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Synthesis and fluorescence study of phenylcoumarin/cyanophenylbenzocoumarin-3-carboxylates

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Abstract: The absorption and fluorescence spectra of phenylcoumarin and cyanophenylbenzocoumarin-3-carboxylates **6a-f** and **9a-e** have been investigated in chloroform, acetonitrile and ethanol**.** The substituting groups with varying electron donating ability such as *N,N*-diethyl amine and morpholine at 7-position, in phenylcoumarin-3-carboxylate **6a-f** exhibits fluorescence at a longer wavelength i.e. 420-460 nm in chloroform and 460-504 nm in acetonitrile. However the morpholine derivatives **6f-j** did not show fluorescence in chloroform. In another series of cyanophenylbenzocoumarin-3-carboxylates **9a-e,** the compound **9c** exhibits fluorescence at 546 nm in ethanol and 256 nm in acetonitrile, and lower emission wavelength i.e. 356 nm in chloroform. Further the compounds **6e**, **9b**, **9d** and **9e** exhibited high quantum yield in ethanol i.e., Φ_F = 0.79, 0.70, 0.80 and 0.74 respectively compare to Rhodamine B (Φ_F = 0.24) in ethanol.

Keywords: Phenylcoumarin-3-carboxylates; cyanophenylbenzocoumarin-3-carboxylates; fluorescence; quantum yield.

1. Introduction

Coumarin fluorescent probes or labels have extensive and diverse applications, as they exhibit extended spectral range and high emission quantum yields.[1] Coumarin-based fluorescent chemodosimeter with salicylaldehyde functionality were used as a binding site for selective detection of cyanide anions over other anions in water at biological pH.[2] Coumarin based copolymer is a class of materials allowing an unprecedented complete and straightforward second-harmonic generation (SHG)-assisted writing-reading-erasing-writing sequence with a high contrast, a process that is particularly appealing for optical data storage applications.[3] Coumarin core moieties have wide biological application, in particular for the imaging of living cells.[4] It is well known that the electron donating groups substituted on coumarin will increase the intermolecular electron transfer and thus enhance the fluorescence of coumarin derivatives. The coumarins are extremely variable in structure,

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due to the various types of substituents in their basic structure, which can influence their optical properties. Thus, the system might be effective for the development of both long wavelength and white-light-emitting chromophores. The coumarins have been promising candidates for the applications in molecular electronics and biological imaging.[5] Coumarins C540A and C485 are good laser additives for laser technology.[6]

Shihai Zhou et al.,[7] have studied 3-(2-benzothiiazolyl) coumarins for their fluorescent properties in which the coumarin acts as a donor while the benzothiazole moiety acts an acceptor. P Moeckli et al.,[8] introduced some new red fluorescent coumarin molecules by keeping electron donating group on 7th position of the coumarin ring and withdrawing group on 3-position. The oxygen atom at the 3-carbonyl group act as a hydrogen bond acceptor and electron donating group on 7th position enhance the fluorescence emission Figure 1a[9] Chiyomi Murata *et al*.,[10] examined coumarin derivatives with both electron donating groups at the 6- and 7-posotions and an electron-withdrawing group at the 3-position, which develop intense fluorescence. Seminaphthofluoresceins (SNAFLs) and naphthofluoresceins, which are recognized as annellated derivatives of fluorescein by one or two aromatic ring exhibited longer emission wavelengths at 623 nm and 663 nm respectively. Hence based on the above observation and in continuation of our work on fluorescent study,[11-14] and synthesis heterocyclic compounds.[15-24] Herein we report the blue fluorescent phenylcoumarin-3-carboxylates and cyanophenylbenzocoumarin-3-carboxylates emits blue light due to electron donating *N,N*-diethyl amino and benzocoumarin groups. Solubility is the main hurdle for the coumarin compounds to investigate their fluorescence property. Hence in order to increase solubility the long chain aliphatic carbon system has been introduced by reacting 4-alkoxyphenols with coumarin-3-carboxylic acids. Hence the synthesized compounds (Figure 1b) showed high fluorescent properties.

Literature Structure

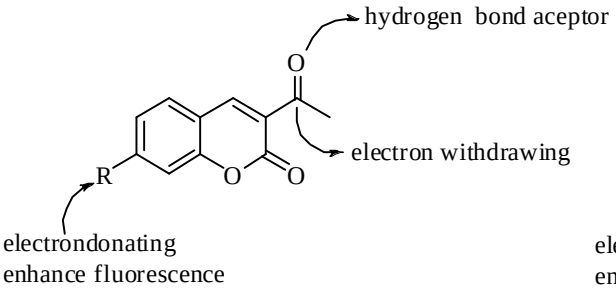


Figure 1a

Synthesized Structure

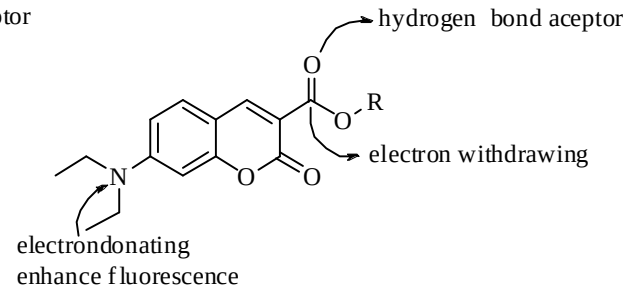
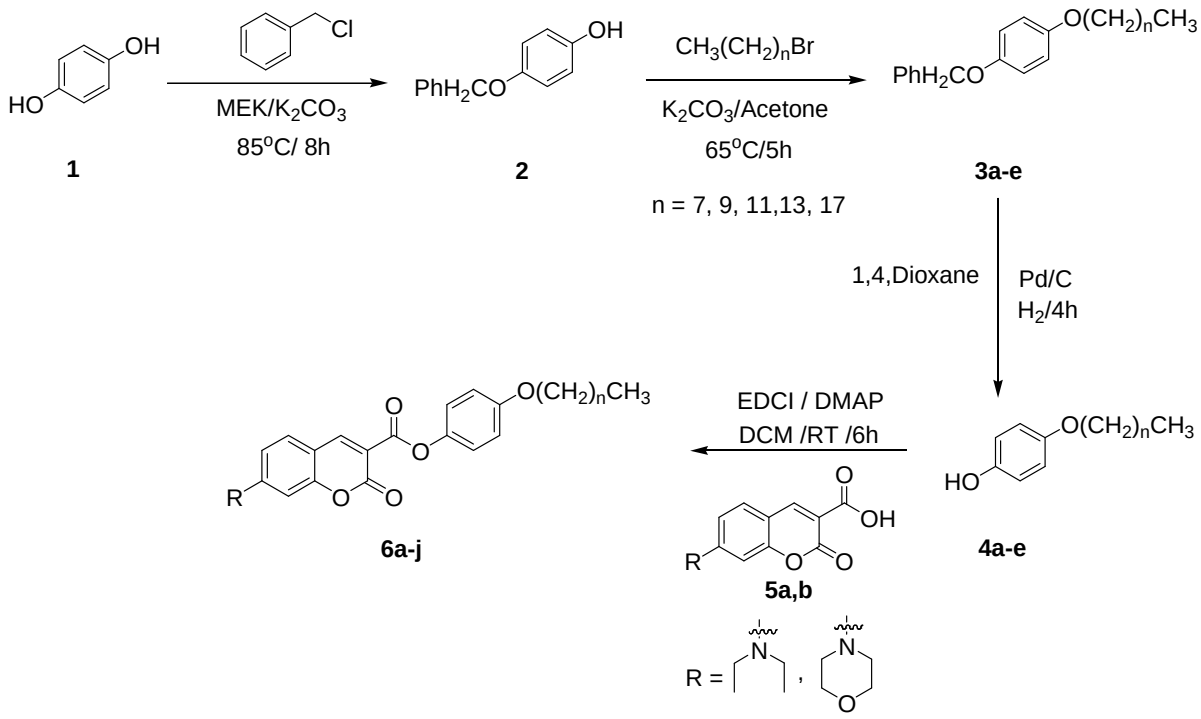


