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Facile Synthesis of 2-(1,3-Benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one as Blue Fluorescent Brighteners

Hosanagara N. Harishkumar, Kittappa M. Mahadevan* and Jagadeesh N. Masagalli

Department of Post Graduate Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta-577 451, Karnataka, India.

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ABSTRACT

A novel synthetic method was developed to prepare new fluorescent 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one derivatives 3a–p by the Knoevenagel condensation between 2-hydroxy-1-naphthaldehyde and benzothiazole-2-yl-aceatates or *N*-methyl benzoxazole-2-yl-acetates using choline chloride/urea ionic liquid as a green catalyst. The results of fluorescence studies revealed that all the compounds show moderate to low emission intensities and are expressed in the form of quantum yields.

KEYWORDS

Benzooxazolyl-3*H*-benzo[*f*]chromen-3-one, benzothiazolyl-3*H*-benzo[*f*]chromen-3-one, choline chloride/urea, fluorescent brighteners.

1. Introduction

Coumarin dyes exhibit unique photochemical and photophysical properties, which make them useful in applications such as optical brighteners, laser dyes, non-linear optical chromophores, solar energy collectors, fluorescent labels and as two-photon absorption (TPA) materials.[1,2] Coumarin dyes have also been used as blue, green and red dopants in organic light-emitting diodes (OLEDs).[3–6]

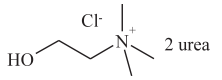
Fluorescent brighteners normally have a system of conjugated double bonds and electron-donating groups that render high efficient fluorescence properties.[7] Typically, coumarin fluorescent dyes contain an electron donor at position-7 and an electron acceptor at position-3.[8] The lasing range covered by coumarin dyes is appreciably extended when they contain a heterocyclic substituent at position-3.[9,10] Further, it is well known that seminaphthofluoresceins (SNAFLs) and naphthofluoresceins have been recognized as annulated derivatives of fluorescein by one or two aromatic ring have longer emission wavelength when compared to fluorescein.[11] Although, the application of various coumarin fluorescent labels has been extensively studied,[12,13] their benzo counterparts, namely benzocoumarins, have been less studied. Recently, Akira *et al.*, reported that coumarins and benzocoumarins coupled with different heterocycles at the 3-position, exhibited strong fluorescent properties.[14]

In our earlier investigation we studied the synthesis and florescent properties of benzocoumarin oxadiazolyl derivatives.[15–17] Kidwai and Kumar[18] have synthesized similar compounds by using 2-hydroxy-1-naphthaldehyde with 5-methyl-1,3,4-thiadiazol-2-ylsulfanyl-, 1*H*-1,2,3,4-tetrazol-1-yl-, 1*H*-indol-3-yl-quinolin-8-yloxy- and 4-methylquinolin-2-yloxy-acetic acids in the presence of DCC–DMSO using microwaves.

On the other hand, with increasing environmental concerns and regulatory constraints, the development of environmentally benign organic reactions has become mandatory. Although several methods have been reported for the synthesis of various benzocoumarin dyes many suffer from disadvantages such as high-temperature requirements, the use of corrosive catalysts, longer reaction times, large solvent volumes, tedious work up methods and often produce low yield. In this context we used choline chloride/urea ionic liquid as the solvent and catalyst. They have gained attention in past few years because of their unique physical and chemical properties.[19–21]

Hence, in view of the above drawbacks and in continuation of our work on the synthesis of fluorescent brighteners[15] and development of new compounds for other applications,[22–29] in this paper we report an environmentally benign one-pot synthesis of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** as new blue fluorescent brighteners by using choline chloride/urea ionic liquid as a green catalyst and as solvent (IL).[19,20]

