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The one-pot synthesis and fluorimetric study of 3-(2′-benzothiazolyl)coumarins

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ABSTRACT

A novel, piperidene-catalysed, one-pot synthesis of 3-(2′-benzothiazolyl)coumarins was undertaken, starting from salicylaldehydes, ethyl cyanoacetate and o-aminobenzenethiols in ethanol. Salicylaldehydes with electron-donating group gave optimum yields. The novel method is characterized by mild reaction conditions, simple procedure and low waste. All compounds were fluorescent in solution emitting either green light (490 nm) or blue light (440–460 nm). Two typical fluorescence peaks were found in the three-dimensional fluorescence spectra.

1. Introduction

Coumarins and their analogues represent an important class of organic heterocycles, which can be found in many natural or synthetic drug molecules and possess versatile biological activities [1–5]. Moreover, coumarin derivatives owe their importance to their sufficient fluorescence in the visible light range, large Stokes shift, high quantum yield of photoluminescence and reasonable solubility, which gives rise to one of the most extensively investigated and commercially significant organic fluorescent materials [6–8]. The coumarin dyes are fluorescing in the blue-green spectral region and widely used in fluorescent probes, coloration of synthetic fibers such as polyester, daylight fluorescent pigments and other functional applications such as tunable dye lasers, solar energy collectors, organic light emitting diodes(LED) [9–15]. The typical coumarin fluorescent dyes generally contain electron donor at the 7-position and electron acceptor benzothiazole, benzimidazole or benzoxazole at the 3-position (Fig. 1).

The method to synthesize 3-heterocycle substituted coumarins can be summarized in two kinds: the coumarin-3-carboxylic acid compounds were synthesized firstly and then reacted with different aryl amines to introduce the heterocyclic structure [16]; or the heterocyclic derivatives prepared firstly reacted with substituted salicylaldehydes to give the coumarin fluorescent dyes [17,18]. Those methods often suffer from corrosive catalyst, laborious multi-step procedures, long reaction time, high reaction temperature and waste problem. We previously reported a facile one-pot synthesis of 3-(2′-benzoxazole)coumarins under the catalysis of benzoic acid from commercially available starting materials [19]. In our further investigation, however, though this benzoic acid catalyzed procedure succeeded in synthesizing 3-(2′-benzimidazolyl)coumarins, it failed in preparing 3-(2′-benzothiazolyl)coumarins. Following our interest on the green synthesis of coumarin fluorescent dyes, here we report a novel one-pot synthesis of 3-(2′-benzothiazolyl)coumarins with salicylaldehydes, o-aminobenzenethiols and ethyl cyanoacetate under the catalysis of piperidine.

2. Experimental

2.1. Chemicals and instruments

All reactants were commercially available and used without further purification. All melting points were uncorrected. Nuclear magnetic resonance spectra were recorded on Bruker Avance III 500 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. Mass spectra were measured using a Thermo Finnigan LCQ Series, Agilent 6210 Series Time-of-Flight Mass Spectrometer (ESI/APCI), Thermo Scientific ITQ 1100 and Waters GCT Premier Mass Spectrometer (EI/CI). Fluorescence spectra were obtained on a Hitachi FL-2500 spectrofluorometer. The widths of the excitation slit and the emission slit were both set to 5 nm with the scanning speed at 1200 nm min^{-1}.

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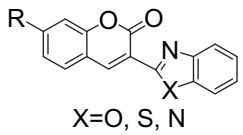


Fig. 1. Typical coumarin fluorescent dyes.

2.2. Synthesis of 2-benzothiazolyl phenol (*B*)

A mixture of salicylaldehyde (2 mmol), ethyl cyanoacetate (2 mmol) and o-aminophenol (2 mmol) in n-butanol (20 mL) containing benzoic acid (0.6 mmol) was refluxed for 7 h. After the solution was cooled, the solid was filtered and washed with water affording a pale yellow solid. Yield 65%; mp 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.50 (s, 1H, ArOH), 7.97(d, J = 8.2 Hz, 1H, 7′-H), 7.89 (d, J = 7.5 Hz, 1H, 4′-H), 7.67 (d, J = 7.8 Hz, 1H, 6′-H), 7.49 (t, J = 8.1 Hz, 1H, 5′-H), 7.41–7.36 (m, 2H, 3-H, 5-H), 7.10 (d, J = 8.3 Hz, 1H, 4-H), 6.95 (t, J = 7.7 Hz, 1H, 6-H); ^{13}C NMR (500 MHz, $CDCl_3$) δ: 169.4, 158.0, 151.9, 132.7, 132.6, 128.4, 126.7, 125.5, 122.2, 121.5, 119.5, 117.9, 116.8; ESI-MS: 228.0 $[M + H]^+$.