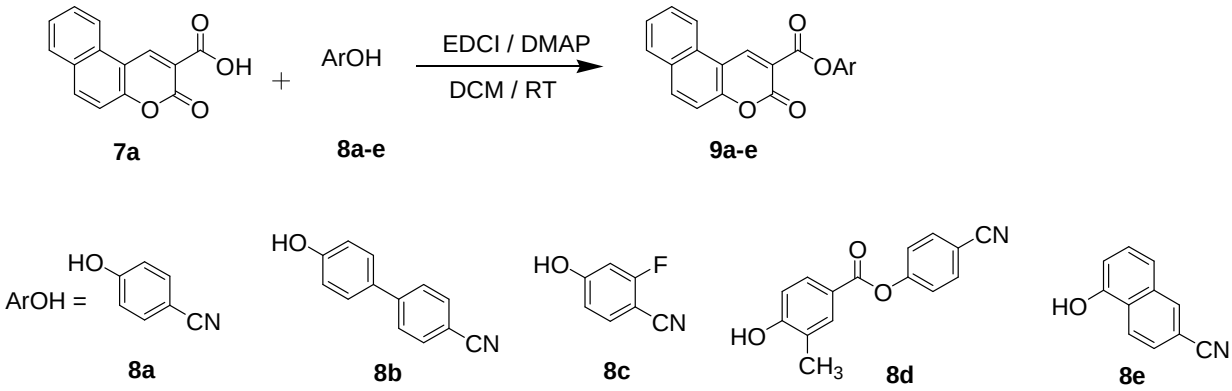
Figure 1b

2. Result and discussion

In this paper, we have reported the synthesis of phenylcoumarin-3-carboxylates **6a-j** (Scheme 1) and cyanophenylbenzocoumarin-3-carboxylates **9a-e** (Scheme 2) by suitable modified synthetic pathway. Initially the benzylation of hydroquinone was carried out by using benzyl chloride in presence of dry K_2CO_3 in methyl ethyl ketone as solvent to get 4-(benzyloxy)phenol **2**. Further, the various 1-(benzyloxy)-4-alkoxybenzenes **3a-e** were prepared by reacting compound **2** with different bromoalkylhalides [25] in presence of dry K_2CO_3 in acetone followed by deprotection of benzyl group by hydrogenolysis [26] using Pd/C in 1,4-dioxane furnished 4-(alkoxy) phenols **4a-e**. Finally the target compound phenylcoumarin-3-carboxylates **6a-j,** were synthesized by reacting compounds **4a-e** with coumarin-3-carboxylic acid **5a,b** in presence EDCI/DMAP as coupling agent. Higher alkoxy chain was introduced in this series of compounds to increase their solubility, in various solvents. Similarly, the compound **9a-e** was synthesized using commercially available compounds **8a-e**. The structures of all the newly synthesized compounds have been characterized by ^{1}H NMR, ^{13}C NMR, LCMS and Elemental analysis and the spectral data are given in the experimental section.



Scheme 1. Synthesis of Phenylcoumarin-3-carboxylates **6a-j**



Scheme 2. Synthesis of Cyanophenylbenzocoumarin-3-carboxylates **9a-e**

Fluorescence properties

The fluorescence properties of novel phenylcoumarin-3-carboxylates **6a-j** were investigated. The effect of different substituents on 3rd and 7th position on coumarin moiety and different solvents with respect to polarity has been studied. The molecules were designed with unique combination of electron donor at the 7th position like *N,N*-diethyl amino, morpholine and electron accepting like phenylcoumarin-3-carboxylates at 3rd position on coumarin moiety leading to the formation of push-pull system as shown in Scheme 1 **6a-j**.[10] In an another series, a benzocoumarin-3-carboxylic acid was converted into various cyanophenylbenzocoumarin-3-carboxylates **9a-e** by coupling with various cyano phenols such as 4-hydroxybenzonitrile, 4'-hydroxybiphenyl-4-carbonitrile, 2-fluoro-4-hydroxybenzonitrile, 4-cyanophenyl 4-hydroxy-3-methylbenzoate, and 5-hydroxy-2-naphthonitriles.

In all these cases the cyano group acts as strong acceptor, where benzocoumarin part served as strong donor[11-14] to constitute a strong push-pull system to exhibit high fluorescent intensities **9a-e**.

The fluorescence spectral data of compounds phenylcoumarin-3-carboxylates **6a-j** and cyanophenylbenzocoumarin-3-carboxylates **9a-e**, are summarized in Table 1. These compounds exhibited varying trend of fluorescent property with 0 to 0.8 quantum yield in chloroform, acetonitrile and ethanol respectively when compared with Rhodamine B. The fluorescent spectra of phenylcoumarin-3-carboxylates **6a-e** and cyanophenylbenzocoumarin-3-carboxylates **9a-e,** were studied in chloroform at a concentration of 1 mg mL^{-1} as shown in Figure 2.

Table 1. Spectral property of phenylcoumarin-3-carboxylates **6a-j** and cyanophenylbenzocoumarin-3-carboxylates **9a-e** in chloroform, acetonitrile and ethanol

Solvent	**Chloroform**				**Acetonitrile**				**Ethanol**			
Compound	Excitation nm	Emission nm	Stokes shift nm	Quantum yield (Φ_F)	Excitation nm	Emission nm	Stokes shift nm	Quantum yield (Φ_F)	Excitation nm	Emission nm	Stokes shift nm	Quantum yield (Φ_F)
6a	438	471	33	0.13	424	467	43	0.12	426	464	38	0.31
6b	429	473	44	0.31	387	463	76	0.50	-	-	-	-
6c	421	495	74	0.12	466	504	38	0.43	434	504	70	0.34
6d	426	483	57	0.54	422	467	45	0.79	395	463	68	0.54
6e	437	471	34	0.12	421	466	45	0.76	439	466	27	0.79
6f	-	-	-	-	406	471	65	0.68	246	303	57	0.58
6g	-	-	-	-	-	-	-	-	411	471	60	0.44
6h	-	-	-	-	354	470	85	0.38	246	304	58	0.66
6i	-	-	-	-	396	469	73	0.63	252	304	52	0.53
6j	-	-	-	-	-	-	-	-	248	304	56	0.49
9a	388	455	67	0.13	417	447	30	0.58	227	304	77	0.54
9b	301	451	150	0.19	-	-	-	-	231	306	75	0.70
9c	356	452	96	0.11	231	450	219	0.15	227	546	319	0.42
9d	320	454	134	0.09	-	-	-	-	248	304	56	0.80
9e	104	351	104	0.13	378	448	70	0.66	246	305	59	0.74

Note: Concentration of the compounds = 1 mg mL^{-1}
(-) Non fluorescence.
Quantum yield of Rhodamine B was taken in acetonitrile (0.34), in ethanol (0.24) and in chloroform (0.43).