Structure of choline chloride/urea ionic liquid

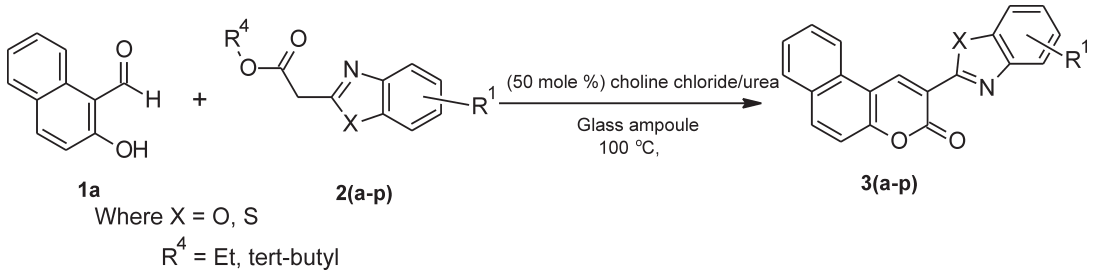


Choline chloride/urea ionic liquid is easy to handle, miscible in water, nonhazardous, and is known to result in faster synthetic transformations. In addition, due to the ionic liquid properties the products can frequently also be isolated more easily. The synthesized products were purified by boiling with MeOH in which the unreacted starting materials dissolve completely and upon filtration, the products were isolated in high purity. Due to the ecofriendly and reusable nature of the catalyst, this procedure is an attractive option compared to existing methods.[32–38]

2. Results and Discussion

2-(1,3-Benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** (Scheme 1, Table 1) were synthesized via two component one-pot reaction of benzoxazol/benzothiazol-2-ylacetate **2a–p** with 2-hydroxy-1-napthaldehyde **1a** in presence of 50 mol% of the choline chloride/urea as catalyst, at reflux temperature on a hot plate for about 1 h. The reaction was quick and immediate product formation was observed in all cases. In

* To whom correspondence should be addressed. E-mail: mahadevan.kmm@gmail.com



Scheme 1
Synthesis of 2-(1,3-benzoxazol/benzothiozol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a-p**.

addition, all the synthesized compounds were confirmed by their spectral data.

Various percentages of choline chloride/urea were employed in order to find out the effective concentration of the catalyst. In our observations 50 mol% of the choline chloride/urea was sufficient for the synthesis of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** with high yields. The increase in the amount of choline chloride/urea to 70 mol%, 90 mol% and 100 mol%, made only marginal differences in the yield and the reaction time. Hence, 50 mol%, choline chloride/urea was used in the synthesis of all compounds **3a–p**. Further, the catalyst was recovered by removing water under reduced pressure and reused three times without any reduction in catalytic activity was noted. It was also observed that the electron-withdrawing group present in benzothiazole-2-yl-acetates and *N*-methyl benzoxazole-2-yl-acetates gave low yields, whereas electron-donating groups yielded more than 90 % with high purity of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo [*f*]chromen-3-ones **3a–p** (Table 1).

2.1. Fluorometric Properties

Absorption spectra of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** were recorded in chloroform and the results of fluorescence studies were expressed in terms of Stoke's shift and quantum yields as shown in Table 1. Zhou *et al.*[8] reported that the fluorescent properties of 3-(2′-benzothiazolyl) coumarins, having electron donor substituents on the 7-position, resulted in red shifts of the fluoresence. A strong intramolecular charge transfer chromophoric system has also been observed in 2-(1,3-benzoxazol/benzotiazol-2-yl)-3*H*-benzo [*f*]chromen-3-one derivatives, where the benzocoumarin ring acts as a donor, while substituents like benzothiazole or benzoxazole moieties in the 3-position act as acceptor groups. The presence of an additional benzene ring in the benzocoumarin structure furthermore enhances the pi conjugation from the donor to the acceptor, with the result that a large red shift with broad emission peaks at 440–570 nm is observed.[8] In addition, the quantum yields reveal that all the synthesized compounds show moderate to low emission intensities with no marked variations. Finally, from Fig. 1 it is evident that varying the substituent on the benzoxazole and benzothiazole rings at the 3-position did not have any significant influence on quantum yields or λ_{max} properties of the fluorphores.