2.3. General procedure for the synthesis of compounds *4a*–*4j*

A mixture of salicylaldehyde (2 mmol), ethyl 2-cyanoacetate (4 mmol) and o-aminophenol (2 mmol) in ethanol (20 mL) containing piperidine (0.3 mmol) was refluxed for 7 h. After the solution was cooled, the solid was filtered, washed with water and then recrystallized from DMF-H_2O to afford the solid **4a**–**4j**.

2.3.1. 3-(2′ -benzothiazolyl)-2H-1-benzopyran-2-one (*4a*)

Yield 68%; yellow solid; mp 221–223 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.09 (s, 1H, 4-H), 8.10 (d, J = 8.2 Hz, 1H, 7′-H), 8.00 (d, J = 7.7 Hz, 1H, 4′-H), 7.75 (d, J = 7.8 Hz, 1H, 5-H), 7.65(t, J = 8.5 Hz, 1H, 7-H), 7.55 (t, J = 8.2 Hz, 1H, 6′-H), 7.46–7.38 (m, 3H, 6-H, 8-H, 5′-H); ESI-MS: 280.5 $[M + H]^+$; HR-ESI-MS for $C_{16}H_{10}NO_2S$: Found: 280.0443, Calcd. 280.0432.

2.3.2. 3-(2′-benzothiazolyl)-6-chloro-2H-1-benzopyran-2-one (*4b*)

Yield 49%; yellow solid; mp 250–252 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.01 (s, 1H, 4-H), 8.12 (d, J = 8.2 Hz, 1H, 7′-H), 8.00 (d, J = 7.9 Hz, 1H, 4′-H), 7.71 (d, J = 2.3 Hz, 1H, 5-H), 7.60–7.56 (m, 2H, 5′-H, 6′-H), 7.46 (t, J = 7.5 Hz, 1H, 7-H), 7.40 (d, J = 8.8 Hz, 1H, 8-H); ESI-MS: 314.2 $[M + H]^+$; HR-ESI-MS for $C_{16}H_9ClNO_2S$: Found: 314.0034, Calcd. 314.0037.

2.3.3. 3-(2′-benzothiazolyl)-6-bromo-2H-1-benzopyran-2-one (*4c*)

Yield 47%; yellow solid; mp 279–280 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.00 (s, 1H, 5-H), 8.10 (d, J = 8.2 Hz, 1H, 7′-H), 8.00 (d, J = 8.0 Hz, 1H, 4′-H), 7.86 (s, 1H, 4-H), 7.74 (d, J = 8.5 Hz, 1H, 7-H), 7.56 (t, J = 7.4 Hz, 1H, 6′-H), 7.46 (t, J = 7.4 Hz, 1H, 5′-H), 7.35(d, J = 8.8 Hz, 1H, 8-H); ESI-MS: 358.4, 360.4 $[M + H]^+$; HR-ESI-MS for $C_{16}H_9BrNO_2S$: Found: 357.9516, 359.9504; Calcd. 357.9537, 359.9537.

2.3.4. 3-(2′-benzothiazolyl)-7-methoxy-2H-1-benzopyran-2-one (*4d*)

Yield: 68%; yellow solid; mp 232–235 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ: 9.04 (s, 1H, 4-H), 8.07 (d, J = 8.2 Hz, 1H, 7′-H), 7.98 (d, J = 7.8 Hz, 1H, 4′-H), 7.65 (d, J = 8.7 Hz, 1H, 5-H), 7.53 (t, J = 7.1 Hz, 1H, 6′-H), 7.42 (t, J = 7.0 Hz, 1H, 5′-H), 6.98–6.96 (m, 1H, 6-H), 6.93 (s, 1H, 8-H), 3.94 (s, 3H, CH_3O); ESI-MS: 310.5 $[M + H]^+$; HR-ESI-MS for $C_{17}H_{12}NO_3S$: Found: 310.0525; Calcd. 310.0532.