The electron donating substituent i.e., *N*,*N*-diethyl amino group present at 7th position of the phenylcoumarin-3-carboxylates **6a-e** exhibited longer emission wavelength ranging from 463 to 504 nm in all solvents. However the compound **6b** did not exhibit fluorescence in ethanol. In case of morpholine substituent on 7th position of **6f-j** did not show emission in the chloroform while other compounds i.e. **6f, 6h** and **6i** showed emission in acetonitrile solvent. However all compounds **6f-j** showed emission in ethanol at shorter wavelength between 303-471 nm when compared with *N*,*N*-diethyl amino derivatives **6a-e**, which may be due to the lesser inductive effect of the morpohline group. The compound **6c** exhibited emission maxima at 504 nm both in ethanol and acetontrile, whereas in chloroform it showed emission maxima at 495 nm with quantum yield 0.581, 0.43 and 0.12 respectively. Fluorescence spectra of compounds **6f-j** showed a blue shift with the increase in solvent polarity from acetonitrile to ethanol due to intramolecular charge transfer (ICT).[10] In chlorinated media intramolecular quenching is very less for compounds **6f-j**, in which molecule gets either distorted in its own plane or twisted out of plane on intramolecular charge transfer.[27, 28] Hence, in the present case the fluorescence intensity of **6f-j** was nil in chloroform. On the other hand compounds **6a-e** showed emission maxima near blue light region in chloroform, acetonitrile and ethanol. But compound **6c** exhibit bathochromic shift (504 nm) in acetonitrile and ethanol but near blue light in chloroform. Thus the fluorescence property of compound **6a-j** were found to be dependent on solvent which either increase the intensity or enhancement the quenching property.

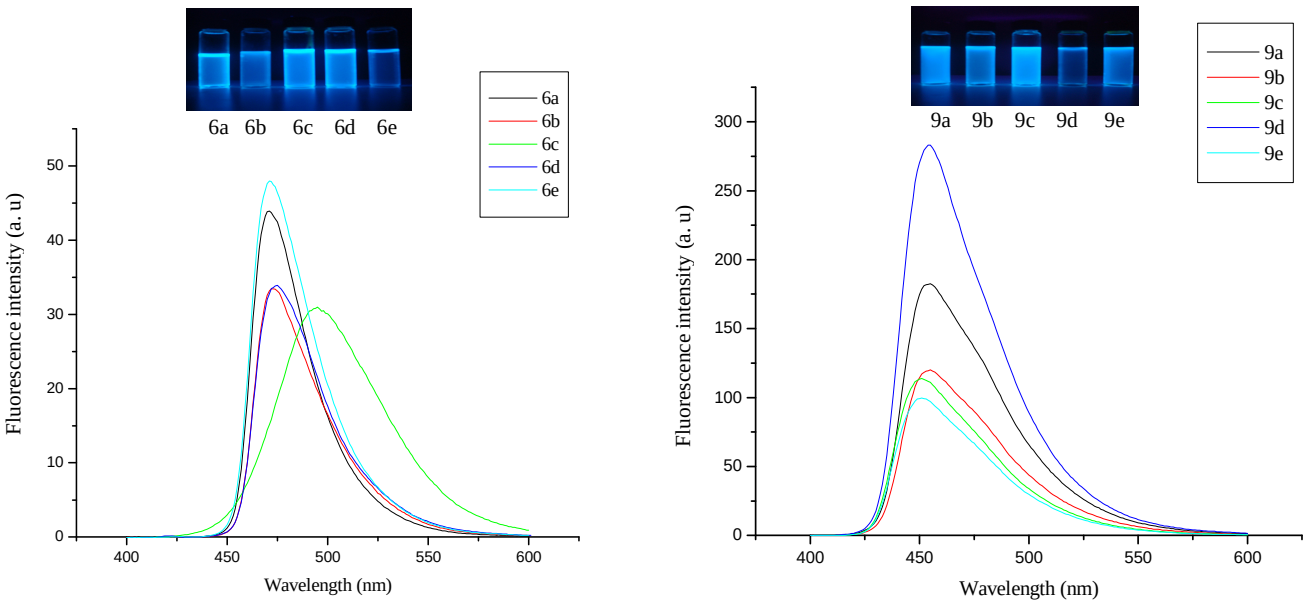


Figure 2. Fluorescent spectra of phenylcoumarin-3-carboxylates **6a-e** and cyanophenylbenzocoumarin-3-carboxylates **9a-e** in chloroform at concentration 1mg mL^{-1}

In an another series of compounds cyanophenylbenzocoumarin-3-carboxylates **9a-e** exhibited fluorescence in all solvent except the compounds **9b** and **9d** in acetonitrile. The compound **9c** showed emission maxima at longer wavelength (546 nm) near to red light in ethanol and near blue light (450 nm) in acetonitrile. Cyanophenylbenzocoumarin-3-carboxylates **9a-e** showed lower emission wavelength ranging from 308 to 388 nm in chloroform and ethanol, whereas in acetonitrile the compounds **9a**, **9c** and **9e** exhibited emission wavelength at 447, 450 and 378 nm respectively near blue region.

Quantum yields of fluorescent derivatives **6a-j**, **9a-e** were studied in various solvents. Among all series **6a-j** and **9a-e**, the cyanophenylbenzocoumarin-3-carboxylates **9a-e** found to exhibit high quantum yield than phenylcoumarin-3-carboxylates **6a-e** as shown in Table 1. In particular the compound **6e**, **9b**, **9d** and **9e** compounds gave high quantum yield 0.79, 0.70, 0.80, and 0.74 respectively in ethanol compare to chloroform which is higher than standard Rhodamine B was found to be 0.43 in chloroform, 0.34 in acetonitrile and 0.24 in ethanol.

The fluorescence property of the compounds depends on the presence of electron donating and electron withdrawing substituents on the acceptor part (Figure 3). In phenylcoumarin-3-carboxylates **6a-e** the compound **6e** acceptor part contains a long chain alkoxy group (**C18**) when compare to compounds **6a-d** (**C8, C10, C12, C14**). Hence due to less positive inductive effect of **6e** (**C18**), the donating tendency becomes less as a result the compound **6e** exhibits high quantum yield 0.79 which is much higher than their homologs **6a-d**. In case of cyanophenylbenzocoumarin-3-carboxylates **9a-e** series the compounds **9b**, **9d** and **9e** exhibited high quantum yield i.e., Φ_F = 0.70, 0.80, and 0.74 respectively when compared to compounds **9a** (0.54), **9c** (0.42) which may be due to the presence of one additional aromatic nucleus in acceptor part which enable extended conjugation, which also intern carries a strong electron withdrawing cyano group (Figure 3).