3. Conclusion

In conclusion, we have demonstrated an efficient and new approach to two component, one-pot synthesis of 2-(1, 3-benzoxazol/benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one derivatives **3a–p** by the reaction of benzoxazol-2-ylacetate/benzothiazol-2-ylaceatate with 2-hydroxy-1-napthaldehyde in presence of choline chloride/urea ionic liquid as catalyst. This method offers advantages over the existing approaches in terms of its efficiency, simplicity and milder reaction conditions. All synthesized compounds are fluorescent in solution with moderate quantum yields that show emission responses in the blue region of the spectrum.

4. Experimental

All the chemicals used were of analytical grade. Melting points were recorded in open capillary and are uncorrected. Purity of

Table 1 Reaction time, yield and melting points of 2-(1,3-benzoxazol/benzothiozol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p**.

Entry	R^1	X	Time/min	Yield/%	Mp/°C (lit. mp)
3a	H	O	30	98	249–250 (263–264)
3b	5-methyl	O	35	93	241–242
3c	6-methyl	O	45	96	251–252
3d	5-chloro	O	30	95	292–293
3e	6-chloro	O	35	96	244–245
3f	5-fluoro	O	45	90	290–291
3g	5-NO_2	O	30	85	280–283
3h	6-NO_2	O	45	75	294–295
3i	6-trifluoromethyl	S	30	90	286–287
3j	5-trifluoromethoxy	S	35	92	211–212
3k	5-trifluoromethyl	S	45	96	285–287
3l	4-chloro	S	30	97	297–298
3m	5,6-difluoro	S	40	90	313–314
3n	6-trifluoromethoxy	S	45	97	245–249
3o	5-cyano	S	30	85	298–299
3p	5-methyl, 6-fluoro	S	45	75	252–255

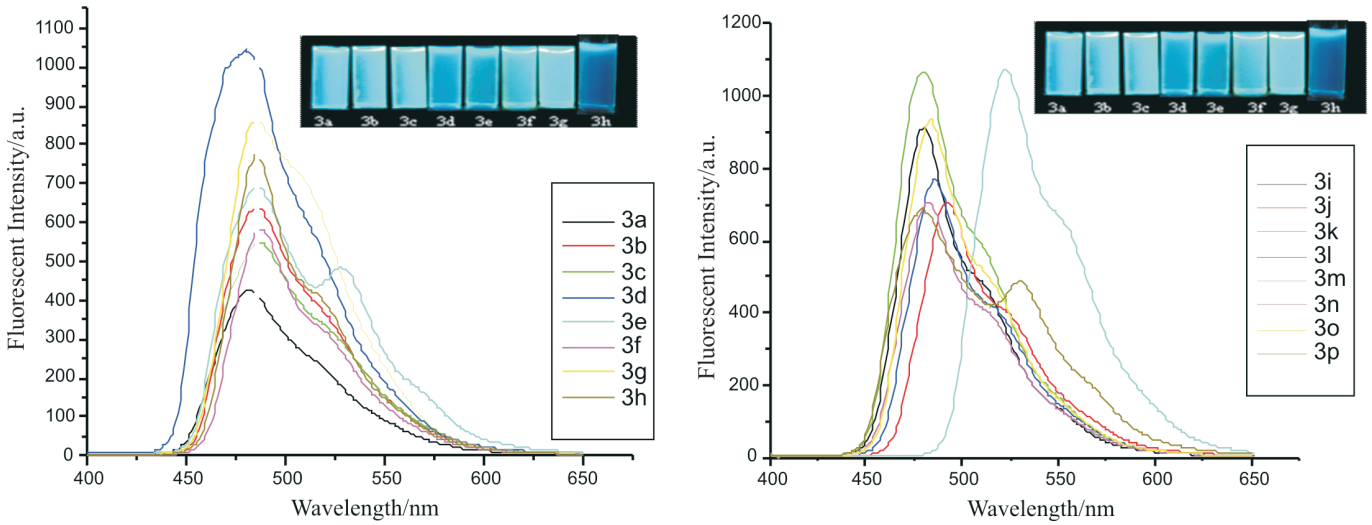


Figure 1 Fluorescence spectra of 2-(1,3-benzoxazol/benzothiozol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** in chloroform at concentration 1 mg mL^{-1}.

