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ORIGINAL ARTICLE

Green Synthesis, Characterization and Electrochemical Behavior of New Thiazole Based Coumarinyl Scaffolds

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Abstract The present paper deals with the synthesis of thiazolo-coumarin derivatives, prepared starting from naphthaldehyde, ethyl acetoacetate and hydrazine in three steps and characterized by spectroscopic analysis. UV-Visible spectra of the compounds was carried out in different solvents DMF, ethanol, methanol, ethyl acetate and acetone and the absorption was observed in the range 338–390 nm. Electrochemical study of thiazoles was conducted in DMF and redox behavior was examined. Fluorescence carried out in ethanol showed sharp emission in the range 440–505 nm.

Keywords Thiazole · Coumarin · Absoption · Emisssion

Introduction

A plethora of literature is available regarding the bioactive nature of coumarins derivatives [1–5]. Installation of thiazole motif to coumarins nucleus further leads to various bioactivities such as antiinflammatory, analgesic, antimicrobial, anti-HIV, antihypertensive and herbicidal activity [6–9]. Coumarins possess a double bond in trans conformation which furnishes strong fluorescence and high fluorescence quantum yield and photostability to coumarin derivatives [11] with the view to highlight this behavior, some thiazole based coumarin scaffolds has been synthesized and they have been passed through the shower of studies (i.e. Cyclic voltammetry, Ultraviolet, and Fluorescence) [12]. It was indicated in the late 1950s that substitutions on the coumarin structure shifted the fluorescence band, electron donating groups when attached at 4 or 7 position bring a bathochromic shift. Addition of electron-repelling groups at the 4-, 6-, or 7-position or electron-attracting groups in the 3-position shift the fluorescence band to longer wavelengths. Changing the solvent or the solution pH also affected the fluorescence spectra [10].

A survey of literature reveals that thiazole based coumarinyl scaffolds show various biological activities [7, 8, 9]. All the synthesized compounds were passed through intelligent eyes having tools to visualize the electrochemical behavior and florescence phenomena and results obtained were highly encouraging. Herein we report a green reaction of thiosemicarbazone (**2a–j**) with 3-bromoacetyl-(6-substituted)coumarin (1) in dry ethanol using silica sulfuric acid catalyst to afford a series of thiazole derivatives appended to coumarin.

Research Highlights:
- Facile synthesis of new thiazole based coumarinyl derivatives has been accomplished.
- Thiazole based coumarinyl derivatives have been found to be highly fluorescent.
- Coumarinyl derivatives exhibited absorptions in the range 338–390 nm.

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Experimental

Apparatus, Reagents and Chemicals

All commercial products were purchased from Sigma-Aldrich. Solvents used were of analytical grade and, when necessary, were purified and dried by the standard methods. Melting points were determined in open capillary tubes on a Stuart melting point apparatus. The IR spectra were run on the

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single beam Nicolet IR 100 (Fourier-Transform); while UV of all the samples were run in water using UV-Genesys spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in DMSO-d_6 using NMR Bruker DPX 300 spectrophotometer operating at 300 MHz TMS was used as internal standard with the deuterium signal of the solvent as the lock and chemical shifts δ recorded in ppm. The elemental analysis (C, H, N, S) of the compounds were performed using Flash EA 1112 elemental analyzer. Compounds were routinely checked by TLC on silica gel G plates using eluting solvents, pet ether: ethyl acetate (7: 3, *v*/v). Also, the developed plates were visualized using a UV lamp for the presence of spots and R_f values were duly calculated.

General Procedure of Synthesis

To a cold mixture of 2-hydroxy-1-naphthalaldehyde (0.1 mol) and ethylacetoacetate (0.1 mol, 12.63 ml) was added 1 g (1.12 ml) of piperdine by the rapid shaking. The solid separated was filtered and washed with ethanol. Crystallization of the solid from pure water provided pure 2-acetyl-3*H*-benzo[f]chromen-3-one. A solution of bromine (0.01 mol, 1.72 g) in chloroform was added by rapidly shaking to a solution 2-acetyl-3*H*-benzo[f]chromen-3-one (0.01 mol, 2.38) in chloroform. The mixture was heated under reflux for 2–3 h and then slowly cooled. The solid separated was crystallized from chloroform–ethanol (2:1) to get pure 2-(2-bromoacetyl)-3*H*-benzo[f]chromen-3-one (3) (0.001 m). The latter was dissolved in 30 mL of ethanol in a round bottom flask fitted with a reflux condenser, and added 0.001 m of KSCN and stirred further at 45–50 °C. After 1 h, suitably substituted aniline (0.0012 m) was added and the reaction mixture was refluxed and the progress of the reaction was monitored by TLC. After 4–5 h, the solid product was obtained either by cooling the reaction mixture or by pouring it into ice-cold water. The solid separated was purified by recrystallization in ethanol. In this way a series of derivatives **5a-j** were synthesized.

