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Synthesis and Photoinduced Fluorescence of 3-(2-Hetarylethenyl)chromen-2-ones

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Abstract—3-(2-Hetarylethenyl)chromen-2-ones were synthesized for the first time, following two different schemes, and their spectral and photochemical properties were studied. The title compounds were found to undergo both reversible and irreversible photoinduced transformations which are accompanied by considerable change of the fluorescence pattern.

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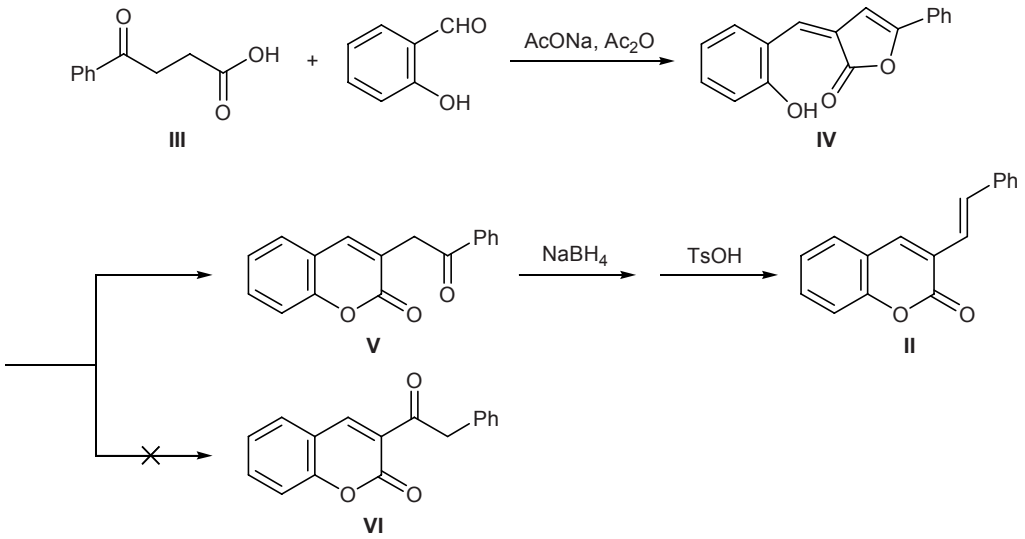
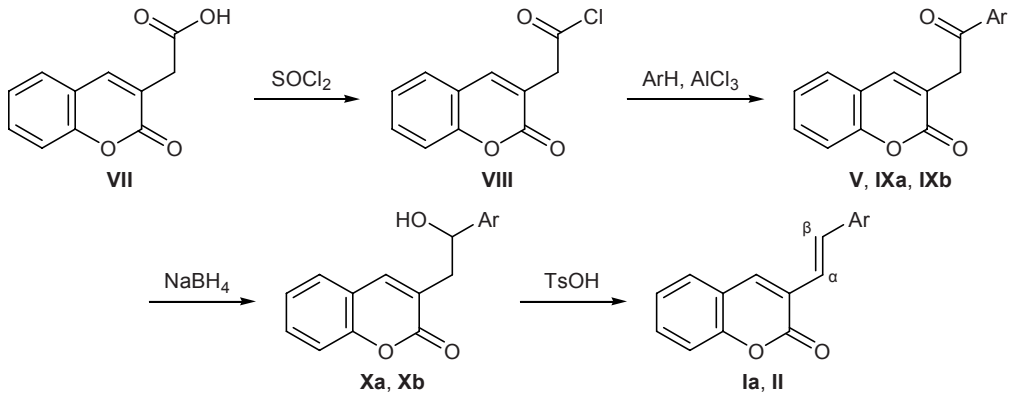
Interest in photochromic dihetarylethenes originates from their possible application as materials for optoelectronic devices, in particular for creation of high-capacity optical data storage media [1]. Here, preference is given to light-sensitive systems capable of changing their fluorescence properties under the action of actinic light [2].

A possible way of building up appropriate compounds consists of introduction into a chromophoric molecule of a fluorophoric fragment, for example, a coumarin moiety. It is known that many coumarin derivatives are effective fluorophores characterized by high fluorescence quantum yields [3]. Taking the above stated into account, we were the first to synthesize coumarine derivatives of the dihetarylethene series. We obtained new unsymmetrical dihetarylethenes **I** containing coumarin and thiophene (or furan) fragments.

Scheme 1.



Scheme 2.



Ia, **IXa**, **Xa**, Ar = 2,5-dimethylthiophen-3-yl; **II**, **V**, **Xb**, Ar = Ph; **IXb**, Ar = 2-methyl-1-benzothiophen-3-yl.