Table 2 Spectral characterization of 2-(1,3-benzoxazol/benzothiozol-2-yl)-3*H*-benzo[*f*]chromen-3-ones **3a–p** in chloroform (λ_{ex}: excitation wavelength in nm; λ_{em}: emission wavelength in nm; θ_F: quantum yield).

Entry	λ_{ex}	λ_{em}	$\Delta\nu$/cm^{-1}	Φ_F
3a	400	482	4260	0.0102
3b	401	486	4360	0.0067
3c	400	486	5000	0.0075
3d	400	486	5000	0.0065
3e	411	486	3830	0.0080
3f	401	488	4500	0.0063
3g	400	484	5000	0.0056
3h	400	487	5000	0.0056
3i	411	481	4000	0.0036
3j	411	482	4000	0.0038
3k	410	480	3500	0.0052
3l	414	485	3500	0.0040
3m	411	482	3600	0.0029
3n	411	482	3600	0.0043
3o	411	484	3700	0.0035
3p	414	478	3200	0.0058

the compounds was checked by TLC on silica gel and purified by recrystallization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 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 were recorded on a JEOL SX 102/DA-6000 (10 kV) FAB mass spectrometer. Elemental analysis was obtained on an 'Elementary vario EL-III instrument'. Fluorescent spectra (Hitachi F-7000 Spectrofluorometer) were recorded by dissolving compounds in chloroform at a concentration of 1 mg mL^{-1}. The excitation wavelength was fixed at the valued obtained from the UV-Visible spectra.

Benzothiazole-2-yl-aceatates and *N*-methyl benzoxazole-2-yl-aceatates were prepared according to literature methods.[30,31] The ^{13}C NMR spectra of some of the products such as **3b**, **3d**, **3e**, **3f**, **3g**, **3h** were not produced due to their low solubility, even in DMSO-d_6.

4.1. Synthesis of:

2-(1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen- 3-one **3**

A mixture of 2-hydroxy-1-naphthaldehyde (5.81 mmol, 1 g) **1a**, an equivalent amount of ethyl 1,3-benzoxazol-2-ylacetate (5.81 mmol, 1.19 g) **2a**, and choline chloride/urea (50 mol%, 0.75 g) was taken in glass ampoule and was heated on a hot plate. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature and poured into crushed ice with stirring. The precipitate thus obtained was filtered, washed with water, and recrystallized using ethanol to get pure **3a**. The other benzocoumarin derivatives were prepared similarly.

2-(1,3-Benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3a)

m.p. 249–250 °C, yield 98 %, IR (KBr): ν = 3086 (ArCH), 1714 (C=O), 1624 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.64 (s, 1H), 8.72 (d, J = 8.40 Hz, 1H), 8.34 (d, J = 9.04 Hz, 1H), 8.11 (d, J = 7.96 Hz, 1H), 7.83 (m, 3H), 7.66 (m, 2H), 7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 159.10, 156.49, 155.11, 150.62, 142.20, 141.69, 136.23, 130.43, 129.52, 129.41, 127.00, 126.57, 125.56, 122.94, 120.54, 117.02, 113.70, 113.06, 111.49 ppm; MS: m/z = 314.3 (m+1), 315.3 (m+2). Anal. Calcd. for $C_{20}H_{11}NO_3$ = C,76.67; H, 3.54; N, 4.47 % Found: C, 76.69; H, 3.82; N, 4.42 %.

