), 7.65–7.76 (m, 4H, Ar−H), 8.20 (s, 1H, C_4 of coumarin), 10.20 (s, 1H,NH) EI-MS 400 $(M+H)^+$. Anal. Calcd. for $C_{19}H_{17}N_3O_5S$: C, 57.13; H, 4.29; N, 10.52. Found: C, 57.10; H, 4.24; N, 10.50%.

(1Z)-1-(1-(6-Bromo-2-oxo-2H-chromen-3-yl)-2-tosyl)ethylidene)semicarbazide (4h). Yield 90%, mp 222–224°C. IR (KBr, γ_{max} cm^{-1}): 1146, 1303 (SO_2), 1459 (C=N), 1723 (NHCO), 1732 (C=O of lactone), 3205 ($CONH_2$), 3376 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.4 (s, 3H, CH_3), 4.70 (s, 2H, CH_2), 7.20–7.65 (m, 9H, Ar−H and NH_2), 8.42 (s, 1H, C_4 of coumarin proton), 9.30 (br, s, NH). Anal. Calcd. for $C_{19}H_{16}BrN_3O_5S$: C, 47.71; H, 3.37; N, 8.79. Found: C, 47.74; H, 3.39; N, 8.70%.

(1Z)-1-(1-(6,8-Dibromo-2-oxo-2H-chromen-3-yl)-2-tosyl)ethylidene)semicarbazide (4i). Yield 88%, mp 236–238°C. IR (KBr, γ_{max} cm^{-1}): 1143, 1319 (SO_2), 1475 (C=N), 1702 (NHCO), 1720 (C=O of lactone), 3206 ($CONH_2$), 3439 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.41 (s, 3H, CH_3),4.90 (s, 2H CH_2), 7.25–7.60 (m, 8H, Ar−H and NH_2), 8.42 (s, 1H, C_4 of coumarin), 9.80 (br, s, NH) Anal. Calcd. for $C_{19}H_{15}Br_2N_3O_5S$: C, 40.95; H, 2.71; N, 7.54. Found: C, 40.98; H, 2.74; N, 7.51%.

(1Z)-1-(1-(6-Chloro-2-oxo-2H-chromen-3-yl)-2-tosyl)ethylidene)semicarbazide (4j). Yield 91%, mp 230°C. IR (KBr, γ_{max} cm^{-1}): 1144, 1320 (SO_2), 1453 (C=N), 1702 (NHCO), 1720 (C=O of lactone), 3250 ($CONH_2$), 3438 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.2 (s, 3H,CH_3), 4.70 (s, 2H, CH_2), 7.12–7.50 (m, 9H, Ar−H and NH_2), 8.40 (s, 1H, C_4 of coumarin), 9.34 (br, s,1H, NH). Anal. Calcd. for $C_{19}H_{16}ClN_3O_5S$: C, 56.60; H, 3.72; N, 9.69. Found: C, 56.62; H, 3.74; N, 9.65%.

(1Z)-1-(1-(6,8-Dichloro-2-oxo-2H-chromen-3-yl)-2-tosyl)ethylidene)semicarbazide (4k). Yield 89%, mp 220–222°C. IR (KBr, γ_{max} cm^{-1}): 1135, 1358 (SO_2), 1475 (C=N), 1692 (NHCO), 1734 (C=O of lactone), 3200 ($CONH_2$), 3415 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.42 (s, 3H,CH_3), 4.90 (s, 2H CH_2), 7.2–7.6 (m, 8H, Ar−H and

NH_2), 8.41 (s, 1H, C_4 of coumarin), 9.80 (br, s, NH) Anal. Calcd. for $C_{19}H_{15}Cl_2N_3O_5S$: C, 48.73; H, 3.23; N, 8.97. Found: C, 48.70; H, 3.20; N, 8.94%.

(1Z)-1-(1-(2-Oxo-2H-benzo[h]chromen-3-yl)-2-tosylethylidene)semicarbazide (4l). Yield 82%, mp 198–200°C. IR (KBr, γ_{max} cm^{-1}): 1144, 1321 (SO_2), 1434 (C=N), 1684 (NHCO), 1721 (C=O of lactone), 3188 ($CONH_2$), 3436 (NHCO), ^1H NMR (DMSO-d_6, δ ppm): 2.40 (s, 3H, CH_3), 4.60 (s, 2H CH_2), 7.21–7.73 (m, 12H, Ar—H and NH_2), 8.40 (s, 1H, C_4 of coumarin), 9.02 (br, s, NH). Anal. Calcd. for $C_{23}H_{19}N_3O_5S$: C, 61.46; H, 4.26; N, 9.35. Found: C, 61.42; H, 4.29; N, 9.38%.

