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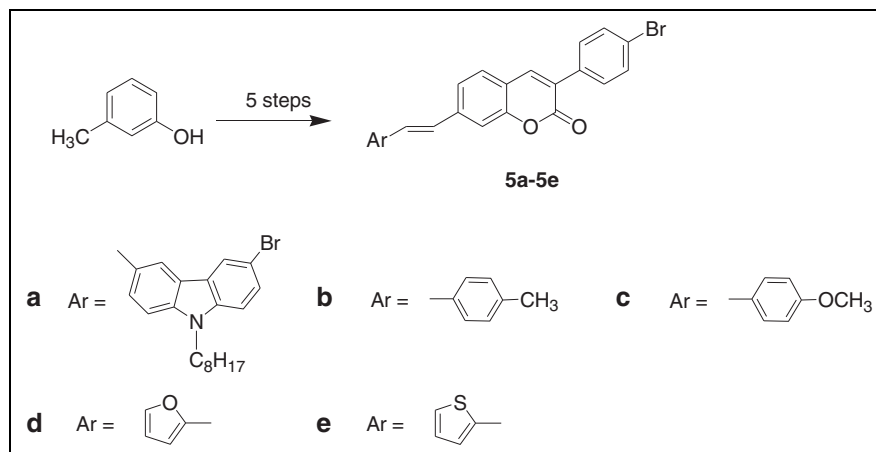
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Received June 1, 2011

DOI 10.1002/jhet.1524

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Five new coumarin derivatives (**5a–5e**) with extending *para*-bromophenyl at the 3-position and substituted vinyl at the 7-position were synthesized and characterized by FT-IR,  $^1\text{H}$  NMR, and element analysis. The absorption and fluorescence characteristics of compounds **5a–5e** showed significant dependences on its molecular structure, which possessed large Stokes shifts (up to  $8309\text{ cm}^{-1}$ ) and high fluorescence quantum yield (up to 0.80) in  $\text{CH}_2\text{Cl}_2$ . These advantageous spectral properties should allow use in many areas.

*J. Heterocyclic Chem.*, **50**, 551 (2013).

## INTRODUCTION

Coumarins and their analogues are an important class of organic heterocyclic dyes, which possess sufficient fluorescence in the visible light range, high quantum yield of photoluminescence, reasonable solubility, and easily optimized structures through variations of substituents at different positions of coumarin core. Based on these unique characteristics, coumarin dyes can be used as fluorescent labels and probes in biology and medicine, optical brighteners, nonlinear optical chromophores, solar energy collectors, laser dyes, and so on [1–7]. However, the undesirable photophysical properties of coumarin fluorophores still constrain the full potential of their applications. For instance, coumarin derivatives have the serious disadvantage of small Stokes shifts, which can lead to serious self-quenching and fluorescence detection errors because of excitation backscattering effects [8]. Therefore, there is a need to develop coumarin derivatives with improved properties. Considerable attention has recently been paid to the exploration of multifluorophores with energy-donor–acceptor architectures such as fluorescence resonance energy transfer (FRET) and through-bond energy transfer (TBET) systems with large pseudo-Stokes shifts and emission shifts [8–11]. However, these cassettes are still

limited by the requirement that the donor emission must have strong or weak overlap with the acceptor absorption.

Generally, hue and fluorescence properties of coumarins can be affected strongly by substituting different groups at the 3-position or 7-position [12,13]. For example, bathochromic shifts in absorption and emission resulting from the extension of stilbene at the 3-position of coumarin were reported [14]. Fluorescence properties of the coumarin compounds can be improved by modifying the electron-accepting ability of the substituent groups at the 3-position. Xu et al. found that 7-styrylcoumarins containing *para*-substituted groups on styrene caused their maximum emission wavelength blue shifts, which increased with their electron-withdrawing ability [15]. Furthermore, it was reported that the coumarin compound that extended at both the 3-position with benzene and 7-position with *para*-chlorostyrene had better fluorescence properties compared with the coumarin with the same extension at 7-position and 4-methyl [15]. From the foregoing, it can be deduced that coumarin fluorescent dyes containing  $\pi$ -conjugated electron donor at the 7-position and  $\pi$ -conjugated electron acceptor at the 3-position should show improved photophysical properties. To our knowledge, few papers have been published so far concerning the synthesis of the extending  $\pi$ -conjugated group of coumarin nucleus at