2-(2-(Mesitylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 238 °C, Yield =69 %, R_f = 0.68 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3380 (N-H), 1712, 1728 (C = O), 3080, 2972, 2952(CH str). 2851 (methyl C–H str), 1510 (C = N str), 1492 (C = C str); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.22(s, 1H, CH), 7.32–8.44 (m, 6H, Ar-H), 7.32 (s, 2H, Ar-H), 9.33(s, 1H, benzocoumarin H-4). 11.92 (s, 1H, NH), 2.39 (s, 3H), 2.21 (s, 6H Ar 2× CH_3); ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 169.3, (C = O), 159.18, (C = N), 152.2 (C = C), 144.8, 137.1, 136.4, 135.8, 134.1, 133.2, 130.5, 129.7, 129.5, 129.1, 128.9, 126.5, 121.9, 120.1, 116.9, 113.6109.16.} (Ar-C), 21.58 (CH_3), 18.27 ($2CH_3$),

2-(2-(2,4-Dimethylphenylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 268 °C, Yield =73 %, R_f = 0.65 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3370 (N-H), 1715, 1738 (C = O), 3060, 2962, 2952(CH str). 2951 (methyl C–H str), 1512 (C = N str), 1495 (C = C str); ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm): 7.23(s, 1H, CH), 7.22–8.42 (m, 6H, Ar-H), 6.9–7.39 (m, 3H Ar-H), 9.23(s, 1H, benzocoumarin H-4). 11.72 (s, 1H, NH), 2.49 (s, 3H), 2.21 (s, 6H Ar 2× CH_3); ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 168.3, (C = O), 158.18, (C = N), 153.2 (C = C), 144.8, 137.1, 136.4, 135.8, 134.1, 133.2, 130.5, 129.7, 129.5, 129.1, 128.9, 126.5, 121.9, 120.1, 116.9, 113.6111.9, 110.5109.1 (Ar-C), 21.54 (CH3), 18.24 (CH3),

2-(2-(2-Chlorophenylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 234 °C, Yield =72 %, R_f = 0.67 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3372 (N-H), 1729 (C = O), 3070, 2962, 2942(CH str). 1511 (C = N str), 1494 (C = C str); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.24 (s, 1H, CH), 7.34–8.42 (m, 6H, Ar-H), 7.75–6.92 (m, 4H, ArH), 9.53(s, 1H, benzocoumarin H-4). 10.92 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 167.3, (C = O), 157.18, (C = N), 150.2 (C = C), 145.8, 143.8, 142.8, 136.1, 135.4, 134.8, 134.2, 133.5, 130.2, 129.5, 129.4, 129.2, 128.7, 124.5, 122.9, 121.1, 117.9, 114.6, 108.1 (Ar-C).

2-(2-(3-Nitrophenylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 248 °C, Yield =77 %, R_f = 0.63 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3378 (N-H), 1727 (C = O), 3071, 2962, 2922(CH str). 1511 (C = N str), 1494 (C = C str); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.20(s, 1H, CH), 7.32–8.32 (m, 6H, Ar-H), 7.89–7.32 (m, 4H, ArH), 9.33(s, 1H, benzocoumarin H-4). 10.55 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 166.3, (C = O), 158.18, (C = N), 152.2 (C = C), 150.8, 144.8, 143.8, 137.1, 134.4, 133.8, 132.2, 131.5, 130.4, 128.5, 128.7, 128.4, 127.7, 123.5, 122.4, 120.1, 114.9, 114.6, 107.1 (Ar-C),

2-(2-(4-Bromophenylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 229 °C, Yield =76 %, R_f = 0.60 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3388 (N-H), 1737 (C = O), 3071, 2972, 2932(CH stretch-ing). 1531 (C = N str), 1493 (C = C str); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.22(s, 1H, CH), 7.32–8.32 (m, 6H, Ar-H), 7.66

(d, 2H, *J* = 7.7 Hz ArH), 7.43(d,2H, *J* = 7.7 Hz ArH) 9.30(s, 1H, benzocoumarin H-4). 11.55 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 167.3, (C = O), 159.18, (C = N), 154.2 (C = C), 152.8, 145.8, 144.8, 138.1, 135.4, 134.4, 133.2, 131.5, 130.3, 129.4, 129.3, 128.2, 127.8, 123.6, 122.5, 121.1, 116.9, 114.6, 109.1 (Ar-C).

2-(2-(4-Chlorophenylamino) thiazol-4-yl)-3H-benzo[f] chromen-3-one

Yellow Solid M.*P* = 245 °C, Yield =72 %, R_f = 0.67 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3378 (N-H), 1739 (C = O), 3081, 2972, 2922(CH stretch-ing). 1531 (C = N str), 1493 (C = C str); ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm): 7.23 (s, 1H, CH), 7.34–8.36 (m, 6H, Ar-H), 7.66 (d, 2H, *J* = 7.60 Hz Ar-H), 7.42(d,2H, *J* = 7.7 Hz ArH) 9.33(s, 1H, benzocoumarin H-4). 11.55 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 169.3, (C = O), 160.18, (C = N), 155.2 (C = C), 153.8, 146.8, 145.8, 138.6, 135.6, 134.6, 133.4, 131.6, 130.4, 129.5, 129.3, 128.6, 127.6, 123.7, 122.7, 121.2, 116.9, 114.8, 109.5 (Ar-C),

2-(2-(4-Methoxyphenylamino)thiazol-4-yl)-3H-benzo[f] chromen-3-one

Light Yellow Solid M.*P* = 236 °C, Yield =76 %, R_f = 0.77 (Pet Ether: Ethyl Acetate 7: 3). FTIR (KBr) cm^{-1}: 3377 (N-H), 1749 (C = O), 3071, 2973, 2942 (CH stretch-ing). 1532 (C = N str), 1494 (C = C str); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.24 (s, 1H, CH), 7.35–8.37 (m, 6H, Ar-H), 7.63 (d, 2H, *J* = 7.60 Hz Ar-H), 7.22(d,2H, *J* = 7.7 Hz ArH) 9.43(s, 1H, benzocoumarin H-4). 11.05 (s, 1H, NH), 3.88 (s, 3H OCH_3), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 169.3, (C = O), 160.18, (C = N), 155.2 (C = C), 155.8, 147.8, 146.8, 138.6, 135.4, 134.6, 133.4, 131.7, 130.4, 129.7, 129.8, 128.8, 127.7, 123.9, 122.5, 121.4, 114.8, 114.7, 109.6 (Ar-C), 60.5 (OMe)

