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Synthesis and fluorescence study of 2-[5-(-2-arylethenyl)-1, 3, 4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones

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ABSTRACT

The syntheses and the fluorescence properties of various 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** as candidate of novel fluorophores emitting in green region has been reported as among the most sensitive and practically useful fluorescent brighteners.

KEYWORDS

Fluoroscence;
Benzocoumarin oxadiazoles;
Antibacterial;
Analgesic.

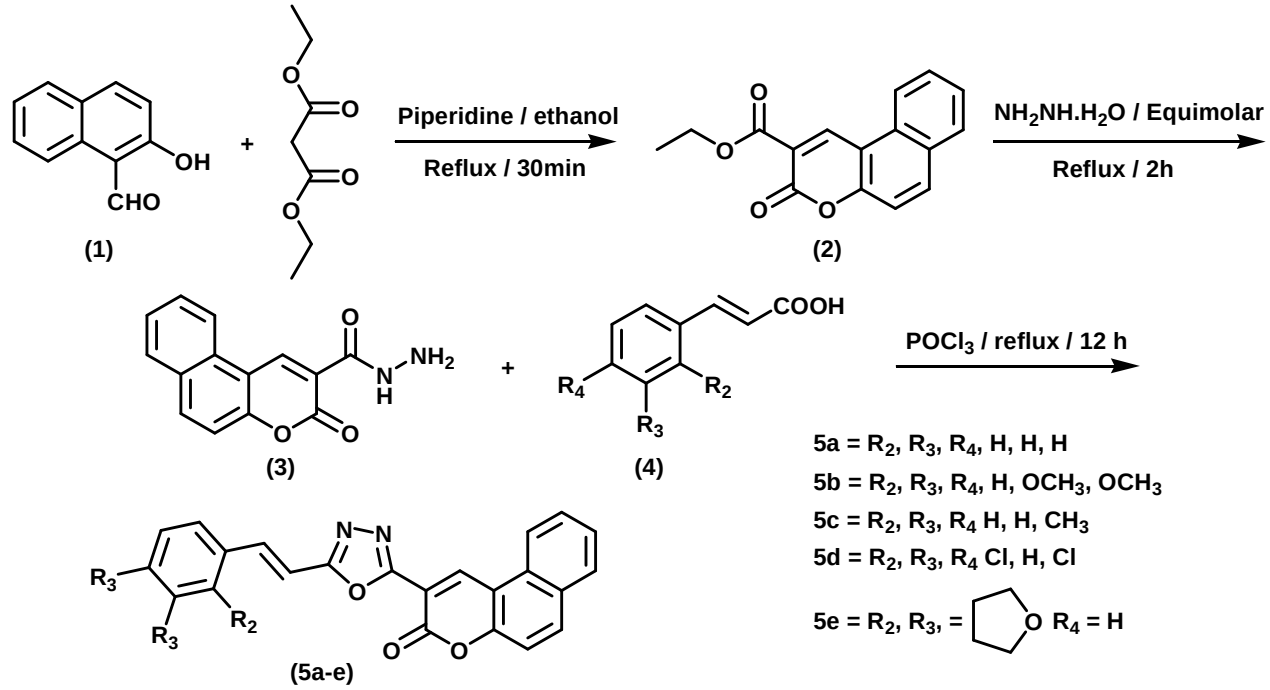
INTRODUCTION

Coumarins posses important photochemical and photophysical properties[1,2] leading to numerous industrial applications[3,4]. Some of the derivatives are also served as fluorescence brighteners[5], Since fluorescence is highly sensitive to physicochemical environments, a variety of such organic fluorescent compounds have been widely used in many scientific fields, for example, as analytical tools such as fluorescent labeling reagents[6], fluorescence probes[7], fluorescence sensors[8], and laser dyes. Several 7-hydroxycoumarins having substituents at 3rd position rank among the most efficient photostable laser dyes, emitting in the blue green region in the visible spectrum. The first industrial optical brightener was produced from coumarin family is 4-methyl-umbelliferone. In 1999, the world production of fluorescent brighteners amounted to 40000 tons of active substances[9]. The lasing range covered by coumarin dyes has been appreciably extended when the substituents at 3rd position is a heterocyclic moiety[10,11]. Therefore, the synthesis and study of electronic properties of coumarins bearing different heterocycles at 3rd position has gained much attention in order to obtain highly sensitive fluorescence coumarin brighteners.