2-(5-Methyl-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3b)

m.p. 241–242 °C, yield 93 %, IR(KBr): ν = 3075 (ArCH), 1730 (C=O), 1603 (C=C), ^{1}H NMR(400 MHz, CD_3OD): δ = 9.68 (s, 1H), 8.63 (d, J = 8.40 Hz, 1H), 8.27 (d, J = 9.24 Hz, 1H), 8.05 (d, J = 7.72 Hz, 1H), 7.84 (t, J = 7.76 Hz, 1H), 7.57–7.69 (m, 4H), 7.32 (d, J = 8.48 Hz, 1H), 2.51 (s, 3H). MS: m/z = 328 (m+1), 329 (m+2). Anal.Calcd. for $C_{21}H_{13}NO_3$= C,77.06; H,4.0; N, 4.28 Found: C,77.03; H, 4.02; N, 4.30 %.

2-(6-methyl-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3c)

m.p. 251–252 °C, yield 96 %, IR(KBr): ν = 3080 (ArCH), 1736 (C=O), 1605 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.62 (s, 1H), 8.71 (d, J = 8.52 Hz, 1H), 8.34 (d, J = 10.36 Hz, 1H), 8.12 (d, J = 7.92 Hz, 1H), 7.82 (t, J = 8.24 Hz, 1H), 7.63–7.65 (m, 3H), 7.38 (t, J = 7.96 Hz, 1H), 7.27 (d, J = 7.44 Hz, 1H), 2.63 (s, 3H) ppm; ^{13}CNMR (100 MHz, DMSO-d_6): 158.36, 155.04, 150.41, 142.01, 140.99, 136.13, 130.71, 130.46, 129.56, 129.51, 129.41, 127.02, 126.30, 125.85, 122.98,117.05.113.96, 113.09. 108.73,16.78 ppm; MS: m/z = 328 (m+1). Anal.Calcd. for $C_{21}H_{13}NO_3$ = C, 77.06; H, 4.0; N, 4.28 % Found: C, 77.03; H, 4.03; N, 4.30 %.

2-(5-Chloro-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3d)

m.p. 292–293 °C, yield 95 %, IR (KBr): ν = 3060 (ArCH), 1714 (C=O), 1579 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.71 (s, 1H), 8.75 (d, *J* = 8.00 Hz, 1H), 8.39 (d, *J* = 9.20 Hz, 1H), 8.14 (d, *J* = 8.16 Hz, 1H), 8.03 (s, 1H), 7.92 (d, *J* = 8.64 Hz, 1H), 7.84 (m, 1H), 7.71 (t, *J* = 8.56 Hz, 2H), 7.55 (d, *J* = 14.92 Hz, 1H). MS: m/z = 348 (m+1), 350 (m+2). Anal.Calcd. for $C_{20}H_{10}ClNO_3$ = C, 69.08; H, 2.90; N, 4.03 % Found: C, 70.33; H, 3.45; N, 3.96 %.

2-(6-Chloro-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3e)

m.p. 244–245 °C, yield 96 %, IR(KBr): ν = 3060 (ArCH), 1730 (C=0), 1605 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.67(s, 1H), 8.72 (d, *J* = 7.12 Hz, 1H), 8.37 (d, *J* = 9.04 Hz, 1H), 8.13 (d, *J* = 8.00 Hz, 1H), 8.07 (s, 1H), 7.92 (d, *J* = 8.48 Hz, 1H), 7.84 (t, *J* = 7.64 Hz, 1H), 7.70 (t, *J* = 9.20 Hz, 2H), 7.55 (d, *J* = 1.40 Hz, 1H) ppm; MS: m/z = 348 (m+1), 350 (m+2). Anal.Calcd. for $C_{20}H_{10}ClNO_3$= C, 69.08; H, 2.90; N, 4.03 % Found: C, 69.05; H, 2.98; N, 4.00 %.

