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Synthesis of styrylcoumarins from coumarin diazonium salts and studies on their spectra characteristics

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Abstract

A facile synthesis of styrylcoumarins based on Palladium-catalyzed reaction of coumarin diazonium salts with substituted styrenes is described. The reactions produced a series of 7-styrylcoumarins in good yields under mild conditions. The absorption and emission spectra of different styrylcoumarins were compared and discussed. Although the $\lambda_{a,max}$ of the styrylcoumarins changed only slightly with a *p*-substituted styrene, the $\lambda_{e,max}$ produced a blue shift which increased with the electron-withdrawing ability of the *p*-substituted group. The *p*-CH_3 of styrylcoumarin caused a red shift of ca. 20 nm and also a higher fluorescence quantum yield. Styrylcoumarins with *o*, *p*-CN obtained well-resolved vibrational bands and the latter possessed higher fluorescence quantum yield. In addition, a coumarin extended at both the 3-positions with benzene and 7-position with p-chlorostyrene had better fluorescence properties.

Keywords: Diazonium salts; Fluorescence quantum yield; Palladium-catalyzed reaction; Styrylcoumarin

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1. Introduction

Coumarin compounds have attracted great interest in recent years in the field of optoelectronic materials [1–3]. Due to the lactone skeleton, coumarins produce stronger fluorescence than open-chain analogs [4,5]. Their strong fluorescence is also closely associated with charge transfer configuration arising from electron transfer from the styryl to the carbonyloxy group [6]. A number of coumarins have been commercialized as optical brighteners [7,8] and also as fluorescent and laser dyes [10–12].

Hue and fluorescence properties of coumarins can been affected strongly by substituting different groups at the 3- or 7-position [7–12]. Fluorescence properties of the coumarin compounds can be improved by modifying the electron-accepting ability of the substituent groups at the 3-position. Previously, we found bathochromatic shifts in absorption and emission resulting from the extension of stilbene at the 3-position of coumarin [13]. In the course of our research, we have become interested in the substituent effect at the 7-positon of coumarin. This paper reports on the relationship between fluorescence properties and coumarin compounds extending styrene at the 7-position, as well as a novel method for preparing 7-styrylcoumarins from coumarin diazonium by

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palladium-catalyzed reaction. The palladium-catalyzed C–C bonding formation is a powerful synthesis tool and has been widely used in organic synthesis [14–16]. Using aryldiazonium as the substrate in the palladium-catalyzed reaction allows the reaction to proceed under mild conditions.

2. Experimental

2.1. Materials and equipment

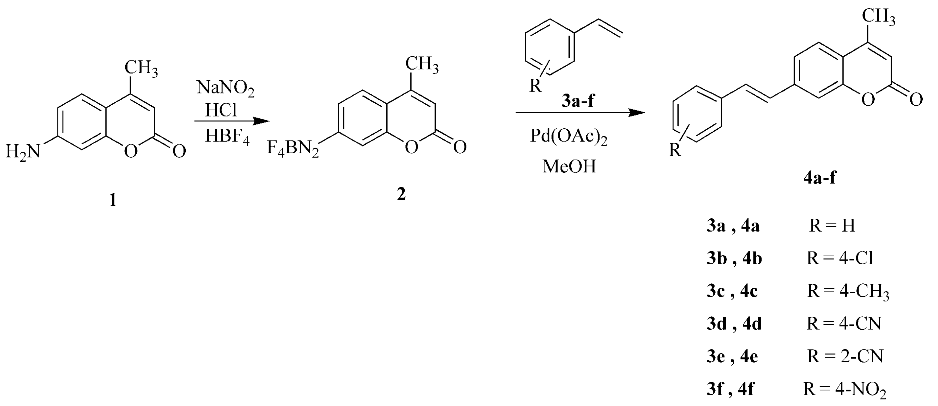
The NMR spectra of ^{1}H were recorded on a Varian Mercury V×300 NMR spectrophotometer with TMS as the internal standard. Silica gel (100–140 mesh) was used for column chromatography. A PerkinElmer 983 was used to determine the IR spectra. UV/Vis absorption spectra were taken on a HP8452A spectrometer. Fluorescence spectra were determined by a PerkinElmer LS-50B fluorescence spectrophotometer. Elemental analyses were recorded on an EA 1108 apparatus.