the 3-position and 7-position. Besides improvement of the range of fluorescent dyes based on coumarins with extending *para*-bromophenyl at the 3-position and different donor groups in 7-position, where substitution of an electron donor group at substituted vinyl with different geometries and electron-donating ability groups (carbazolyl, 4'-methylphenyl, 4'-methoxyphenyl, furyl, thienyl) was used, the aim of this research was investigation of relationship between molecular structure and photophysical properties of novel coumarin compounds (**5a–5e**). For **5a–5e**, push–pull chromophores involved electron-donor and electron-acceptor interacting through a  $\pi$ -conjugating spacer. These moieties could increase the conjugative effect and surely benefit the fluorescence of the compounds, expecting to understand the effect of substituents in coumarin skeleton on the photoluminescent properties of coumarin. The synthetic pathway is shown in Scheme 1.

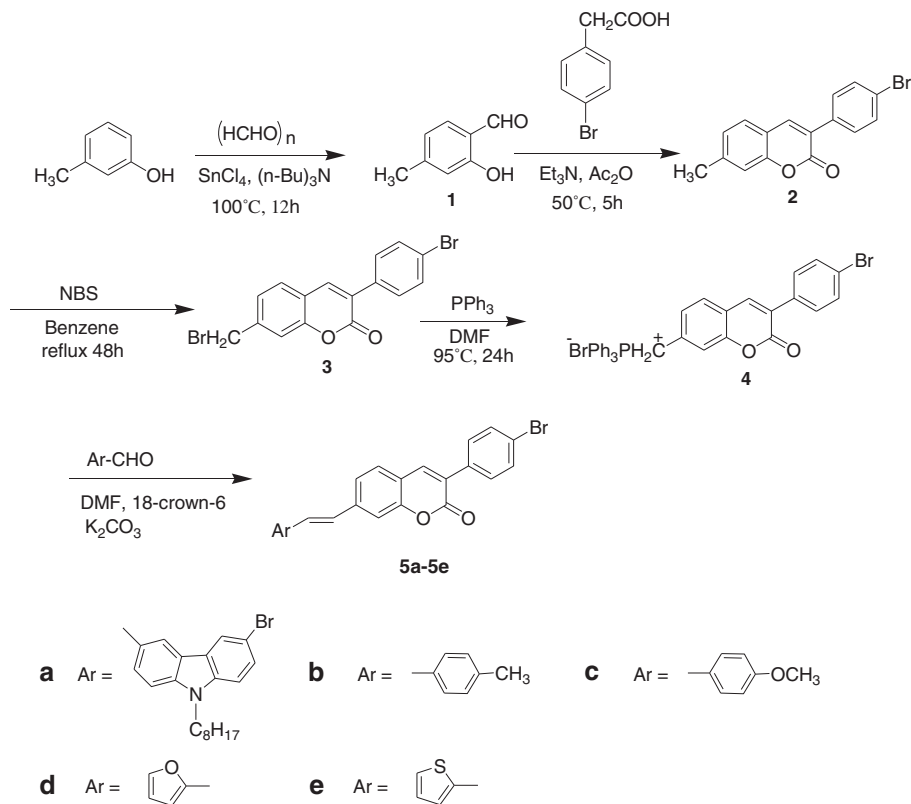
## RESULTS AND DISCUSSION

**Synthesis.** Commercially available 4-methyl phenols underwent the formylation reaction in presence of tri (*n*-butylamine), stannicchloride, and paraformaldehyde at 100°C to furnish 4-methyl-2-hydroxybenzaldehyde (**1**). The classical Perkin condensation is perhaps the most direct and simple method known for the preparation of

3-arylcoumarins [18]. Subsequent Perkin condensation reaction of compound **1** and 4-bromophenylacetic acid was carried out by use of acetic anhydride and triethylamine as catalysts at 50°C, for 5 h, resulting in the formation of 3-(*para*-bromophenyl)-7-(methyl) coumarin (**2**). Comparing the synthetic route herein proposed with previously reported that with *N,N*-dicyclohexylcarbodiimide (DCC) as dehydrating agent, in DMSO, at 110°C reflux, for 24 h to afford 3-phenylcoumarins [19], one can verify that our synthetic method is more effective and more mild. Benzylic bromination of the coumarins with *N*-bromosuccinimide under standard conditions yielded the 3-(*para*-bromophenyl)-7-(bromomethyl) coumarin (**3**). The quaternary phosphonium salts (**4**) were formed by addition of triphenylphosphine to compound **3**. It was subjected to Wittig olefination with aromatic aldehydes to afford 3-(*para*-bromophenyl)-7-(substituted vinyl) coumarins (**5a–5e**) in 60–75% yields.

