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Synthesis of New Benzocoumaryl Oxadiazolyls as Strong Blue-Green Fluorescent Brighteners

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ABSTRACT

The benzocoumarin-3-ethylcarboxylate 2 on treatment with hydrazine hydrate at room temperature afforded benzocoumarin-3-carbohydrazide 3. The compound 3 served as key intermediate in the synthesis of the title compounds. Thus, benzocoumarin-1,3,4-oxadiazolyls 6a–e were obtained in two ways, *i.e.* one by direct cyclization of benzocoumarin-3-carbohydrazide 3 with substituted benzoic acids in $POCl_3$ and the other by cyclization of Schiff bases of compounds 5a–e in the presence of bromine/acetic acid. The structures of the novel benzocoumaryl oxadiazolyls 6a–e were confirmed by spectral analysis. The benzocoumarin-1,3,4-oxadiazolyls 6a–e exhibited strong blue and green fluorescent properties. The Stoke's shifts range from 43 to 165 nm. The absorption and fluorescence maxima of the benzocoumaryl oxadiazolyls showed good bathochromic shifts.

KEYWORDS

Benzocoumarin-3-ethylcarboxylate, benzocoumaryl oxadiazolyls, fluorescent brighteners.

1. Introduction

Coumarin dyes has been of significant interest for the application of dye-sensitized solar cells and many organic devices in the application of light-emitting diodes.[1] The performance of these devices depend mainly on the properties of the structure of coumarin dyes. Hence, many coumarin dyes were designed and found to be successful as photosensitizers in dye sensitized solar cell (DSSC).[2] Further, Daniel *et al.* reported the Light-Harvesting Arrays with Ru(II) complexes of 1,10-phenanthroline derivatives of coumarin donors as metal-to-ligand charge transfer (MLCT) acceptors.[3] An injection and recombination limitation of coumarin dye-sensitized solar cell upon device performance was reported by Koops *et al.* 2010.[4] Wang *et al.* have reported that NKX-2753 and NKX-2586 (Structures 1 and 2) coumarin dyes as an alternative sensitizers to Ruthenium complexes in DSSCs.[5] Beside this, in support of our investigation, benz-annulated coumarin derivatives have also found to be useful dyes in organic light-emitting devices and were used as electron-transporting emitters.[6,7] Among these benzocoumarins, benzocoumarin-3-ethylcarboxylate and 3-acetylbenzocoumarin exhibited high fluorescence intensity. The results apparently show that the fluorescence intensity of the benzocoumarins is influenced by the direction of annulations and by the electronic effects of substituent at position-3. Based on this observation, we have reported fatty acid derivatives of various benzocoumaryl oxadiazolyls as a bright-blue fluorophores[12] (Fig. 1). Hence, in continuation of our work on synthesis and fluorescent studies on benzocoumarins[12] and development of new heterocyclic moieties in our laboratory[8–19], we report in this paper the convenient synthesis of benzocoumaryl oxadiazolyls as very strong blue and green fluorescent brighteners.

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2. Experimental

All the chemicals used were that of analytical grade. Melting points were determined in open capillary and were uncorrected; purity of the compounds was checked by TLC on silica gel and were purified by using chromatography. ^{1}H NMR spectra was recorded in a Bruker supercon FT NMR (400 MHz) spectrometer using $CDCl_3$ and DMSO as the solvents, TMS as an internal standard for reference and the chemical shifts are expressed in δ units. IR spectra were recorded in JASCO FT/IR-300 E spectrometer. Mass spectra were recorded in a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer.

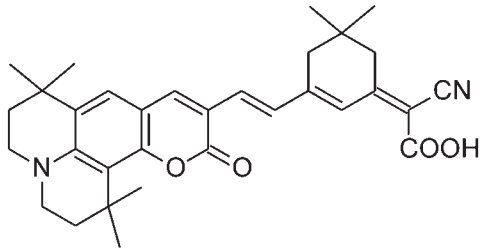
2.1. Synthesis of ethyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate (2)

A mixture of 2-hydroxy-1-naphthaldehyde (2.9 mmol, 0.5 g) **1** and diethyl malonate (2.9 mmol, 0.464 g) was dissolved in absolute ethanol (30 mL) and catalytic amount of piperidine was added. The reaction mixture was refluxed on a water bath for about 30 minutes. The reaction mixture was cooled to room temperature and poured in to 100 g of crushed ice with stirring. The precipitate obtained was filtered, washed with water, dried under vacuum and recrystallized by using ethanol to get pure compound.

2.1.1. *Ethyl 3-oxo-3*H*-benzo[f]chromene-2-carboxylate* (**2**; $C_{16}H_{12}O_4$)[12]

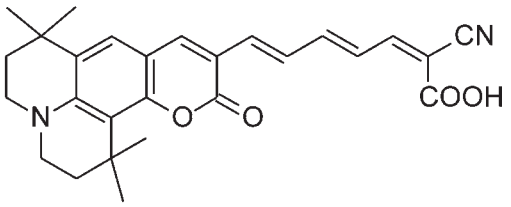
Yellow crystalline solid; (94 %); m.p.117 °C; IR (KBr): ν = 1748.2 (C=O) cm^{-1}, 1698 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, J=10.7 Hz, 3H, CH_3), 4.39–4.45 (m, 2H, CH_2), 7.41 (d, J=9.0 Hz, 1H, ArH), 7.53 (t, J=11.3 Hz, 1H), 7.74 (t, J = 11.7 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 9.35 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 163.37, 156.47, 155.56, 144.35, 136.47, 130.19, 129.44, 129.42,

Structure 1



NKX-2753

Structure 1



NKX-2586

129.39, 126.86, 122.64, 116.90, 116.87, 112.29, 61.76, 14.55 ppm; MS: m/z = 269.2 (M+1).