3-(5-(Phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5)

Semicarbzone **4** (0.001 mol) was added portionwise to the thionylchloride (1.5 ml) at 0–5°C.Then the mixture was heated at reflux temperature over 4 h. The reaction mixture was cooled to room temperature, and the reaction mixture decomposed with saturated sodium carbonate solution. The solid that separated was filtered, washed with water, dried, and purified by column chromatography (silica gel 60–120 mesh,, hexane:ethylacetate, 8:2).

3-(5-(Phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5a). Yield 92%, mp 110–112°C. IR (KBr, γ_{max} cm^{-1}): 1152, 1331 (SO_2), 1446 (N=N), 1608 (C=C), 1723 (C=O of lactone), ^1H NMR ($CDCl_3$, δ ppm): 7.41–7.69 (m, 9H, Ar—H), 8.14 (s, 1H, C_4 of coumarin) EI-MS 371 $(M+H)^+$. Anal. Calcd. for $C_{17}H_{10}N_2O_4S_2$: C,55.12; H, 2.72; N,7.56. Found: C,55.10; H,2.75; N, 7.52%.

6-Bromo-3-(5-(phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5b). Yield 90%, mp 122–123°C.IR (KBr, γ_{max} cm^{-1}): 1156, 1346 (SO_2), 1447 (N=N), 1619 (C=C), 1746 (C=O of lactone), ^1H NMR ($CDCl_3$, δ ppm): 7.62–7.90 (m, 8H, Ar—H), 9.05 (s, 1H, C_4 of coumarin) Anal. Calcd. for $C_{17}H_9BrN_2O_4S_2$: C, 45.44; H, 2.02; N, 6.23. Found: C, 45.41; H, 2.00; N, 6.26%.

6,8-Dibromo-3-(5-(phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5c). Yield 90%, mp 156–158°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1330 (SO_2), 1446 (N=N), 1602 (C=C), 1735 (C=O of lactone), ^1H NMR ($CDCl_3$, δ ppm): 7.35–8.0 (m, 7H, Ar—H), 8.06 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{17}H_8Br_2N_2O_4S_2$: C, 38.66; H, 1.53; N, 5.30; Found: C, 38.68; H, 1.50; N, 5.32%.

6-Chloro-3-(5-(phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5d). Yield 92%, mp 118–120°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1325 (SO_2), 1447 (N=N), 1607 (C=C), 1734 (C=O of lactone), ^1H NMR ($CDCl_3$, δ ppm): 7.51–7.58 (m, 6H, Ar—H), 7.79–7.80 (m, 2H, Ar—H), 8.20 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{17}H_9ClN_2O_4S_2$: C, 50.43; H, 2.24; N, 6.92. Found: C, 50.45; H, 2.26; N, 6.95%.

6,8-Dichloro-3-(5-(phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5e). Yield 89%, mp 142–144°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1324 (SO_2), 1447 (N=N), 1606 (C=C), 1725 (C=O of lactone), ^1H NMR ($CDCl_3$, δ ppm): 7.40–7.69 (m, 7H, Ar—H), 8.14 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{17}H_8Cl_2N_2O_4S_2$: C, 46.48; H, 1.84; N, 6.38. Found: C, 46.40; H, 1.90; N, 6.42%.

3-(5-(Phenylsulfonyl)-1,2,3-thiadiazol-4-yl)-2H-benzo[h]chromen-2-one (5f). Yield 84%, mp 178–180°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1331 (SO_2), 1438 (N=N), 1627 (C=C), 1726 (C=O of lactone),^1H NMR ($CDCl_3$, δ ppm): 7.50–7.90 (m, 11H, Ar—H), 8.95 (s, 1H, C_4 of coumarin).Anal. Calcd. for $C_{21}H_{12}N_2O_4S_2$: C, 59.99; H, 2.88; N, 6.66; Found: C, 59.96; H, 2.86; N, 6.69%.