2.2. Synthesis of coumarin diazonium salts

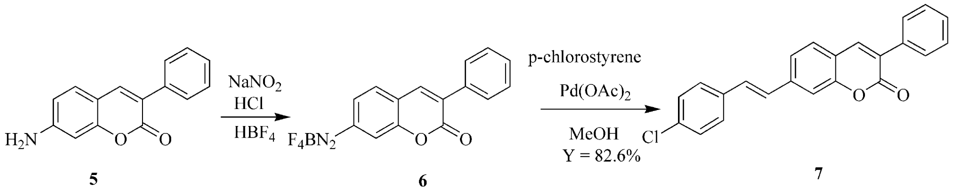
Coumarin diazonium salts were prepared by the following method: 12 ml of 2.75 M $NaNO_2$ was added dropwise to an ice-cold mixture of coumarin **1** (Scheme 1) or **5** (Scheme 2) (32 mmol) in 18% HCl (18 ml, 10.5 mmol). After 1 h of stirring at 0 °C, 40% HBF_4 (9.1 g, 41 mmol) was added, then stirring continued for another hour at 0 °C. The mixture was filtered and washed with cold water, followed in turn by washing in cold methanol and ether. After drying at room temperature, the product obtained was a light brown powder. The resulting products were 4-methylcoumarin-7-diazonium tetrafluoroborate (**2**) (7.45 g, 85.1% yield, Scheme 1), with a decomposition temperature of 132 °C, or 3-phenylcoumarin-7-diazonium tetrafluoroborate (**6**) (4.4 g, 40.9% yield, Scheme 2), with decomposition at 196 °C.

2.3. Preparation of styrylcoumarin derivatives

The general procedure for the Heck reaction coupling coumarin diazonium salts and the six substituted styrenes was as follows: 0.72 mmol coumarin diazonium salt and 0.031 mmol palladium acetate were placed in a 25-ml sealed flask. The flask was evacuated and purged with nitrogen gas. Ten ml of methanol and a 1.44 mmol corresponding substituted styrene, prepared by the method described by Butcher, were added by syringe. The reaction was continued until the solution color changed. Methanol was removed by evaporation at atmospheric pressure. Dichloromethane was added, the mixture was washed twice with water, dried with Na_2SO_4 and concentrated under atmospheric pressure. Chromatography of the residue over silica gel gave pure products.



Scheme 1. Synthesis of 4-methyl-7-styrylcoumarins. Reagents and reaction conditions: (i) $NaNO_2$, HCl, 40% HBF_4; (ii) substituted styrene, $Pd(OAc)_2$, MeOH, 40 °C, 5 min–2 h.



Scheme 2. Synthesis of 3-phenyl-7-styrylcoumarin. Reagents and reaction conditions: (i) NaNO$_2$, HCl, 40% HBF$_4$; (ii) *p*-chlorostyrene, Pd(OAc)$_2$, MeOH, 40 °C, 35 min.

2.3.1. 7-Styryl-4-methylcoumarin (4a)

Yellow flake (0.159 g, 84.2% yield), m.p. 188 °C; ^{1}H NMR (CDCl$_3$) $\delta = 2.45$ (*d*, *J* = 1.5 Hz, 3H, CH$_3$), 6.27 (*d*, *J* = 1.5 Hz, 1H), 7.03 (*d*, *J* = 16.5 Hz, 1H), 7.24 (*d*, *J* = 16.5 Hz, 1H), 7.28–7.61 (*m*, 8H). IR (KBr) 1715, 1703, 1605, 1540, 1490, 1450, 1410, 1385, 1365, 1255, 1215, 1145, 1060, 1015, 970, 945, 885, 840, 810, 750, 685, 620, 575, 490, 430 cm^{-1}; Anal. Calcd for: C, 82.42%; H, 5.38%. Found: C, 82.44%; H, 5.50%.