The structure and purity of the resulting new compounds (**5a–5e**) were confirmed by spectral data and elemental analysis. In the IR spectra of these compounds, the strong bands at around 1707–1723  $\text{cm}^{-1}$  confirm the presence of coumarin skeletons. Bands at about 920–954  $\text{cm}^{-1}$  indicate the formation of *trans* olefin double bonds in these compounds. Presence of aromatic skeleton is verified by peaks at 3047–3061  $\text{cm}^{-1}$  corresponding to aromatic

**Scheme 1.** Synthesis of novel 3-(*para*-bromophenyl)-7-(substituted vinyl) coumarins (**5a–5e**).



C–H stretching. The  $^1\text{H}$  NMR spectra of compounds **5a–5e** showed clearly distinguishable intense peaks at 7.79–8.39 ppm for H-4 of the coumarin nucleus. Such signals are characteristic for coumarin system protons [20]. Moreover, the chemical shifts of *trans*-olefinic protons are located in the range of 7.01–7.28 ppm in double peaks or single peak at 6.47 ppm for compounds **5a–5e**.

**UV-vis properties.** The different substituents in the coumarin nucleus strongly influence the photophysical properties of the resulting derivatives. The absorption spectra of compounds **5a–5e** in  $\text{CH}_2\text{Cl}_2$  solution are shown in Figure 1, and the characteristic data are summarized in Table 1.

As shown in Scheme 1, structural modification occurs only in one terminal moiety of compounds **5a–5e**, where carbazolyl, 4-methylphenyl, 4-methoxyphenyl, furyl, and thienyl were linked to vinyl at 7-position of coumarin core. Such modifications could be expected to result in notable changes in the  $\pi$ -conjugated length and co-plane characteristic. In general, the absorption profiles and the absorption maxima are mainly dominated by the nature of the excited state  $\pi$ -electron system. Some molecules with small geometries and good co-plane characteristics are found to possess much simple absorption band structures. From Figure 1, compounds **5a** and **5e** display weak absorption bands at around 280–320 nm and strong absorption bands at 350–450 nm, which is in agreement with the previously reported that absorption spectrum of coumarin showing two peaks at 281 and 320 nm [21]. On the other hand, the two-peak profiles in absorption spectra indicate that compounds **5a** and **5e** in the excited state suffer structure distortions in the  $\pi$ -conjugated frameworks. However, compounds **5b**, **5c**, and **5d** only show one strong absorption band with  $\lambda_{\text{a,max}}$  at 376, 381, and 338 nm, respectively. The absorption spectrum of compound **5a** ( $\lambda_{\text{a,max}}$  at 402 nm with molar extinction coefficient ( $\epsilon$ ) of  $68,500 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ) is most red-shifted in comparison with that of compounds **5b–5e** ( $\lambda_{\text{a,max}}$  in 338–381 nm range). From the location of  $\lambda_{\text{a,max}}$ , the extent of the excited state  $\pi$ -electron system in compound **5a** seems to be greater than that in other compounds. Moreover, from their extinction coefficients, it can be further confirmed that compound **5a** had the best conjugation chain.

For comparison, absorption spectrum of compound **3** in  $\text{CH}_2\text{Cl}_2$  was also shown in Figure 1. Compound **3** showed  $\lambda_{\text{a,max}}$  at 336 nm with a shoulder peak at 312 nm, which was slightly red-shifted 8 nm than that of **2** ( $\lambda_{\text{a,max}} = 328$  nm) because of their similar structures. The longer absorption bands in 338–402 nm range for compounds **5a–5e** present bathochromic shift as the result of the electron-releasing substituted vinyl in 7-position and electron-withdrawing *para*-bromophenyl group in 3-position that can increase conjugative effect of the molecules. Compared with compound **3**, 66-nm red shift in the absorption

peak together with significant increase in molar extinction coefficient (about 2.50-fold) was found for compound **5a**. The broader spectral response and higher molar absorption coefficient of compound **5a** mainly resulted from a stronger electron-donating ability of carbazolyl vinyl donor than that of bromomethyl donor,  $\pi$ - $\pi^*$  transition in the coumarin ring, *para*-bromophenyl, and substituted vinyl skeleton as well as introducing extended  $\pi$ -conjugated group at the 7-position.