2.2. Synthesis of 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide (3)

A mixture of ethyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate **2** (3.8 mmol, 1.0 g) and hydrazine hydrate (3.8 mmol, 0.19 g) was dissolved in ethanol and refluxed on a water bath for 2 h. Then the reaction mixture was cooled to room temperature and poured onto 150 g crushed ice with stirring. The separated solid was filtered, washed with water, dried under vacuum and recrystallized with ethanol to get pure yellow compound **3**.

2.2.1. *3-Oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide* (**3**; $C_{14}H_{10}N_2O_3$)

Yellow crystalline solid; (95 %); m.p. 260 °C; IR (KBr): ν = 3320 cm^{-1}, 1708.5 cm^{-1}, 1621 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.77 (s, 2H, NH_2), 7.68 (t, J = 7.8 Hz, 2H), 7.78–7.82 (m, 1H), 8.11 (d, J = 8.0 Hz,1H), 8.33 (d, J = 9.0 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 9.43 (s, 1H), 9.69 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.47, 160.89, 154.93, 143.95, 136.07, 130.41, 129.49, 129.26, 129.17, 126.85, 121.97, 116.37, 115.94, 113.22 ppm; MS: m/z = 255 (M+1). Anal. Calcd. for $C_{14}H_{10}N_2O_3$ = C, 66.14; H, 3.96; N 11.02 %. Found: C, 66.03; H, 3.83; N, 10.86 %.

2.3. Synthesis of 4-amino-3-oxo-3,4-dihydrobenzo[*f*]quinoline-2-carbohydrazide (4)

A mixture of ethyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate **2** (3.8 mmol, 1.0 g) and hydrazine hydrate (20 mmol, 0.38 g) was dissolved in ethanol and refluxed on a water bath for 2 h. Then the reaction mixture was cooled to room temperature and poured into 150 g crushed ice with stirring. The solid thus separated was filtered dried and purified by column chromatography (ethyl acetate: methanol) to get compound **4**.

2.3.1. *4-Amino-3-oxo-3,4-dihydrobenzo[*f*]quinoline-2-carbohydrazide* (**4**; $C_{14}H_{12}N_4O_2$)[12]

White crystalline solid; (97 %) m.p. 183 °C; IR (KBr): ν = 3500 cm^{-1}, 3020 cm^{-1}, 1765 cm^{-1}, 1605 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 2H, NNH_2), 5.55 (s, 2H, $CONH_2$), 7.20 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 10.4 Hz, 1H), 7.45–7.52 (m, 1H), 7.74–7.80 (m, 2H), 8.05 (d , J = 8.5 Hz, 1H) 8.81 (s, 1H), 12.32 (s, 1H, NH) ppm; MS: m/z = 268.1 (M+1).

2.4. Synthesis of *N*′-benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazides (5)

A mixture of 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide **3** (2.0 mmol, 0.50 g) and benzaldehyde (2.0 mmol, 0.212 g) was dissolved in sufficient quantity of DMF with stirring, then refluxed for 12 h on a water bath. The reaction mixture was cooled and then poured into crushed ice. The solid thus separated was filtered and recrystallised from DMF to obtain pure compound **5a**. Similarly the compounds **5b–e** were synthesized.

2.4.1. N′-*Benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide* (**5a**; $C_{21}H_{14}N_2O_3$)

Yellow crystalline solid; (86 %), m.p. 233–235 °C; IR (KBr): ν = 3429 cm^{-1}, 1706 cm^{-1}, 1566 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.70 (d, J = 8.0 Hz, 3H), 7.80 (d, J = 11.4 Hz, 5H), 8.10 (t, J = 7.5 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H), 8.48 (s,