There are no published data on the synthesis of 3-(2-hetarylethenyl)chromen-2-ones. Some synthetic approaches to fluorescent arylethenes containing a coumarin fragment have been reported, but the available data are contradictory. For example, various 3-styrylcoumarin derivatives **II** were obtained according to Scheme 1 [4]. Condensation of salicylaldehyde with 4-phenyl-4-oxobutanoic acid (**III**) gave butenolide **IV** which underwent rearrangement into acyl coumarin derivative under acidic [4, 6] or basic conditions [5]. However, the data on the product structure were ambiguous. According to [5, 6], the product had 3-phenacylcoumarin structure **V**, whereas Chodankar et al. [4] presumed formation of phenylacetyl-substituted coumarin **VI**. In both cases, the assignment was based only upon IR spectral data. We reproduced the synthesis of compound **V** described in [4]. The physical constants of butenolide **IV** differed from those reported in [4], and the mass spectrum of ketone **V** contained a peak with *m*/*z* 105, corresponding to benzoyl ion. These data indicate that the rearrangement of butenolide **IV** yields 3-phenacylcoumarin (**V**) rather than 3-(phenylacetyl)coumarin (**VI**) as presumed in [4]. The subsequent reduction of **V** with sodium tetrahydridoborate and dehydration of the alcohol thus formed afforded 3-styrylcoumarin (**II**).

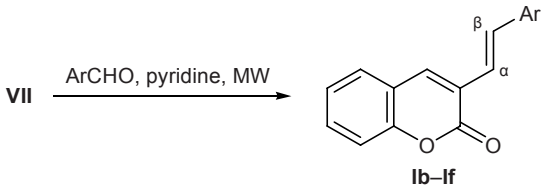
However, analogous syntheses of heteroanalogs of ketone **V** as key compounds for the preparation of new photochromes (Scheme 1), cannot be regarded as promising, for at least to steps in this scheme, the formation of butenolide **IV** and its rearrangement into ketone **V**, are characterized by fairly moderate yields (45 and 52%, respectively). Therefore, we made an attempt to reduce the number of steps and improve the overall yield of ketone **V** and its heteroanalogs via acylation of benzene and the corresponding hetarenes with (2-oxo-2*H*-chromen-3-yl)acetyl chloride (**VIII**). (2-Oxo-2*H*-chromen-3-yl)acetic acid (**VII**) was synthesized by reaction of salicylaldehyde with succinic anhydride. The yield of acid **VII** was greater when triethylamine rather than sodium succinate [7] was used as base (57 and 40%, respectively). Treatment of acid **VII** with excess thionyl chloride at room temperature (reaction time 12 h) gave (2-oxo-2*H*-chromen-3-yl)acetyl chloride (**VIII**), and the latter was used to acylate benzene in the presence of anhydrous aluminum chloride at 50°C (3 h). As a result, ketone **V** was obtained in 75% yield (Scheme 2).

Following Scheme 2, we succeeded in synthesizing heterocyclic analogs of 3-phenacylcoumarin (**V**). In particular, the acylation of 2,5-dimethylthiophene and 2-methyl-1-benzothiophene with chloride **VIII** in the presence of $AlCl_3$ as catalyst at –5 to –10°C gave ketones **IXa** and **IXb** in 71 and 63% yield, respectively. The subsequent reduction of ketone **IXa** with sodium tetrahydridoborate and dehydration of alcohol **Xa** gave dihetarylethene **Ia** (Scheme 2). The reduction of ketone **IXb** under analogous conditions occurred in a complicated fashion, and we failed to isolate the corresponding alcohol.

One more synthetic approach to 3-styrylcoumarins is based on the condensation of (2-oxo-2*H*-chromen-3-yl)acetic acid (**VII**) with substituted benzaldehydes, which leads to the formation of the target products in one step (Scheme 3) [4]. Attack by the activated methylene carbon atom in acid **VII** on the aldehyde carbonyl group is followed by decarboxylation, yielding disubstituted alkene.

We tried to extend this approach to the synthesis of 3-(2-hetarylethenyl)coumarins. In fact, by reaction of acid **VII** with heterocyclic aldehydes in pyridine in the

Scheme 3.



Ar = 2-methyl-1-benzothiophen-3-yl (**b**), 2-thienyl (**c**), 5-methylthiophen-2-yl (**d**), 2-furyl (**e**), 5-methylfuran-2-yl (**f**).

presence of piperidine we obtained compounds **Ib**–**If**. We also found that the reaction can be activated by microwave irradiation. For example, the yield of compound **Ib** in the thermal reaction (heating under reflux on an oil bath) was as poor as 23%, while microwave-assisted reaction gave 47% of **Ib**. In the latter case, the isolation procedure was considerably simpler: no by-products that could complicate chromatographic separation of the target compounds were formed.