2.3.5. 3-(2′-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one (*4e*)

Yield 60%; orange solid; mp 213–215 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (s, 1H, 4-H), 8.02 (d, J = 8.2 Hz, 1H, 7′-H), 7.94 (d, J = 7.9 Hz, 1H, 4′-H), 7.50–7.48 (m, 2H, 5′-H, 6′-H), 7.36 (t, J = 7.6 Hz, 1H, 5-H), 6.67 (dd, $J_{6,5}$ = 8.9 Hz and $J_{6,8}$ = 2.3 Hz, 1H, 6-H), 6.57 (d, J = 2.2 Hz, 1H, 8-H), 3.46 (q, J = 7.1 Hz, 4H, NCH_2CH_3), 1.26 (t, J = 7.1 Hz, 6H, NCH_2CH_3); ESI-MS: 351.6 $[M + H]^+$; HR-ESI-MS for $C_{20}H_{19}N_2O_2S$: Found: 351.1170; Calcd. 351.1162.

2.3.6. 3-(5′-chloro-2′-benzothiazolyl)-2H-1-benzopyran-2-one (*4f*)

Yield 58%; yellow solid; mp 271–273 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.08 (s, 1H, 4-H), 8.07 (d, J = 1.9 Hz, 1H, 4′-H), 7.90 (d, J = 8.5 Hz, 1H, 7′-H), 7.75 (d, J = 7.7 Hz, 1H, 5-H), 7.67 (t, J = 8.6 Hz, 1H, 7-H), 7.46 (d, J = 8.3 Hz, 1H, 6′-H), 7.42–7.39 (m, 2H, 6-H, 8-H); EI-MS: 313.1 $[M]^+$; HR-EI-MS for $C_{16}H_8ClNO_2S$: Found: 312.9963; Calcd. 312.9964.

2.3.7. 6-chloro-3-(5′-chloro-2′-benzothiazolyl)-2H-1-benzopyran-2-one (*4g*)

Yield 48%; yellow solid; mp 296–297 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.99 (s, 1H, 4-H), 8.08 (d, J = 2.0 Hz, 1H, 4′-H), 7.89 (d, J = 8.6 Hz, 1H, 7′-H), 7.72 (d, J = 2.4 Hz, 1H, 5-H), 7.60 (dd, $J_{6',7'}$ = 8.7 Hz and $J_{6',4'}$ = 2.4 Hz, 1H, 6′-H), 7.43–7.40 (m, 2H, 7-H, 8-H); EI-MS: 347.1 $[M + H]^+$; HR-EI-MS for $C_{16}H_8Cl_2NO_2S$: Found: 346.9580; Calcd. 346.9575.

2.3.8. 6-bromo-3-(5′-chloro-2′-benzothiazolyl)-2H-1-benzopyran-2-one (*4h*)

Yield 50%; yellow solid; mp 295–297 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.99 (s, 1H, 5-H), 8.08 (d, J = 1.9 Hz, 1H, 4-H), 7.91 (d, J = 8.5 Hz, 1H, 7′-H), 7.88 (d, J = 2.3 Hz, 1H, 4′-H), 7.74 (dd, $J_{7,8}$ = 8.8 Hz and $J_{7,5}$ = 2.3 Hz, 1H, 7-H), 7.42 (dd, $J_{6',7'}$ = 8.6 Hz and $J_{6',4'}$ = 1.9 Hz, 1H, 6′-H), 7.35 (d, J = 8.8 Hz, 1H, 8-H); EI-MS: 391.1, 393.1[M + H]$^+$; HR-EI-MS for $C_{16}H_8BrClNO_2S$: Found: 390.9065, 392.9041; Calcd. 390.9069, 392.9069.