2-(2-(Thiazol-5-ylamino)thiazol-4-yl)-3H-benzo[f] chromen-3-one

Yellow Solid, M.*P* = 224 °C, Yield = 65 %, R_f = 0.70 (Pet Ether: Ethyl Acetate 7: 3) FTIR (KBr) cm^{-1}: 3189.8 (N-H, str), 2989.7 (Aromatic C-H, str), 1686.5 (C = O, str), 1511.8 (C-C, str), 1421.5 (C-H, bending), 1289.3 (C = S, str). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm): 7.27 (s, 1H, CH), 7.38–8.67 (m, 6H, Ar-H), 7.69–7.26 (d, 2H, ArH 9.43(s, 1H, benzocoumarin H-4). 13.05 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 169.3, (C = O), 160.18, 154.6 (C = N), 155.2, 154.2 (C = C), 157.8, 145.8, 146.6, 138.4, 135.4, 134.4133.4, 131.8, 130.1, 129.7, 126.8, 125.7, 123.9, 113.3 (Ar-C),

2-(2-(Benzylamino)thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 235 °C, Yield = 78 %, R_f = 0.68 (Pet Ether: Ethyl Acetate 7: 3) FTIR (KBr) cm^{-1}: 3199.8 (N-H, str), 2979.7 (Aromatic C-H, str), 1687.5 (C = O, str), 1511.8 (C-C, str), 1421.5 (C-H, bending), 1289.3 (C = S, str). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm): 7.28 (s, 1H, CH), 7.37–8.67 (m, 6H, Ar-H), 7.26–6.9 (dd, 3H, ArH),3.95(s, 2H), 9.43(s, 1H, benzocoumarin H-4). 13.05 (s, 1H, NH), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 169.5, (C = O), 160.3, 154.7 (C = N), 155.4, 154.5 (C = C), 157.6, 145.7, 146.8, 138.5, 135.1, 134.4, 133.5, 131.7, 130.1, 129.7, 127.8, 125.7, 123.9 (Ar-C), 46.5

2-(2-(p-toluidino) thiazol-4-yl)-3H-benzo[f]chromen-3-one

Yellow Solid M.*P* = 250 °C, Yield =77 %, R_f = 0.63 (Pet Ether: Ethyl Acetate 7: 3) FTIR (KBr) cm^{-1}: 3367 (N-H), 1759 (C = O), 3171, 2973, 2943 (CH str). 1534 (C = N str), 1495 (C = C str); ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm): 7.24 (s, 1H, CH), 7.36–8.38 (m, 6H, Ar-H), 7.63 (d, 2H, *J* = 7.60 Hz ArH), 7.24(d,2H, *J* = 7.7 Hz ArH) 9.44(s, 1H, benzocoumarin H-4). 12.05 (s, 1H, NH), 2.88 (s, 3H CH_3), ^{13}C-NMR (75 MHz, DMSO-*d*6): δ (ppm): 167.3, (C = O), 162.18, (C = N), 156.2 (C = C), 154.8, 148.8, 145.8, 139.6, 136.4, 135.6, 133.4, 131.7, 130.4, 129.7, 129.8, 128.8, 127.7, 123.9, 122.5, 121.4, 114.8, 114.7, 109.6 (Ar-C), 27.5 (Me).

Results and Discussion

Synthesis

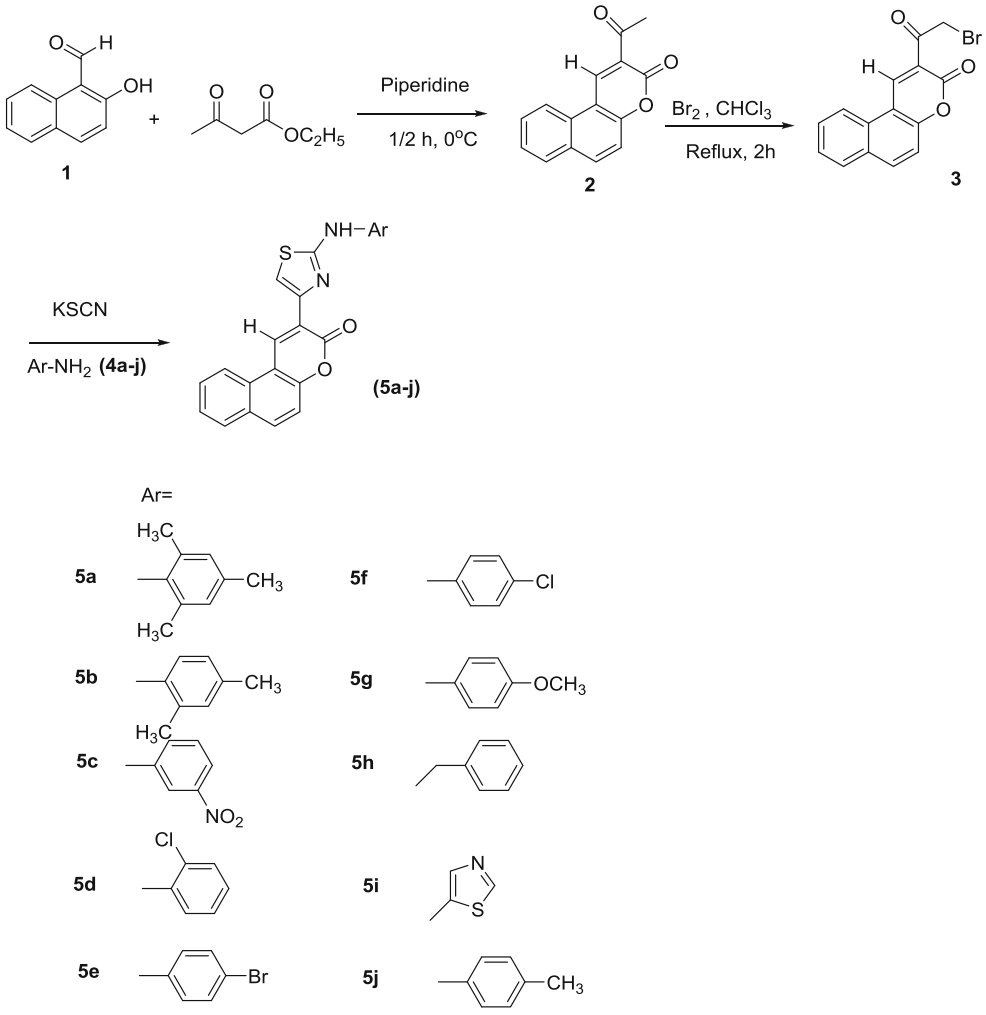
Coumarinyl derivatives **5a-j** have been synthesized well in excellent yields and high purity through synthetic route depicted in Scheme 1. These derivatives were synthesized in order to obtain coumarin derivatives potentially applicable as drugs and bioimaging materials. Thus, 3-acetyl coumarin was (2) synthesized by reacting naphthaldehyde and ethyl acetoacetate which was further converted to target thiazolocoumarin derivatives (5a-j) by bromination and condensation of intermediate (2) with different substituted aniline derivatives **4a-j** at reflux (Scheme 1).