According to the ^{1}H NMR data, all isolated compounds **I** and **II** were *trans* isomers with respect to the exocyclic double bond. Their ^{1}H NMR spectra contained two doublets at δ 7.88–7.70 and 7.08–6.84 ppm with a coupling constant ^3J of 16–16.5 Hz, which is typical of *trans*-oriented protons (Table 1).

We examined photochromic and fluorescent properties of 3-(2-hetaryl)coumarins **Ia**–**If** and **II**. Their spectral parameters are collected in Table 2. It is seen that these compounds are characterized by absorption in the UV region and fluorescence in the visible region. Irradiation induces photochemical transformations which are accompanied by reduction of the absorption and fluorescence intensity as compared to the initial *E* isomer. Figures 1 and 2 show photoinduced variations in the electronic absorption and fluorescence spectra of compound **Ib** upon irradiation at λ 365 nm (filtered light). Irradiation of a solution of **Ib** with UV light (λ 365 nm) leads to reduction in the absorption intensity at λ 371 nm and decrease in the fluorescence intensity at λ 458 nm. Simultaneously, a weak absorption band appears in the visible region of the spectrum. Analogous changes were observed for compounds **Ia** and **II**. These transformations are reversible. Figure 3 illustrates variations of the spectral pattern upon irradiation of a solution of the photoinduced form of compound **II** with filtered light at λ 436 nm. However, the intensity of the original absorption band is restored only partly.

The other compounds displayed no variations in the in the visible region of the electronic absorption spectra. On the other hand, new bands appear in the UV region (Fig. 4). The photoinduced transformations are also reversible. In the course of the reversible transformations, the photoinduced optical density monotonously decreases as a result of decomposition of the initial photochrome or the corresponding photoinduced form. This also follows from the disappearance of isosbestic point from the absorption spectra after prolonged irradiation with actinic light. Compounds **Ia** and **Ib** are characterized by high thermal stability of the photoinduced form; the latter disappears in the dark very slowly.

Taking into account that initial compounds **Ia**–**If** and **II** have *trans* configuration, the observed photochemical transformations may be rationalized as follows using dihetarylethene **Ib** as an example (Scheme 4). Presumably, the first step is *E*–*Z* isomerization. Such isomerization is typical of *trans*-alkenes

Table 1. Chemical shifts and coupling constants of protons at the exocyclic double bond in 3-(2-hetarylethenyl)-2*H*-chromen-2-ones **Ia**–**If** and **II**

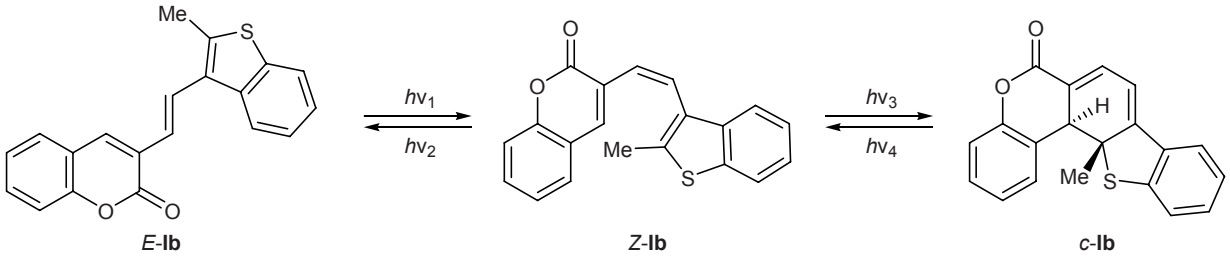
Compound no.	δ_α, ppm	δ_β, ppm	J, Hz
Ia	7.57	6.84	16.3
Ib	7.83	7.08	16.5
Ic	7.88	6.91	16.0
Id	7.80	6.91	16.0
Ie	7.64	6.99	16.1
If	7.54	6.93	16.0
II	7.62	7.14	16.3

Table 2. Spectral parameters[a] of 3-(2-hetarylethenyl)-2*H*-chromen-2-ones **Ia**–**If** and **II**

Comp. no.	λ_{init}, nm	ε, l mol^{-1} × cm^{-1}	λ_{ph}, nm	ΔD at λ_{init}	ΔD at λ_{ph}	λ_{fl}, nm
Ia	378	22200	450	0.15	<0.1	452
Ib	371	11500	442	0.15	<0.1	458
Ic	378	13000	<300	0.25	<0.1	442
Id	385	23700	<300	0.51	<0.1	450
Ie	380	23400	<300	0.03	<<0.1	453
If	390	22200	323	0.47	<0.1	465
II	362	28000	433	0.92	~0.1	440

[a] λ_{init}, λ_{ph}, and λ_{fl} stand for absorption maxima of the initial and photoinduced forms and fluorescence maximum of the photoinduced form; ε is the molar absorption coefficient of the initial form, and ΔD stands for the photoinduced change in the optical density at the absorption maxima corresponding to the initial (λ_{init}) and photoinduced forms (λ_{ph}).