2.3.2. 7-(4-Chlorostyryl)-4-methylcoumarin (4b)

Yellow needle (0.150 g, 70.3% yield), m.p. 200 °C; ^{1}H NMR (CDCl$_3$) $\delta = 2.44$ (*d*, *J* = 1.2 Hz, 3H, CH$_3$), 6.27 (*d*, *J* = 1.2 Hz, 1H), 7.08 (*d*, *J* = 16.2 Hz, 1H), 7.17 (*d*, *J* = 16.2 Hz, 1H), 7.35 (*d*, *J* = 8.4 Hz, 2H), 7.42 (*s*, 1H), 7.43 (*dd*, *J* = 8.4,1.8 Hz, 1H), 7.48 (*d*, *J* = 8.4 Hz, 2H), 7.58 (*d*, *J* = 8.4 Hz, 1H). IR (KBr) 1720, 1695, 1605, 1590, 1540, 1490, 1415, 1385, 1360, 1315, 1285, 1260, 1230, 1220, 1180, 1150, 1090, 1060, 1010, 980, 970, 960, 940, 885, 870, 850, 840, 820, 730, 710, 680, 625, 575, 540, 520, 500, 460, 430, 400 cm^{-1}; Anal. Calcd for: C, 72.85%; H, 4.42%; Found: C, 73.08%; H, 4.54%.

2.3.3. 7-(4-Methylstyryl)-4-methylcoumarin (4c)

Yellow needle (0.147 g, 74% yield), m.p. 186 °C; ^{1}H NMR (CDCl$_3$) $\delta = 2.38$ (*s*, 3H, CH$_3$), 2.43 (*d*, *J* = 1.2 Hz, 3H, CH$_3$), 6.25 (*q*, *J* = 1.2 Hz, 1H), 7.06 (*d*, *J* = 16.2 Hz, 1H), 7.20 (*d*, *J* = 16.2 Hz, 1H), 7.19 (*d*, *J* = 8.7 Hz, 2H), 7.41 (*s*, 1H), 7.43 (*dd*, *J* = 8.4,1.8 Hz, 1H), 7.44 (*d*, *J* = 8.7 Hz, 2H), 7.56 (*d*, *J* = 8.4 Hz, 1H). IR (KBr) 1715, 1695, 1600, 1540, 1510, 1500, 1440, 1415, 1385, 1360, 1315, 1290, 1280, 1250, 1230, 1215, 1180, 1140, 1060, 1010, 970, 950, 880, 850, 840, 820, 800, 750, 720, 710, 680, 620, 570, 550, 540, 520, 500, 430 cm^{-1}; Anal. Calcd for: C, 82.58%; H, 5.84%. Found: C, 82.59%; H, 6.00%.

2.3.4. 7-(4-Cyanostyryl)-4-methylcoumarin (4d)

Yellow needle (0.164 g, 79.5% yield), m.p. 220 °C; ^{1}H NMR (CDCl$_3$) $\delta = 2.45$ (*d*, *J* = 1.5 Hz, 3H, CH$_3$), 6.30 (*q*, *J* = 1.5 Hz, 1H), 7.18 (*d*, *J* = 16.5 Hz, 1H), 7.24 (*d*, *J* = 16.5 Hz, 1H), 7.45 (*s*, 1H), 7.46 (*dd*, *J* = 8.7,1.8 Hz, 1H), 7.61 (*d*, *J* = 8.7 Hz, 1H), 7.62 (*d*, *J* = 8.7 Hz, 2H), 7.67 (*d*, *J* = 8.7 Hz, 2H). IR (KBr) 2220, 1730, 1605, 1600, 1540, 1495, 1440, 1415, 1385, 1360, 1290, 1260, 1250, 1220, 1185, 1170, 1135, 1060, 1015, 970, 950, 885, 875, 855, 820, 750, 705, 680, 620, 575, 550, 520, 435 cm^{-1}; Anal. Calcd for: C, 79.43%; H, 4.56%; N, 4.88%. Found: C, 79.23%; H, 4.63%; N, 4.84%.

