# Synthesis, structures, and photochromic properties of 3-[(*E*)-alk-1-enyl]-4-(1-alkyl-5-methoxy-2-methyl-1*H*-indol-3-yl)furan-2,5-diones

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New hetarylethenes, *viz.*, 3-[(E)-alk-1-enyl]-4-(1-alkyl-5-methoxy-2-methyl-1*H*-indol-3-yl)furan-2,5-diones, exhibiting photochromic properties in solution were synthesized. The molecular and crystal structure of 3-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)-4-[(*E*)-prop-1-enyl]furan-2,5-dione was determined by X-ray diffraction. The initial and photoinduced forms of hetarylethenes are characterized by thermal stability. The open-ring isomers of furandiones exhibit fluorescence with quantum yields of up to 0.1.

**Key words:** furan-2,5-dione, synthesis, structure, X-ray diffraction study, photochromism, fluorescence, molecular switches.

Dihetarylethenes, including hetaryl-substituted furandiones (maleic anhydrides), whose photochromic transformations occur by the mechanism involving the reversible hexatriene-cyclohexadiene rearrangement, are generally characterized by thermal stability of isomeric forms and high resistance to photodegradation. Due to this fact, dihetarylethenes are considered as one of the most promising classes of molecular systems for the use in optical memory devices and as molecular switches.<sup>1,2</sup>

We found that the starting open-ring isomers of 3-[(E)-alk-1-enyl]-4-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)-furan-2,5-diones exhibit efficient fluorescence.<sup>3</sup> The fluorescence of one of isomeric forms shows promise for the design of media for 3D data recording and molecular switches with a fluorescent signaling property.<sup>4-7</sup>

With the aim of studying the influence of substituents of different nature in the indole and maleic anhydride moieties of 3-[(E)-alk-1-enyl]-4-(1,2-alkyl-5-methoxy-1H-indol-3-yl)furan-2,5-diones on their photochromicand fluorescence properties and investigating the energyand structural mechanisms of photoinduced transformations, we synthesized new <math>3-[(E)-alk-1-enyl]-4-(1-benzyl-5-methoxy-2-methyl-1H-indol-3-yl)furan-2,5-dionescontaining different alkyl substituents in the heterocyclicand olefinic moieties and performed a comparative studyof the spectroscopic and photochromic properties of *N*-methyl- and *N*-benzylindolyl-substituted furan-2,5-diones.

In addition, to determine the geometric parameters and the degree of preparedness of the molecules in the solid state for exhibiting optical properties, we obtained single crystals of 3-[(E)-but-1-enyl]-4-(5-methoxy-1,2dimethyl-1H-indol-3-yl)furan-2,5-dione and studiedthem by X-ray diffraction.

## **Results and Discussion**

The starting compounds, *viz.*, 5-methoxy-1,2-dimethylindole (1) and 1-benzyl-5-methoxy-2-methylindole (2), were synthesized according to known procedures.<sup>8,9</sup> The acylation of indoles 1 and 2 with oxalyl chloride<sup>10</sup> afforded the corresponding acid chlorides 3 and 4. The reactions of compounds 3 and 4 with (*E*)-3-alkenoic acids gave 3-[(*E*)-alk-1-enyl]-4-(5-methoxy-1,2-dimethyl-1*H*indol-3-yl)furan-2,5-diones (**5a**-**c**) and 3-[(*E*)-alk-1enyl]-4-(1-benzyl-5-methoxy-2-methyl-1*H*-indol-3-yl)furan-2,5-diones (**5d,e**) (Scheme 1).