2-(5-Fluoro-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3f)

m.p. 290–291 °C, yield 90 %, IR(KBr): ν = 3080 (ArCH), 1736 (C=O), 1605 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.69 (s, 1H), 8.74 (d, *J* = 8.08 Hz, 1H), 8.38 (d, *J* = 8.64 Hz, 1H), 8.14 (d, *J* = 8.04 Hz, 1H), 7.91 (t, *J* = 4.24 Hz, 1H), 7.82 (dd, *J* = 8.28, 21.96 Hz, 2H), 7.54 (t, *J* = 8.52 Hz, 2H), 7.38 (t, *J* = 9.36 Hz, 1H) ppm; MS: m/z = 332 (m+1), 333 (M+2). Anal.Calcd. for $C_{20}H_{10}NO_3$= C, 72.51; H, 3.04; N, 4.23 % Found:C, 73.33; H, 3.28; N, 4.30 %.

2-(5-nitro-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3g)

m.p. 280–283 °C, yield 85 %, IR(KBr): ν = 3055(ArCH), 1736(C=O), 1615 (C=C), ^{1}H NMR(400 MHz, DMSO-d_6): δ = 9.80 (s, 1H), 8.42 (d, *J* = 9.32 Hz, 1H), 8.13 (d, *J* = 8.64 Hz, 2H), 7.90 (m, 2H), 7.86 (t, *J* = 7.88 Hz, 1H), 7.75 (d, *J* = 14.80 Hz, 1H), 7.45 (m, 2H) ppm; MS: m/z = 359 (m+1). Anal.Calcd. for $C_{20}H_{10}N_2O_5$= C, 67.04; H, 2.81; N, 7.82 %. Found: C, 67.08; H, 2.82; N, 7.86 %.

2-(6-nitro-1,3-benzoxazol-2-yl)-3*H*-benzo[*f*]chromen-3-one(3h)

m.p. 294–295 °C, yield 75 %, IR (KBr): ν = 3060 (ArCH),1708 (C=O), 1602 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.75 (s, 1H), 8.74 (d, *J* = 9.84 Hz, 1H), 8.67 (d, *J* = 7.88 Hz, 1H), 8.12 (t, *J* = 5.96 Hz, 3H), 7.84 (t, *J* = 7.00 Hz, 2H), 7.69 (d, *J* = 8.56 Hz, 2H) ppm; MS: m/z = 359 (m+1). Anal.Calcd. for $C_{20}H_{10}N_2O_5$= C, 67.04; H, 2.81; N, 7.82 % Found: C, 66.72; H, 3.08; N, 7.68 %.

2-[6-(Trifluoromethyl)-1,3-benzothiazol-2-yl]-3*H*-benzo[*f*]chromen-3-one (3i)

m.p. 286–287 °C, yield 90 %, IR (KBr): ν = 3060 (ArCH), 1714 (C=O), 1652 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.84 (s, 1H), 8.69 (d, *J* = 7.96 Hz, 2H), 8.35 (dd, *J* = 8.6 Hz, 21.68 Hz, 2H), 8.29 (d, *J* = 8.60 Hz, 1H), 8.11 (d, *J* = 8.04 Hz, 1H), 7.82–7.88 (m, 2H), 7.69 (t, *J* = 16.56 Hz,2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 163.80, 159.36, 154.06, 138.11, 136.26, 135.85, 130.06, 129.16, 129.03, 126.68, 125.48, 123.23, 122.40, 120.56, 117.90, 116.53, 113.03 ppm; MS: m/z = 398 (m+1), 399 (m+2). Anal.Calcd. for $C_{21}H_{10}F_3NO_2S$=C, 63.47; H, 2.54; N, 3.52 % Found: C, 63.44; H, 2.55; N, 3.50 %.