2.3.5. 7-(2-Cyanostyryl)-4-methylcoumarin (4e)

Yellow needle (0.175 g, 83.3% yield), m.p. 225 °C; ^{1}H NMR (CDCl$_3$) $\delta = 2.46$ (*d*, *J* = 1.2 Hz, 3H, CH$_3$), 6.29 (*q*, *J* = 1.2 Hz, 1H), 7.29 (*d*, *J* = 16.5 Hz, 1H), 7.39 (*t*, *J* = 7.5 Hz, 1H), 7.43 (*s*, 1H), 7.55 (*d*, *J* = 16.5 Hz, 1H), 7.55–7.65 (*m*, 3H), 7.68 (*d*, *J* = 7.5 Hz, 1H), 7.83 (*d*, *J* = 7.5 Hz, 1H). IR (KBr) 2220, 1720, 1605, 1540, 1475, 1450, 1415, 1385, 1370, 1310, 1280, 1175, 1150, 1070, 1015, 990, 970, 950, 885, 875, 860, 810, 760, 700, 625, 570, 490, 430 cm^{-1}; Anal. Calcd for: C, 79.43%; H, 4.56%; N, 4.88%. Found: C, 79.01%; H, 4.72%; N, 4.85%.

2.3.6. 7-(4-Nitrostyryl)-4-methylcoumarin (4f)

Light brown crystal (0.291g, 65.9% yield), m.p. 288–290 °C; ^{1}H NMR (DMSO-d_6) $\delta = 2.49$ (*d*, *J* = 1.2 Hz, 3H, CH$_3$), 6.36 (*t*, *J* = 1.2 Hz, 1H), 7.60 (*s*, 2H), 7.66 (*d*, *J* = 9.0 Hz, 1H), 7.67 (*s*), 7.78 (*d*, *J* = 9.0 Hz, 1H), 7.89 (*d*, *J* = 8.7Hz, 2H), 8.25 (*d*, *J* = 8.7 Hz, 2H). IR (KBr) 1715, 1705, 1610, 1590, 1510, 1440, 1420, 1385, 1365, 1335, 1190, 1150, 1110, 1065, 1015, 990, 975, 880, 870, 840, 745, 705, 690, 630, 580, 540, 495, 420 cm^{-1}; Anal. Calcd for: C, 70.35%; H, 4.26%; N, 4.56%. Found: C, 69.78%; H, 4.57%; N, 4.65%.

2.3.7. 7-(4-Chlorostyryl)-3-phenycoumarin (7)

Yellow needle (0.213 g, 82.6% yield), m.p. 216 °C; ^{1}H NMR ($CDCl_3$) $\delta = 7.11$ (*d*, $J = 16.5$ Hz, 1H), 7.19 (*d*, $J = 16.5$ Hz, 1H), 7.36 (*d*, $J = 8.4$ Hz, 2H), 7.41–7.47 (*m*, 5H), 7.49 (*d*, $J = 8.4$ Hz, 2H), 7.52 (*d*, $J = 8.7$ Hz, 1H), 7.72 (*dd*, $J = 7.8$ Hz, 2H), 7.81 (*s*, 1H). IR (KBr) 1715, 1695, 1610, 1600, 1585, 1485, 1440, 1420, 1155, 1135, 1125, 1085, 1005, 960, 910, 885, 865, 825, 780, 720, 695, 625, 570, 550, 510, 410 cm^{-1}; Anal. Calcd for: C, 76.99%; H, 4.21%. Found: C, 76.68%; H, 4.34%.

2.4. Determination of the fluorescence quantum yield

Fluorescence quantum yields were determined using a previously adopted procedure [6]. The determination was carried out in a polar aproton solvent THF.

3. Results and discussion

3.1. Synthesis of different substituted styrylcoumarin derivatives

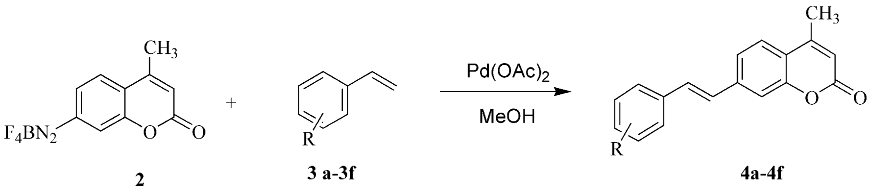
4-Methyl-7-styrylcoumarins (compounds **4a**–**f**) were prepared with coumarin diazonium salts and substituted styrene (Scheme 1). 3-Phenyl-7-styrylcoumarin (compound **7**) was similarly produced (Scheme 2).