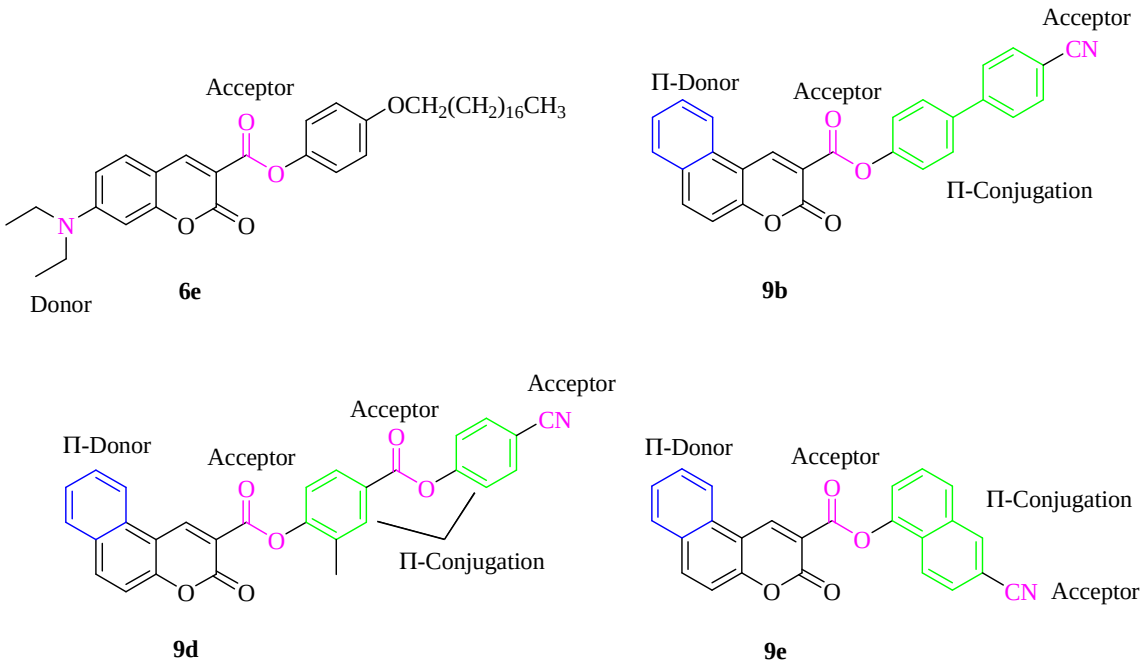


Figure 3. The compounds **9b**, **9d** and **9e**

3. Conclusion

A New class of phenylcoumarin-3-carboxylates **6a-j** and cyanophenylbenzocoumarin-3-carboxylates **9a-e** has been reported. The fluorescence properties of all the synthesized compounds were studied in chloroform, acetonitrile, and ethanol. The results obtained were interesting that the compounds **6e**, **9b**, **9d** and **9e** shows fluorescent in ethanol with high quantum yield i.e., Φ_F = 0.79, 0.70, 0.80 and 0.74 respectively than Rhodamine B (Φ_F =.0.24) Whereas in case of chloroform and acetonitrile the quantum yield was moderate to nil for compounds **6f-j** which may be due to distortion of molecule in its own plane or twisted out of plane on intramolecular charge transfer caused by solvents.

4. Experimental

All the chemicals used were of analytical grade. Melting points were uncorrected, determined in open capillary. Purity of the compounds was checked by TLC on silica gel and compounds were purified by recrystalisation method. ^{1}H NMR spectra were 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. Mass spectra's were recorded on a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer. The elemental analysis was obtained by "Elementary vario EL-III instrument".

Spectral measurements

The fluorescence spectra were recorded on Hitachi F-7000 spectrofluorometer in chloroform, ethanol and acetonitrile at a concentration of 1 mg mL^{-1}. The fluorescence spectra were recorded using excitation into the maximum of the longest wavelength absorption band program. Origin 6.1(Microsoft) was used for data plotting. The fluorescence of the solution was measured in a $1cm^3$ cuvette in the right angle arrangement. The quantum yield of the compound **6a-j** and **9a-e** derivative was determined using Rhodamine B as the standard in the respective medium, it was found to be 0.43 in chloroform 0.34 in acetonitrile, and 0.24 in ethanol. The fluorescence spectra were taken by the excitation into the maximum of the longest wavelength absorption band. The fluorescence spectra of

Rhodamine B excited were at 536, 473 and 512 nm in ethanol, acetonitrile and chloroform respectively.

Calculation of the quantum yield

$\Phi_x = \Phi_s[A_s/A_x][R_s/R_x][D/D_s]$
Φ= Fluorescence quantum yield
Subscritps x and s denotes test and standard respectively
R = refractive index of the solvent
D = area under the corrected, extrapolated emission spectra.

The synthesis of intermediate 1-(benzyloxy)-4-alkoxybenzenes **3a-e** and 4-(alkoxy) phenols **4a-e** were reported in literature[25,26] and were used here as key intermediates for the synthesis of the new phenylcoumarin-3-carboxylates **6a-j.** The synthesis of coumarin-3-carboxylic acid **5a,b** were reported previously in our laboratory[18]

Typical procedure for synthesis of 4-(octyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate(6a): A mixture of 7-Diethylamino coumarin-3-carboxylic acid **5a** (1 g, 5.25 mmol), 1(3-dimethylaminopropyl-3-ethylcarbodiimide. hydrochloride) (EDCI) (1.1 g, 5.78 mmol) and DMAP (dimethyl amino pyridine, 0.70 g, 5.78 mmol) were taken in dichloromethane. To the reaction mixture, 4-alkoxy phenol **4a** (1.28 g, 5.78 mmol) was added, stirred at room temperature for 5 h and the progress of the reaction was monitored by TLC (ethyl acetate: pet ether, 1:1). After the completion of the reaction, the reaction mass was diluted with water (50 mL) and extracted with DCM (25 mL × 2). The organic layer was washed with saturated brine solution and was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography, by using ethyl acetate: petroleum ether (2:8) as eluent, followed by recrystalization by ethanol to yield 1.78 g of *4-(octyloxy)*phenyl 7-(diethylamino)-2-oxo-2*H*-chromene-3-carboxylate **6a**. Similarly, above procedure was applied for synthesis of phenylcoumarin-3-carboxylates **6b-j** and cyanophenylbenzocoumarin-3-carboxylates **9a-e (**Table 2).

***4-(octyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (*6a):** IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1757(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.39 (d, *J* = 9.20 Hz, 1H), 7.11 (dd, *J* = 2.40, 6.80 Hz, 2H), 6.90 (dd, *J* = 2.00, 6.80 Hz, 2H), 6.63 (dd, *J* = 2.40, 9.00 Hz, 1H), 6.50 (d, *J* = 2.40 Hz, 1H), 3.95 (t, *J* = 6.80 Hz, 2H), 3.44-3.46 (m, 4H), 1.76-1.81 (m, 2H), 1.43-1.47 (m, 2H), 1.32-1.34 (m, 14H), 0.90 (t, *J* = 3.20 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 163.14, 158.79, 158.05, 156.83, 153.24, 150.09, 144.20, 131.32, 122.52, 114.99, 109.68, 107.95, 107.81, 96.80, 68.42, 45.17, 31.82, 29.37, 29.30, 29.24, 26.05, 22.66, 14.10, 12.45 ppm; LCMS *m/z*= 466(M+1). Anal.Calcd. for $C_{28}H_{35}NO_5$ = C, 72.23%, H, 7.58%, N, 3.01% Found: C,72.24%, H,7.59%, N, 3.03%.