The physical data of these coumarinyl derivatives is shown in Table 1.

Spectral Characterization of Coumarinyl Thiazoles (5a-j)

The structures of newly synthesized coumarinyl derivatives **5a-j** were elucidated by UV, FTIR and NMR studies. The UV-visible absorption spectra of the coumarins **5a-j** (1×10^{-6} M) were obtained at room temperature in

Scheme 1 Synthetic pathway to thiazole coumarin derivatives (**5a-j**)



different solvents (Fig. 1) and the selected spectral data is summarized in Table 2.

UV-visible spectra of all coumarinyl derivatives 5a-j were taken in DMF, ethanol, methanol, ethyl acetate and acetone. It was observed from their UV-visible spectra of coumarin 5a-j, that all compounds exhibited the only absorption maximum at 338–390 nm (Fig. 1) due to π-π* transition of naphthalene and benzene rings common in all derivatives [13]. The λ_{max} for **5b** is 390 nm is due to π-π* transitions of benzene and heterocyclic rings present in the molecule and this is largest among all the coumarinyl derivatives. There is more and more availability of electrons causing the bathochromic shift within the molecule. Thereby it has lager λ_{max}. In case of 5 h the λ_{max} is 338 nm while that of **5e, 5c-g** and **5i-j** is in the range 360–384 nm in given solvents. All this is due to π-π* and n-π* transitions of lone pairs and π-bonded electrons. The lowest λ_{max} of **5 h** is attributed to the intervening methylene functionality between the aryl and heterocyclic coumarin motif which vanishes the conjugation between the rings and causes hypsochromic shift. The UV-visible study of these coumarinyl compounds is different in different solvents due to the nature of solvents as it was conducted in different solvents and there is no larger change in λ_{max} for a given compound with respect to solvent polarity. This shows that the π-π* transitions

Table 1 Physical characteristics of coumarinyl derivatives **5a-j**

Compound	Colour	Melting Point (°C)	R_f Value
5a	Yellow Solid	238	0.68
5b	Yellow Solid	268	0.65
5c	Yellow Solid	234	0.67
5d	Yellow Solid	248	0.63
5e	Yellow Solid	229	0.60
5f	Yellow Solid	245	0.67
5 g	Light Yellow Solid	236	0.77
5 h	Yellow Solid	224	0.70
5i	Yellow Solid	235	0.68
5j	Yellow Solid	250	0.63

