

Synthesis and Properties of Dihetaryl-Substituted Furanones. Synthesis of Photochromic Dithienylethenes Containing a Furanone Bridging Fragment

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Abstract—The reaction of 2,5-dimethylthiophen-3-ylacetic acid with 2,5-dimethylthiophen-3-ylacetyl chloride gave 3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5*H*)-one which was converted into a series of 5-methylidene and 5-arylmethylidene derivatives.

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We previously synthesized a wide series of various photochromic dihetarylethenes which are promising for the design of photochemical molecular switches and materials for optical data storage devices [1–6]. Transformations of most of these compounds are thermally irreversible. However, the results of our studies in this field show that, among numerous structurally related structures, only those dihetarylethenes in which carbon atoms rather than heteroelements are linked through bridging double bonds are characterized by high cycling number (Scheme 1). Examples are derivatives of cyclopentane, cyclohexane, and maleic anhydride; the corresponding cycling numbers amount to several thousands. The cycling number of compounds having a dioxolone, oxazolone, thiazolone, or pyrrole (at the *b* bond) bridging fragments does not exceed several tens. Therefore, development of procedures for the synthesis of new dihetarylethenes with a C=C bridging fragment seems to be an important problem.

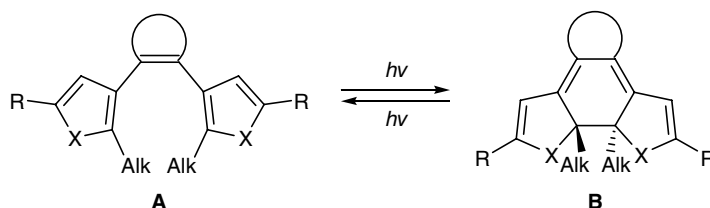
Furanones like **I** are close analogs of dithienylethenes based on maleic anhydride. Compounds **I**

attract interest as such, and they may be used as convenient starting materials for subsequent transformations into various photochromic derivatives.