**Fluorimetric properties.** Coumarin itself is not fluorescent; however, the addition of various electron-donating substituents at the 6-position and 7-position and electron-acceptor at the 3-position results in a red shift and enhanced fluorescence intensity. Compounds **2** and **3** have identical emitting wavelengths with  $\lambda_{\text{e,max}} = 410$  nm. The fluorescence spectra of compounds **5a–5e** were measured in  $\text{CH}_2\text{Cl}_2$  and shown in Figure 2.

As compared with compound **3**, the introduction of substituted vinyl group at the 7-position enlarges the conjugation of compounds **5a–5e**, causing red shifts (52–115 nm) in  $\lambda_{\text{e,max}}$ . The efficient  $\pi$ -conjugation in molecule is known to be responsible for charge-transfer nature of the emissive excited state. From Figure 2, it can be observed that all compounds are fluorescent in solution and the substituents have an important effect on their fluorescence spectra. Compound **5a** possesses the emission peaks at 525 nm emitting green light, whereas compounds **5b–5e** have the emission peaks lie in 462–495 nm range, indicating that they emit blue lights.

Compound **5b** had the highest fluorescence quantum yield than that of other compounds. This may be related with the electron-donating ability of substituted vinyl at the 7-position of compounds **5a–5e**. Compound **5b** has weakest electron-donating ability substituents at the 7-position among them. Intramolecular charge-transfer (ICT) between electron-donor at the 7-position and the electron-acceptor at the 3-position makes electron cloud density on the double bond of compound **5b** lower than other compounds accordingly, which reduces the chance of free rotation of the double bond. As a result, the fluorescence quantum yield of compound **5b** was enhanced. In other words, the fluorescence quantum yields increase with the decrease of the electron-donating ability of the 2'-groups in vinyl, because the increase of electron cloud density on the double bond readily leads to *trans-cis* transfer. Thus its fluorescence quantum yield is lowered.

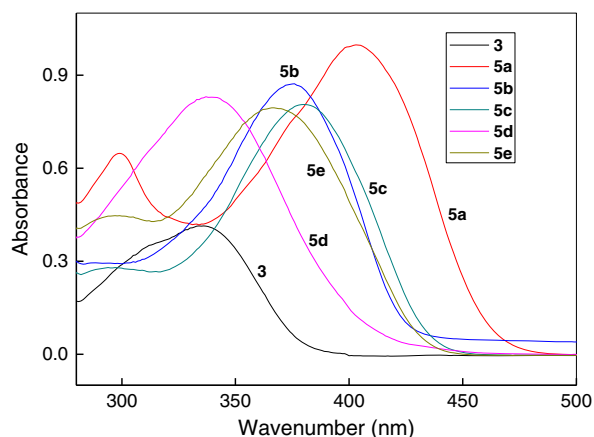
Quantum yield of dye is affected by solvent polarity. Low quantum yields of compounds **5a–5e** were observed in more polar solvent DMF than that of in  $\text{CH}_2\text{Cl}_2$  (Table 1). This behavior indicates the strong interaction of polar nonprotic solvent with the electronic excited state of compounds **5a–5e**. Generally, polarity-induced modulation of non-radiative rates (rotation) in polar solvents leads to a decrease of fluorescence intensity, expressed as low

quantum yield. This fall-off in quantum yield may be ascribed to the conversion of the planar ICT state to a conformer displaying full charge separation, a twisted ICT state [22], which is non-emissive in a polar solvent such as DMF, and by the acceleration of ICT between the electron-donating substituted vinyl at the 7-position and electron-withdrawing *para*-bromophenyl at the 3-position. Danko et al. [23] reported similar results for coumarin fluorophores in different polar solvents. From these results, it can be seen that the quantum yield data of such coumarins are strongly dependent upon solvent polarity and ICT between the electron-withdrawing *para*-bromophenyl group and the C7-substituents.