Recently we have reported the synthesis and fluorescent properties of 2-(5-alkyl-1,3,4-oxadiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones as strong blue fluorescent compounds[12]. In connection to this we report in this paper, the syntheses and the fluorescence properties of various 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** as candidate of novel fluorophores emitting in green region, which could be among the most sensitive and practically useful fluorescent brighteners. This work was encouraged by our previous investigation on new routes and new synthesis of various heterocyclic compounds[12-22].

RESULTS AND DISCUSSION

The 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide 3 served as key intermediate in the synthesis of a new range of fluorescent 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)**. Thus the various 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** were synthesized from 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide 3 by reacting with various Cinnamic acids in presence of $POCl_3$ in one pot at reflux temperature on water bath (Scheme 1). Keeping in view of the electronic properties of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)**, the various Cinnamic acids which contains electron donating substituents such as $–OCH_3$, tetrahydrofuran and weak donating group like $-CH_3$ was selected. On the other hand electron withdrawing group like -Cl was also selected to find out the differences in the electronic properties of compounds **(5a-e)**. These groups significantly change the absorption and emission maxima in the visible spectrum which are as shown in TABLE 1.



Scheme 1 : Synthesis of ethyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate 2, 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide 3, and 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones (5a-e).

All the newly synthesized compounds have been characterized by elemental analysis and spectroscopic data. The spectral details of all these new compounds are given in experimental section.

The formation of **(5a-e)** was verified with ^{1}H NMR and mass spectroscopic analysis. For example, ^{1}H NMR spectra of **(5a)** indicates that the appearance of two doublet at δ 7.83 and δ 6.09 are due to olefin CH protons. The remaining peaks resonating between δ 8.1-7.02 correspond to 11 aromatic protons of benzo[*f*]chromen-3-one ring as well as phenyl ring. A singlet at δ 9.58 ppm attribute to the proton present at 4th position of the lactone ring in benzo[*f*]chromen-3-one nucleus. Further the structure of compound **(5a)** was confirmed by its mass spectrum. Thus the compound **(5a)** gave molecular ion peak at MS (M+1) 367 (100 %) which is corresponds to its molecular formula confirms the structure of the product.

Photo physical properties

The structures of all synthesized novel 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** are shown in Figure 2. These molecules are planar with extend conjugation, hence, results in notable changes in the pi-conjugated length and red-shifts in the absorption and emission spectra. Fluorescence absorption spectra of these molecules in chloroform are given in Figure 3.

To improve the fluorescence characteristics, of

these coumarins especially emission wavelength, here we have selected unsaturated aromatic carboxylic acids. As a result it was observed that the fluorescence property of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e) (5a)**, (E_M = 481.8) and **(5d)**, (E_M = 478), **(5c)**, (E_M = 485.6), **(5e)**, (E_M = 510.2), **(5b)**, = (E_M = 524.6) increases shifts with increasing planarity and extended conjugation **(5a-e)**. Further, it was noticed that the fluorescence properties, depend on the substituents on the fluorophores. Fluorescence emission increases with electron donating groups such as methoxy and tetrahydrofuran in compound **(5b)** and **(5e)**, whereas decreases with electron withdrawing groups like chlorine in compound **(5a)**, and no substituents in **(5d)**.

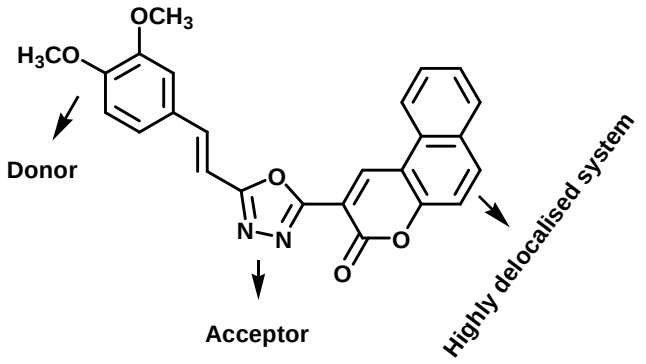


Figure 1 : Showing parts of donor, aceptor and delocalised system

All the synthesized compounds showed excellent fluorescence properties with Stoke's shift ranges from 35.8 to 107.6. In this study, new green fluorescent dyes based on coumarin, has high fluorescence yield and chemical stability.