2.3.9. 3-(5′-chloro-2′-benzothiazolyl)-7-methoxy-2H-1-benzopyran-2-one (*4i*)

Yield 80%; **y**ellow solid; mp 279–280 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.02 (s, 1H, 4-H), 8.04 (d, J = 2.0 Hz, 1H, 4′-H), 7.87 (d, J = 8.4 Hz, 1H, 7′-H), 7.64 (d, J = 8.7 Hz, 1H, 5-H), 7.38 (dd, $J_{6',7'}$ = 8.6 Hz and $J_{6',4'}$ = 1.9 Hz, 1H, 6′-H), 6.97 (dd, $J_{6,5}$ = 8.7 Hz and $J_{6,8}$ = 2.3 Hz, 1H, 6-H), 6.93 (d, J = 2.3 Hz, 1H, 8-H), 3.94 (s, 3H, CH_3O); ESI-MS: 344.5 $[M + H]^+$; HR-ESI-MS for $C_{17}H_{11}ClNO_3S$: Found: 344.0140; Calcd. 344.0143.

2.3.10. 3-(5′-chloro-2′-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one (*4j*)

Yield 58%; orange solid; mp 259–261 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.90 (s, 1H, 4-H), 7.99 (d, J = 1.9 Hz, 1H, 4′-H), 7.83 (d, J = 8.5 Hz, 1H, 7′-H), 7.50 (d, J = 9.0 Hz, 1H, 5-H), 7.33 (dd, $J_{6',7'}$ = 8.5 Hz and $J_{6',4'}$ = 2.0 Hz, 1H, 6′-H), 6.69 (dd, $J_{6,5}$ = 9.0 Hz and $J_{6,8}$ = 2.5 Hz, 1H, 6-H), 6.57 (d, J = 2.4 Hz, 1H, 8-H), 3.47 (q, J = 7.1 Hz, 4H, NCH_2CH_3), 1.26 (t, J = 7.1 Hz, 6H, NCH_2CH_3); ESI-MS: 385.1 $[M + H]^+$; HR-ESI-MS for $C_{20}H_{18}ClN_2O_2S$: Found: 385.0764; Calcd. 385.0772.

3. Results and discussion

3.1. One-pot synthesis of 3-(2′-benzothiazolyl)coumarins

We have ever reported the preparation of 3-(2′-benzoxazolyl) coumarins in good yields by three-component one-pot synthesis under the catalysis of benzoic acid [19]. In the following work to

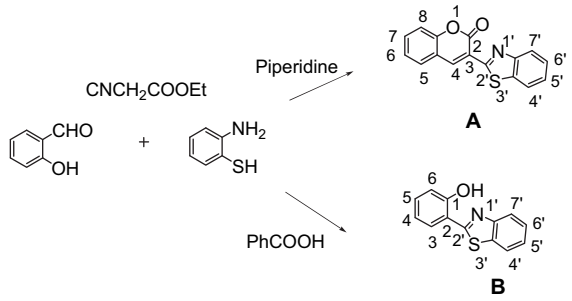
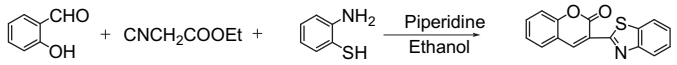


Fig. 2. Piperidine-catalyzed and PhCOOH-catalyzed one-pot reaction with salicylaldehyde, ethyl cyanoacetate and o-aminophenol.

obtain 3-(2′-benzothiazolyl)coumarin, salicylaldehyde, ethyl cyanoacetate and o-aminobenzenethiol were reacted in n-butanol at reflux in the presence of benzoic acid, and a yellow fluorescent product mistaken firstly to be **A** was obtained in 65% yield (Fig. 2). However, the peak related to 4-H of **A** can't be found in its ^{1}H NMR, which generally occurred in 8–9 ppm. Moreover, a single peak appeared in 12–13 ppm. The further characterization of this product by ^{13}C NMR and MS proved that it is 2-benzothiazolyl phenol (Fig. 2, **B)** formed by the reaction of salicylaldehyde and o-aminobenzenethiol under the catalysis of benzoic acid.