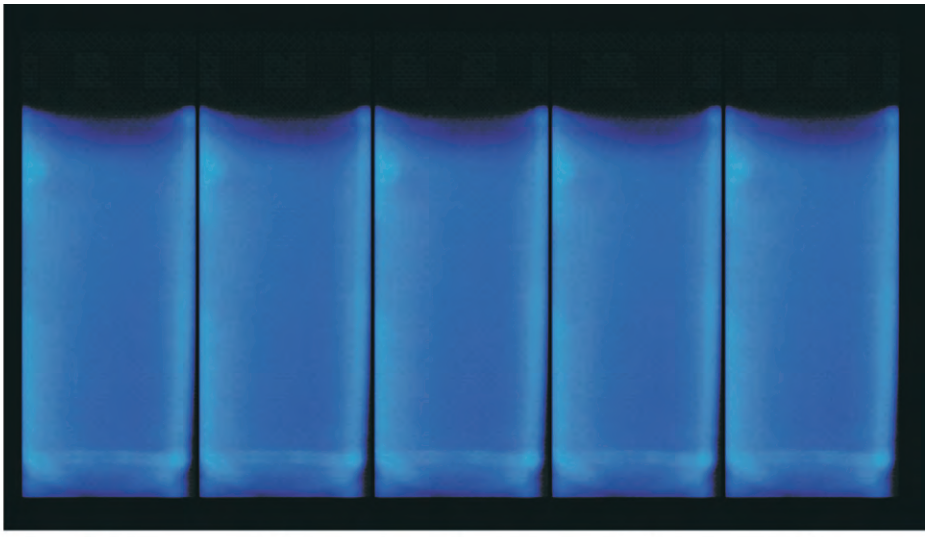


Figure 1 Fluorescent properties of substituted *N*′-benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazides (**5a–e**).

1H), 9.51 (s, 1H), 11.82 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.62, 158.34, 154.36, 149.25, 142.87, 135.83, 133.95, 130.32, 129.96, 129.07, 129.01, 128.78, 127.29, 126.59, 122.37, 118.32, 116.37, 112.69 ppm; MS: m/z = 343.3 (M+1) Anal. Calcd. for $C_{21}H_{14}N_2O_3$ = C, 73.68; H, 4.12; N, 8.18 % Found: C, 73.46; H, 3.94; N, 7.99 %.

2.4.2. N′-*(2-Chlorobenzylidene)-3-oxo-3*H-*benzo[f]chromene-2-carbohydrazide* (**5b**; $C_{21}H_{13}ClN_2O_3$)

Yellow crystalline solid; (81 %); m.p. 257–259 °C; IR (KBr): ν = 3320 cm^{-1}, 1709 cm^{-1}, 1621.2 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.23 (d, J = 8.7 Hz, 1H), 7.38–7.44 (m, 3H), 7.51 (d, J = 1.4 Hz,1H), 7.76 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 7.8 Hz, 2H), 8.13 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 9.08 Hz, 1H), 8.63 (d, J = 8.6 Hz, 1H), 9.50 (s, 1H), 12.11 (s, 1H, NH) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.10, 158.52, 156.21, 149.74, 147.53, 145.21, 138.55, 135.14, 134.12, 132.43, 132.31, 132.15, 130.72, 130.61, 130.55, 128.43, 127.12, 124.87, 124.36, 123.55, 112.42 ppm; MS: m/z = 377 (M+1). Anal. Calcd. for $C_{21}H_{13}ClN_2O_3$ = C, 66.94; H, 3.48; N, 7.43 % Found: C, 66.75; H, 3.33; N, 7.24 %.

2.4.3. N′-*(3-Nitrobenzylidene)-3-oxo-3*H-*benzo[f]chromene-2-carbohydrazide* (**5c**; $C_{21}H_{13}N_3O_5$)

Yellow crystalline solid; (89 %); m.p. 254–256 °C; IR (KBr): ν = 3310 cm^{-1}, 1708 cm^{-1}, 1622 cm^{-1}; ^{1}H NMR (300Mz, DMSO-d_6): δ = 7.22 (d, J = 9.0 Hz, 1H), 7.55–7.62 (m, 1H), 7.93 (d, 1H, J = 8.0 Hz), 8.05 (d, 2H, J = 8.4 Hz), 8.14 (d, 2H, J = 8.3 Hz), 8.24 (d, 1H, J = 7.6 Hz), 8.31 (d, 1H, J = 8.1 Hz), 8.35 (d, 1H, J = 9.1 Hz), 8.58–8.66 (m, 1H), 9.51 (s, 1H), 12.07 (s, 1H, NH) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.82, 160.17, 157.21, 149.55, 148.46, 145.73, 138.58, 137.38, 132.54, 132.45, 132.25, 131.06, 130.43, 130.26, 128.41, 127.55, 126.28, 125.43, 124.55, 123.19, 113.12 ppm; MS: m/z = 388 (M+1). Anal. Calcd. for $C_{21}H_{13}N_3O_5$ = C, 65.12; H, 3.38; N, 10.85 % Found: C, 64.89; H, 3.17; N, 10.69 %.

2.4.4. N′-*(4-Chlorobenzylidene)-3-oxo-3*H-*benzo[f]chromene-2-carbohydrazide* (**5d**; $C_{21}H_{13}ClN_2O_3$)

Yellow crystalline solid; (88 %); m.p. 244–246 °C; IR (KBr): ν = 3321 cm^{-1}, 1711 cm^{-1}, 1622 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21 (d, 1H, J = 8.8 Hz), 7.55 (d, 2H, J = 8.1 Hz), 7.67–7.74 (m, 2H), 7.80–7.87 (m, 3H), 8.04 (d, 1H, J = 8.9 Hz,), 8.16 (d, 1H, J = 8.1 Hz), 8.34 (d, 1H, J = 9.0 Hz), 8.62 (t, 1H, J = 8.6 Hz), 9.53 (s, 1H), 11.80 (s, 1H, NH) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ = 159.52, 158.33, 156.62, 149.56, 147.54, 145.48, 138.29, 135.33, 134.03, 132.19, 132.15, 132.11, 130.55, 130.21, 129.54, 128.88, 126.49, 124.52, 123.51, 123.41, 112.49 ppm; MS: m/z = 377 (M+1). Anal. Calcd. for $C_{21}H_{13}ClN_2O_3$ = C, 66.94; H, 3.48; N, 7.43 % Found: C, 66.71; H, 3.31; N, 7.22 %.