The scope of the palladium catalyzed coupling of coumarin diazonium salts with substituted styrene is shown in Table 1. The reactions were carried out in the presence of 4 mol% $Pd(OAc)_2$ in methanol under N_2 at 40 or 60 °C and it is notable that the E-form coupled products were produced with high yields (Table 1, Entries 1,2,4–7). *p*-Chloro substituted styrylcoumarin **4b** was achieved in a low yield of 14% at 60 °C in MeOH under N_2, (Table 1, Entry 3) [7–24]. When the reaction temperature was 40 °C, a higher yield of 70.3% can be reached in a few minutes (Table 1, Entry 2). Under similar conditions, compound **4a** and p-methyl substituted compound **4c** were produced in yields of 84.2 and 74.0% respectively (Table 1, Entries 1,4). Electronwithdrawing *p*- and *o*-cyanostyrene substituted compounds **4d** and **4e** were also produced in yields of 79.5% and 83.3% under the above-stated conditions (Table 1, Entries 5, 6). Otherwise, the reaction proceeded for a longer time as a lower yield when using strong electronwithdrawing *p*-nitrostyrene (Table 1, Entry 7).

3.2. Absorption and emission spectra of prepared styrylcoumarin derivatives

A series of substituted 7-styrylcoumarins were synthesized. The absorption-emission spectra were

Table 1
Palladium-catalyzed reaction of 4-methylcoumarin-7-diazonium tetrafluoroborate with substituted styrene



Entry	Styrene (**3a**–**3f**)	Temperature (°C)	Product[a]	Yield (%)
1	**3a** R = H	40	**4a**	84.2
2	**3b** R = 4-Cl	40	**4b**	70.3
3	**3b** R = 4-Cl	60	**4b**	14.0
4	**3c** R = 4-CH_3	40	**4c**	74.0
5	**3d** R = 4-CN	40	**4d**	79.5
6	**3e** R = 2-CN	40	**4e**	83.3
7	**3f** R = 4-NO_2	40	**4f**	65.9

[a] Reaction conditions: 4 mol% $Pd(OAc)_2$, MeOH, under N_2, 5 min–2 h.

Table 2
Absorption and emission maxima, Stokes shift, fluorescence quantum yield and extinction coefficient of tested compounds

Entry	Compounds	$\lambda_{a,max}$ (nm)	$\lambda_{e,max}$ (nm)	$\Delta\lambda$ (nm)	ε/mol l^{-1} cm^{-1} ($\times 10^4$)	Φ
1	**4a**	350	407	57	2.97	0.117
2	**4b**	352	406	54	3.85	0.144
3	**4c**	354	422	68	3.26	0.303
4	**4d**	356	403	47	5.05	0.365
5	**4e**	352	400	48	3.53	0.176
6	**4f**	352	396	44	2.03	0.005
7	**7**	372	448	76	5.35	0.650

studied and the fluorescence quantum yields were determined. Table 2 lists the UV–vis absorption maxima ($\lambda_{a,max}$), emission maxima ($\lambda_{e,max}$), Stokes shift ($\Delta\lambda$), extinction coefficient (ε/mol l^{-1} cm^{-1}), and fluorescent quantum yield (Φ) of tested compounds.

In a comparison of compounds **4a**–**f** (Table 2, entries 1–6), it can be seen that the $\lambda_{a,max}$ changed slightly and, from their extinction coefficients, that compound **4d** had the best conjugation chain. Their emission spectra are showed in Figs. 1 and 2, the emission spectra of compounds.

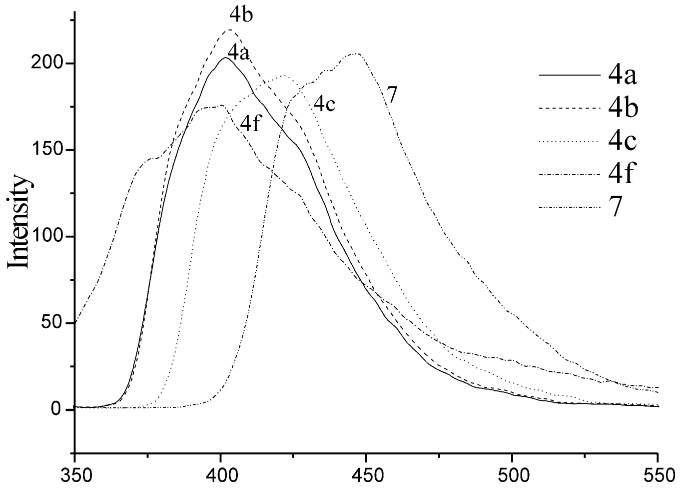


Fig. 1. Emission spectra (nm) of **4a**–**c**, **4f** and **7** in THF.