Since 3-(2′-benzothiazolyl)coumarin can't be obtained through the acid catalyzed one-pot synthesis, the base catalyzed reaction was attempted. Piperidine, pyridine and triethylamine were chosen to catalyze one-pot synthesis of salicylaldehyde, ethyl cyanoacetate and o-aminobenzenethiol (Table 1, Entry 1–3). Among those catalysts tested, piperidine gave the better yield 29% for **4a** (Table 1, Entry 3). When ethyl cyanoacetate was replaced with malonic acid, diethyl malonate or malononitrile, trace product was obtained. To further improve the yield, the effects of the solvent and catalyst amount were investigated. The product obtained in n-butanol was a little dark, which was perhaps due to the oxidation of the reactant or intermediate caused by high reaction temperature. Therefore methanol and ethanol were selected to replace n-butanol, which improved the yield up to above 40% (Table 1, Entry 4–5), and ethanol was preferred. In addition, when the piperidine amount was reduced to 0.15 equivalent, it afforded the comparable yield (Table 1, Entry 6); while either the further reduce of piperidine amount to 0.1 equivalent or the increase to 0.5 equivalent was unfavorable to the yields (Table 1, Entry 7–8). On the other hand, the mole ratios of ethyl cyanoacetate **2** or o-aminobenzenethiol **3** to salicylaldehyde **1** were increased to facilitate the reaction. The yields improved with the increase of the mole ratio of **2** to **1** and **3** (Table 1, Entry 9–11), and it bolstered to 68% when the mole ratio of **2** to **1** and **3** doubled (Table 1, Entry 11). However the increase of o-aminobenzenethiol amount had less help (Table 1, Entry 12).

Table 1
Synthesis of 3-(2′-benzohiazolyl)coumarin **4a** by one-pot reaction with salicylaldehyde, ethyl cyanoacetate and 2-aminobenzenethiol[a].



1 **2** **3** **4a**

Entry	Reactant ratio [b]	Catalyst	Catalyst amount/equiv.	Solvent	Yield/%
1	1:1:1	Et_3N	0.3	n-butanol	15%
2	1:1:1	pyridine	0.3	n-butanol	15%
3	1:1:1	piperidine	0.3	n-butanol	29%
4	1:1:1	piperidine	0.3	methanol	42%
5	1:1:1	piperidine	0.3	ethanol	43%
6	1:1:1	piperidine	0.15	ethanol	42%
7	1:1:1	piperidine	0.1	ethanol	38%
8	1:1:1	piperidine	0.5	ethanol	36%
9	1:1.2:1	piperidine	0.15	ethanol	46%
10	1:1.5:1	piperidine	0.15	ethanol	57%
11	1:2:1	piperidine	0.15	ethanol	68%
12	1:1:2	piperidine	0.15	ethanol	47%

[a] The reaction condition: salicylaldehydes(2 mmol), solvent (20 mL), reaction time (7 h) at reflux.
[b] Reactant ratio: salicylaldehydes:ethyl cyanoacetate:2-aminobenzenethiol.

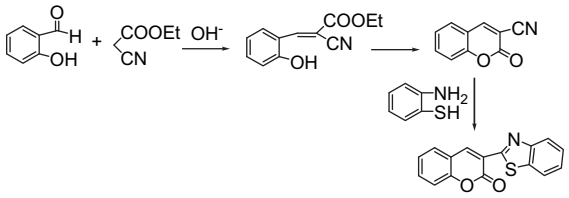


Fig. 3. A mechanistic rationalization for piperidine-catalyzed one-pot synthesis.

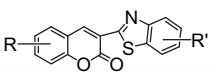
A mechanistic rationalization for this reaction is provided in Fig. 3 based on this piperidine catalyzed reaction. The Knoevenagel reaction of salicylaldehyde and ethyl cyanoacetate under the catalysis of piperidine and subsequent cyclization afford 3-cyanocoumarin, then the condensation of 3-cyanocoumarin with o-aminobenzenethiol leads to the formation of 3-(2′-benzothiazolyl) coumarin.