***4-(decyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (*6b):** IR(KBr): *v* = 1726(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.91(t, *J* = 8.4 Hz, 2H), 6.71-6.68(m, 1H), 6.55(d, *J* = 1.6 Hz, 1H), 3.95(t, *J* = 6.8 Hz, 2H), 3.50-3.44(m, 4H), 1.81-1.74(m, 2H), 1.47-1.42(m, 2H), 1.32-1.24(m, 18H), 0.878(t, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 162.11, 158.77, 158.07, 156.84, 153.23, 150.08, 144.20, 131.31, 122.51, 114.97, 109.62, 107.90, 107.79, 96.77, 68.41, 45.16, 31.92, 29.70, 29.61, 29.41, 29.35, 29.30, 26.05, 22.67, 14.13, 12.44 ppm; GCMS = 493. Anal.Calcd. for $C_{30}H_{39}NO_5$ C, 72.99%, H, 7.96%, N, 2.84% Found, C, 73.01%, H, 7.95%, N, 2.83%.

4-(dodecyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (6c): IR(KBr): *v* = 1726(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H),7.16-7.12 (m, 2H), 6.94-6.90 (m, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.50-3.44(m, 4H), 1.75-1.82 (m, 2H), 1.42-1.47 (m, 2H), 1.32-1.28 (m, 22H), 0.88

(t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 161.42, 157.31, 155.43, 154.92, 147.92, 143.62, 130.41, 122.13, 121.48, 120.24, 120.11, 115.17, 114.41, 68.49, 31.91, 29.58, 29.40, 29.31, 29.27, 26.05, 22.68, 14.11 ppm; GCMS = 521.2. Anal.Calcd. for $C_{32}H_{43}NO_5$ = C, 73.67%, H, 8.31%, N, 2.68%. Found: C, 73.61%, H, 8.29%, N, 2.66%.

4-(tetradecyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (6d): IR(KBr): *v* = 1725(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.40 (d, *J* = 9.20 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 2H), 6.91 (d, *J* = 2.0 Hz, 2H), 6.64 (dd, *J* = 2.80, 9.00 Hz, 1H), 6.50 (m, 1H), 3.95 (t, *J* = 6.40 Hz, 2H), 3.41-3.50 (m, 4H), 1.77-1.79 (m, 2H), 1.43-1.48 (m, 2H), 1.20-1.23 (m, 26H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm; LCMS *m/z*= 550(M+1). Anal.Calcd. for $C_{34}H_{47}NO_5$ = C, 74.28%, H, 8.62%, N, 2.55% Found: C, 74.10%, H, 8.61%.N, 2.33%.

4-(octadecyloxy)phenyl 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylate (6e): IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.39 (d, *J* = 8.80 Hz, 1H), 7.09-7.12 (m, 2H), 6.88-6.91 (m, 2H), 6.62 (dd, *J* = 2.40, 9.20 Hz, 1H), 6.49 (d, *J* = 2.0 Hz, 1H), 3.94 (t, *J* = 6.40 Hz, 2H), 3.48-3.43(m, 4H), 1.74-1.79 (m, 2H), 1.43-1.47 (m, 2H), 1.23-1.26 (m, 34H), 0.88 (t, *J* = 7.20 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 163.12, 158.78, 158.06, 156.83, 153.24, 150.09, 144.20, 131.33, 122.51, 114.98, 109.69, 107.91, 107.80, 96.78, 68.42, 45.17, 31.93, 29.70, 29.61, 29.42, 29.36, 29.31, 26.06, 22.69, 14.12, 12.45 ppm; LCMS *m/z*= 606(M+1). Anal.Calcd. for $C_{38}H_{55}NO_5$: C, 75.33%, H, 9.15%, N, 2.31% Found: C, 74.98%, H, 9.16%, N, 2.30%.

4-(Octyloxy)phenyl 7-morpholino-2-oxo-2H-chromene-3-carboxylate (6f): IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.46 (d, *J* = 9.20 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 2H), 6.89-6.92 (m, 2H), 6.82 (dd, *J* = 2.40, 8.80 Hz, 1H), 6.68 (d, *J* = 2.40 Hz, 1H), 3.94 (t, *J* = 6.8 Hz, 2H), 3.85 (t, *J* = 4.8 Hz, 4H), 3.40 (t, *J* = 4.8 Hz, 4H), 1.71-1.81 (m, 2H), 1.41-1.47 (m, 2H), 1.23-1.34 (m, 8H), 0.88-0.90 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 162.70, 158.20, 157.52, 156.95, 155.66, 149.92, 144.03, 131.02, 128.71, 122.41, 116.04, 115.58, 114.67, 111.28, 110.79, 109.65, 99.45, 68.44, 66.30, 47.03, 31.82, 29.36, , 26.05, 22.65, 14.09 ppm; GCMS = 480. Anal.Calcd. for $C_{28}H_{33}NO_6$: C, 70.13, H, 6.94%, N, 2.92% Found: C, 70.15%, H, 6.96%, N 2.93%.

4-(decyloxy)phenyl 7-morpholino-2-oxo-2H-chromene-3-carboxylate (6g): IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 7.48 (d, *J* = 8.80 Hz, 1H), 7.27 (s, 2H), 7.11-7.13 (m, 2H), 6.91 (t, *J* = 2.16 Hz, 1H), 6.69 (d, *J* = 2 Hz, 1H), 3.88 (t, *J* = 9.72 Hz, 4H), 3.42 (t, *J* = 9.80 Hz, 4H), 1.79-1.82 (m, 3H), 1.75-1.77 (m, 3H), 1.44-1.46 (m, 12H), 0.89 (t, *J* = 4.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 149.91, 158.22, 131.02, 122.41, 115.42, 115.04, 111.27, 109.67, 115.04, 99.48, 68.70, 68.44, 66.31, 47.03, 31.92, 26.05, 22.69, 14.11 ppm; Anal.Calcd. for $C_{30}H_{37}NO_6$: C, 70.98%, H, 7.35%, N, 2.76% Found: C, 70.99%, H, 7.36% N 2.68%.

***4-(dodecyloxy)phenyl 7-morpholino-2-oxo-2H-chromene-3-carboxylate (6h)*:** IR(KBr): *v* = 1726(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.62 (s, 1H), 7.48 (d, *J* = 9.20 Hz, 1H), 7.13 (d, *J* = 4.00 Hz, 2H), 6.92 (d, *J* = 4.40 Hz, 2H), 6.83 (d, *J* = 4.80 Hz, 2H), 3.88 (t, *J* = 5.20 Hz, 4H), 3.42 (t, *J* = 4.80 Hz, 4H), 1.75-1.80 (m, 3H), 1.46-1.50 (m, 3H), 1.42-1.46 (m, 16H), 0.89 (t, *J* = 1.20 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 158.19, 156.94, 149.86, 131.00, 122.40, 115.02, 111.24, 109.66, 99.47, 68.44, 66.31, 47.04, 31.93, 29.70, 29.41, 29.36, 26.05, 22.69, 14.12 ppm; GCMS = 535 Anal.Calcd. for $C_{32}H_{41}NO_6$: C, 71.75%, H, 7.71%, N, 2.61% Found: C, 71.79%, H, 7.72%, N, 2.62%.