The results showed that the fluorescence absorption of compound **(5b)** exhibited maximum absorption is 417 nm and emission maxima is 524.6 nm compared to other compounds as they contains electron withdrawing substitution particularly in compound **(5d)**. Because, as compound **(5a)** contains donor moiety like dimethoxy phenyl group which is connected to acceptor oxadiazole moiety through a -C=C- maintains coplanarity between them. Also benzo[*f*]chromen-3-one moiety helps for delocalization of the excited electron in the entire dye structure since there is a planarity throughout the dye molecule. Emission maxima was found to be 524.6 nm resulted in a strong bathochromic shift (417e 524.6nm).

Hence, 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** were depends on their molecular structures. The first absorption band of compounds starts in the region 446e 481nm which is due to highly electron accepting character of oxadiazole moiety, as a result, the red-shift of absorption can possibly occur.

Since all new 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-

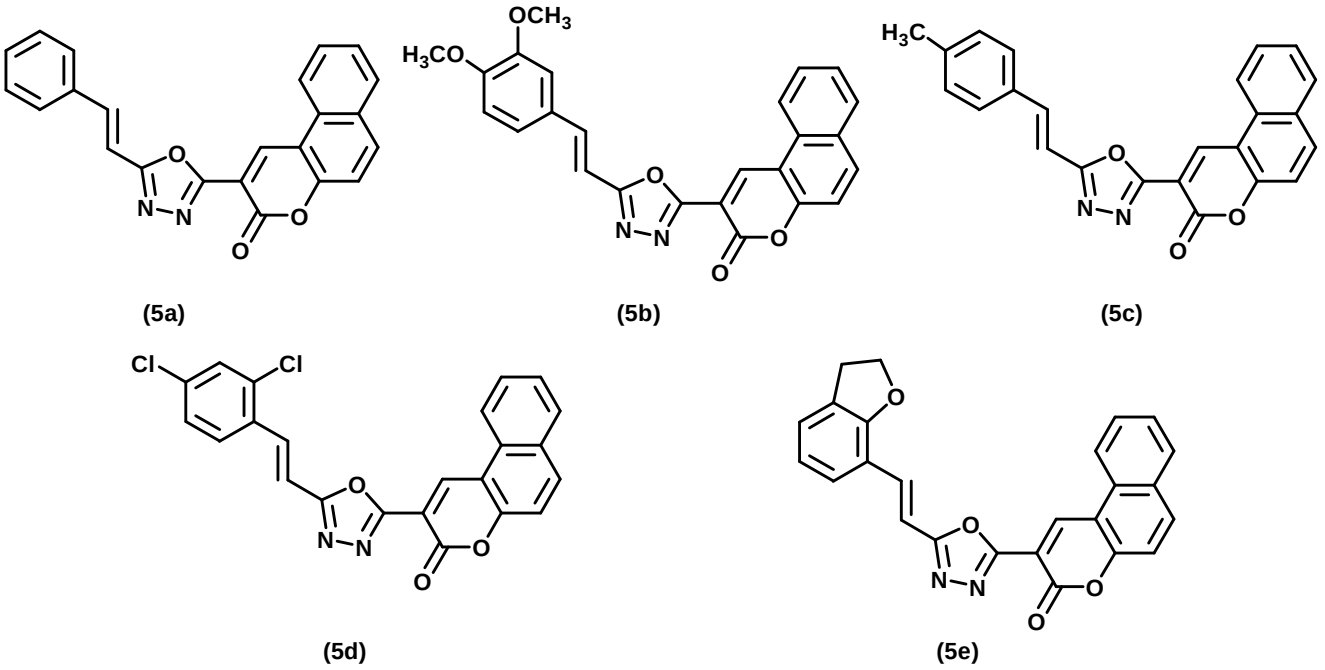


Figure 2 : Structure of (5a-e)

2-yl}-3*H*-benzo[*f*]chromen-3-ones **(5a-e)** has an extended conjugation, displays an unconstrained delocalization. Hence, in the visible region the absorption bands of all the compounds experiences a good bathochromic shift, the Stoke's shift ranges from 35.8 to 107.6 nm. The newly synthesized compounds **(5a-e)** emit green region of the visible spectrum that is better than any other coumarin fluorophores.