To investigate the scope of this one-pot synthesis, different salicylaldehydes and o-aminobenzenethiols were reacted with ethyl cyanoacetate and the results were listed in Table 2. The reaction proceeded smoothly giving 47–80% yield with salicylaldehydes and o-animobenzenethiols bearing different substituents. Moreover, salicylaldehydes containing electron-donating group provided better yields than those with electron-withdrawing group. Especially salicylaldehyde with methyloxy group gave the best yield 80%. Though the diethylamino group was a superior electron-donating group to methyloxy group, salicylaldehyde with diethylamino group gave lower yield than that with methyloxy group probably due to the easy oxidation of diethylamino group.

3.2. Fluorimetric properties

The fluorescence spectra of 3-(2′-benzothiazolyl)coumarins were measured in $CHCl_3$ (Fig. 4) and the relevant data were listed in Table 3. 3-(2′-benzothiazolyl)coumarins is a well-known strong intramolecular charge-transfer chromophoric system in which the coumarin ring acts as a donor while the benzothiazole moiety acts as an accepter. Π-conjugations through the donor to the acceptor

Table 2
One-pot synthesis of 3-(2′-benzothiazolyl)coumarins.



Compound	R	R′	Yield(%)
4a	H	H	68
4b	6-Cl	H	53
4c	6-Br	H	47
4d	7-CH_3O	H	68
4e	7-NEt_2	H	60
4f	H	5′-Cl	58
4g	6-Cl	5′-Cl	48
4h	6-Br	5′-Cl	50
4i	7-CH_3O	5′-Cl	80
4j	7-NEt_2	5′-Cl	58

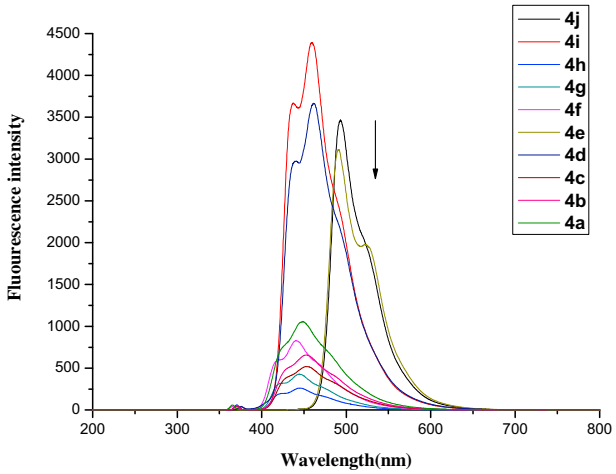


Fig. 4. Fluorescence spectra of 3-(2′-benzothiazolyl)coumarins in $CHCl_3$ at concentration 5×10^{-6} mol L^{-1}.

produce strong donor-acceptor system. From Fig. 4, it can be observed that all compounds are fluorescent in solution and the subtituents have an important effect on their fluorescence spectra. Compounds **4e**, **4j** bearing the strongest electron-donating diethylamino group presents a green emission of fluorescence, while the other compounds have the emission peaks located at ~440–460 nm, indicating that they emit blue lights. The emission intensity results were agreed well with the earlier recognition of the substituent effect, and compounds **4d**, **4e**, **4i**, and **4j** displayed stronger emission intensity due to the charge-transfer in the 3-(2′-benzothiazolyl)coumarin molecules from the strong electron-donating diethylamino or methoxy group at C-7 position to the benzothiazole ring. Besides, compounds **4e**, **4j** showed the lowest Stoke's shift than other compounds.

Table 3
Fluorescence spectra data for **4a**–**4j**.[a]

Compound	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	Stoke's Shift (nm)
4a	365	448	83
4b	370	452	82
4c	370	453	83
4d	375	461	86
4e	445	491	46
4f	365	441	76
4g	370	445	75
4h	370	445	75
4i	375	459	70
4j	445	493	48

[a] The fluorescence spectra were measured in chloroform.

The three-dimensional fluorescence spectra are a rising fluorescence analysis technique in recent years. The excitation wavelength, the emission wavelength and the fluorescence intensity can be used as the axes in order to investigate the synthetically information of the samples, and the contour spectra can also provide a lot of important information [20]. The three-dimensional fluorescence spectra of compounds **4d**, **4e**, **4i** and **4j** were shown in Fig. 5 and characteristic parameters were summarized in Table 4. Two typical fluorescence peaks could be easily found in all three-dimensional fluorescence spectra, which were in accordance with those observed in the three-dimensional fluorescence contour map (Fig. 6).