2.4.5. N′-*(2-Hydroxybenzylidene)-3-oxo-3*H-*benzo[f]chromene-2-carbohydrazide* (**5e**; $C_{21}H_{14}N_2O_4$)

Yellow crystalline solid; (90 %); m.p. 234-236 °C; IR (KBr) ν = 3320 cm^{-1}, 1715 cm^{-1}, 1622.5 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.92 (s, 1H, OH), 7.19–7.26 (m, 2H), 7.43 (d, 1H, J = 7.3 Hz), 7.54 (m, 2H, J = 7.1 Hz), 7.81 (t, 1H, J = 7.4 Hz), 7.95 (d, 1H, J = 7.9 Hz), 8.05 (d, 1H, J = 9.0 Hz), 8.16 (d, 2H, J = 8.1 Hz), 8.34 (t, 1H, J = 7.4 Hz), 8.58–8.64 (m, 1H), 9.51 (s, 1H), 11.94 (s, 1H, NH) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.13, 159.56, 157.35, 149.62, 148.21, 145.33, 138.56, 137.71, 132.57, 132.73, 132.47, 131.31, 130.83, 130.27, 128.62, 127.31, 126.17, 125.07, 124.52, 122.56, 112.22 ppm; MS: m/z = 359 (M+1). Anal. Calcd. for $C_{21}H_{14}N_2O_4$ = C, 70.39; H, 3.94; N, 7.82 % Found: C, 70.04; H, 3.8; N, 7.61 %.

2.5. Synthesis of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones (6)

2.5.1. *Method I*

To the mixture of 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide **3** (2.0 mmol, 0.5 g) and benzoic acid (2.0 mmol, 0.27 g) 10 mL of $POCl_3$ was added and refluxed for about 12–15 h on a water bath. After it was cooled to room temperature, the reaction mixture was poured in to 200 g of crushed ice with stirring and was neutralized by saturated sodium bicarbonate solution. The yellow precipitate thus obtained was filtered washed with water, dried under vacuum and purified through column chromatography by using ethyl acetate and petroleum ether (1:9 v/v) as eluent to obtain analytically pure compound of **6a.** Similarly the compounds **6b–e** was synthesized.

2.5.2. *Method II*

To the mixture of *N′*-benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide **5a** (3.0 mmol, 1.0 g) and anhydrous sodium acetate (33 mmol, 0.246 g) in 25 mL glacial acetic acid the solution of bromine (0.24, 0.003 mol) in 10 mL glacial acetic acid was added slowly at room temperature with stirring. The stirring was continued for 4 h and the reaction mixture was kept overnight. It was refluxed for further 2 h, cooled to room temperature, and poured onto 250 g crushed ice with stirring. The solid obtained was filtered, washed with water, dried under vacuum and purified through column chromatography by using ethyl acetate and petroleum ether (1:9 v/v) as eluent to obtain analytically pure compound of **6a.** Similarly the compounds **6b–e** were synthesized. The yields are recorded for $POCl_3$ cyclization method (route 1, Scheme 2).

2.5.3. *2-[5-Pheny)-1,3,4-oxadiazol-2-yl]-3*H-*benzo[f]chromen-3-one* (**6a**; $C_{21}H_{12}N_2O_3$)