The IR spectra of compounds 5a - e show characteristic bands at 1750 and 1820 cm<sup>-1</sup> corresponding to vibrations of two exocyclic carbonyl groups of the furandione moiety. The <sup>1</sup>H NMR spectra of compounds 5a - e in CDCl<sub>3</sub> contain all signals of the indole and (*E*)-alk-1-

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Scheme 1

1, 3: R<sup>1</sup> = Me; 2, 4: R<sup>1</sup> = Bn; 5: R<sup>1</sup> = R<sup>2</sup> = Me (a); R<sup>1</sup> = Me, R<sup>2</sup> = Et (b); R<sup>1</sup> = Me, R<sup>2</sup> = C<sub>6</sub>H<sub>13</sub> (c); R<sup>1</sup> = Bn, R<sup>2</sup> = Me (d); R<sup>1</sup> = Bn, R<sup>2</sup> = Et (e)



enyl substituents. At low field, there are two signals for ethylene protons with the spin-spin coupling constant J = 16 Hz and the characteristic spin-spin coupling of these protons with the protons at the carbon atom of the alkyl substituent nearest to the double bond. This indicates that the compounds were isolated in the open form A containing the alkenyl substituent in the *E* configuration (see Scheme 2 and the Experimental section).

The structure of 3-[(E)-but-1-enyl]-4-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)furan-2,5-dione (**5b**) in the crystalline state was determined by X-ray diffraction (Fig. 1). It was shown that there are two crystallographi-



Fig. 1. X-ray diffraction structures of two independent molecules in the crystal structure of compound 5b (the numbering of the second molecule was set by adding 20 to the numbers of the corresponding atoms in the first molecule).

#### Scheme 2

cally independent molecules in the crystal structure of compound **5b**.

It should be noted that two independent molecules have similar structures with the only difference that the hydrogen atoms of the methyl groups at the nitrogen atoms N(1) and N(21) are rotated by approximately  $60^{\circ}$  with respect to the plane of the pyrrole ring and, correspondingly, with respect to each other upon superimposition.

The distances between the reactive carbon atoms in compound **5b** are 4.399 and 4.402 Å in two independent molecules, which are shorter than that in the non-photochromic crystal of  $3-(1,2-\text{dimethyl}-1H-\text{indol}-3-\text{yl})-4-[(E)-\text{prop}-1-\text{enyl}]furan-2,5-dione (6);^{10} however, these distances are too long for the photocyclization to occur in the crystal to form the cyclohexadiene ring. In solutions of compound$ **5b**, the free rotation around single bonds, through which the indole and alkenyl moieties are bound to the furandione ring, provides the necessary distance between the reaction centers.

The electronic absorption spectra of solutions of furan-2,5-diones 5a—e are characterized by long-wavelength absorption bands of a similar shape with maxima at 442-445 nm and the molar extinction coefficients of  $9760-10980 \text{ Lmol}^{-1} \text{ cm}^{-1}$  (Table 1). The introduction of the electron-releasing methoxy group at position 5 of the indole moiety in compounds 5a-e causes a bathochromic shift ( $\Delta\lambda$  are 6, 7, 8, 5, and 8 nm, respectively) of the longwavelength absorption maximum of the form A compared to the open form A of model compound 6, viz., 3-(1,2dimethyl-1H-indol-3-yl)-4-[(E)-prop-1-enyl]furan-2,5dione,<sup>10</sup> whose long-wavelength absorption maximum is observed at lower wavelengths ( $\lambda_{max}^{abs} = 437$  nm,  $\varepsilon = 7330 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ). *N*-Methylindole derivatives **5a**-**c** are characterized by a weak ( $\Delta \lambda = 1 - 3$  nm) bathochromic shift of the long-wavelength absorption of the form A

**Table 1.** Spectral-absorption and fluorescence characteristics of the isomeric starting (A) and photoinduced (B) forms of compounds 5a-e and 6 in heptane at 293 K

Com- pound	Form <b>A</b>				Form <b>B</b>
	Absorption $\lambda_{max}^{abs}/nm$ $(\epsilon_{max} \cdot 10^{-3}/$ $L mol^{-1} cm^{-1})$	Fluorescence			Absorption $\lambda_{max}^{abs}/nm$
		$\lambda_{max}^{ex}$	$\lambda_{max}^{\ \ em}$	Φ	max / min
5a	443 (8.84)	446	524	0.09	530
5b	444 (10.93)	448	525	0.07	528
5c	445 (10.34)	450	525	0.09	530
5d	442 (9.76)	448	528	0.06	530
5e	442 (10.98)	446	523	0.08	530
6	437 (7.33)	442	522	0.03	495 shoulder