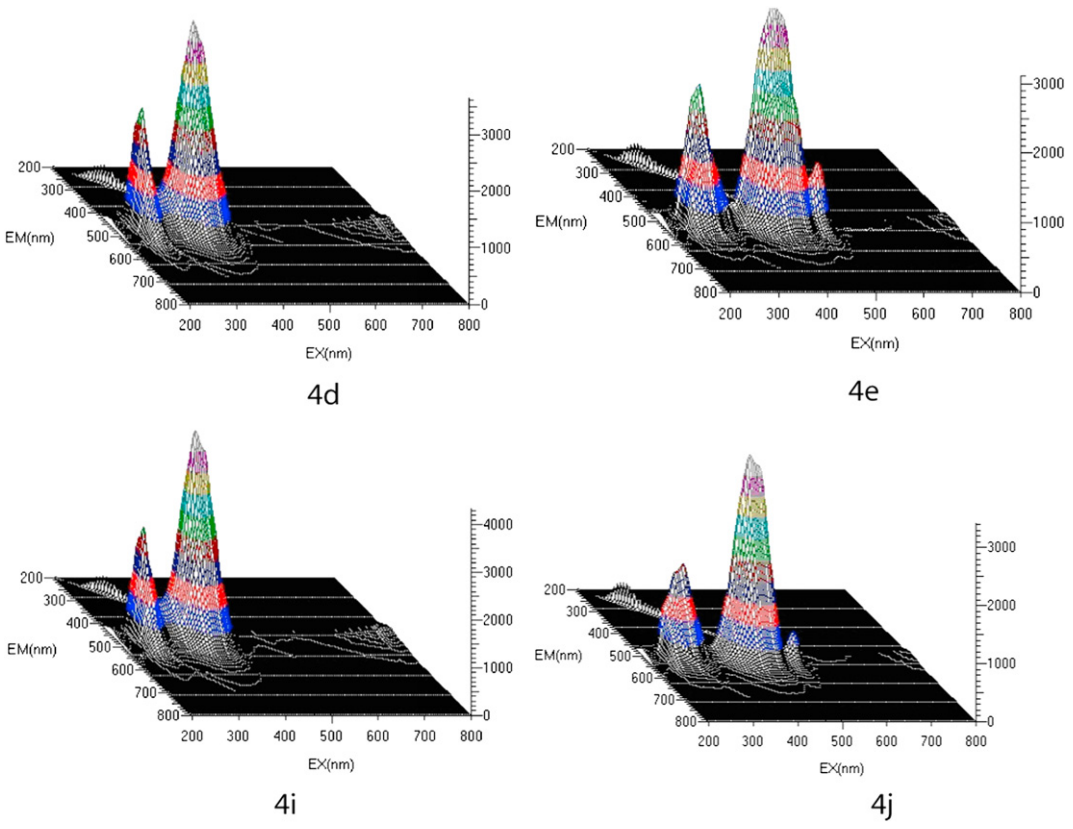


Fig. 5. Three-dimensional fluorescence spectra of compounds **4d**, **4e**, **4i** and **4j** in $CHCl_3$ at concentration 5×10^{-6} mol L^{-1}.

Table 4
Some characteristic parameters of three-dimensional fluorescence spectra.

Compound	Parameter	Peak one	Peak two
4d	Peak position (λex/λem, nm/nm)	265.0/460.0	375.0/461.4
	Relative intensity	2093.0	3666
	Stokes shift **Δλ**/nm	195	86.4
4e	Peak position (λex/λem, nm/nm)	290.0/490.0	445.0/491.2
	Relative intensity	1938	3115
	Stokes shift **Δλ**/nm	200	46.2
4i	Peak position (λex/λem, nm/nm)	265.0/460.0	375.0/459.2
	Relative intensity	2306	4395
	Stokes shift **Δλ**/nm	194.2	84.2
4j	Peak position (λex/λem, nm/nm)	295.0/495.0	445.0/493.4
	Relative intensity	1564	3468
	Stokes shift **Δλ**/nm	200	48.4