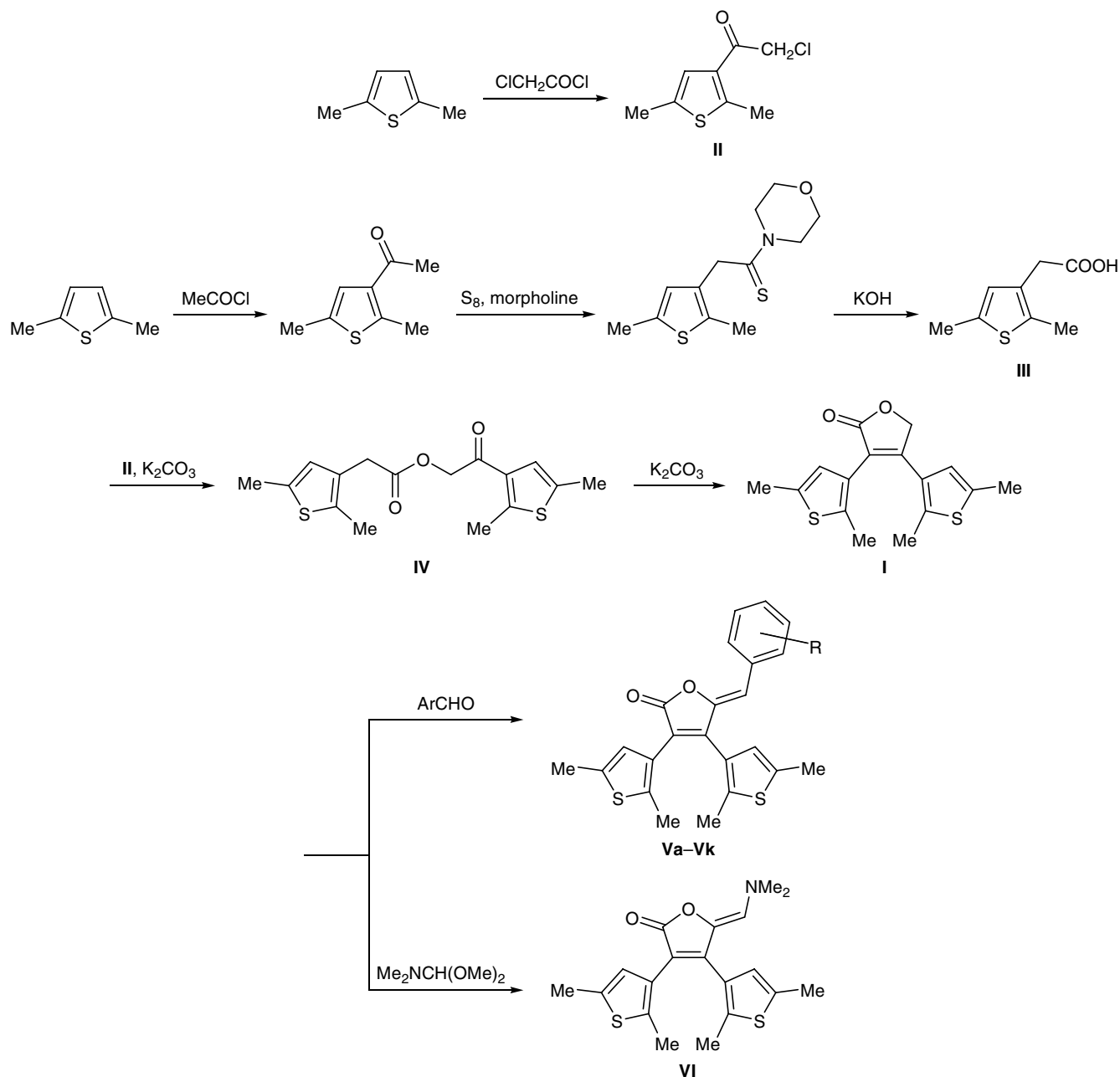
The goal of the present work was to improve the procedure for the preparation of initial furanone **I** and to synthesize photochromic dimethylaminomethylidene-furanones and arylmethylidene-furanones on its base. As previously, 2,5-dimethylthiophen-3-yl fragment was used as heteroaromatic substituent. A general procedure for the synthesis of structurally related diaryl-substituted furanones was reported in [4, 5]. The procedure is based on the condensation of the corresponding α -halo ketone with arylacetic acid. It is simple, and heteroaromatic substituents at the double bond in the resulting dihetarylethene can be varied over a wide range. By analogy, we have synthesized 3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5*H*)-one (**I**) (Scheme 2).

Initial α -chloro ketone **II** was obtained by acylation of 2,5-dimethylthiophene with chloroacetyl chloride in the presence of aluminum chloride [6]. The corre-

Scheme 1.



Scheme 2.



R = H (a), 4-Me (b), 4-Br (c), 3-Cl (d), 2-Cl (e), 4-MeO (f), 3-MeO (g), 2-MeO (h), 3,4-OCH₂O (i), 2-Cl-6-F (j), 4-Me₂N (k).

sponding thienylacetic acid **III** was prepared from 3-acetyl-2,5-dimethylthiophene by the Willgerodt-Kindler reaction, followed by hydrolysis of the thioacetomorpholide thus formed in aqueous alkali [7]. The reaction of thienylacetic acid **III** with α -chloro ketone **II** in the presence of a base gave ester **IV** which was subjected to cyclization on heating with potassium carbonate in dimethylformamide in an inert atmosphere to obtain compound **I** in 70–75% yield. It should

be noted that the last two stages can be performed without isolation of intermediate ester **IV**.