Scheme 4.



E-**Ib** *Z*-**Ib** *c*-**Ib**

upon UV irradiation [8]. Photoinduced formation of the *Z* isomer from compounds **Ia**, **Ib**, and **II** is likely to promote the subsequent reversible photocyclization. In fact, comparison of the observed variations in the electronic absorption spectra of these compounds with those typical of photoinduced electrocyclization of dithienylethenes [1] suggests formation of cyclic structures. The appearance of a new absorption band at longer wavelengths ($\Delta\lambda$ = 70–72 nm, relative to λ_{max} of the initial structure) is typical of cyclic forms of dithienylethenes. In this case, the fluorescence intensity decreases as a result of rupture of conjugation between the coumarin and hetaryl fragments in going to the cyclic structure.

It is most probable that compounds **Ic**, **Id**, and **If** do not undergo photoinduced cyclization but give rise to reversible *E*–*Z* photoisomerization, as follows from the appearance of short-wave absorption bands in their electronic spectra (Fig. 3), which is typical of *cis*-stilbenes and their analogs [8]. The positions of absorption maxima of the *E* and *Z* isomers of compounds **I** were calculated in terms of the INDO/S approximation. The results showed that the absorption maxima of the *Z* isomers are displaced to the blue region by 20–30 nm as compared to the *E* isomers, which is consistent with the experimental data. No transformations of compound **Ie** were observed upon irradiation.

Thus the results of our spectral and kinetic studies indicate that the mechanism of photoinitiated transformations of 3-(2-hetarylethenyl)coumarins is determined by the substrate structure. The process can involve both reversible *E*–*Z* photoisomerization and subsequent photocyclization. In all cases, the transformations are accompanied by considerable change in the fluorescence intensity, which may be useful for the development of light-sensitive materials with photocontrolled fluorescence.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Bruker AC-200 spectrometer from solutions in $CDCl_3$ and DMSO-d_6. The melting points were determined on a Boetius melting point apparatus. The mass spectra

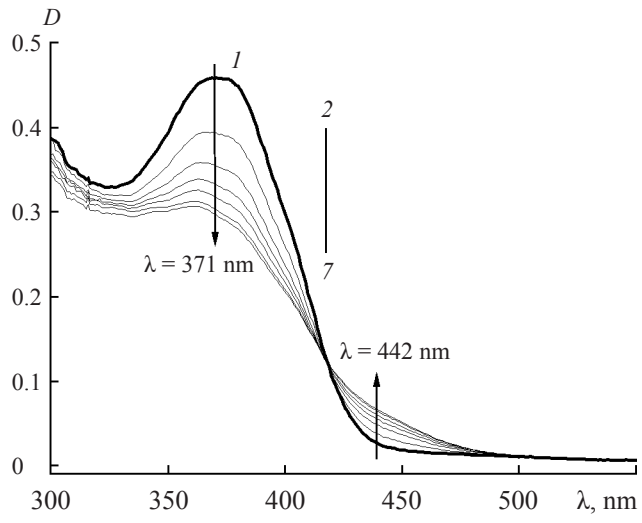


Fig. 1. Electronic absorption spectra of a solution of 3-[(*E*)-2-(2-methyl-1-benzothiophen-3-yl)vinyl]-2*H*-chromen-2-one (**Ib**) in toluene (*1*) before and after irradiation at λ 365 nm for (*2*) 5, (*3*) 10, (*4*) 15, (*5*) 20, (*6*) 30, and (*7*) 180 s.