3-(5-Tosyl-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5g). Yield 94%, mp 124–126°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1330 (SO_2), 1454 (N=N), 1608 (C=C), 1729

(C=O of lactone), ^{1}H NMR ($CDCl_3$, δ ppm): 2.75 (s, 3H, CH_3), 7.12–7.40 (m, 8H, Ar—H), 8.42 (s, 1H, C_4 of coumarin), EI-MS 385 $(M+H)^+$. Anal. Calcd. for $C_{18}H_{12}N_2O_4S_2$: C, 56.24; H, 3.15; N, 7.29; Found: C, 56.28; H, 3.18; N, 7.27%.

6-Bromo-3-(5-tosyl-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5h). Yield 91%, mp 138–140°C. IR (KBr, γ_{max} cm^{-1}): 1156, 1332 (SO_2), 1451 (N=N), 1601 (C=C), 1735 (C=O of lactone), ^{1}H NMR ($CDCl_3$, δ ppm): 2.43 (s, 3H, CH_3), 7.31–7.34 (m, 2H, Ar—H), 7.69–7.84 (m, 5H, Ar—H), 9.05 (s, 1H, C_4 of coumarin), Anal. Calcd. for $C_{18}H_{11}BrN_2O_4S_2$: C, 46.66; H, 2.39; N, 6.05; Found: C, 46.68; H, 2.44; N, 6.00%.

6,8-Dibromo-3-(5-tosyl-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5i). Yield 85%, mp 145–146°C. IR (KBr, γ_{max} cm^{-1}): 1155, 1326 (SO_2), 1444 (N=N), 1615 (C=C), 1736 (C=O of lactone), ^{1}H NMR($CDCl_3$, δ ppm): 2.46 (s, 3H, CH_3), 7.20–7.30 (m, 3H, Ar—H), 7.70–7.8 (m, 3H, Ar—H), 8.05 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{18}H_{10}Br_2N_2O_4S_2$: C, 39.87; H, 1.86; N, 5.17; Found: C, 39.89; H, 1.88; N, 5.19%.

6-Chloro-3-(5-tosyl-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5j). Yield 88%, mp 136–138°C. IR (KBr, γ_{max} cm^{-1}): 1154, 1326 (SO_2), 1455 (N=N), 1606 (C=C), 1732 (C=O of lactone), ^{1}H NMR ($CDCl_3$, δ ppm): 2.70 (s, 3H, CH_3), 7.20–7.40 (m, 2H, Ar—H), 7.60–7.75 (m, 5H, Ar—H), 8.52 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{18}H_{11}ClN_2O_4S_2$: C, 51.61; H, 2.65; N, 6.69; Found: C, 51.63; H, 6.67; N, 2.68%.

6,8-Dichloro-3-(5-tosyl-1,2,3-thiadiazol-4-yl)-2H-chromen-2-one (5k). Yield 88%, mp 128–130°C. IR (KBr, γ_{max} cm^{-1}): 1125, 1333 (SO_2), 1447 (N=N), 1605 (C=C), 1726 (C=O of lactone), ^{1}H NMR ($CDCl_3$, δ ppm): 2.40 (s, 3H, CH_3), 7.2–7.4 (m, 2H, Ar—H), 7.60–7.90 (m, 4H, Ar—H), 8.40 (s, 1H, C_4 of coumarin).Anal. Calcd. for $C_{18}H_{10}Cl_2N_2O_4S_2$: C, 47.69; H, 2.22; N, 6.18; Found: C, 47.67; H, 2.24; N, 6.21%.

3-(5-Tosyl-1,2,3-thiadiazol-4-yl)-2H-benzo[h]chromen-2-one (5l). Yield 80%, mp 188–190°C. IR (KBr, γ_{max} cm^{-1}): 1127, 1343 (SO_2), 1414 (N=N), 1623 (C=C), 1716 (C=O of lactone), ^{1}H NMR ($CDCl_3$, δ ppm): 2.29 (s, 3H, CH_3), 7.10–7.20 (m, 10H, Ar—H), 7.96 (s, 1H, C_4 of coumarin). Anal. Calcd. for $C_{22}H_{14}N_2O_4S_2$ C, 60.82; H, 3.25; N, 6.45; Found: C, 60.84; H, 3.21; N, 6.42%.

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