Furanones like **I** possess an activated methylene group [8], which makes it possible to readily modify this structure. We have found that furanone **I** readily reacts with aromatic aldehydes on heating in ethanol in the presence of piperidine as base catalyst to give arylmethylidene furanones **Va–Vk** in 70–85% yield. The nature of substituent in the aldehyde component has no

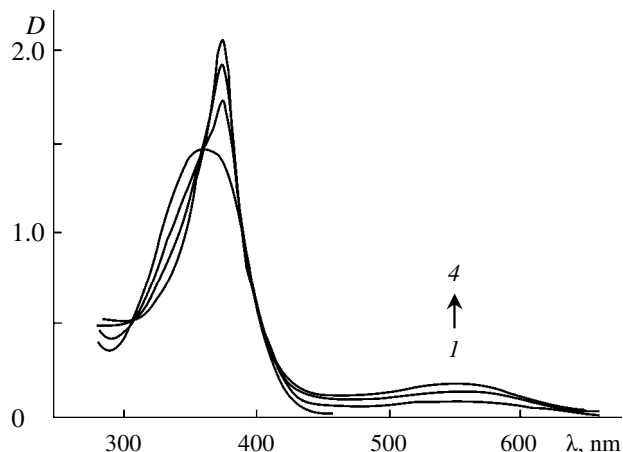


Fig. 1. Electronic absorption spectra of compound **Va** in toluene (*1*) before and (*2–4*) after irradiation at $\lambda = 365$ nm.

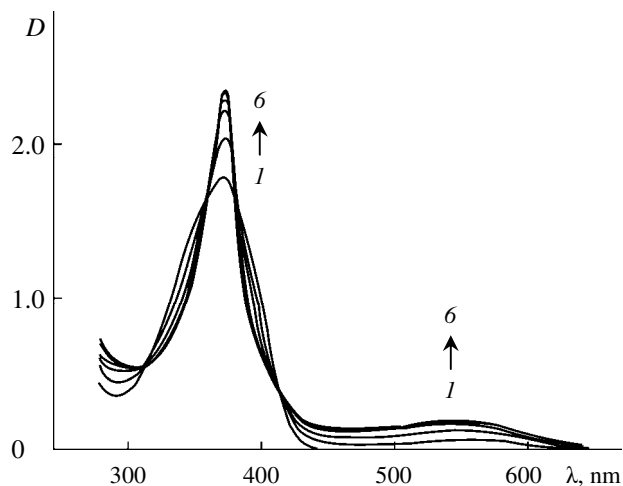


Fig. 2. Electronic absorption spectra of compound **Vb** in toluene (*1*) before and (*2–6*) after irradiation at $\lambda = 365$ nm.

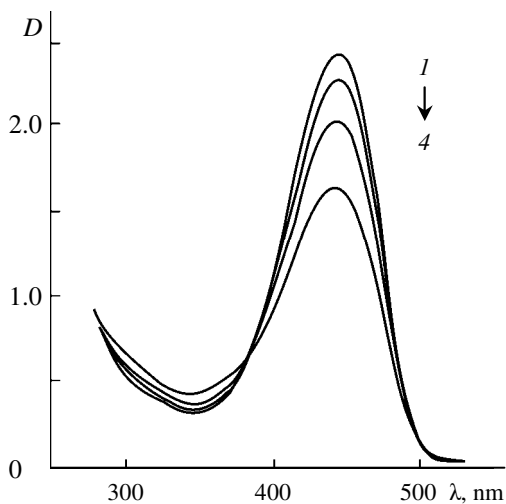


Fig. 3. Electronic absorption spectra of compound **Vk** in toluene (*1*) before and (*2–4*) after irradiation at $\lambda = 436$ nm.

appreciable effect on the condensation process. By condensation of **I** with dimethylformamide dimethyl acetal we obtained dimethylaminomethylidene-furaneone **VI** in a high yield (Scheme 2).

The spectral parameters and kinetic parameters of photochemical transformations of compounds **Va–Vk** and **VI** are presented in table and Figs. 1–4. Dithienyl-furanones **Va–Vi** showed similar variations in the electronic absorption spectra upon irradiation. Open-chain isomers **A** are characterized by absorption maxima in the λ range from 355 to 395 nm, and their position only slightly depends on the substituent nature. As an example, Fig. 1 shows the electronic absorption spectra of the initial and photoinduced forms of compound **Va** in toluene.

Introduction of electron-withdrawing substituents into different positions of the benzene ring (compounds **Vc** and **Ve**) either does not affect the position of the absorption maximum of open-chain isomer **A** or slightly displaces it to the short-wave region. Electron-donor substituents induce red shift of the absorption maximum by 10 (**Vb**, **Vf**, **Vg**) or 20 nm (**Vi**). Unlike initial forms **A**, cyclic isomers **B** absorb at λ 550 nm, and the position of the absorption maximum does not depend on the substituent in the benzene ring.