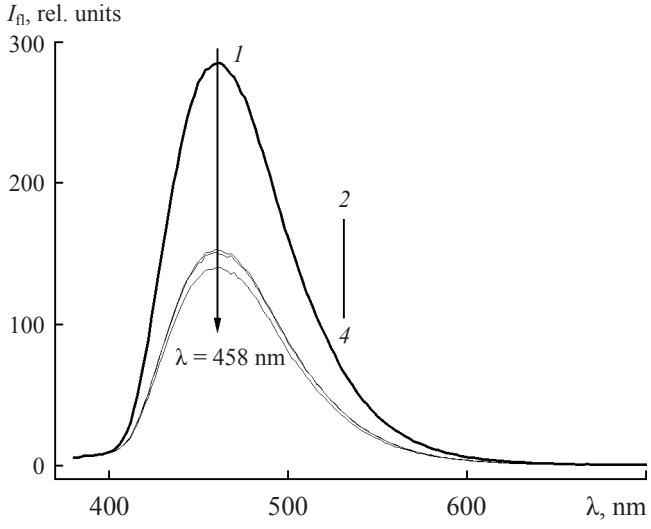


Fig. 2. Fluorescence spectra of a solution of 3-[(*E*)-2-(2-methyl-1-benzothiophen-3-yl)vinyl]-2*H*-chromen-2-one (**Ib**) in toluene (*1*) before irradiation and after irradiation at λ 365 nm for (*2*) 15, (*3*) 60, and (*4*) 105 s.

(electron impact, 70 eV) were obtained on a Kratos MS-30 instrument with direct sample admission into the ion source. Thin-layer chromatography was performed using Merck 60 F_{254} plates. The electronic absorption spectra were recorded on a Varian Cary UV-50 single-beam spectrophotometer. The fluorescence spectra were measured on a Varian Cary Eclipse spectrofluorimeter. The spectral studies were performed using 1-cm cells and toluene of spectroscopic grade as solvent; solutions with a concentration of 4×10^{-5} M (electronic absorption spectra) or 4×10^{-6} M (fluorescence spectra) were prepared. A mercury–xenon gas-discharge lamp was used as a source of UV and visible irradiation; a required wavelength was isolated using a set of glass light filters. Microwave-assisted reactions were carried out in a Rolsen MS1770SA domestic microwave furnace.

5-(2-Hydroxybenzylidene)-3-phenylfuran-2(5*H*)-one (IV). A mixture of 2.44 g (20 mmol) of salicylaldehyde, 3.56 g (20 mmol) of 4-phenyl-4-oxobutanoic acid [9], 1.64 g (20 mmol) of anhydrous sodium acetate, and 7 ml of acetic anhydride was stirred for 12 h on heating on a boiling water bath. The mixture was poured into cold water and was left overnight, and the precipitate was filtered off and recrystallized from ethanol. Yield 2.4 g (45%), orange crystals, mp 172–174°C; published data [4]: mp 140°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.26 br.s (1H, OH), 6.64–6.98 m (4H, H_{arom}), 7.13 s (1H, 4′-H), 7.41–7.80 m (6H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (100) $[M]^+$, 158 (34), 118 (70), 105 (40). Calculated: *M* 264.28.

3-(2-Oxoethyl-2-phenyl)-2*H*-chromen-2-one (V). *a*. Butenolide **IV**, 4 g (15 mmol), was dissolved in 30 ml of acetic acid, an equal volume of concentrated hydrochloric acid was added, and the mixture was heated for 4 h on a boiling water bath. The mixture was cooled, and the precipitate was filtered off and recrystallized from ethyl acetate. Yield 2.08 g (52%), colorless crystals, mp 165–166°C [5, 6].

b. (2-Oxo-2*H*-chromen-3-yl)acetyl chloride (**VIII**), 4 mmol (880 mg), was dissolved in 20 ml of anhydrous benzene, 1200 mg (8.8 mmol) of $AlCl_3$ was added under stirring, and the mixture was stirred for 3 h on heating on a boiling water bath. The warm mixture was poured into a mixture of concentrated hydrochloric acid with ice, the organic phase was separated, the aqueous phase was extracted with ethyl acetate, the extract was combined with the organic phase and dried over anhydrous $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was recrystallized from ethyl acetate. Yield 790 mg (75%), colorless crystals, mp 165–166°C [5, 6]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.21 s (2H, CH_2), 7.22–8.03 m (10H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (10) $[M]^+$, 105 (100) $[PhCO]^+$, 76 (63), 51 (25). Found, %: C 77.29; H 4.62. $C_{17}H_{12}O_3$. Calculated, %: C 77.26; H 4.58. *M* 264.28.