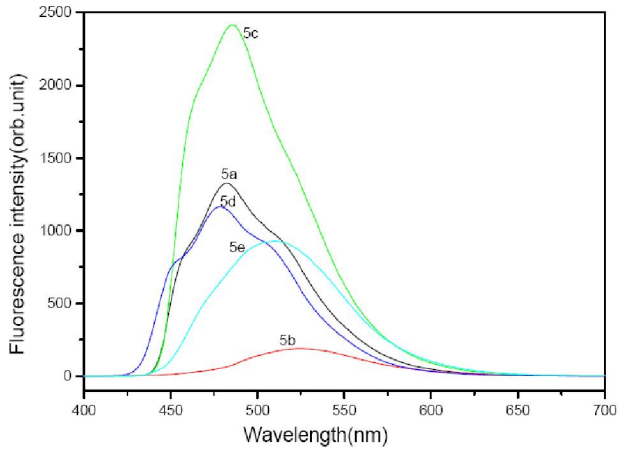


Figure 3 : The absorption and fluorescence spectra of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones (5a-e) in chloroform

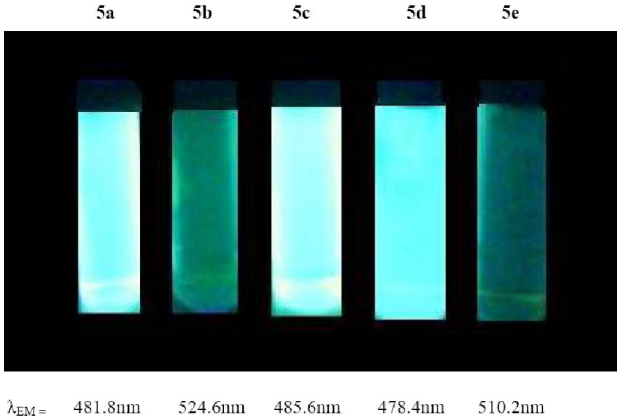


Figure 4 : Appearance of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones 5a-e in UV chamber

TABLE 1 : Absorption and fluorescence characteristics of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]-chromen-3-ones (5a-e) in chloroform

Compound	Maximum wavelength (nm)		Stoke's shift (nm)	Δv/cm^{-1}
	Excitation	Emission		
5a	446	481.8	35.8	16660
5b	417	524.6	107.6	48968
5c	449	485.6	36.6	20328
5d	436	478.4	42.4	16786
5e	440	510.2	70.2	31271

Antibacterial activity[23]

All the synthesized compounds (TABLE 2) were tested for their antibacterial activity against various bacterial strains belonging to Gram positive *Staphylococcus aureus, Bacillus subtilis, Streptococcus-haemolytius,* Gram negative, *Salmonella typhi, Escherichia coli, Pseudomonas aeruginosa, and Klebsiella species.* Streptomycin was used as standard drug for comparison. All the synthesized compounds were found to active against all bacteria. The maximum activity was found in compounds **(5a)**, **(5d)**, and where as **(5c)** moderately active and **(5b)**, **(5e)** are less active.