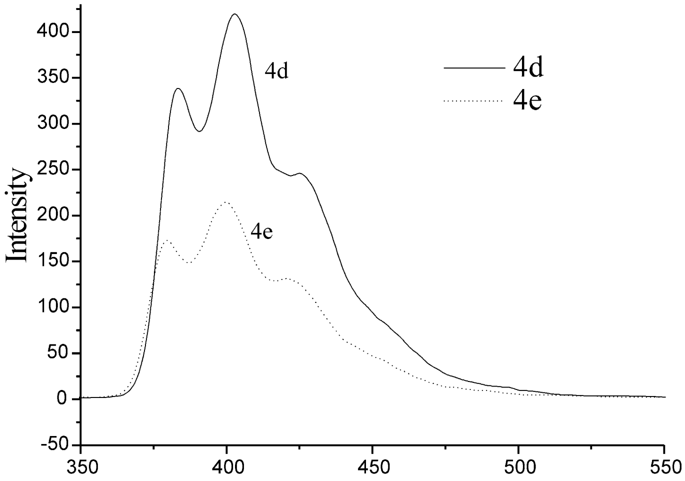


Fig. 2. Emission spectra (nm) of **4d** and **4e** in THF.

4a, **4b** (Fig. 1), **4d** and **e** (Fig. 2) were located between 360–550 nm, with a $\lambda_{e,max}$ at ca. 400 nm and two shoulders at ca. 380 and 422 nm. The vibration bands of **4d** were located at 382, 403 and 422 nm and those of **4e** were at 379, 400, 422 nm. The fluorescence quantum yield of **4d** was higher than **4e** (Table 2, entries 4, 5). The well-resolved vibrational bands of compounds **4d** and **e** showed that the interval of their energy levels leading to the different conformation of the compounds at ground state were larger (Fig. 2). Compound **4c** had a greater fluorescence quantum yield and Stokes shift, with a red-shifted emission spectrum occurring between 370–530 nm (Fig. 1) with a $\lambda_{e,max}$ at 422 nm, than **4a** and **b** (Table 2, Entries 1–3). The strong electron-withdrawing *p*-nitro substituted compound **4f** had a blue shift of 11 nm compared with unsubstituted compound **4a** and produced a strong extinction effect on its fluorescence intensity (Table 2, Entries 1,6). In general, the $\lambda_{e,max}$ produced a blue shift which increased with the electron-withdrawing ability of the *p*-substituted group (Table 2, Entries 1–4,6).

Compound **7** extended at both the 3-position with benzene and 7-position with *p*-chlorostyrene (Scheme 2) was produced under similar conditions in good yield. It is notable that this compound, with the extension at 3-position, produced a 20 nm bathochromic shift of the absorption maximum, greater Stokes shift of 76 nm (Fig. 1) and considerable enhancement of fluorescence quantum yield from 0.144 to 0.650 (Table 2, Entries 2, 7). Compound **7** has better fluorescence properties and its application work is undergoing.

4. Conclusions

Coumarin diazonium salts were used as the substrate, allowing the reaction to proceed under mild condition in good yield for the preparation of novel styrylcoumarins. *p*-Substituted groups on styrene at the 7-position of these coumarins caused their $\lambda_{e,max}$ blue shifts, which increased with their electron-withdrawing ability. The *p*-CH_3 and *p*-CN substituted styrylcoumarin had higher fluorescence quantum yield. In addition, a coumarin compound extended at both the 3-position with benzene and 7-position with *p*-chlorostyrene had better fluorescence properties compared with coumarin with the same extension at 7-position and 4-methyl.