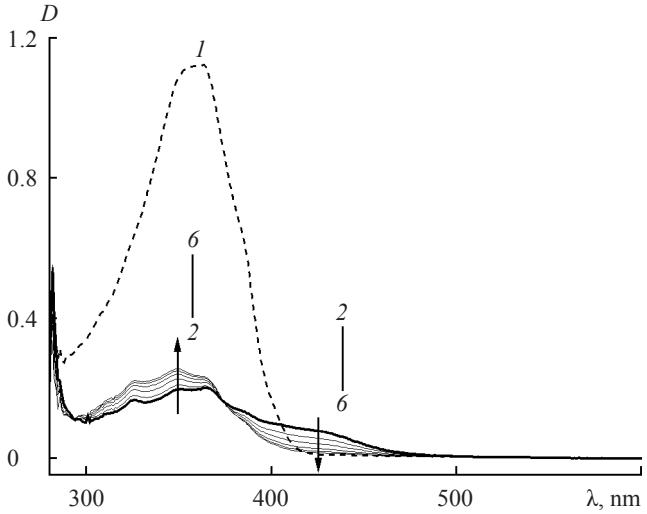


Fig. 3. Electronic absorption spectra of a solution of 3-[(*E*)-2-phenylvinyl]-2*H*-chromen-2-one (**II**) in toluene (*1*) before irradiation, (*2*) after irradiation at λ 365 nm for 210 s, and after subsequent irradiation at λ 436 nm for (*3*) 5, (*4*) 15, (5) 30, and (*6*) 45 s.

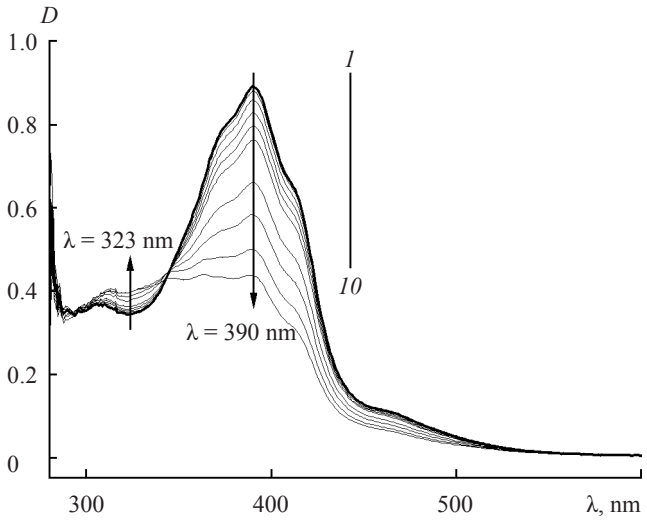


Fig. 4. Electronic absorption spectra of a solution of 3-[(*E*)-2-(5-methylfuran-2-yl)vinyl]-2*H*-chromen-2-one (**If**) in toluene (*1*) before irradiation and after irradiation at λ 365 nm for (*2*) 5, (*3*) 15, (*4*) 30, (*5*) 45, (*6*) 60, (*7*) 120, (*8*) 180, (*9*) 240, and (*10*) 300 s.

3-(2-Hydroxy-2-phenylethyl)-2*H*-chromen-2-one (Xb). Ketone **V**, 132 mg (0.5 mmol), was dissolved in

15 ml of methanol, and sodium tetrahydridoborate was added in 50-mg portions at 1-h intervals, the progress of the reaction being monitored by TLC. When the reaction was complete, the mixture was poured into cold water and acidified with 5 ml of 10% hydrochloric acid. The precipitate was filtered off, dried, and recrystallized from 75% ethanol. Yield 108 mg (81%), colorless crystals, mp 179–180°C; published data [4]: mp 155°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.56 br.s (1H, OH), 2.85–3.11 m (2H, CH_2), 5.07–5.13 m (1H, C**H**OH), 7.20–7.51 m (10H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 266 (10) $[M]^+$, 160 (23), 107 (100) $[PhCH_2O]^+$. Found, %: C 76.50; H 5.39. $C_{17}H_{14}O_3$. Calculated, %: C 76.68; H 5.30. *M* 266.30.

3-[(*E*)-2-Phenylvinyl]-2*H*-chromen-2-one (II). *p*-Toluenesulfonic acid, 100 mg, was added to a solution of 133 mg (0.5 mmol) of compound **Xb** in 5 ml of acetic acid, and the mixture was kept for 24 h at room temperature and poured into water. The precipitate was filtered off and purified by column chromatography using methylene chloride as eluent. Yield 113 mg (91%), greenish crystals, mp 168–169°C; published data [4]: mp 166°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 d (1H, β-H, *J* = 16.3 Hz), 7.24–7.54 m (9H, H_{arom}), 7.62 d (1H, α-H, *J* = 16.3 Hz), 7.81 s (1H, 4-H, chromene). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (100) $[M]^+$, 231 (18), 219 (31), 203 (15), 189 (21), 165 (13). Found, %: C 82.07; H 4.98. $C_{17}H_{12}O_2$. Calculated, %: C 82.24; H 4.87. *M* 248.28.