The Stokes shift ( $\Delta\lambda$ ) is an important parameter for fluorescent dyes. The Stokes shift represents the differences in the properties and structure of the fluorescent compounds between the ground state and the first excited state. The Stokes shifts of all dyes were determined by Eq. (1) [24]:

$$\Delta\lambda = (1/\lambda_A - 1/\lambda_F) \times 10^7 \quad (1)$$

where  $\Delta\lambda$  is Stokes shift, and  $\lambda_A$  and  $\lambda_F$  are absorption and fluorescence maxima, respectively. Expect compound **5b** (Stokes shift:  $4950\text{ cm}^{-1}$ ), other compounds have large Stokes shifts in  $5828\text{--}8309\text{ cm}^{-1}$  range, which is larger than that of compound **3** (Stokes shift:  $5371\text{ cm}^{-1}$ ). Larger Stokes shift generally implies more prominent charge transfer in the excited state that indicates better stabilization of the excited state for compounds **5a** and **5c–5d**. UV-vis and fluorescence data indicate that the high  $\pi$ -conjugated molecule structure enhances the light absorption and the fluorescence emission ability of compounds **5a–5e** because of the contribution of *para*-bromophenyl and substituted vinyl groups.



**Figure 1.** Absorption spectra (nm) of compounds **3** and **5a–5e** in  $\text{CH}_2\text{Cl}_2$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com)].

## CONCLUSIONS

Five new coumarin derivatives (**5a–5e**) containing electron-withdrawing *para*-bromophenyl at 3-position and electron-donating substituted vinyl at 7-position were successfully synthesized and verified by means of IR,  $^1\text{H}$  NMR measurements. The absorption and fluorescence characteristics of **5a–5e** show significant dependences on its molecular structure. The key features of the novel class of compounds **5a–5e** include large Stokes shifts (up to  $8309\text{ cm}^{-1}$ ) and high fluorescence quantum yield (up to 0.80) in  $\text{CH}_2\text{Cl}_2$ . These advantageous spectral properties should allow use of compounds **5a–5e** in many areas.

## EXPERIMENTAL

**Chemicals and instruments.** All reactants were commercially available and used without further purification. All melting points were uncorrected. The IR spectra were measured on a Nicolet/Nexus-870 FT-IR spectrometer with KBr pellets in the range  $4000\text{--}400\text{ cm}^{-1}$ . Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 MHz and chemical shifts are expressed in parts per million using TMS as an internal standard. The UV-vis absorption spectra were recorded using a Helios Alpha UV-vis scanning spectrophotometer. 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  $1200\text{ nm min}^{-1}$ .

**Preparation of 3-bromo-*N*-octyl-6-formylcarbazole.** To a flask containing DMF (5 mmol) in anhydrous chloroform (10 mL) at  $0^\circ\text{C}$ ,  $\text{POCl}_3$  (5 mmol) was added drop by drop and the resulting mixture was stirred for 40 min at room temperature. The reaction mixture again comes down to  $0^\circ\text{C}$  and a solution of 3-bromo-*N*-octyl-carbazole (1 mmol) in chloroform (10 mL) was added dropwise. The resulting reaction mixture was stirred at  $90^\circ\text{C}$  for 8 h (monitored by TLC) and then cooled to room temperature. The reaction mixture was then poured into ice-cold water, NaOH aqueous solution ( $2\text{ mol L}^{-1}$ ) was carefully added to neutralize the acids, and the mixture was extracted with chloroform ( $3 \times 10\text{ mL}$ ). The organic part was then dried with sodium sulfate and evaporated. Purification of the residue was performed by silica gel column chromatography [petroleum ether–ethylacetate (80 : 1, v/v)] to give 0.308 g 3-bromo-*N*-octyl-9-formylcarbazole in 80% yield. m. p.  $86\text{--}87^\circ\text{C}$ , IR(KBr,  $\text{cm}^{-1}$ )  $\nu = 3061, 2926, 2854, 2732, 1692, 1625, 1590, 1480, 1282, 804, 627$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 10.08$  (s, 1H, CHO), 8.55 (s, 1H, Ar-H), 8.27(d, 1H,  $J = 8\text{ Hz}$ , Ar-H), 8.03 (d, 1H,  $J = 8\text{ Hz}$ , Ar-H), 7.61 (d, 1H,  $J = 8\text{ Hz}$ , Ar-H), 7.498(d, 1H,  $J = 8\text{ Hz}$ , Ar-H), 7.33 (d, 1H,  $J = 8\text{ Hz}$ , Ar-H), 4.31 (t, 2H,  $\text{CH}_2$ ), 1.90–1.83 (m, 2H,  $\text{CH}_2$ ), 1.40–1.23 (m, 10H,  $(\text{CH}_2)_5$ ), 0.86 (t, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 191.5, 144.2, 139.8, 129.4, 128.9, 127.5, 124.7, 124.3, 123.5, 122.0, 113.1, 110.8, 109.3, 43.6, 31.7, 29.3, 29.1, 28.9, 27.2, 22.6, 14.1$ .