2-[5-(Trifluoromethoxy)-1,3-benzothiazol-2-yl]-3*H*-benzo[*f*]chromen-3-one (3j)

m.p. 211–212 °C, yield 98 %, IR (KBr): ν = 3032 (ArCH), 1706 (C=O), 1605 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.83 (s, 1H), 8.71 (d, *J* = 8.48 Hz, 1H), 8.36 (d, *J* = 9.12 Hz, 2H), 8.24 (d, *J* = 8.92 Hz, 1H), 8.13 (d, *J* = 7.96 Hz, 1H), 7.84 (dd, *J* = 1.16, Hz, 15.32 Hz 2H), 7.68–7.73 (m, 2H), 7.59 (dd, *J* = 1.76, Hz,8.88 Hz 1H) ppm; ^{13}CNMR (100 MHz, *DMSO*-d_6): 162.38, 154.43, 151.29, 138.11, 137.61, 136.09, 130.59, 129.62, 129.54, 127.15, 124.37, 122.93, 121.02, 118.60, 117.05, 113.58 ppm; MS: m/z = 414.3 (m+1), 415.3 (m+2). Anal.Calcd. for $C_{21}H_{10}F_3NO_3S$=C, 61.02; H, 2.44; N, 3.39 % Found: C, 61.19; H, 3.55; N,3.10 %.

2-[5-(Trifluoromethyl)-1,3-benzothiazol-2-yl]-3H-benzo[*f*]chromen-3-one (3k)

m.p. 285–287 °C, yield 96 %, IR (KBr): ν = 3010 (ArCH), 1707 (C=O), 1602 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.90 (s, 1H), 8.72 (d, *J* = 8.52 Hz, 1H), 8.49 (d, *J* = 7.32 Hz, 2H), 8.40 (d, *J* = 9.08 Hz, 1H), 8.16 (d, *J* = 8.00 Hz, 1H), 7.83 (m, 2H), 7.74 (dd, *J* = 7.68 Hz,14.04 Hz 2H) ppm; ^{13}CNMR (100 MHz, DMSO-d_6): 162.36, 159.90, 154.43, 152.02, 140.04, 138.09, 135.49, 130.51, 129.56, 129.24, 129.11, 126.80, 122.49, 122.08, 121.55, 120.06, 118.42, 116.62, 113.54 ppm; MS: m/z = 398. (m+2), 399 (m+2). Anal.Calcd. for $C_{21}H_{10}F_3NO_2S$=C, 63.47; H, 2.54; N, 3.52 % Found:C, 63.46; H, 2.56; N, 3.57 %.

2-(4-Chloro-1,3-benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3l)

m.p. 297–298 °C, yield 97 %, IR (KBr): ν = 3072 (ArCH), 1706 (C=O), 1604 (C=C), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 8.60 (d, *J* = 8.44 Hz, 1H), 8.13 (d, *J* = 9.00 Hz, 1H), 7.97 (d, *J* = 7.96 Hz, 1H), 7.9 (t, *J* = 0.64 Hz, 1H), 7.8 (dd, *J* = 0.92 Hz, 11.3 Hz, 1H), 7.66 (t, *J* = 7.28 Hz, 1H), 7.56–7.59 (m, 1H), 7.37 (t, *J* = 7.84 Hz 2H) ppm; ^{13}C NMR (100 MHz, *DMSO*-d_6): 156.29, 155.24, 149.57, 144.84, 133.56, 133.26, 130.54, 125.76, 124.77, 124.41, 124.25, 123.08, 122.00, 121.92, 121.04, 117.53, 115.62, 113.84, 111.86, 108.80 ppm; MS: m/z = 364 (m+1). Anal.Calcd. for $C_{20}H_{10}ClNO_2S$=C, 66.03; H, 2.77; N, 3.85 % Found: C, 66.05; H, 2.70; N, 3.80 %.

2-(5,6-Difluoro-1,3-benzothiazol-2-yl)-3*H*-benzo[*f*]chromen-3-one (3m)

m.p. 313–314 °C, yield 90 %, IR (KBr): ν = 3050 (ArCH), 1706 (C=O), 1620 (C=C), ^{1}H NMR (400 MHz, , DMSO-d_6): δ = 9.64 (s,1H) 8.74 (d, *J* = 7.60 Hz, 1H), 8.36 (d, *J* = 8.72 Hz, 1H), 8.13 (d, *J* = 7.52 Hz, 1H), 7.82 (s, 1H), 7.69 (m, 3H), 7.32 (d, *J* = 6.80 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 159.17,155.08, 148.91, 142.03, 141.94, 136.16, 135.03, 130.45, 129.52, 127.64, 127.02, 122.99, 120.24, 117.05, 113.84, 113.11, 110.90 ppm; MS: m/z = 366 (m+1), 367.3 (m+2). Anal.Calcd. for $C_{20}H_9F_2NO_2S$ = C, 65.75; H, 2.48; N, 3.83 % Found: C, 65.70; H, 2.49; N,3.81 %.