(2-Oxo-2*H*-chromen-3-yl)acetic acid (VII). A mixture of 30 g (0.3 mol) of succinic anhydride, 12.2 g (0.1 mol) of salicylaldehyde, and 13.1 g (0.13 mol) of triethylamine was heated under stirring to the boiling point. After 1–1.5 h, abundant solid separated. The mixture was cooled and treated with concentrated hydrochloric acid, and the precipitate was filtered off and dried. The product was dissolved in a warm saturated aqueous solution of sodium hydrogen carbonate, the solution was filtered, finely powdered activated charcoal was added to the filtrate, the mixture was stirred for 15 min and filtered, and the filtrate was acidified with concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and dried in air until constant weight. Yield 11.2 g (57%), colorless crystals, mp 163–164°C; published data [7]: mp 164°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.66 s (2H, CH_2), 7.29–7.57 m (4H, 5-H, 6-H, 7-H, 8-H), 7.70 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 204 (25) $[M]^+$, 160 (100) $[M - CO_2]^+$, 131 (71).

(2-Oxo-2*H*-chromen-3-yl)acetyl chloride (VIII). (2-Oxo-2*H*-chromen-3-yl)acetic acid (**VII**), 204 mg (1 mmol), was dispersed in 10 ml of anhydrous methylene chloride, and 360 mg (3 mmol) of thionyl chloride and 2 drops of dimethylformamide were added. After 12 h, the transparent solution was evaporated on a rotary evaporator to obtain acid chloride **VIII** as yellow–brown crystals which were used in further syntheses without additional purification.

3-[2-(2,5-Dimethylthiophen-3-yl)-2-oxoethyl]-2*H*-chromen-2-one (IXa). A solution of 667 mg (3 mmol) of (2-oxo-2*H*-chromen-3-yl)acetyl chloride (**VIII**) and 308 mg (2.75 mmol) of 2,5-dimethylthiophene in 50 ml of anhydrous methylene chloride was cooled to –10°C using an ice–salt bath, 850 mg (6.3 mmol) of $AlCl_3$ was added in portions under stirring over a period of 15 min, and the mixture was stirred for 2.5 h on cooling and poured into a mixture of concentrated hydrochloric acid with ice. The organic phase was separated and dried over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator, and the residue was recrystallized from petroleum ether–acetone (1:1). Yield 71%, colorless crystals, mp 155–156°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, 5′-CH_3), 2.68 s (3H, 2′-CH_3), 4.07 s (2H, CH_2), 7.15 s (1H, 4′-H), 7.27–7.50 m (4H, 5-H, 6-H, 7-H, 8-H), 7.66 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 298 (12) $[M]^+$, 187 (13), 139 (100). Found, %: C 68.36; H 4.88; S 10.59. $C_{17}H_{14}O_3S$. Calculated, %: C 68.44; H 4.73; S 10.75. *M* 298.36.

3-[2-(2-Methyl-1-benzothiophen-3-yl)-2-oxoethyl]-2*H*-chromen-2-one (IXb) was synthesized as described above for compound **IXa** by acylation of 2-methyl-2-benzothiophene with acyl chloride **VIII**. Yield 61%, colorless crystals, mp 185–186°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.84 s (3H, Me), 4.21 s (2H, CH_2), 7.27–7.81 m (9H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 336 (30) $[M]^+$, 296 (31), 205 (25), 175 (100). Found, %: C 71.86; H 4.19; S 9.55. $C_{20}H_{14}O_3S$. Calculated, %: C 71.84; H 4.22; S 9.59. *M* 334.40.

3-[2-(2,5-Dimethylthiophen-3-yl)-2-hydroxyethyl]-2*H*-chromen-2-one (Xa) was synthesized as described above for alcohol **Xb** from ketone **IXa**. Yield 74%, colorless crystals, mp 167–168°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, 5′-CH_3), 2.37 br.s (1H, OH), 2.41 s (3H, 2′-CH_3), 2.92–2.95 m (2H, CH_2), 5.07–5.13 m (1H, C**H**OH), 6.75 s (1H, 4′-H), 7.50–7.27 m (4H, 5-H, 6-H, 7-H, 8-H), 7.53 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 300 (4) $[M]^+$,

160 (18), 141 (100), 131 (15), 113 (62). Found, %: C 68.12; H 5.42; S 10.79. $C_{17}H_{16}O_3S$. Calculated, %: C 67.98; H 5.37; S 10.67. *M* 300.38.

3-[(*E*)-2-(2,5-Dimethyltiophen-3-yl)vinyl]-2*H*-chromen-2-one (Ia) was synthesized as described above for alkene **II** from alcohol **Xa**. Yield 97%, yellow crystals, mp 154–155°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, 5′-CH_3), 2.50 s (3H, 2′-CH_3), 6.84 d (1H, β-H, *J* = 16.3 Hz), 6.94 (1H, 4′-H), 7.49–7.27 m (4H, 5-H, 6-H, 7-H, 8-H), 7.57 d (1H, α-H, *J* = 16.3 Hz), 7.73 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 282 (100) $[M]^+$. Found, %: C 72.15; H 4.91; S 11.51. $C_{17}H_{14}O_2S$. Calculated, %: C 72.31; H 5.00; S 11.36. *M* 282.36.