TABLE 2 : Antibacterial activity of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones (5a-e), and inhibition zone was measured in mm

Compound	Streptococcus-haemolyticus	Staphylococcus aureus	Salmonella typhi	Pseudomonas aeruginosa	Escherichia coli	Bacillus subtilis	Klebsiella species
5a	23	22	23	22	24	21	23
5b	19	18	20	18	19	19	20
5c	24	20	22	20	20	21	22
5d	25	23	24	23	26	23	25
5e	20	19	21	19	21	20	21
Standard	22	23	24	22	23	22	23
Control	00	00	00	00	00	00	00

Note: Standard drug used: Streptomycin (40 µg/mL); Compounds used: (40 µg/mL); Control: DMSO (Dimethyl sulphoxide)

Analgesic activity[24]

Male Swiss albino mice were produced from Virus Diagnostic Laboratory, Shivamogga. Karnataka, India. Analgesic activity was calculated as the percentage maximum possible effect (%MPE) and the results are recorded in (TABLE 3)

Analgesic properties of test compounds were compared with the activity of standard drug aspirin having percentage of protection value 54. The compounds **(5e)**, exhibited almost equipotent percentage protection as compared with standard aspirin and compounds **(5a)** and **(5d)** showed more significant percentage protection and compounds **(5b)**, **(5c)**, are showed less percentage protection compared to standard.

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TABLE 3 : Analgesic activity of 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones (5a-e)

Compound	Dose mg/kg	Mean no. of writhing		% MPE
		Before drug	After drug	
Standard	100	24.00±1.41	11.00±1.26	54.00
Control	100	33.66±0.816	33.33±1.0	1
5a	100	40.6±2.1	15.8±1.43	61.1*
5b	100	33.33±0.683	16.16±0.577	51.52
5c	100	34.16±06	16.08±0.57	50.73
5d	100	40.6±2.1	13.8±0.43	61.3*
5e	100	35.05±0.57	16.16±0.60	54.47*

Analgesic activity, *P<0.001 vs. Control, student's t-test, n = 6

EXPERIMENTAL

General

All the chemicals used were of analytical grade. Melting points were uncorrected, determined in an open capillary. Purity of the compounds was checked by TLC on silica gel and was purified by using column chromatography. ^{1}H NMR spectra was recorded on a Bruker supercon FT NMR (400 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 and, TMS as an internal standard. The chemical shifts are expressed in δ units. IR spectra were recorded by using JASCO FT/IR-300 E spectrometer from a KBr pelleted sample. Mass spectra was recorded on a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer. A fluorescence spectrum was recorded by F-7000 FL (SL. NO 1911-004, ROM 5J14000 03) Spectrophotometer. The Elemental analysis was obtained by "Elementar vario EL-III instrument".

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

A mixture of 2-hydroxy-1-naphthaldehyde (2.9 mmol) 1, an equivalent amount of diethyl malonate (2.9 mmol), and catalytic amount of piperidine in ethanol (30 ml) was refluxed for 30 minutes on water bath. After the reaction was completed, the reaction mixture was cooled to room temperature and poured into crushed ice with stirring. The precipitate obtained was then filtered, washed with water, dried and recrystallised using ethanol to get ethyl 3-oxo-3*H*-benzo[*f*]chromene-2-carboxylate. m.p. 115–116 °C.

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) and hydrazine hydrate (3.8 mmol) was dissolved in ethanol and stirred at r.t for one day. After the completion of the reaction, the reaction mixture was cooled to room temperature and poured into crushed ice with stirring. The separated solid was filtered, washed with water, dried and recrystallised with ethanol to get pure yellow 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide 3. M.p. 261-263 ºC (M.p. 260-262 ºC[11]).

Synthesis of 2-[5(-2-phenylethenyl)-1, 3, 4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-one (5a)

Phosphorous oxychloride 10ml was added to the mixture of 3-oxo-3*H*-benzo[*f*]chromene-2-carbohydrazide (1.97 mmol, 0.5 g) and cinnamic acid (1.97 mmol, 0.29 g). The reaction mixture was then refluxed for about 10-12 hr on water bath and cooled to room temperature. The mixture was poured into crushed ice with stirring and it was neutralized by using saturated sodium bicarbonate solution. The yellow precipitate obtained was filtered, washed with water, dried and purified through column chromatography using ethyl acetate and petroleum ether (2:8) as eluent. Similarly, the compounds **(5b-e)** were synthesized.