*Note*.  $\lambda_{max}^{ex}$  and  $\lambda_{max}^{em}$  are the fluorescence excitation and emission maxima, respectively;  $\Phi$  is the fluorescence quantum yield.

compared to *N*-benzylindolyl-substituted furan-2,5-diones **5d**,e.

An increase in the length of the alkyl substituent in the alkenyl moiety at position 4 of furan-2,5-dione in going from 4-[(E)-prop-1-enyl]- (**5a,d**) to 4-[(E)-but-1-enyl]- (**5b,e**) and then to 4-[(E)-oct-1-enyl]furan-2,5-dione (**5c**) has virtually no effect on the spectral-absorption characteristics of the isomers **A** (see Table 1).

Solutions of the compounds under study in heptane at room temperature were found to exhibit fluorescence with maxima at 523–528 nm for hetarylethenes 5a-e and at 522 nm for compound **6** (see Table 1). Figure 2 illustrates the fluorescence excitation and emission spectra of a solution of compound **5c** in heptane. The fluorescence excitation spectra are in good agreement with the absorption spectra, which unambiguously indicates that the observed fluorescence corresponds to the open isomers **A** (see Table 1). The fluorescence quantum yields of compounds **5a**–**e** are 0.06-0.09, and they are two—three times higher than that of compound **6** (0.03 in heptane).

The UV irradiation of solutions of compounds 5a-eand 6 in heptane with a mercury lamp ( $\lambda = 436$  nm) leads to their coloration associated with the appearance of new bands in the long-wavelength region of the electronic absorption spectra with maxima at 528–530 nm (see Table 1 and Fig. 3). This absorption is characteristic of the closed isomeric forms **B** of dihetarylethenes<sup>1,10</sup> (see Scheme 2). The positions of the long-wavelength absorption maxima of the cyclic isomers **B** are virtually independent of the structures of compounds 5a-e. It should be noted that the presence of the methoxy group in the indole moiety of hetarylethenes 5a-e leads to a bathochromic shift of the long-wavelength absorption maximum of the form **B** in these compounds by more than 30 nm compared to model compound **6**.



**Fig. 2.** Fluorescence excitation (1) and emission (2) spectra of a solution of compound **5c** in heptane ( $C = 4 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ , T = 293 K).



**Fig. 3.** Electronic absorption spectra of compound **5c** in heptane  $(C = 4 \cdot 10^{-5} \text{ mol } \text{L}^{-1}, T = 293 \text{ K})$  before (*1*) and after irradiation at 436 nm for 1 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), 10 (*6*), and 20 min (*7*).

Unlike the starting open form **A**, the closed isomers **B** of hetarylethenes do not exhibit fluorescence.

The irradiation of colored solutions of compounds 5a-eand 6 at long-wavelength absorption bands of the cyclic forms **B** ( $\lambda = 546$  nm) leads to their bleaching accompanied by the recovery of the initial (before irradiation at 436 nm) spectral patterns. This is evidence for the backward photoreaction **B** $\rightarrow$ **A**, resulting in the recovery to the initial state of the system. The isomeric forms **A** and **B** are thermally stable (after the irradiation was stopped, the contents of the forms **A** and **B** remained unchanged with time even as the temperature was increased). Therefore, hetarylethenes 5a-e exhibit photochromic properties and possess bistability, *i.e.*, they can exist in two thermally stable structurally-mediated states.