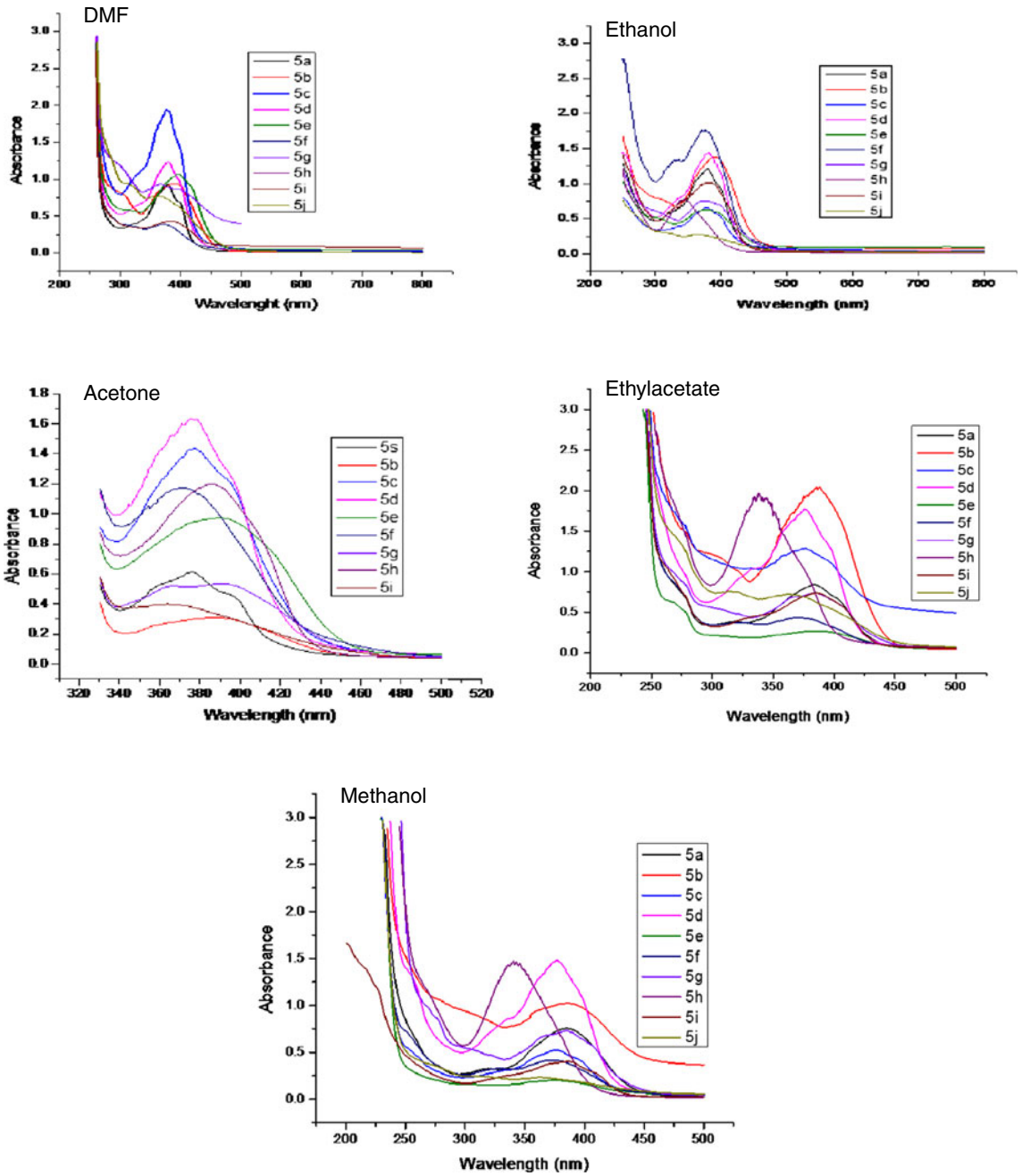


Fig. 1 UV-visible spectra of thiazole coumarin derivatives (5a-j) in DMF, ethanol,methanol, ethyl acetate and acetone

occurring over here is of B-type bands which are independent of the nature of solvent. So these compounds are not showing the phenomenon of solvatochromism.

The FTIR spectra of thiazole coumarin derivatives (5a-j) exhibited absorption bands due to N-H, Ar-H, C = O of lactone, C = N of imine, C = C, C = S and C-O, stretchings and bending vibrations at 3370–3399, 2980–3170, 1727–1749, 1620–1652, 1510–1533, 1411–1431, 1280–1295, 1105–1155, 836–860 and 793–818 cm^{-1}respectively. In case of coumarin **5d**, ester motif was confirmed by the appearance of peak at 1727 due to the carbonyl group of cyclic six membered esters. Presence of peak at 1149 cm^{-1} was result of C-O-C functionality. The absorption bands at 1630, 1533 and 859 cm^{-1} depicted the presence of C = C stretching and bending vibrations respectively. FTIR spectrum of dye **5e**, showed NH group peak at 3380 cm^{-1} and C = C-H stretching vibrations at 3168 cm−1.

The ^{1}H-NMR spectrum of compound **5a** (Fig. 2) showed 6H singlet at 2.21 ppm and 3H singlet at 2.39 ppm due to three CH_3 substituents attached to benzene. Singlet peak at

Table 2 Wavelength of maximum absorption (λ_{max}/nm) of coumarinyl derivatives **5a-j** in different solvents

Compound	DMF λ_{max}	Ethanol λ_{max}	Methanol λ_{max}	Ethyl acetate λ_{max}	Acetone λ_{max}
5a	378	379	384	376	383
5b	390	388	385	386	388
5c	377	377	376	377	396
5d	379	381	377	375	375
5e	379	377	375	384	381
5f	368	376	373	371	369
5 g	366	369	377	390	384
5 h	342	344	343	340	338
5i	384	376	387	386	385
5j	364	363	362	363	360

11.92 ppm is assigned to N-H substituted by heterocyclic and phenyl rings of coumarin. The multiplets at 7.32–8.44 ppm are due to six mutually coupled aromatic protons attached to coumarin part of molecule. The distinguishing peak for all coumarins is the presence of coumarin H-4 at 9.33 ppm. Difference among **5a-j** series is due to condensed substituted aromatic moieties. The ^{13}C-NMR of **5a** showed peaks for different carbon atoms present within the molecule (Fig. 3). The carbonyl and imine carbons were observed are at 169.3 and 159.1 ppm respectively. Three methyl carbons at benzene ring in **5a** appeared at at 21.5 and 18.2 ppm. Similarly the rest of compounds **5b-j** were confirmed by ^{1}H-NMR and ^{13}C-NMR spectra. The ^{1}H- and ^{13}C-NMR spectrum of coumarin derivative **5a** are shown in (Figs. 2 and 3) respectively.