2-[5-[2-phenylethenyl]-1, 3, 4-oxadiazol-2-yl]-3H-benzo[*f*]chromen-3-one (5a)

Yellow brown Solid, Yield 70%; m.p.135-138ºC (ethyl acetate); ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 9.58 (s, 1H, CH), 7.83 (d, 1H, J = 9.4 Hz), 7.74 (m, 1H), 7.59 (d, 2H, J = 10.8 Hz), 7.36 (d, 2H, J = 6.27 Hz), 7.29 (m, 4H), 7.02 (t, 1H, j = 8.19 Hz), 6.09 (d, 2H, j = 1.89 Hz): ^{13}CNMR (400 MHz, DMSO-d_6) δ (ppm): 166.7 (s), 160.3 (s), 155.8(s), 153.9(s), 141.3 (d), 135.8 (d), 134.9 (s), 134 (d), 130.1(s), 129.2 (d), 129.2 (d), 129.1 (s), 128.4 (d), 128.4, 127.7 (d), 126.9 (d), 126.2 (d), 126.2 (d), 124.8 (d), 122.1 (d), 116.6 (d), 113.6 (s), 112.1 (s): IR (KBr) ν (cm^{-1}): 1768 (s) (C=O pyrone), 1602 (s) (C=N); MS (m/z): 367 (M+1). $C_{23}H_{14}N_2O_3$ = C,75.40; H, 3.85; N, 7.65 Found: C, 74.69; H, 4.20; N, 7.58.

2-[5-[2-(3, 4-dimethoxyphenyl) ethenyl]-1, 3, 4-oxadiazol-2-yl]-Hbenzo[*f*]chromen-3-one (5b)

Redish Solid. Yield 85%; m.p.164-167°C (ethyl acetate); ^{1}H NMR (300 MHz, *DMSO-d*$_6$) δ (ppm): 9.4 (s, 1H, CH), 8.68 (m, 1H), 8.34 (d, 1H, *J* = 9.06 Hz), 8.1 (d, 1H, *J* = 7.6 Hz), 7.80 (m, 6H), 7.04 (d, 1H, *J* = 7.0 Hz), 6.7 (d, 1H, *J* = 2.0 Hz), 3.8 (d, 6H, *J* = 6 Hz): ^{13}CNMR (400MHz, DMSO-*d*$_6$) δ (ppm): 166.7 (s), 160.1 (s), 155.6(s), 153.9(s), 148.0, (s), 147.2, (s) 141.1 (d), 135.8 (d), (s), 134 (d), 130.6 130.1(s), 129.2 (d), 129.2 (d), 129.1 (s), 128.0, 127.7 (d), 126.9 (d), 122.2 (d), 122.2 (d), 122.1 (d), 116.6 (d), 113.6 (s), 112.1, 55.9, 55.9: IR (KBr) ν (cm^{-1}): 1761 (s) (C=O pyrone), 1626 (s) (C=N); MS (m/z): 427.4 (M+1). Anal. Calcd. For $C_{25}H_{18}N_2O_5$ = C, 70.42; H, 4.25; N, 6.57 Found: C, 70.29; H, 4.06.; N 6.51.

2-[5-[2-(4-methylphenyl) ethenyl]-1, 3, 4-oxadiazol-2-yl]-3H-benzo[*f*]chromen-3-one (5c)

Bright Yellow Solid, Yield 80 %; m.p.148-151ºC (ethyl acetate); ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ (ppm): 9.62 (s, 1H, CH), 8.81 (d, 1H, *J* = 8.9 Hz), 8.3 (d, 1H, *J* = 9.2 Hz), 8.1 (d, 1H, *J* = 9.0 Hz), 7.8 (t, 2H, *J* = 7.4 Hz), 7.75 (m, 4H), 7.42 (d, 1H, *J* = 16.8), 7.3 (d, 2H, *J* = 8.52 Hz), 2.48 (s, 3H, CH_3): ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ (ppm): 166.7 (s), 160.6 (s), 155.8(s), 154.0(s), 141.8 (d), 137(s) 135.9(d), 134.9 (s), 134 (d), 130.3(s), 129.4 (d), 129.4 (d), 129.2 (s), 129.2 (d), 129.2, 127 (d), 125.9 (d), 125.9 (d), 124.7 (d), 122.1 (d), 116.1 (d), 113.7 (s), 112.6 (s), 20.6: IR (KBr) ν (cm^{-1}): 1764 (s) (C=O pyrone), 1618 (s) (C=N); MS (m/z): 381.39 (M+1). Anal. Calcd. For $C_{24}H_{16}N_2O_3$: = C, 70.42; H, 4.25; N, 6.57 Found: C, 70.31; H, 4.17; N, 6.67.