The continuous irradiation of solutions of compounds 5a - e and 6 at the long-wavelength absorption band of the form A does not lead to the complete conversion into the colored form **B** but results in the establishment of the photostationary state as a consequence of the substantial overlap of the long-wavelength absorption bands of the photoactive isomeric forms A and B. Since the presence of the methoxy group at position 5 of the indole moiety of hetarylethenes 5a - e leads to a bathochromic shift of the long-wavelength absorption maxima of the closed isomers **B** compared to unsubstituted compound **6**, whereas the positions of the long-wavelength absorption maxima of the open forms A remain virtually unchanged, the content of the colored forms in the photostationary state of compounds 5a-e is higher than that of the previously synthesized hetarylethene **6**.

To quantitatively characterize the phototransformations of furan-2,5-diones  $5\mathbf{a}-\mathbf{e}$  in heptane, we used the product of the quantum yield ( $\Phi$ ) of the photoreaction by the molar extinction coefficient at the long-wavelength absorption maximum of the photoinduced form  $(\epsilon_{max}^{B})$  corresponding to one of the concepts of "photo-colorability".<sup>11</sup>

The efficiencies of the photocyclization reactions  $\mathbf{A} \rightarrow \mathbf{B}$ of furan-2,5-diones  $\mathbf{5a} - \mathbf{e}$  in heptane at room temperature in terms of the photocolorability ( $\Phi_{AB} \cdot \varepsilon_{max}^{B}$ ) are given in Table 2.

The photocyclization quantum yields ( $\Phi_{AB}$ ) estimated with the use of the average molar extinction coefficient  $\varepsilon_{max}^{B} = 7300 \text{ L mol}^{-1} \text{ cm}^{-1}$  (see Refs 12–17) are 0.10–0.16 for compounds **5a–e** and 0.11 (0.10 in hexane<sup>10</sup>) for compound **6**.

The efficiencies of the photorecyclization reactions  $\mathbf{B} \rightarrow \mathbf{A}$  estimated as  $\Phi_{\mathbf{BA}} \cdot \varepsilon_{\max}{}^{\mathbf{B}}$  (see Table 2) depend only slightly on the nature of the substituents and are 2190–2493 L mol<sup>-1</sup> cm<sup>-1</sup> for compounds **5a**–**e** and 2488 L mol<sup>-1</sup> cm<sup>-1</sup> for compound **6**.

The ratios of the quantum yields of the forward and backward photoreactions ( $\Phi_{AB}/\Phi_{BA}$ ) for compounds **5a**—**e** are 0.32—0.55. This indicates that the efficiency of the ring-opening photoreactions is much higher (see Table 2). The estimated quantum yields of the backward photoreactions are 0.30—0.34 for compounds **5a**—**e** and 0.34 for compound **6** (0.32 for compound **6** in hexane<sup>10</sup>).

Maleic anhydrides 5a - e exhibit resistance to photodegradation. The repeated ten photocoloration-photobleaching cycles showed that the spectroscopic characteristics of the colored and bleached solutions remained unchanged.

To sum up, we synthesized new photochromic hetarylethenes containing the 5-methoxy-substituted indole moiety. These compounds are characterized by a high content of colored forms in the photostationary state compared to the unsubstituted analog. Due to the thermal stability of isomeric forms, quite efficient fluorescence of openring isomers, and resistance to photodegradation, the resulting hetarylethenes can be considered as promising compounds for the design of materials for optical data recording and molecular switches with a fluorescent-signaling property.

Table 2. Characteristics of the photochromic transformations of compounds 5a - e and 6 in heptane at 293 K

Com-	$\Phi_{AB} \cdot \epsilon_{max}^{B}$	$\Phi_{BA} \cdot \varepsilon_{max}^{B}$	$\Phi_{\rm AB}/\Phi_{\rm BA}$
pound	L mol <sup>-1</sup>		
5a	1095	2275	0.41
5b	930	2493	0.48
5c	1164	2307	0.55
5d	724	2238	0.32
5e	755	2190	0.34
6	796	2468	0.32

*Note*.  $\Phi_{AB} \cdot \varepsilon_{max}^{B}$  is photocoloration (cyclization) and  $\Phi_{BA} \cdot \varepsilon_{max}^{B}$  is photobleaching (recyclization).