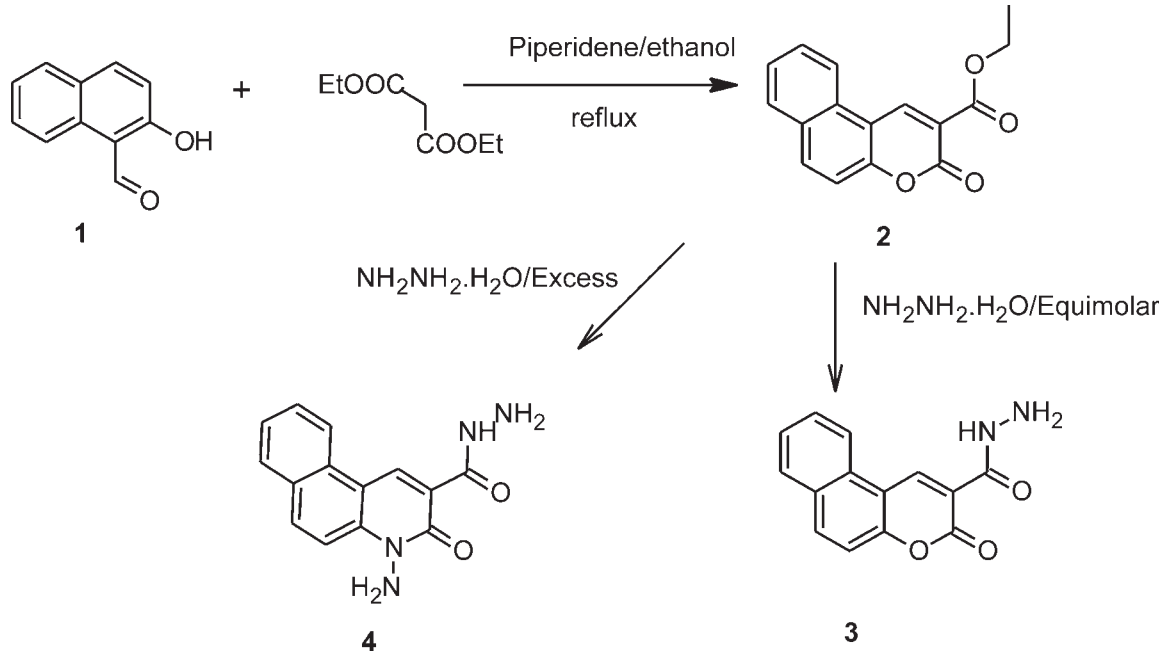
Yellow crystalline solid; (51 %); m.p. 197–199 °C; IR (KBr): ν = 3060 cm^{-1}, 1737 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.72 (m, 5H), 7.85 (t, H, J = 7.9 Hz), 8.13 (d, 1H, J = 8.2 Hz), 8.26 (d, 2H, J = 1.6 Hz), 8.35 (d, 1H, J = 9.0 Hz), 8.87 (d, 1H, J = 7.2 Hz), 9.63 (s, 1H) ppm; MS: m/z = 341 (M+1). ^{13}C NMR (300 MHz, $CDCl_3$): 172.33, 165.53, 163.23, 152.16, 144.13, 132.93,131.19, 130.47, 130.33, 130.21, 129.71, 129.51, 129.41, 128.56, 128.53, 127.82,127.26, 124.63, 122.34,118.82, 118.74.Anal. Calcd. for $C_{21}H_{12}N_2O_3$ = C, 74.11; H 3.55; N 8.23 % Found: C, 73.88; H 3.36; N 8.01 %.

2.5.4. *2-[5-(2-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-3*H-*benzo[f]chromen-3-one* (**6b**; $C_{21}H_{11}Cl\ N_2O_3$)

Yellow crystalline solid; (58 %); m.p. 221–223 °C; IR (KBr): ν = 3050 cm^{-1}, 1747 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d_6) δ = 7.21 (d, 1H, J = 8.9 Hz,), 7.26 (d, 3H, J = 8.8 Hz), 8.32 (d, 2H, J = 8.5 Hz), 8.36 (d, 2H, J = 9.0 Hz), 8.63 (d, 1H, J = 8.4 Hz), 8.65 (d, 1H, J = 8.6 Hz), 9.61 (s, 1H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): 171.33, 165.56, 163.05,151.69, 147.14, 135.97, 133.35, 132.96, 131.22, 131.14, 130.47, 130.44, 129.92, 129.82, 129.55, 128.43, 127.86, 124.65, 123.38, 118.82, 118.71. MS: m/z = 375 (M+1). Anal. Calcd. for $C_{21}H_{11}Cl\ N_2O_3$ = C, 67.30; H, 2.96; N,7.47 %Found: C, 67.06; H, 2.79; N,7.22 %.

2.5.5. *2-[5-(3-Nitrophenyl)-1,3,4-oxadiazol-2-yl]-3*H-*benzo[f]chromen-3-one* (**6c**; $C_{21}H_{11}N_3O_5$)

Yellow crystalline solid; (53 %); m.p. 223–225 °C; IR (KBr): ν = 3070 cm^{-1}, 1727 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.24 (t, J = 5.1 Hz, 2H), 7.83 (t, J = 7.4 Hz, 1H), 7.91 (t, J = 7.9 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 8.37 (t, J = 8.9 Hz, 2H), 8.56 (d, J = 7.4 Hz, 1H), 8.62 (d, J = 7.5 Hz, 1H), 8.93 (t, J = 16.2 Hz, 1H), 9.72 (s, 1H) ppm;



Scheme 1

General synthetic procedure for ethyl 3-oxo-3*H*-benzo[*f*]chromene-2- carboxylate **2**, 3-Oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide **3** and 4-amino-3-oxo-3,4-dihydrobenzo[*f*]quinoline-2-carbohydrazide **4**.

^{13}C NMR (300 MHz, $CDCl_3$): 170.66, 165.56, 163.22, 151.61, 149.94, 147.12, 134.67,132.93, 131.26, 131.12, 130.44, 129.82, 129.53, 128.11, 127.85, 124.62, 123.37, 123.18, 122.16, 118.83, 118.75. MS: m/z = 386 (M + 1). Anal. Calcd. for $C_{21}H_{11}N_3O_5$ = C, 65.46; H, 2.88; N, 10.90 % Found: C, 65.08; H, 2.64; N, 10.76 %.