Electrochemical Properties

The electrochemical characterization of these coumarinyl derivatives (5a-j) was conducted by cyclic voltammetry (Fig. 4) using ethanol having 0.1 M TBAPF6 as a supporting electrolyte. All redox potentials, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) were calculated from cyclic voltammograms (Fig. 4).

Redox Potentials ($E_{1/2}$)

Synthesized coumarin derivatives (**5a-j**) showed oxidation and reduction potentials on conducting their cyclic voltammetric analysis. From the cyclic voltammograms redox potentials was observed shown in Table 3. The lowest redox

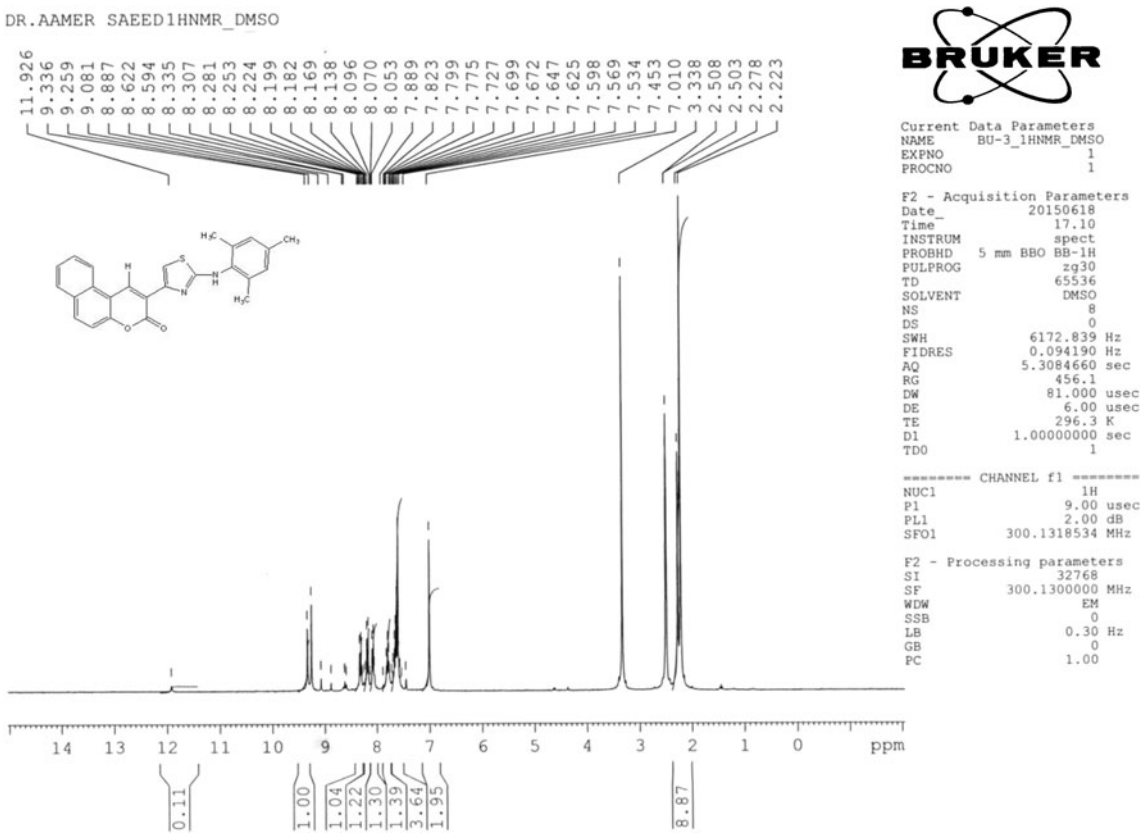


Fig. 2 ^{1}H-NMR of coumarin derivative (5a)