## **Experimental**

The electronic absorption spectra were measured on a Cary 100 spectrophotometer (Varian); the optical path length was 1 cm. The fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian). The fluorescence quantum yields were determined by the Parker-Rees method<sup>18</sup> with the use of a solution of 3-methoxybenzanthrone in toluene as the reference luminophore.19 The solutions were irradiated in a quartz cell (l = 1 cm) with a DRSh-250 mercury lamp equipped with a kit of interference light filters to select lines of the mercury spectrum. The kinetic curves for the photocoloration of solutions of dihetarylethenes were measured directly during irradiation on a Cary 50 spectrophotometer (Varian) equipped with a temperature-controlled cell holder. A xenon lamp equipped with a monochromator to produce narrow spectral lines (Newport) was used as the radiation source. The optical radiation intensity was determined with a Newport 2935 optical power meter. The optical radiation intensity at the wavelengths used (436 and 546 nm) was  $2.94 \cdot 10^{15}$  and  $6.30 \cdot 10^{15}$  photon s<sup>-1</sup>, respectively. To determine the photocolorability  $(\Phi_{AB} \cdot \epsilon_{max}{}^B)$ , the slope of the tangent line at the initial instant was calculated from the kinetic curves for the photocoloration.

The IR spectra in Nujol mulls were recorded on a Varian Excalibur 3100 FT-IR instrument. The <sup>1</sup>H NMR spectra were measured in  $CDCl_3$  on a Varian Unity-300 instrument (300 MHz) with hexamethyldisiloxane as the external standard.

5-Methoxy-1,2-dimethylindole (1) was synthesized according to a known procedure,<sup>8</sup> m.p. 67-68 °C.

**1-Benzyl-5-methoxy-2-methylindole (2)** was synthesized according to a procedure published earlier, <sup>9</sup> m.p. 114–115 °C.

3-(5-Methoxy-1,2-dimethyl-1H-indol-3-yl)-4-[(E)-prop-1enyl]furan-2,5-dione (5a). Oxalyl chloride (0.26 mL, 3 mmol) was added dropwise to a solution of dimethylindole 1 (0.53 g,3 mmol) in dry 1,2-dichloroethane (5 mL) at 5 °C. The reaction mixture was stirred at 5 °C for 10 min. Then a solution of (E)-pent-3-enoic acid (0.3 mL, 3 mmol) and triethylamine (1 mL, 3.2 mmol) in 1,2-dichloroethane (7 mL) was added dropwise at 5 °C. The reaction mixture was stirred for 1 h, and the solution was concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform as the eluent). The yield of the product was 0.26 g (28%), red crystals, m.p. 185–187 °C. IR, v/cm<sup>-1</sup>: 1750, 1820 (C=O). <sup>1</sup>H NMR, δ: 1.94 (dd, 3 H, Me,  $J_1 = 7.0$  Hz,  $J_2 = 1.7$  Hz); 2.43 (s, 3 H, Me); 3.74 (s, 3 H, NMe); 3.80 (s, 3 H, OMe); 6.26 (dq, 1 H, CH,  $J_1 = 16.0$  Hz,  $J_2 = 1.7$  Hz); 6.79 (d, 2 H, H<sub>Ar</sub>, J = 2.4 Hz); 6.90 (dd, 1 H, H<sub>Ar</sub>,  $J_1 = 8.9$  Hz,  $J_2 = 2.4$  Hz); 7.10–7.30 (m, 2 H, H<sub>Ar</sub>). Found (%): C, 69.32; H, 5.41; N, 4.46. C<sub>18</sub>H<sub>17</sub>NO<sub>4</sub>. Calculated (%): C, 69.44; H, 5.50; N, 4.50.