4-(tetradecyloxy)phenyl 7-morpholino-2-oxo-2H-chromene-3-carboxylate (6i): IR(KBr): *v* = 1726(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 2.4Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.9 (s, 1H), 6.83 (d, *J* = 4.0 Hz, 2H), 3.90 (t, *J* = 6.8 Hz, 4H), 3.40 (t, *J* = 6.4 Hz, 4H), 1.75-1.79 (m, 3H), 1.46-1.50 (m, 23H), 0.90 (t,

J = 1.20 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 162.71, 156.86, 149.91, 144.03, 131.02, 128.74, 122.44, 116.04, 115.58, 115.04, 111.30, 110.80, 109.65, 46.69, 44.67, 32.47, 47.04, 31.87, 29.38, 29.28, 29.36, 26.05, 22.69, 14.11 ppm; Anal.Calcd. for $C_{34}H_{45}NO_6$: C, 72.44%, H, 8.05%, N, 2.48% Found: C, 72.45%, H 8.06%, N 2.49%.

4-(octadecyloxy)phenyl 7-morpholino-2-oxo-2H-chromene-3-carboxylate (6j): IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.11 (dd, *J* = 2.40, 6.80 Hz, 2H), 6.90 (dd, *J* = 2.00, 6.80 Hz, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 3.95 (t, *J* = 6.4 Hz, 4H), 3.42 (t, *J* = 4.8 Hz, 4H), 1.74-1.80 (m, 2H), 1.42-1.47 (m, 2H), 1.26-1.32 (m, 30H), 0.88 (t, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 158.21,156.95,149.89, 131.0, 122.41, 115.03, 111.26, 109.67, 99.48, 68.44, 66.31, 47.04, 31.93, 26.05, 22.69, 14.12 ppm; LCMS *m/z*= 620(M+1). Anal.Calcd. for $C_{38}H_{53}NO_6$ = C, 73.63%, H, 8.62%, N, 2.26% Found: C, 73.65%, H, 8.64%, N, 2.27%.

4-cyanophenyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (9a): IR(KBr): *v* = 1722(aromatic C=O) cm^{-1}, 1761(ester C=O) cm^{-1}, ^{1}H NMR(300 MHz, DMSO-d_6): δ 9.74 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.72-7.66(m, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), ^{13}C (100 MHz, DMSO-d_6): 161.07, 156.35, 154.35, 146.81, 137.60, 134.63, 130.38, 129.74, 129.65, 127.16, 123.91, 123.02, 118.83, 117.08, 115.11, 112.55, 109.55, LCMS *m/z* = 342.2(M+1), 343.2(M+1). Anal. Cald. for $C_{21}H_{11}NO_4$,: C, 73.90 %, H%, 3.25%, N, 4.10. Found; C, 73.95%, H, 3.43%, N, 4.10%.

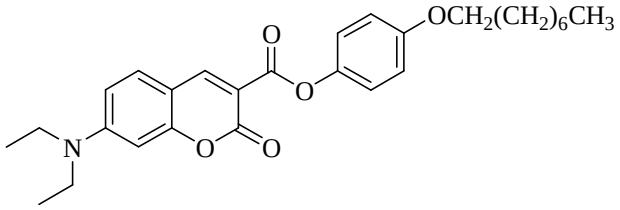
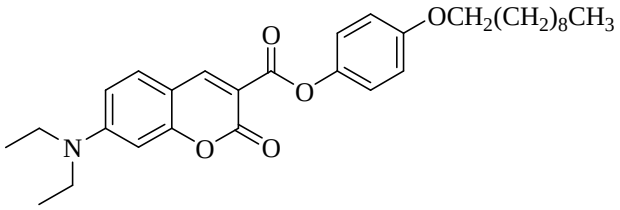
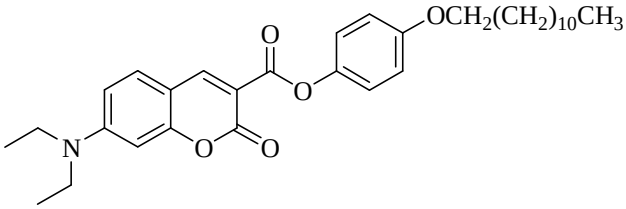
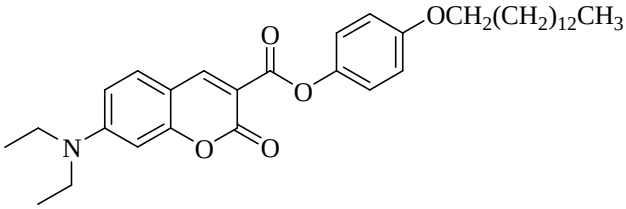
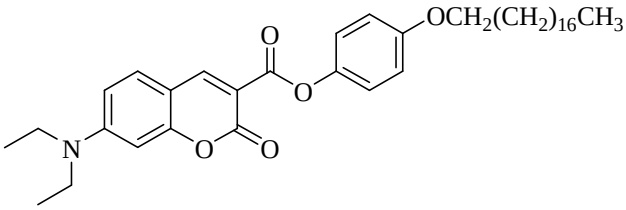
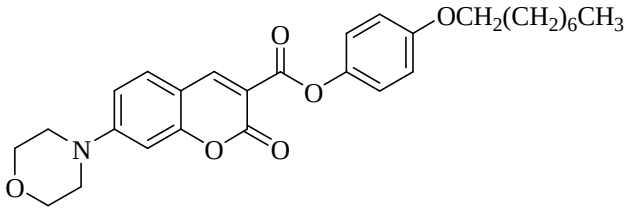
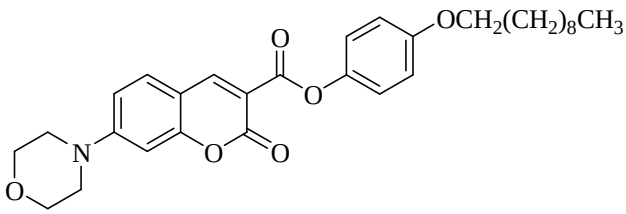
4-cyano-biphyneyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (9b): IR(KBr): *v* = 1732(aromatic C=O) cm^{-1}, 1757(ester C=O) cm^{-1}, ^{1}H NMR(300 MHz, DMSO-d_6): δ 9.55 (s, 1H), 8.38 (d, *J* = 9.2 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.63-7.81 (m, 8H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.41-7.43 (m, 2H), ^{13}C (100 MHz, $CDCl_3$):162.10, 156.60, 151.50, 146.03, 144.70, 137.27, 137.01, 132.68, 130.29, 129.43, 128.44, 127.75, 126.80, 122.44, 121.50, 118.83, 116.73, 115.31, 112.34, 111.18. LCMS, *m/z* = 464(M+1), 465(M+2), 466(M+3).Anal Cald for $C_{27}H_{15}NO_4$: C, 77.61%; H%, 3.62%; N%, 3.36%. Found: C, 77.59%; H, 3.79%; N, 3.30%