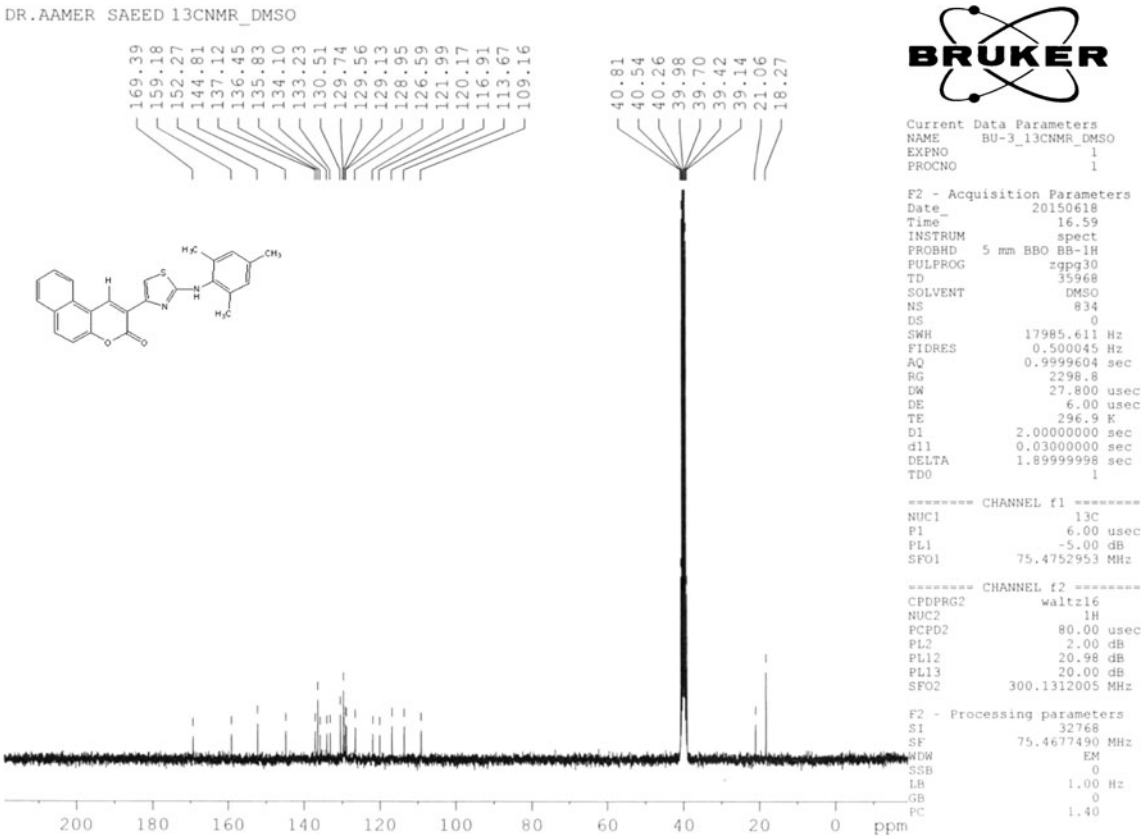


Fig. 3 ^{13}C-NMR of coumarin derivative 5a

potential was observed for compounds **5a** having 2,4,6-trimethyl ligands on the chromophore and highest redox potential was observed for **5 h** and **5i** containing different benzyl and heterocyclic moieties attached at thiazole ring [14]. It can be visualized from the data in Table 3 that coumarinyl derivatives bearing electron withdrawing groups have low redox potentials while those having electron donating groups have high redox potential values [15]. Behavior of derivative 5 h based on benzyl functionality was different from coumarin containing methyl groups.

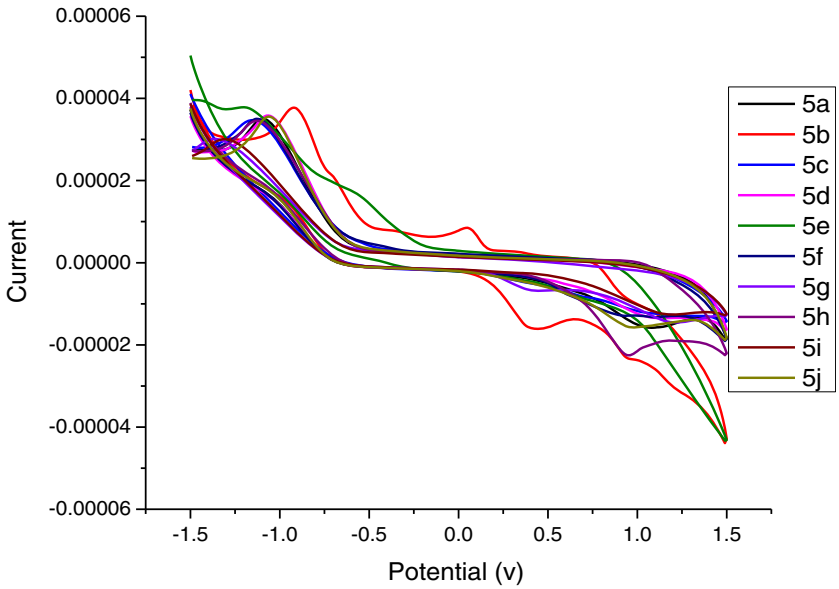


Fig. 4 Combined cyclic voltammogram of coumarin derivatives (5a-j) in ethanol

Lowest Unoccupied Molecular Orbital (LUMO)

In order to calculate the absolute energies of LUMO level with respect to the vacuum level, the redox data are standardized to the ferrocene/ferricenium couple which has a calculated absolute energy of – 4.8 eV. The data related to LUMO level energies of dyes are presented in Table 3.

It is inferred from LUMO energy levels, which varies from −4.71 to −5.92 eV that electron donating groups on the coumarinyl motives decrease the energy of LUMO levels while electron withdrawing groups increase the energy of LUMO energy levels. The energy of LUMO levels is varied only by increasing the delocalization of electrons through alternating single and double bonds and it is noticed that energy difference decreases with increasing conjugation and vice versa.

Band Gap Energy (Eg)

The optical band gap values were calculated using the standard procedure. The band gap energy is the span of energies that lies between the valence and conduction bands for insulators and semiconductors. Every solid has its own characteristic energy-band structure. This variation in band structure is responsible for the wide range of electrical characteristics observed in various materials. Band gap energy of these coumarinyl derivatives is given in Table 3.The band gap energy varied from 3.17 to 3.68 eV which is highest for dyes **5 g, 5 h, 5j** and minimum for dyes **5b** and **5i** which depend upon substituents attached to chromophore as well as on the precursor utilized for synthesis of coumarins. In case of compound5bmethyl groups are attached to coumarin motif while **5i** has a thiazole ring which increases the electron density of chromophore and energy levels get close to each other and decrease the band gap energy.