**3-[(***E***)-But-1-enyl]-3-(5-methoxy-1,2-dimethyl-1***H***-indol-4yl)furan-2,5-dione (5b) was synthesized by analogy with compound 5a from dimethylindole 1 and (***E***)-hex-3-enoic acid. The yield was 0.32 g (32.7%), red crystals, m.p. 175–177 °C. IR, v/cm^{-1}: 1750, 1820 (C=O). <sup>1</sup>H NMR, \delta: 1.05 (t, 3 H, Me, J = 7.4 Hz); 2.26 (q.d, 2 H, CH<sub>2</sub>, J\_1 = 7.3 Hz, J\_2 = 1.6 Hz); 2.44 (s, 3 H, Me); 3.75 (s, 3 H, NMe); 3.80 (s, 3 H, OMe); 6.22 (dt, 1 H, CH, J\_1 = 16.0 Hz, J\_2 = 1.6 Hz); 6.78 (d, 1 H, H<sub>Ar</sub>, J = 2.4 Hz); 6.90 (dd, 1 H, H<sub>Ar</sub>, J\_1 = 8.9 Hz, J\_2 = 2.4 Hz); 7.16–7.30 (m, 2 H, H<sub>Ar</sub>). Found (%): C, 70.02; H, 5.63; N, 4.21. C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>. Calculated (%): C, 70.14; H, 5.69; N, 4.30.**  **3-(5-Methoxy-1,2-dimethyl-1***H***-indol-3-yl)-4-[(***E***)-oct-1enyl]furan-2,5-dione (5c) was synthesized by analogy with compound 5a from dimethylindole 1 and (***E***)-dec-3-enoic acid. The yield was 0.3 g (26.4%), red crystals, m.p. 112–114 °C. IR, v/cm<sup>-1</sup>: 1750, 1820 (C=O). <sup>1</sup>H NMR, \delta: 0.86 (br.t, 3 H, Me, J=7.0 Hz); 1.16–1.35 (m, 6 H, CH<sub>2</sub>); 1.36–1.48 (m, 2 H, CH<sub>2</sub>); 2.20 (q, 2 H, CH<sub>2</sub>, J = 7.0 Hz); 2.42, 3.73, and 3.79 (all s, 3 H each, NMe, C(2)Me, OMe); 6.21 (br.d, 1 H, CH, J=16.0 Hz); 6.78 (d, 1 H, H<sub>Ar</sub>, J = 2.3 Hz); 7.16–7.30 (m, 2 H, H<sub>Ar</sub>). Found (%): C, 72.86; H, 7.01; N, 3.54. C<sub>23</sub>H<sub>27</sub>NO<sub>4</sub>. Calculated (%): C, 73.00; H, 7.15; N, 3.68.** 

**3-(1-Benzyl-5-methoxy-2-methyl-1***H***-indol-3-yl)-4-[(***E***)-<b>prop-1-enyl]furan-2,5-dione (5d)** was synthesized by analogy with compound **5a** from 1-benzylindole **2** and (*E*)-pent-3-enoic acid. The yield was 0.29 g (31%), red crystals, m.p. 150–152 °C. IR,  $\nu/cm^{-1}$ : 1750, 1820 (C=O). <sup>1</sup>H NMR,  $\delta$ : 1.95 (dd, 3 H, Me,  $J_1 = 7.0$  Hz,  $J_2 = 1.6$  Hz); 2.38 (s, 3 H, Me); 3.80 (s, 3 H, OMe); 5.36 (s, 2 H, CH<sub>2</sub>); 6.24–6.32 (dq, 1 H, CH,  $J_1 = 16.0$  Hz,  $J_2 = 1.6$  Hz); 6.82–6.95 (m, 2 H, H<sub>AT</sub>); 7.00–7.12 (m, 2 H, H<sub>AT</sub>); 7.14–7.22 (m, 2 H, H<sub>AT</sub>); 7.24–7.38 (m, 3 H, H<sub>AT</sub>). Found (%): C, 74.36; H, 5.41; N, 3.60. C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub>. Calculated (%): C, 74.40; H, 5.46; N, 3.62.