2.5.6. *2-[5-(4-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-3*H*-benzo[f] chromen-3-one* (**6d**; $C_{21}H_{11}Cl\,N_2O_3$)

Yellow crystalline solid; (56 %); m.p. 214–216 °C; IR (KBr): ν = 3065 cm^{-1}, 1755 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.61 (d, 1H, *J* = 8.3 Hz), 7.74 (d, 5H, *J* = 8.1 Hz), 7.96 (d, 1H, *J* = 8.2 Hz), 8.13 (d, 1H, *J* = 8.1 Hz,), 8.22 (d, 1H, *J* = 8.1 Hz), 8.35 (d, 1H, *J* = 8.8 Hz) 9.61 (s, 1H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): 169.87, 165.57, 163.77,151.65, 147.17, 135.24, 132.97, 131.13, 130.57, 130.41, 130.33, 130.12, 129.87, 129.83, 129.52, 127.81, 125.32, 124.63, 123.35, 118.83, 118.72. MS: m/z = 375 (M + 1). Anal. Calcd. for $C_{21}H_{11}Cl\,N_2O_3$ = C, 67.30; H, 2.96; N, 7.47 % Found: C, 67.15; H, 2.80; N, 7.21 %.

2.5.7. *2-[5-(2-Hydroxyphenyl)-1,3,4-oxadiazol-2-yl]-3*H*-benzo[f] chromen-3-one* (**6e**; $C_{21}H_{12}N_2O_4$)

Yellow crystalline solid; (55 %); m.p. 205–207 °C; IR (KBr): ν = 3422.4, 3080 cm^{-1}, 1770 cm^{-1} ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.03 (m, 1H, *J* = 8.5 Hz), 7.61 (m, 1H, *J* = 4.0 Hz), 7.74 (d, 3H, *J* = 8.4 Hz), 7.85 (t, 2H, *J* = 6.7 Hz), 8.13 (m, 2H, *J* = 7.0 Hz), 8.35 (d, 1H, *J* = 8.5Hz), 8.72 (d , 1H, *J* = 8.0 Hz,), 9.63 (s, 1H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): 171.15, 166.5, 163.55, 156.36, 152.64, 145.17, 132.93, 131.26, 131.13, 130.47, 129.96, 129.83, 129.56, 127.84, 124.64, 123.32, 122.95, 118.81, 118.73, 117.42, 113.21. MS: m/z = 357 (M+1). Anal. Calcd. for $C_{21}H_{12}N_2O_4$ = C, 70.78; H, 3.39; N, 7.86 % . Found: C, 70.55; H, 3.12; N, 7.69 %.

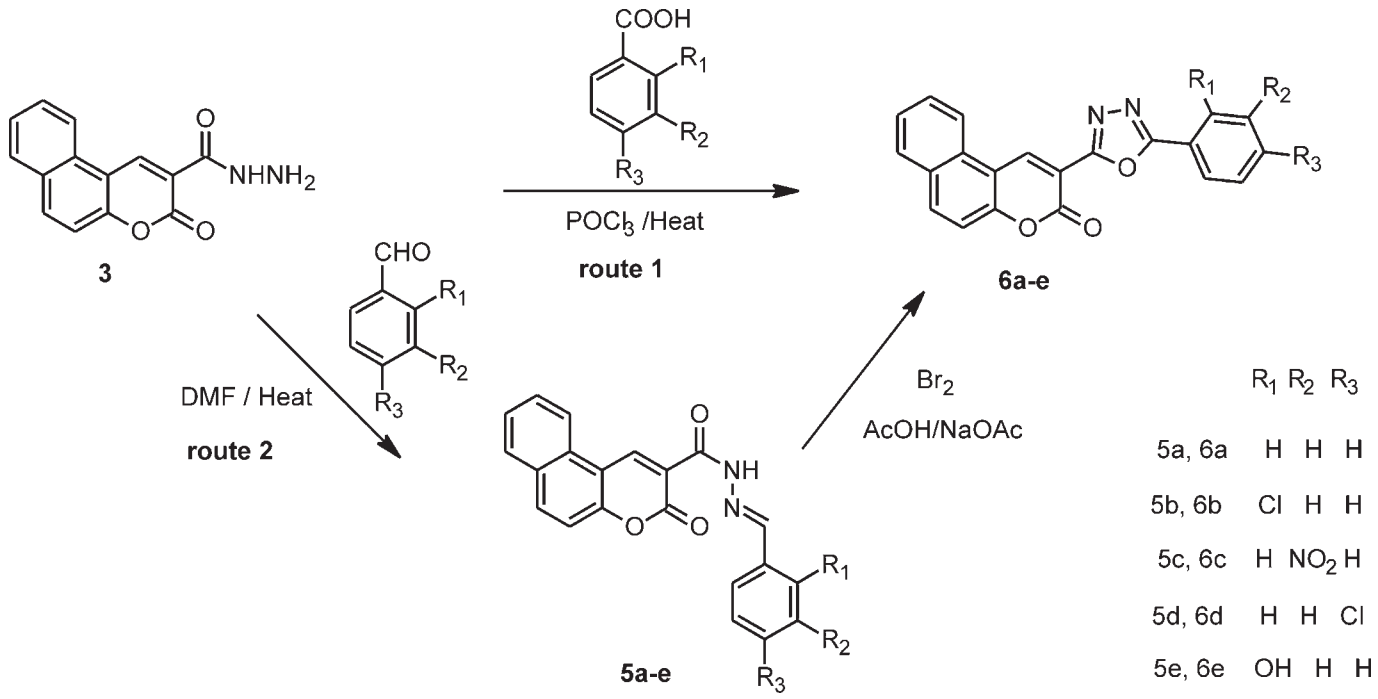
2.6. Recording of UV-visible and Fluorescence Spectral Data