2-[5-[2-(2, 4-dichlorophenyl) ethenyl]-1,3,4-oxadiazol-2-yl]-3H-benzo[*f*]chromen-3-one (5d)

Yellow Solid. Yield 50%; m.p.181-184ºC (ethyl acetate); ^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm): 9.6 (s, 1H), 8.8 (d, 1H, *J* = 8.4 Hz), 8.37 (d, 1H, *J* = 9.0 Hz), 8.13 (d, 1H, *J* = 11.0 Hz), 7.89 (m, 6H), 7.49 (d, 1H, *J* = 5.88 Hz), 7.45 (d, 1H, *J* = 16 Hz); ^{13}CNMR (400M Hz, DMSO-*d*$_6$) δ (ppm): 166.7 (s), 160.3 (s), 155.8(s), 153.9(s), 141.3 (d), 138.5 (s), 135.8 (d), 135, 134.9 (s), 134 (d), 133, 130.1(s), 129.2 (d), 129.2 (d),129.2 (d)126.9 (d), 129.0, 126.5 (d), (d), 124.9 (d), 122.1 (d), 116.6 (d), 113.6 (s), 112.1 (s): IR (KBr) ν (cm^{-1}): 1763 (s) (C=O pyrone), 1612 (s) (C=N); MS (m/z): 436.25 (M+1). Anal. Calcd. For $C_{23}H_{12}N_2O_3$: = C, 63.47; H, 2.78; N, 6.44 Found: C, 63.36; H, 2.69; N, 6.18.

2-[5-[2-(2, 3-dihydro-1-benzofuran-7-yl) ethenyl]-1, 3, 4-oxadiazol-2-yl]-3H- benzo[*f*]chromen-3-one (5e)

Redish Solid. Yield 60% m.p.192-194ºC (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.41 (s, 1H, CH), 8.40 (d, 1H, *J* = 8.4 Hz), 8.14 (d, 1H, *J* = 9.0 Hz), 7.98 (d, 2H, *J* = 8.0 Hz), 7.80 (t, 2H, *J* = 7.2 Hz), 7.60 (t, 1H, *J* = 7.5 Hz), 7.54 (d, 1H, *J* = 9.0 Hz), 7.14 (d, 1H, *J* = 6.1 Hz), 6.9 (d, 2H, *J* = 7.4 Hz), 4.5 (t, 2H, *J* = 7.7 Hz), 3.1 (t, 2H, *J* = 7.5 Hz) : ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ (ppm): 166.7 (s), 160.3 (s), 158.8 (s), 155.8(s), 153.9(s), 141.3 (d), 135.8 (d), 134.9 (s), 134 (d), 130.1(s), 129.2 (d), 129.2 (d), 129.1 (s), 127.7 (d), 126.9 (d), 126.2 (d), 124.8 (d), 124 (q), 122.1 (d), 118 (d), 116.6 (d), 113.6 (s), 112.1 (s), 29.1, 29.1: IR (KBr) ν (cm^{-1}; 1765 (s) (C=O pyrone), 1621 (s) 1621 (s) (C=N); MS (m/z): 409.4 (M+1). Anal. Calcd. For $C_{25}H_{16}N_2O_4$: = C, 73.52; H, 3.95, N, 6.86 Found: C, 73.29; H, 3.89, N, 6.73.

CONCLUSION

Highly planar and delocalized 2-{5-[2-aryl ethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones has been produced through simple and convenient route. The results shown that due to increase in planarity and extended conjugation, all 2-{5-[2-aryl ethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones displayed a largest bathochromic shifts. All the synthesized compounds are hitherto unknown in literature and are observed to possess excellent fluorescence and pharmacological properties. Hence 2-{5-[2-arylethenyl]-1,3,4-oxadiazol-2-yl}-3*H*-benzo[*f*]chromen-3-ones could be a very useful fluorescent dyes for industrial applications.

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