Table 3 LUMO/eV energy levels of thiazole coumarin derivatives (**5a-j**)

Compound.	$E_{1/2}$ (V)	LUMO (eV)
5a	−0.012	−4.788
5b	0.241	−5.04
5c	−0.049	−4.75
5d	0.075	−4.87
5e	0.690	−5.4
5f	−0.087	−4.71
5 g	−0.031	−4.76
5 h	1.015	−5.81
5i	1.127	−5.92
5j	0.218	−5.01

Table 4 HOMO/eV energy levels and band gap energy coumarinnyl derivatives (5a-j)

Compound	E_g(V)	HOMO (eV)
5a	3.28	−8.08
5b	3.17	−7.97
5c	3.28	−8.08
5d	3.27	−8.07
5e	3.27	−8.07
5f	3.36	−8.16
5 g	3.38	−8.18
5 h	3.68	8.48
5i	3.20	8.00
5j	3.4	8.20

Highest Occupied Molecular Orbital (HOMO)

Table 4 depicts the highest occupied molecular orbital energy levels, which are calculated using the standard reported procedure. Considering the energy range from −7.97 to −8.48 eV for coumarin derivatives **5a-j**, it was observed that for coumarin **5 h** the HOMO energy levels are at very low energy because the benzyl group is present in the chromophore while 5 hhas high HOMO energy levels due to inductive effect of methyl groups present in the molecule. It is observed that there is the effect of electron donating groups on the HOMO energy levels is to increase their energy while electron withdrawing groups definitely decrease the energy of HOMO levels by increasing the energy gap between HOMO and LUMO.

Fluorescence Studies

Fluorescence study of all the coumarin derivatives was made by preparing the ethanolic solution of compounds **(5a-j)** and all the compounds were found to highly fluorescent (Table 5).

Table 5 Fluorescence data of thiazole coumarin derivatives (**5a-j**) in ethanol

Compound	Excitation wavelength (nm)	Emission wavelength (nm)	Stoke shift	FLQ
5a	445	456	16	0.56
5b	445	463	18	0.65
5c	450	465	15	0.76
5d	450	460	10	0.81
5e	450	461	11	0.66
5f	436	450	14	0.79
5 g	440	456	16	0.73
5 h	460	505	45	0.48
5i	440	455	15	0.78
5j	440	456	16	0.61

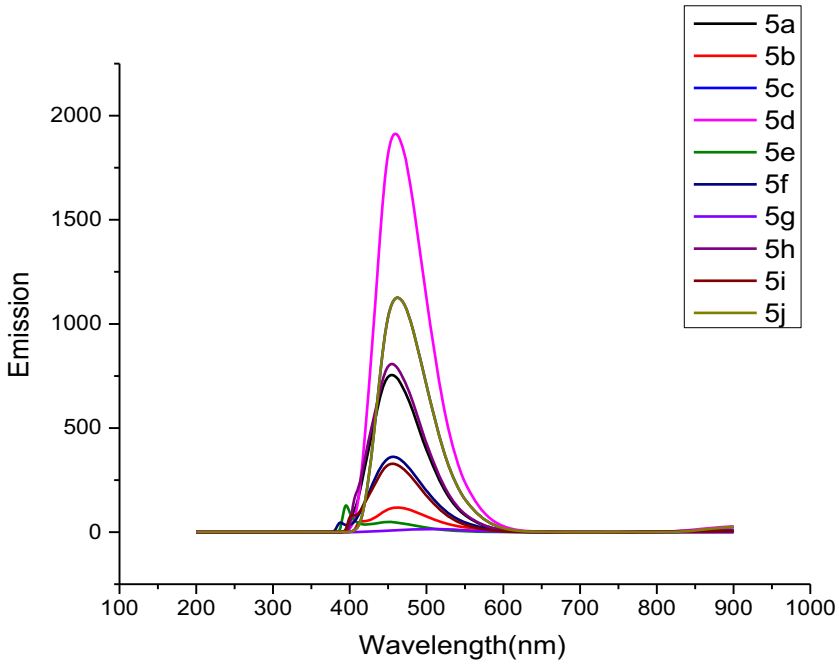


Fig. 5 Fluorescence spectrum of thiazole coumarin derivatives (5a-j) in ethanol

These coumarin derivatives fulfilled the premier requirement of fluorescence as these molecules were highly conjugated and were devoid of rotational or vibrational motions as a whole molecule [16]. Fluorescence spectrum of all derivatives **5a-j** is shown in Fig. 5, which was recorded by selecting different excitation wavelengths of the source. Fluorescence spectrum provides the intensity contribution to the observed emission at a given wavelength by different excitation wavelengths for which the samples were exposed. The fluorescence spectrum showed only one emission for all dyes. The emission peak of highest emission wavelength was noted for 5 h at 505 nm on excitation of ethanolic solution at a concentration 10^{-7} to 10^{-8} M.

High fluorescence of these coumarinyl derivatives enables them to be used for bio labeling and bio imaging [17]. Therefore these derivatives can be applied where usual fluorescent compounds are being used. Fluorescence quantum (FLQ) yield of coumarinyl derivatives **5a-j** was determined by preparing an equimolar solution (1×10^{-5} M) of synthesized dyes and fluorescein and comparing the emission intensity of dyes with reference compound. FLQ value of these coumarinyl derivatives is approximately half of the fluorescein [18].

Conclusion

A series of coumarinyl derivatives **5a-j** have been synthesized in high yields via a short and easily accessible route. All these derivatives are yellow colored which exhibit absorptions in the range 370–395 nm. The $_{max}$ of all the dyes was found to be maximum in DMF, which was in accordance with the general rule that polar solvents shift the π-π* transitions to higher wavelength. Solvatochromic behavior was observed for the derivatives and the absorption maxima underwent a bathochromic shift on increasing the polarity of solvents. Fluorescence study of these derivatives was conducted in ethanol and high stoke shift values were observed and maximum emission was noted for compound 5 h. The coumarinyl derivatives bearing methoxy group have lowest band gaps and high energy HOMO levels.

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