Fluorescence spectra were recorded on a F-7000 FL (SL. NO 1911-004, ROM 5J14000 03) spectrophotometer. A solution of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-one (**6a–e**) in chloroform was prepared (1 mg/mL), which was taken in cuvettes and was placed in probe. First absorption maxima was recorded and it was fixed. Then UV absorption maxima and fluoroscence emission maxima of the sample was recorded.

3. Results and Discussion

The various benzocoumaryl oxadiazoles **6a–e** have been synthesized by using benzocoumaryl-3-ethylcarbohydrazide **3** as key intermediate. The benzocoumarin-3-carbohydrazide **3** was prepared in an excellent yield from benzocoumarin-3-ethylecarboxylate **2** on treatment with hydrazine hydrate in ethanol. The benzocoumarin-3-ethylcarboxylate was obtained by Knoevenagel condensation between 2-hydroxy-1-napthaldehyde and diethylmalonate in presence of catalytic amount of piperidine. While preparing the key intermediate **3**, it was interesting to note that, the reaction of compound **2** with hydrazine hydrate with its mole ratio at room temperature furnished only compound **3**,[12] whereas the reaction of compound **2** with excess of hydrazine hydrate yielded another interesting new heterocycle, such as 1-amino 3,4-dihydrobenzo-[*f*]quinoline-3-carbohydrazide **4** (Scheme 1). It was also noticed that the compound **3** was insoluble in ethanol while compound **4** is soluble in ethanol. From the difference in solubility of these two compounds, it can be easily identified physically during their synthesis. So that either compounds could be easly prepared depending upon requirement. Since compound **4** contains active functional groups (-NH_2 and $CONHNH_2$), it could be synthetically exploited to generate a series of new quinoline derivatives.The research work in this context is under progress in our laboratory.

The structures of all the newly synthesized compounds were characterized by analytical and spectral studies. ^{1}H NMR of compound **3** revealed the presence of a singlet at δ 9.9 ppm for one proton of NH (D_2O exchangeable) group and another singlet at δ 4.7 ppm for two protons of NH_2 (D_2O exchangeable) group that confirms conversion of benzocoumarin carboxylate to benzocoumarin carbohydrazide **3**. Compound **4** exhibited a singlet at δ 1.4 ppm due to two protons corresponding to N-NH_2 (D_2O exchangeable) confirming its assigned structure. The formation of compounds **3** and **4** were also supported by their



Scheme 2

General synthetic procedure for *N*′-benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazides (**5a–e**) and 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3–ones (**6a–e**).

Table 1 Reaction time, yield and melting points of *N*′-benzylidene-3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide (**5a–e**).

Entry	Reaction time/h	Yield/% *	Mp/°C
5a	14	86	233–235
5b	11	81	257–259
5c	13	89	254–256
5d	12	88	244–246
5e	11	90	234–236

* The yields were recorded for $POCl_3$ cyclization method (route 1, Scheme 2).

Table 2 Reaction time, yield and melting points of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones **(6a–e)**.

Entry	Reaction time/h	Yield/%	Mp/°C
6a	12	51	197–199
6b	15	58	221–223
6c	11	53	223–225
6d	14	56	214–216
6e	12	55	205–207

mass spectral analysis. The molecular ion peak were observed at MS (M^+) 255 (100 %) for compound **3** and MS (M^+) 268 (100 %) for compound **4**, respectively. Compound **3** has been exploited to construct various oxadiazole moiety linked to benzocoumarin at position 3 in two different routes (Scheme 2). Thus on refluxing compound **3** with various benzoic acids in the presence of $POCl_3$ afforded the benzocoumarin-3-oxadiazoles **6a–e** (route 1, Scheme 2).[22]

In route 2, on refluxing compound **3** with various benzaldehydes in DMF produced *N*-(aryl-methylene) substituted benzocoumarin-3-carbohydrazides **5a–e** (Table 2).[23] Compounds **5a–e** were made to undergo cyclization on treating with bromine in acetic acid and anhydrous sodium acetate to afford **6a–e** (Table 3). All the newly synthesized compounds have been characterized by elemental analysis and spectroscopic data.

3.1. UV-visible and Fluorescence Spectral Data Analysis

Coumarin by itself is not fluorescent, it's derivatives with both electron donating groups at 6 and 7 positions and electron withdrawing group at position 3 develops intense fluorescence as shown in Table 1. The experimental UV-visible spectra of benzocoumarin derivatives **6a–e** in chloroform were obtained. The spectra of compounds **6a–e** are reproduced in Figs. 2 and 3.