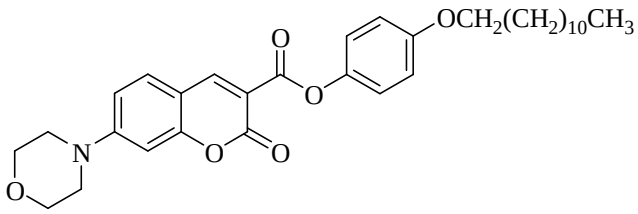
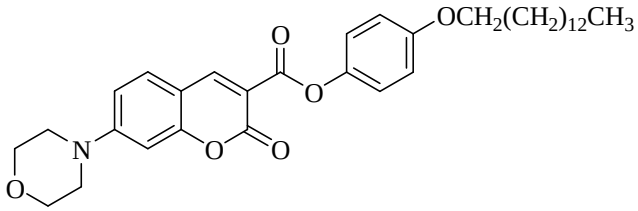
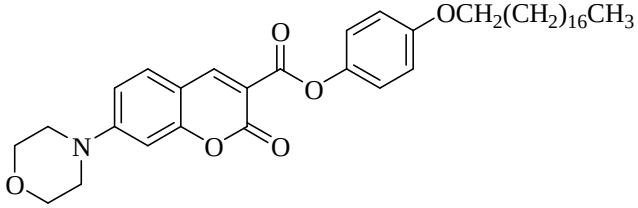
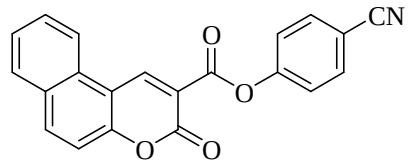
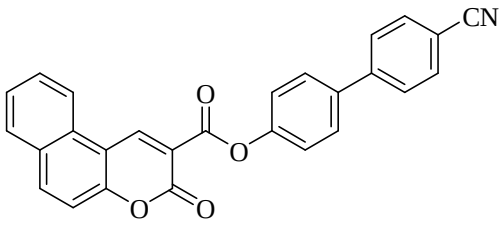
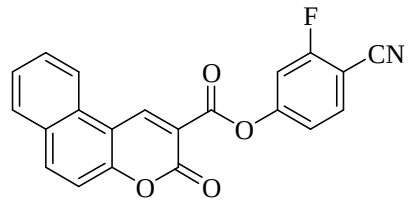
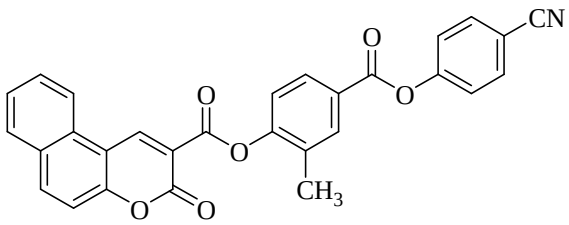
4-cyano-3-fluorophenyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (9c): IR(KBr): *v* = 1732(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}, ^{1}H NMR(400 MHz, DMSO-d_6): δ 9.53 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.80-7.83 (m, 1H), 7.71-7.75 (m, 1H), 7.65-7.67 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.28-7.31 (m, 2H), ^{13}C (100 MHz, $CDCl_3$).161.08, 156.93, 156.19, 146.83, 137.63, 134.19, 130.30, 129.65, 129.49, 126.97, 121.42, 118.79, 116.70, 114.24, 113.36, 112.28, 111.24, 111.01, LCMS, *m/z* = 360(M+1), 361(M+2). Anal. Cald. for $C_{21}H_{10}FNO_4$: C, 70.20%; H%, 2.81%; N, 3.90%, Found, C, 70.40%, H, 2.89%, N, 3.91%.

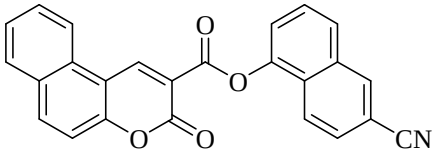
4-((4-cyanophenoxy) carbonyl)-2-methylphynyl 3-oxo-3H-benzo[f]chromene-2-carboxylate (9d): IR(KBr): *v* = 1732(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.11-8.15 (m, 3H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.83 (t, *J* = 7.2 Hz, 1H), 7.67-7.73 (m, 2H), 7.53-7.61 (m, 3H), 2.38(s, 3H), ^{13}C (100 MHz, $CDCl_3$).163.54, 161.48, 155.58, 150.48, 135.22, 133.78, 129.99, 129.87, 128.16, 127.47, 125.15, 123.56, 122.92, 122.20, 117.75, 117.04, 111.24, 111.01, LCMS, *m/z* = 475(M+1). Analysis cal, for $C_{29}H_{17}FNO_6$; C, 73.26%; H, 3.60%; N; 2.95%, Found, C, 73.35%, H, 3.89%, N, 2.91%.

6-cyanonaphthalen-1-yl 3-oxo-3H-benzo[f]chromene-2-carboxylate (9e): IR(KBr): *v* = 1728(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.76 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.67 (s, 1H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.13-8.24 (m, 3H), 8.07 (s, 1H), 7.81-7.87 (m, 2H), 7.66-7.74 (m, 3H). ^{13}C (100 MHz, DMSO-d_6).161.70, 156.43, 156.29, 150.96, 146.57, 137.47, 135.47, 134.78, 130.87, 130.51, 130.38, 129.71, 129.61, 127.65, 127.13, 124.01, 123.01, 119.69, 119.53, 117.08, 115.45, 112.58, 108.89. LCMS, *m/z* = 392(M+1). 393(M+2).Anal. Calcd. for $C_{25}H_{13}NO_4$. C, 76.72%; H, 3.35%; N, 3.58%; Found; C 76.68%, H, 3.38%, N, 3.61%.

Table 2. Physical data of phenylcoumarin-3-carboxylates **6a-j** and cyanophenylbenzocoumarin-3-carboxylates **9a-e**

Entry	Product	Yield (%)*	M. P. (°C)*
6a		94	108-112
6b		90	106-110
6c		94	99-101
6d		97	92-95
6e		93	120-126
6f		97	147-148
6g		83	150-152

6h		87	161-163
6i		89	142-145
6j		95	150-154
9a		93	238-240
9b		88	257-259
9c		78	242-243
9d		95	237-240

9e		81	263-265

* Isolated yield, melting point were uncorrected

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Reference

[1] Ivana, K.; Andrea, J.; Pavol, K. Synthesis of coumarin or ferrocene labeled nucleosides via Staudinger ligation. *Beilstein J, Org. Chem.* **2006**, *2*, No. 23.

[2] Lee, K. S.; Kim, H. J.; Kim, G. H.; Shin, I.; Hong, J. I. Fluorescent chemodosimeter for selective detection of cyanide in water. *Org. Lett*. **2008,** *10(1)*,49-51.

[3] Illiopoulos, K.; Krupka, O.; Gindre, D.; Salle, M. Reversible two-photon optical data storage in coumarin-based copolymers, *J. Am. Chem. Soc*. **2010**, *132*, 14343-14345.