**Preparation of 4-methyl-2-hydroxybenzaldehyde (1).** 4-methyl-2-hydroxybenzaldehyde (**1**) was synthesized from 4-methyl phenols in the presence of tri(*n*-butylamine), stannicchloride, and paraformaldehyde at  $100^\circ\text{C}$  following the method reported previously [16]. m. p.  $60\text{--}61^\circ\text{C}$ ,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 11.03$  (s, 1H, CHO), 9.82 (s, 1H, OH), 7.40 (d, 1H, Ar-H), 6.80 (d, 1H, Ar-H), 6.79(s, 1H, Ar-H), 2.37(s, 3H,  $\text{CH}_3$ ).

Table 1

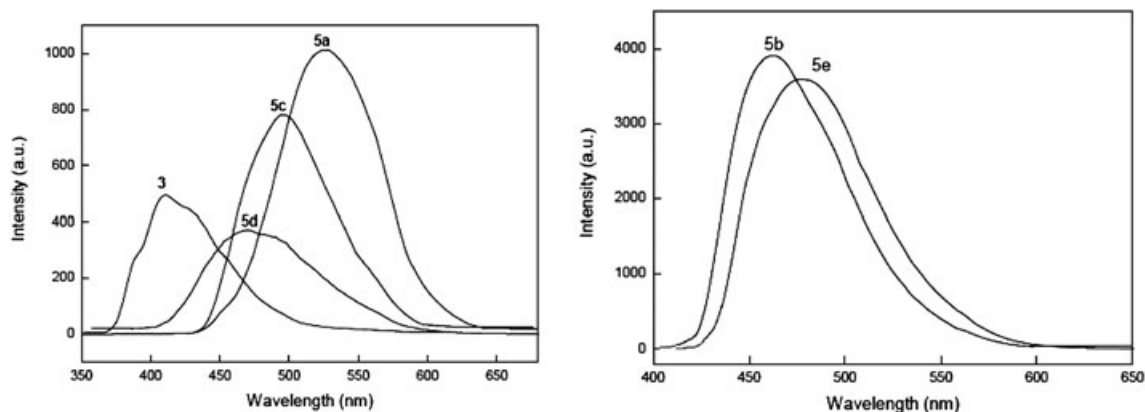
Absorption and emission maxima, Stokes shift, fluorescence quantum yield, and extinction coefficient of compounds **5a–5e**.<sup>a</sup>

Entry	Compounds	$\lambda_{a,max}$ (nm)	$\lambda_{e,max}$ (nm)	$\Delta\lambda$ (cm <sup>-1</sup> )	$\epsilon/mol\ L^{-1}\cdot cm^{-1}$ ( $\times 10^4$ )	$\Phi^b$	$\Phi^c$
1	<b>2</b>	328	410	6097	5.28	0.35	0.25
2	<b>3</b>	336	410	5371	2.74	0.26	0.21
3	<b>5a</b>	402	525	5828	6.85	0.42	0.31
4	<b>5b</b>	376	462	4950	5.82	0.80	0.57
5	<b>5c</b>	381	495	6044	5.86	0.32	0.21
6	<b>5d</b>	338	470	8309	5.61	0.28	0.19
7	<b>5e</b>	367	477	6283	5.34	0.75	0.46

<sup>a</sup>Absorption and emission spectra of dyes measured in CH<sub>2</sub>Cl<sub>2</sub> with the concentrate of solution  $1.0 \times 10^{-5} M$ ,  $\epsilon$  is the extinction coefficient at  $\lambda_{max}$  of absorption.

<sup>b</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>c</sup>Measured in DMF.

Figure 2. Emission spectra (nm) of compounds **3** and **5a–5e** in CH<sub>2</sub>Cl<sub>2</sub>.