Acknowledgements

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References

[1] Avramenbo LF, Grigorenko TF, Kondratenko PA. Structure and spectral properties of substituted 3-phenylcoumarin derivatives. Ukr Khim, Zh 1996;62(5–6):44–9.

[2] El-Ansary SL, Mikhail AN, Taliawi GMEl, Farag NAH. New furobenzopyrone analogs as photochemotherapeutic agents. Bull Fac Pharm 1998;36(3):73–83.

[3] Vijayan KK. One step synthesis of 3-Phenylcoumarins and benzylidene coumaran-2-ones. Indian J Heterocyclic Chem 1998;8:1–6.

[4] Kazuyoshi O, Hinohara T, Matsui K. Kogyo Kagaku Zasshi 1968;71(7):1010–5.

[5] Fan MG. Photochemistry fundamental principles and photon material science. Science Press; 2001.

[6] Hinohara T, Honda M, Amano K, Cho S, Matsui K. Excited states and fluorescence properties of 7-substituted coumarins. Nippon Kagaku Zasshi 1981;4:477–80.

[7] Siegrist AE, Eckhardt C, Kaschig J, Schmidt E. Ullmann. 5th ed. Weinheim: VCH Verlagsges; 1991.

[8] Harold J, McElhone J. Kirk-Othmer, vol. 11. 4th ed. New York: John Wiley & Sons; 1994.

[9] Wheelock CE. The fluorescence of some coumarins. J Am Chem Soc 1959;81:1348.

[10] Ayyangar NR, Srinivasan KV, Daniel T. Polycyclic compounds part VII. Synthesis, laser characteristics and dyeing behaviour of 7-diethylamino-2H-1-benzopyran-2-ones. Dyes and Pigments 1991;16:197–204.

[11] Griffiths J, Millar V. The influence of chain length and electron acceptor residues in 3-substituted 7-*N*,*N*-diethylaminocoumarin dyes. Dyes and Pigments 1995;28:327–39.

[12] Dai ZH, Wu SK. Photophysical properties of coumarins derivatives in solvents. Wuli Huaxue Xuebao 1999;15(12):1076–81.

[13] Zhang YY, Meng XM, Wang XL, Xu LH. Studies on the synthesis and spectra characteristics of stilbenylcoumarin organic materials. Dyes and Pigments 2003;156(3):189–94.

[14] Heck RF. Org React. New York: John Wiley & Sons; 1982. vol. 27.

[15] Schiedel MS, Briehn CA, Bäuerle P. Mini review C-C cross-coupling reactions for the combinatorial synthesis of novel organic materials. J Organomet Chem 2002;653: 200–8.

[16] Tsuji J. Palladium reagents and catalysts: innovations in organic synthesis. Chichester: John Wiley & Sons; 1995.

[17] Kikukawa K, Nagira K, Matsuda T. Synthesis of 4′-vinylbenzo-15-crown-5. Bull Chem Soc 1977;50(8):2270.

[18] Kikukawa K, Nagira K, Wada F, Matsuda T. Reaction of diazonium salts with transition metals—III. Tetrahedron 1981;37:31–6.

[19] Brunner H, Courcy NLCC. (Nathale Le Cousturier de Courcy), Genêt JP. Heck reactions using aryldiazonium salts towards phosphonic derivatives. Synlett 2000; 2:201–4.

[20] Wang Y, Pang Y, Zhang Z, Hu H. Arylation of camphene with arenediazonium salts catalyzed by palladium acetate. Synthesis 1991:967.

[21] Kikukawa K, Matsuda T. Reaction of diazonium salts with transition metals i. arylation of olefins with arenediazonium salts catalyzed by zero valent palladium. Chem Lett 1977:159–62.

[22] Sengupta S, Bhattacharya S. Heck reaction of arenediazonium salts: a palladium-catalysed reaction in an aqueous medium. J Chem Soc Perkin Trans 1 1993; 1943.

[23] Darses S, Pucheault M, Genêt JP. Efficient access to perfluoroalkylated aryl compounds by Heck reaction. Eur J Org Chem 2001:1121–8.

[24] Andrus MB, Song C, Zhang J. Palladium-imidazolium carbene catalyzed mizoroki-Heck coupling with aryl diazonium ions. Org Lett 2002;4(12):2079–82.