[4] Signore, G.; Nifosi, R.; Albertazzi, L.; Storti, B.; Bizzarri, R. Polarity-sensitive coumarins tailored to live cell imaging. *J. Am. Chem. Soc*. **2010**, *132*, 1276-1288.

[5] Sun, Y. F.; Xu, S. H.; Wu, R. T.; Wang, Z. Y.; Zheng, Z. B.; Li, J. K.; Cui, Y. P. The synthesis, structure and photoluminescence of coumarin-based chromophores. *Dyes and Pigments.* **2010,** *87(2),* 109-118.

[6] Vijila, C.;.Ramalingam, A. Photophysical characteristics of coumarin 485 dye doped poly(methyl methacrylate) modified with various additives. *J. Mat. Chem*. **2001**, *11*, 749-755.

[7] Zhou, S. H.; Jia, J. H.; Gao, J. R.; Han, L.; Li, Y. J.; Sheng, W. J.. The one-pot synthesis and fluorimetric study of 3-(2-benzothiazolyl)coumarins. *Dyes and Pigments*. **2010**, *86*, 123-128.

[8] Moeckli, P. Preparation of some new red fluorescent 4-cyanocoumarin dyes. *Dyes and Pigments.* **1980,** *1*, 3-15.

[9] Kuo, P. Y.; and Yang, D. Y. Design of a coumarin-based triketone as a fluorescent protecting group for primary amines. *J. Org. Chem.* **2008**, *73*, 6455-6458.

[10] Murata, C.; Masuda, T.; Kamochi, Y.; Todoroki, K.; Yoshida, H.; Nohta, H.; Yamaguchi, M.; Takadate, A. Improvement of fluorescence characteristics of coumarins; syntheses and fluorescence properties of 6-methoxycoumarin and benzocoumarin derivatives as novel fluorophores emitting in the longer wavelength region and their application to analytical reagents, *Chem.Pharm. Bull*. **2005,** *53(7),* 750-758.

[11] Rajesha.; Naik, H. S. B.; Kumar, H. N. H.; Hosamani, K. M.; Mahadevan, K. M. Studies on the synthesis and fluorescent properties of long-chained 2-(5-alkyl-1, 3, 4-oxadiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones. *Arkivoc*. **2009**, *(ii)*, 11-19.

[12] Rajesha, G.; Kumar, H. C. K.; Naik, H. S. B.; Mahadevan, K. M. Synthesis of new benzocoumaryl oxadiazolyls as strong blue-green fluorescent brighteners. *S. Afr. J. Chem*. **2011**, *64*, 88-94.

[13] Rajesha, Kiran K.H.C.; Bhojya, N. H. S.; Mahadevan, K. M. Synthesis and fluorescence study of 2-[5-(-2-arylethenyl)-1, 3, 4-oxadiazol-2-yl]-3*H*-benzo[*f*]chromen-3-ones. *Org. Chem. Indian J.* **2012**, *8(1)*, 34-40.

[14] Harishkumar, H. N.; Mahadevan K. M.; Masagalli, J.N. Facile synthesis of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one as blue fluorescent brighteners. *S. Afr. J. Chem*, **2012**, *65*, 5-9.

[15] Harishkumar, H.N.; Hulikal, V. K.; Mahadevan, K. M. Aqueous synthesis of *N*-phenyl/alkyl-2-quinolinone-3-carboxylic acids from coumarin-3-carboxylic acids. *Synth. Commun.* **2010**, *40*, 3281-3289.

[16] Varma, P. P.; Mahadevan, K. M.; Abdul, K.; Vijaykumar, H. One pot synthesis of 2-hydroxy pyrrolidine derivatives. *Org. Commun*. **2011**, *4:3*, 52-57.

[17] Varma, P. P.; Srinivasa, A.; Mahadevan, K. M. Efficient $InCl_3/H_2O$ catalyzed one-pot stereo selective synthesis of *cis*-2-methyl-4-amido-1,2,3,4-tetrahydroquinoline derivatives. *Synth. Commun.* **2011,** *41*, 2186-2194.

[18] Harishkumar, H.N.; Mahadevan, K.M.; Kiran, K. H. C.; Satyanarayan, N. D. A facile, choline chloride/urea catalyzed solid phase synthesis of coumarins via Knoevenagel condensation. *Org. Commun.* **2011**, *4:2*, 26-32.

[19] Harishkumar, H. N.; Mahapatra, S.; Venugopala, K. N.; Mahadevan, K. M. 3-(2-Bromoacetyl)-6-fluoro-2*H*-chromen-2-one. *Acta Cryst*. **2011**, *E67*, 2264.

[20] Rajesha, G. Mahadevan, K. M.; Satyanarayan, N. D.; Naik, H. S. B. Synthesis, antibacterial, and analgesic activity of novel 4-hydroxy-3-(phenylthio)-2*H*-chromen-2-ones and 4-hydroxy-3-[imidazol/tetrazolo-2-yl)thio]-2*h*chromen-2-ones. *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 1733-1743.

[21] Rajesha, Kiran, K. H. C.; Bhojya, N. H. S.; Mahadevan, K. M. Aqueous synthesis of coumarins using tetramethylammonium hydroxide as surfactants. *Org. Chem. Indian J.* **2011**, *7*, 365-368.

[22] Bindu, P. J.; Mahadevan, K. M.; Satyanarayan, N. D.; Naik, T. R. R. Synthesis and DNA cleavage studies of novel quinoline oxime esters. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 898-900.

[23] Bindu, P. J.; Mahadevan, K. M.; Naik, T. R. R. Sm(III)nitrate-catalyzed one-pot synthesis of furano[3,2c]-1,2,3,4-tetrahydroquinolines and DNA photocleavage studies. *J. Mol. Struct.* **2012**, *1020*, 142-147.

[24] Kiran, K. H. C.; Mahadevan, K. M.; Prabhakara, V. P.; Srinivasa, A. One pot synthesis of medicinally important *cis*-2-methyl-4-amino substituted-1,2,3,4-tetrahydroquinoline. *Chin. J. Chem.* **2012**, *30*, 534-540.

[25] Sadashiva, B. K.; Prasad, V. Mesomorphic properties of 1-(4 dodecylbiphenyl-4-yl)-3-(2 or 3 alkoxyphenyl) propane-1,3 diones: The influence of alkoxy substituent position. *J, Chem, Soc. Perkin Trans*, **1996,** *2*, 755-759.

[26] Radhika, S.; Srinivasa, H. T.; Sadashiva, B. K. Anticlinic smetic c phase in new and novel five-ring hockey stick-shaped compounds. *Liq. Cryst.* **2011,** *38*, 785-792 and references cited therein.

[27] Danko, M.; Szabo, E.; Hrdlovic, P. Synthesis and spectral characteristics of fluorescent dyes based on coumarin fluorophore and hindered amine stabilizer in solution and polymer matrices. *Dyes and Pigments*, **2011**, *90*, 129-138 and references cited therein.

[28] Vijila, C. and Ramalingam, A. Photophysical characteristics of coumarin 485 dye doped poly(methyl methacrylate) modified with various additives. *J. Mater. Chem.* **2001**, *11*, 749-755 and references cited therein.

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