**Preparation of 3-(para-bromophenyl)-7-methylcoumarin (2).** Compound **1** (1.36 g, 10 mmol), 4-bromophenylacetic acid (2.26 g, 10.5 mmol) and acetic anhydride (6 mL) were placed in a 100-mL round-bottom flask. After the solids were dissolved, triethylamine (4 mL) was added and white precipitation was obtained. The mixtures were heated at 50°C for 5 h and cooled to room temperature. The precipitate was filtered and washed with ethanol three times. The solids were dried *in vacuo* to afford 2.09 g compound **2** in 66% yield. m.p. 221–222°C; IR(KBr, cm<sup>-1</sup>):  $\nu = 3085, 3044, 2954, 1687, 1401, 1356, 1334, 956, 732$ ; <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.79(s, 1H, Ar-H), 7.61–7.55 (m, 4H, Ar-H), 7.43 (d, 1H,  $J=8$  Hz, Ar-H), 7.18(s, 1H, Ar-H), 7.12 (d, 1H,  $J=8$  Hz, Ar-H), 2.47 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 160.5, 153.7, 143.1, 140.0, 133.8, 131.6, 130.1, 127.7, 125.9, 125.8, 123.0, 117.1, 116.7, 21.9$ .

**Preparation of 3-(para-bromophenyl)-7-(bromomethyl)-coumarin (3).** Compound **2** (500 mg, 1.59 mmol), *N*-bromosuccinimide (325 mg, 1.83 mmol), and BPO (22 mg, 0.09 mmol) were placed in a round-bottom flask containing 25 mL of dried benzene. The contents were heated at reflux for 48 h under a nitrogen atmosphere. After this period, the reaction mixture was cooled and the solvent removed *in vacuo*. Water was added in residue and extracted with dichloromethane (3  $\times$  20 mL). The combined extracts were

dried over anhydrous sodium sulfate. The crude product was passed through a short silica-gel column using ethyl acetate/petroleum ether (1:20, v/v) as the eluting solvent to give 488 mg of light yellow solid **3** in 78% yield. m.p. 185–187°C; IR(KBr, cm<sup>-1</sup>)  $\nu = 3058, 1716, 1610, 1488, 1252, 736, 638, 517$ ; <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.80(s, 1H, Ar-H), 7.61–7.56 (m, 4H, Ar-H), 7.543 (d, 1H,  $J=8$  Hz, Ar-H), 7.38 (s, 1H, Ar-H), 7.34 (d, 1H,  $J=8$  Hz, Ar-H), 4.54 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 160.0, 153.4, 141.8, 139.2, 133.4, 131.3, 130.1, 128.4, 127.6, 125.4, 123.4, 119.3, 116.8, 31.9$ .

**Preparation of phosphonium salts (4).** Triphenylphosphine (320 mg, 1.23 mmol) and compound **3** (400 mg, 1.02 mmol) were dissolved in dry DMF (10 mL) and heated at 95°C for 24 h. Subsequently, the contents were cooled to afford a white solid, which was filtered, washed several times with petroleum ether, and dried to yield 599 mg (90%) of crude product **4** that was used without further purification.

**General procedure for the synthesis of 3-(para-bromophenyl)-7-(substituted vinyl) coumarins (5a–5e).** To a solution of aromatic aldehyde (1.00 mmol) in dried DMF (5 mL) was added potassium carbonate (276 mg, 2.00 mmol) and several drops of 18-Crown-6 under a nitrogen atmosphere. After stirring the reaction mixture for 15 min at room temperature, a solution of compound **4** (1.30 mmol) in dried DMF (5 mL) was added

dropwise and stirred for another 12 h. Then methanol was added to the reaction mixture to give crude solids, which was purified by recrystallization by use of dichloromethane/methanol to give compounds **5a–5e**.