Condensation of (2-oxo-2*H*-chromen-3-yl)acetic acid (VII) with aldehydes (*general procedure*). An ampule was charged with 1 mmol of the corresponding heterocyclic aldehyde, 1.1 mmol of acid **VII**, and 2 ml of pyridine, two drops of piperidine was added, and the ampule was tightly capped with a heat-resistant stopper and irradiated for 20 min in a microwave furnace at a power of 210 W. The mixture was cooled and poured into ice water acidified with hydrochloric acid. The precipitate was filtered off or extracted into methylene chloride, and the product was finally purified by column chromatography using methylene chloride as eluent.

3-[(*E*)-2-(2-Methyl-1-benzothiophen-3-yl)vinyl]-2*H*-chromen-2-one (Ib). Yield 47%, yellow crystals with greenish tint, mp 183–184°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.70 s (3H, Me), 7.08 d (1H, β-H, *J* = 16.5 Hz), 7.27–7.55 m (6H, H_{arom}), 7.78 d (1H, H_{arom}, *J* = 7.9 Hz), 7.82 s (1H, 4-H), 7.83 d (1H, α-H, *J* = 16.5 Hz), 7.98 d (1H, H_{arom}, *J* = 8.0 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 318 (100) $[M]^+$, 258 (16), 184 (23), 171 (25), 67 (20), 43 (38). Found, %: C 75.40; H 4.47; S 9.99. $C_{20}H_{14}O_2S$. Calculated, %: C 75.45; H 4.43; S 10.07. *M* 318.40.

3-[(*E*)-2-(2-Thienyl)vinyl]-2*H*-chromen-2-one (Ic). Yield 51%, yellow crystals, mp 157–158°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.91 d (1H, β-H, *J* = 16 Hz), 7.02–7.54 m (7H, H_{arom}), 7.72 s (1H, 4-H), 7.88 d (1H, α-H, *J* = 16 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 254 (100) $[M]^+$. Found, %: C 70.81; H 4.00; S 12.42. $C_{15}H_{10}O_2S$. Calculated, %: C 70.85; H 3.96; S 12.61. *M* 254.31.

3-[(*E*)-2-(5-Methylthiophen-2-yl)vinyl]-2*H*-chromen-2-one (Id). Yield 41%, yellow crystals, mp 166–167°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 s (3H, Me), 6.69 d (1H, 4′-H, *J* = 3.4 Hz), 6.91 d (1H, β-H, *J* = 16 Hz), 6.96 d (1H, 3′-H, *J* = 3.5 Hz), 7.52–7.25 m (4H, 5-H, 6-H, 7-H, 8-H), 7.69 s (1H, 4-H), 7.80 d (1H, α-H, *J* = 16 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 268 (100) $[M]^+$. Found, %: C 71.70; H 4.35; S 12.03. $C_{16}H_{12}O_2S$. Calculated, %: C 71.62; H 4.51; S 11.95. *M* 268.34.

3-[(*E*)-2-(2-Furyl)vinyl]-2*H*-chromen-2-one (Ie). Yield 36%, yellow crystals, mp 142–143°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.99 d (1H, β-H, *J* = 16.1 Hz), 7.25–7.53 m (7H, H_{arom}), 7.64 d (1H, α-H, *J* = 16.1 Hz), 7.70 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 238 (73) $[M]^+$, 181 (100). Found, %: C 75.49; H 4.20. $C_{15}H_{10}O_3$. Calculated, %: C 75.62; H 4.23. *M* 238.25.

3-[(*E*)-2-(5-Methylfuran-2-yl)vinyl]-2*H*-chromen-2-one (If). Yield 42%, orange crystals, mp 151–152°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (3H, Me), 6.05 d (1H, 4′-H, *J* = 2.8 Hz), 6.36 d (1H, 3′-H, *J* = 3.1 Hz), 6.93 d (1H, β-H, *J* = 16.0 Hz), 7.28–7.53 m (4H, 5-H, 6-H, 7-H, 8-H), 7.54 d (1H, α-H, *J* = 16.0 Hz), 7.68 s (1H, 4-H). Mass spectrum, *m*/*z* (I_{rel}, %): 252 (100) $[M]^+$, 237 (17), 209 (15), 181 (55), 152 (43). Found, %: C 75.98; H 4.94. $C_{16}H_{12}O_3$. Calculated, %: C 76.18; H 4.79. *M* 252.27.

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