**3-(1-Benzyl-5-methoxy-2-methyl-1***H***-indol-3-yl)-4-[(***E***)-<b>but-1-enyl]furan-2,5-dione (5e)** was synthesized by analogy with compound **5a** from 1-benzylindole **2** and (*E*)-hex-3-enoic acid. The yield was 0.29 g (30%), red crystals, m.p. 148–149 °C. IR,  $v/cm^{-1}$ : 1750, 1820 (C=O). <sup>1</sup>H NMR,  $\delta$ : 1.05 (t, 3 H, Me, J = 7.3 Hz); 2.27 (q.d, 2 H, CH<sub>2</sub>,  $J_1 = 7.2$  Hz,  $J_2 = 1.5$  Hz); 2.37 (s, 3 H, Me); 3.80 (s, 3 H, OMe); 5.36 (s, 2 H, CH<sub>2</sub>); 6.25 (dt, 1 H, CH,  $J_1 = 16.0$  Hz,  $J_2 = 1.5$  Hz); 6.82–6.95 (m, 2 H, CH, H<sub>Ar</sub>); 7.00–7.12 (m, 2 H, H<sub>Ar</sub>); 7.14–7.22 (m, 2 H, H<sub>Ar</sub>); 7.28–7.40 (m, 3 H, H<sub>Ar</sub>). Found (%): C, 74.77; H, 5.69; N, 3.44. C<sub>25</sub>H<sub>23</sub>NO<sub>4</sub>. Calculated (%): C, 74.80; H, 5.77; N, 3.49.

3-(1,2-Dimethyl-1*H*-indol-3-yl)-4-[(*E*)-prop-1-enyl]furan-2,5-dione (6) was synthesized according to a known procedure, <sup>10</sup> m.p. 199–200 °C.

X-ray diffraction study. The unit cell parameters were measured and the three-dimensional X-ray diffraction data set was collected on an Enraf-Nonius CAD-4 automated diffractometer (Mo-Ka radiation, graphite monochromator) at room temperature. Dark-red transparent crystals of compound **5b** ( $C_{19}H_{19}NO_4$ , M = 325.35) are triclinic, space group  $P\overline{1}$ , a = 10.463(3) Å, b = 11.118(3) Å, c = 17.107(4) Å,  $\alpha = 71.66(2)^{\circ}$ ,  $\beta = 76.54(3)^{\circ}$ ,  $\gamma = 62.72(3)^{\circ}$ , V = 1669.6(8) Å<sup>3</sup>, Z = 4,  $d_{calc} = 1.294$  g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 0.91 cm<sup>-1</sup>. The intensities of 6220 reflections were measured in the angle range  $2\theta \le 50.04^\circ$  using the  $\omega/2\theta$  scanning technique from a single crystal of dimensions  $0.42 \times 0.25 \times 0.25$  mm; 5887 reflections ( $R_{int} = 0.071$ ) were independent, 4057 reflections were with  $F^2 > 4\sigma(F^2)$ . The structure was solved by direct methods using the SHELXTL program package<sup>20</sup> and refined by the full-matrix least-squares method based on  $F^2$  with anisotropic displacement parameters for nonhydrogen atoms using the SHELXTL program package.<sup>20</sup> All hydrogen atoms were located in difference Fourier maps. Then the atomic coordinates and the isotropic temperature factors for all H atoms were refined by the least-squares method using a riding model. In the last cycle of the full-matrix refinement, the absolute shifts of all 434 variable parameters of the crystal structure of 5b were smaller than 0.001 $\sigma$ . The final *R* factors were  $R_1 = 0.054$ ,  $wR_1 = 0.150$ based on 4057 observed reflections with  $I \ge 2\sigma(I)$ ;  $R_2 = 0.081$ ,  $wR_2 = 0.163$  based on all measured reflections; GOOF = 1.004.

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