**3-(4'-bromophenyl)-7-(N'-octyl-6'-bromo-3'-carbazolyl vinyl)-2H-chromen-2-one (5a)**: orange solid in 60% yield. m. p. 210–213°C. IR(KBr,  $\text{cm}^{-1}$ )  $\nu$ =3047, 2920, 2852, 1716, 1597, 1478, 1444, 1276 1133, 948, 516;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.39 (1H, s, Ar-H), 8.20 (1H, s, Ar-H), 7.80(1H, s, Ar-H), 7.72 (d, 1H,  $J$ =8 Hz, Ar-H), 7.63–7.39 (m, 10H, Ar-H), 7.28(d, 1H,  $J$ =16 Hz, olefin H), 7.16(d, 1H,  $J$ =16 Hz, olefin H), 4.27 (t, 2H,  $\text{CH}_2$ ), 1.87–1.84 (m, 2H,  $\text{CH}_2$ ), 1.33–1.23 (m, 10H,  $(\text{CH}_2)_5$ ), 0.86 (t, 3H,  $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{37}\text{H}_{33}\text{NO}_2\text{Br}_2$  (%): C, 65.02, H, 4.87; N, 2.05. Found: C, 65.20; H, 4.60; N, 2.23.

**3-(4'-bromophenyl)-7-(4'-methylphenyl vinyl)-2H-chromen-2-one (5b)**: light yellow solid in 70% yield. m. p. 247–249°C. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ =3058, 2922, 2854, 1712, 1597, 1462, 1422, 1262, 1163, 920, 508;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.80 (s, 1H, Ar-H), 7.63–7.87 (m, 9H, Ar-H), 7.51(d, 2H,  $J$ =8 Hz, Ar-H), 7.09(d, 2H,  $J$ =16 Hz, olefin H), 2.38 (s, 3H,  $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{24}\text{H}_{17}\text{O}_2\text{Br}$  (%): C, 69.08, H, 4.11. Found: C, 69.21; H, 4.22.

**3-(4'-bromophenyl)-7-(4'-methoxyphenyl vinyl)-2H-chromen-2-one (5c)**: light yellow solid in 65% yield. m. p. 235–237°C. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ =3047, 2922, 2854, 1707, 1596, 1458, 1422, 1256, 1163, 954, 517;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.80 (s, 1H, Ar-H), 7.61–7.43 (m, 10H, Ar-H), 6.91(d, 1H,  $J$ =8 Hz, Ar-H), 7.01(d, 2H,  $J$ =16 Hz, olefin H), 3.85 (s, 3H,  $\text{OCH}_3$ ). Anal. Calc. for  $\text{C}_{24}\text{H}_{17}\text{O}_3\text{Br}$  (%): C, 66.53, H, 3.95. Found: C, 66.43; H, 3.82.

**3-(4'-bromophenyl)-7-(2'-furyl vinyl)-2H-chromen-2-one (5d)**: yellow solid in 72% yield. m. p. 182–184°C. IR(KBr,  $\text{cm}^{-1}$ )  $\nu$ =3049, 2922, 2854, 1723, 1607, 1460, 1424, 1260, 1108, 943, 515;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.79 (s, 1H, Ar-H), 7.62–7.56 (m, 5H, Ar-H), 7.46 (s, 1H, Ar-H), 7.41–7.39 (m, 2H, Ar-H), 7.04(d, 2H,  $J$ =4 Hz, Ar-H), 6.47(s, 2H, olefin H). Anal. Calc. for  $\text{C}_{21}\text{H}_{13}\text{O}_3\text{Br}$  (%): C, 64.14, H, 3.33. Found: C, 64.26; H, 3.56.

**3-(4'-bromophenyl)-7-(2'-thienyl vinyl)-2H-chromen-2-one (5e)**: light yellow solid in 75% yield. m. p. 216–217°C. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ =3061, 2921, 2852, 1714, 1597, 1483, 1418, 1266, 1128, 953, 509;  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.81 (s, 1H, Ar-H), 7.50 (d, 2H,  $J$ =12 Hz, Ar-H), 7.40 (d, 2H,  $J$ =12 Hz, Ar-H), 7.62–7.57 (m, 6H, Ar-H), 6.55(d, 1H,  $J$ =12 Hz, olefin H), 6.80(d, 1H,  $J$ =12 Hz, olefin H). Anal. Calc. for  $\text{C}_{21}\text{H}_{13}\text{O}_2\text{BrS}$  (%): C, 61.62, H, 3.20. Found: C, 61.84; H, 3.39.

**Determination of the fluorescence quantum yield.** Fluorescence quantum yields were determined using a previously adopted procedure [17]. The determination was carried out in  $\text{CH}_2\text{Cl}_2$ .

**Acknowledgments.** The supports by the National Natural Science Foundation of China (20904010) and the Fundamental Research Funds for the Central Universities (2009ZM0170) are gratefully acknowledged.

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