The spectroscopic properties fluorescence excitation (λ_{EX}), fluorescence emission (λ_{EM}), Stoke's shift ($\Delta\nu$) are listed in Table 1. It was observed that the λ_{EM} values of the compounds with electron withdrawing groups such as **6b**, **6c** and **6d** shifted to the longer wave length region with larger $\Delta\nu$ values than those of the non-substituted derivatives **6a** and the compound bearing an electron donating group **6e**. In the visible region, the absorption band of all the compounds experiences a good bathochromic shift. The fluorescence spectral properties of compounds **6a–e** are not identical to each other and gave Stoke's shifts ranging from 43 to 165 nm, and their differences were found to be high because of different substituents. In the case of compounds **6a** and **6e**, although they absorb at higher wavelengths the fluores-

Table 3 Fluorescence spectral data of compounds **6a–e** in chloroform.

Compound	Maximum wavelength/nm		Stoke's shift/nm	$\Delta\nu$/cm^{-1}
	Excitation	Emission		
6a	368	453	85	5098
6b	368	464.8	96.8	5612
6c	365	462.6	97.6	5780
6d	299	464	165	11893
6e	418	461	43	2270

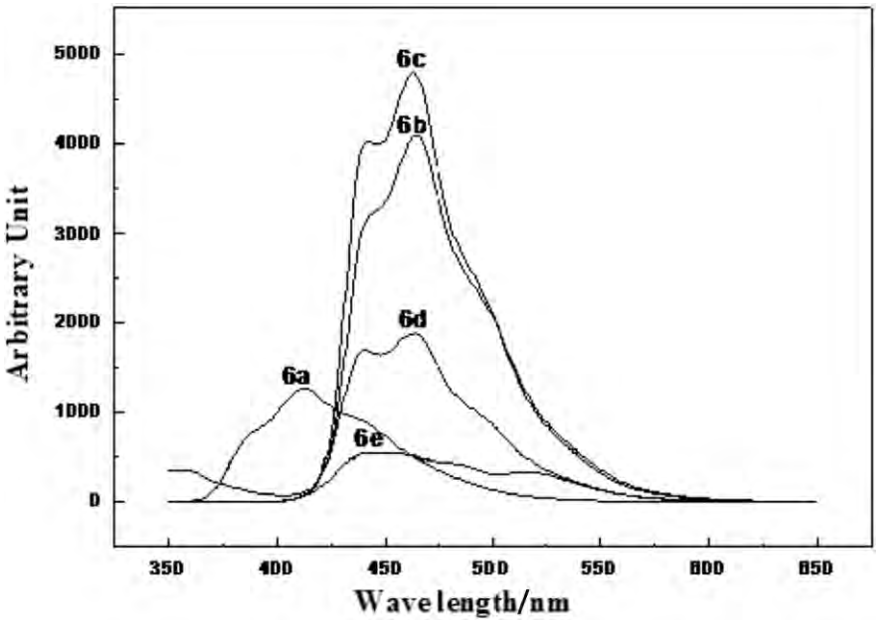


Fig. 2 Fluorescence spectra of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones **6a–e** in chloroform.

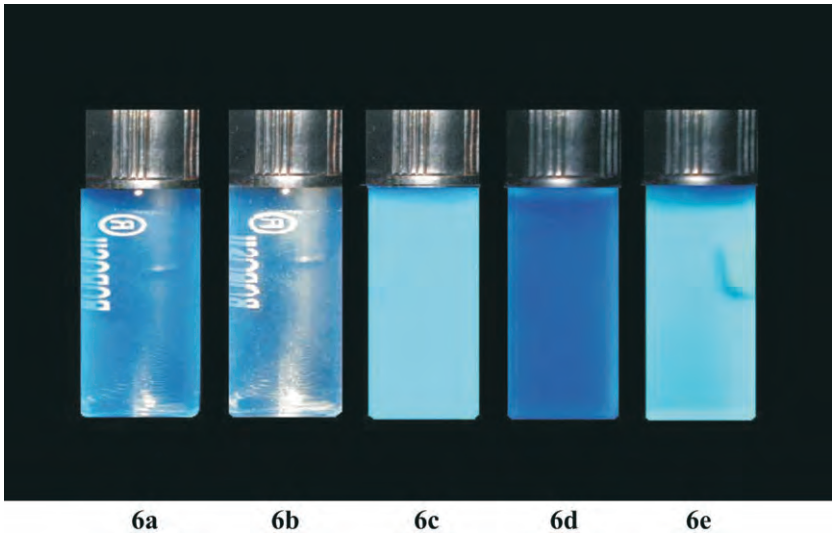


Fig. 3 Appearance of 2-[5-phenyl-1,3,4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones **6a–e** in a UV chamber.

cent intensities are very small when compared to **6b, 6c** and **6d**. These benzocoumaryl oxadiazolyls show excellent blue fluorescent properties when compared to recently reported coumarin fluorescent labels.[20,21]

4. Conclusion

In conclusion, a simple, efficient and general method has been developed for the synthesis of benzocoumarin oxadiazolyl compounds **6a–e** through a one-pot reaction of aromatic carboxylic acids and benzocoumarin-3-carboxyhydrazide in the presence of $POCl_3$ at reflux condition. All these compounds are hitherto unknown in literature and are observed to exhibit excellent fluorescence properties.

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