2-[6-(Trifluoromethoxy)-1,3-benzothiazol-2-yl]-3*H*-benzo[*f*]chromen-3-one (3n)

m.p. 245–249 °C, yield 97 %, IR (KBr): ν = 3020 (ArCH), 1709 (C=O), 1610 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.88 (s, 1H), 8.76 (d, *J* = 8.60 Hz, 1H), 8.39 (d, *J* = 9.16 Hz, 2H), 8.27 (d, *J* = 8.88 Hz, 1H), 8.16 (d, *J* = 8.28 Hz, 1H), 7.87 (t, *J* = 8.36 Hz, 1H), 7.71–7.77 (m, 2H), 7.62 (d, *J* = 8.00 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 162.32, 159.86, 154.40, 151.26, 145.91, 138.04, 137.60, 136.07, 130.57, 129.59, 129.51, 127.1 3, 124.34, 122.88, 120.97, 118.55, 117.01, 115.59, 113.54, 56.49, 19.02 ppm; MS: m/z = 414 (m+1). Anal.Calcd. for $C_{21}H_{10}F_3NO_3S$=C, 61.02; H, 2.44; N, 3.39 % Found: C, 61.08; H, 2.45; N, 3.40 %.

2-(3-Oxo-3*H*-benzo[*f*]chromen-2-yl)-1,3-benzothiazole-5-carbonitrile (3o)

m.p. 298–299 °C, yield 85 %, IR (KBr): ν = 3080 (ArCH), 1716

(C=O), 1652 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.82 (s, 1H), 8.78 (s, 1H), 8.42 (d, J = 8.28 Hz, 1H), 8.37 (d, J = 8.80 Hz, 1H), 8.26 (d, J = 8.28 Hz, 1H), 8.12 (d, J = 8.04 Hz, 2H), 7.95 (d, J = 7.88 Hz, 1H),7.85(d, J = 7.52 Hz, 2H) ppm; ^{13}C.(100 MHz, DMSO-d_6): 163.80, 159.36, 154.06, 138.11, 136.26, 135.85, 130.06, 129.16, 129.03, 126.68, 125.48, 123.23, 122.40, 120.56, 117.90, 116.53, 113.03 ppm; MS: (m/z) = 355 (M+1), 356 (M+2). Anal.Calcd. for $C_{21}H_{10}N_2O_2S$=C, 71.17; H, 2.84; N, 7.90 % Found: C, 70.45; H, 2.91; N, 7.83 %.

2-(6-Fluoro-5-methyl-1,3-benzothiazol-2-yl)-3*H*-benzo[*f*] chromen-3-one (3p)

m.p. 252–255 °C, yield 75 %, IR (KBr): ν = 3065 (ArCH), 1760 (C=O), 1607 (C=C), ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.71 (s, 1H), 8.65 (d, J = 8.24 Hz, 1H), 8.32 (d, J = 9.00 Hz, 1H), 8.11 (d, J = 8.04 Hz, 1H), 7.99 (dd, J = 9.4 Hz,16.62 Hz, 2H), 7.83 (t, J = 15.44 Hz, 1H), 7.69 (t, J = 8.84 Hz, 2H), 2.37 (s, 3H) ppm; MS: (m/z) = 362 (m+1). Anal.Calcd. for $C_{21}H_{12}FNO_2S$=C, 69.79; H, 3.35; N, 3.38 % Found: C, 69.15; H, 3.31; N, 3.81 %.

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