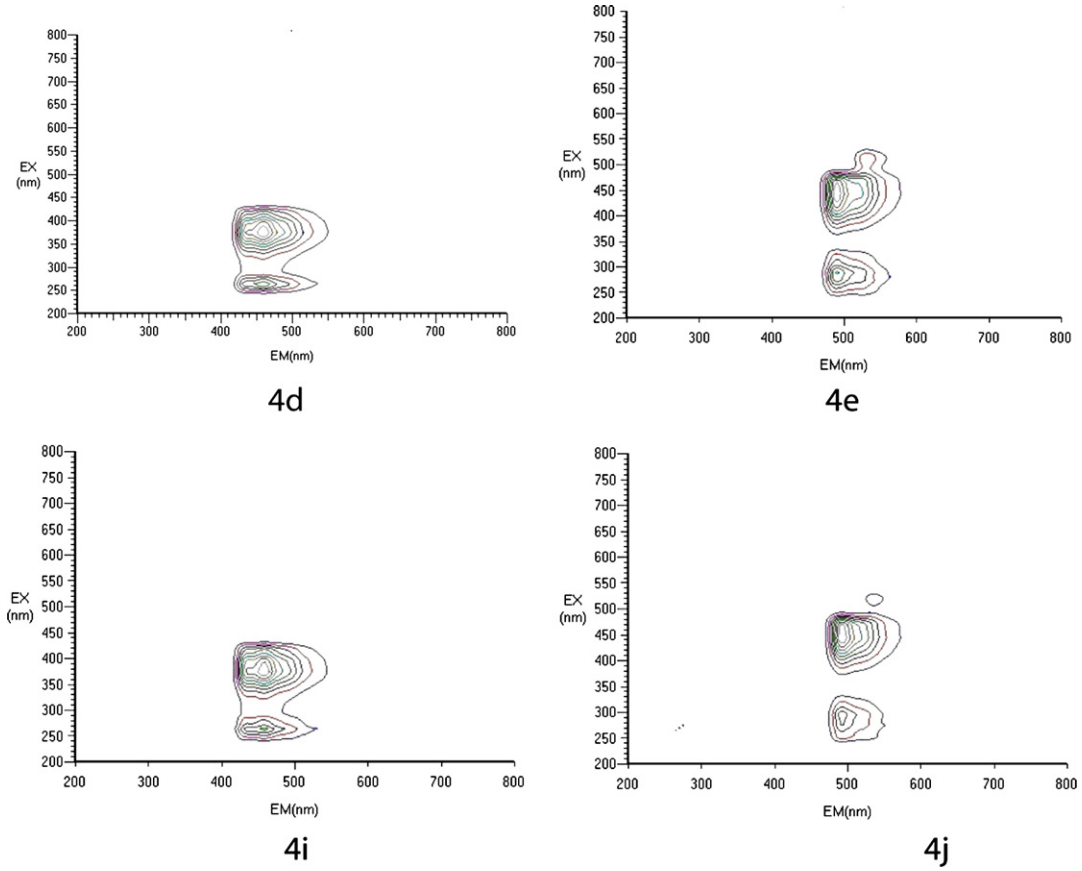


Fig. 6. Three-dimensional fluorescence contour map of compounds **4d**, **4e**, **4i** and **4j** in $CHCl_3$ at concentration 5×10^{-6} mol L^{-1}.

4. Conclusions

In conclusion, we have demonstrated a convenient and efficient method for the preparation of an important class of 3-(2′-benzothiazolyl)coumarins with salicylaldehydes, ethyl cyanoacetate and o-aminobenzenethiols. This piperidine catalyzed one-pot synthesis has a wide substrate scope and the salicylaldehydes containing electron-donating group afford better yields. Short reaction time, mild reaction condition, simple workup and less waste are significant advantages of this method presented here.

All synthesized compounds are fluorescent in solution, with compounds **4e**, **4j** emitted green light (490 nm) whilst other compounds emitting blue light (440–460 nm). The substituents have a conspicuous effect on the fluorescence spectra, and the electron-donating groups of the coumarin moiety enhance the fluorescent efficiency. Besides, two typical fluorescence peaks are found in the three-dimensional fluorescence spectra.

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