Comparison of the kinetic parameters of photochemical transformations of the compounds under study showed that they are characterized by approximately similar sensitivities to UV light; this follows from almost coinciding photoinduced optical densities at the absorption maximum of the cyclic form (D_B^{\max}). The corresponding rate constants for photobleaching ($k_{B \rightarrow A}$) indicated their almost similar sensitivities to visible light (except for compound **Ve**). The rate constants for the transformation **A** \rightarrow **B** ($k_{A \rightarrow B}$) show a larger dispersion due to different degrees of overlap of the absorption bands of the open-chain and cyclic forms at the activating wavelength (λ 365 nm). This is clearly seen from comparison of the absorption spectra shown in Fig. 2 with those given in Fig. 1. It should be emphasized that introduction of an electron-donor substituent into the *ortho* position of the benzene ring (compound **Ve**), as well as into the *para* position (**Vf**, **Vi**), sharply increases the efficiency of photodecomposition.

Compound **Vk** having a dimethylamino group in the *para* position of the benzene ring shows no photochromic properties. The electronic spectrum of **Vk** before irradiation contains an absorption band with its maximum at λ 445 nm; this band slowly and irreversibly

Spectral parameters and kinetic parameters of photochemical transformations of dihetaryl-substituted furanones **Va–Vc**, **Ve–Vg**, **Vi**, **Vk**, and **VI**^a

Compound no.	λ_A , nm	λ_B , nm	D_B^{\max}	$k_{A \rightarrow B}$, s ⁻¹	$k_{B \rightarrow A}$, s ⁻¹	$\tau_{1/2}$, °C
Va	365	550	0.55	0.68	0.11	120
Vb	375	550	0.67	0.46	0.11	150
Vc	365	550	0.62	0.47	0.11	150
Ve	355	550	0.60	2.40	0.37	45
Vf	375	550	0.51	1.0	0.12	70
Vg	375	550	0.63	0.56	0.17	140
Vi	395	550	0.55	0.68	0.10	70
Vk	445	–	–	–	–	500
VI	390	490	–	–	–	50

^a λ_A (nm) is the long-wave absorption maximum of the initial open-chain isomer (optical density at a concentration c of 2×10^{-4} M and layer thickness d of 0.2 cm); λ_B (nm) is the long-wave absorption maximum of the colored cyclic form (optical density at $c = 2 \times 10^{-4}$ M, $d = 0.2$ cm); D_B^{\max} is the optical density of the photostationary state upon irradiation of a solution ($c = 2 \times 10^{-4}$ M, $d = 1$ cm) with a DRSh-250 mercury lamp ($\lambda = 365$ nm); $k_{A \rightarrow B}$ (s⁻¹) is the rate constant for photocyclization upon irradiation ($c = 2 \times 10^{-4}$ M, $d = 1$ cm) with a DRSh-250 mercury lamp ($\lambda = 365$ nm); $k_{B \rightarrow A}$ (s⁻¹) is the rate constant for ring opening upon irradiation ($c = 2 \times 10^{-4}$ M, $d = 1$ cm) with a DRSh-250 mercury lamp ($\lambda = 578$ nm); and $\tau_{1/2}$ (s) is the time during which the optical density at the absorption maximum of the cyclic form decreases by half upon continuous irradiation with full spectrum of a DRSh-250 mercury lamp.

sibly disappears upon irradiation at the absorption maximum (Fig. 3). Compound **VI** in which the dimethylamino group is directly attached to the bridging fragment is characterized by low efficiency of photochromic transformation and fast photodecomposition (Fig. 4).

Thus we have synthesized a series of new photochromic arylmethylidene-substituted dithienylfuranones and shown that electron-donor and electron-withdrawing substituents in the benzene ring (except for dimethylamino group) almost do not affect the spectral parameters of their open-chain and cyclic forms and the sensitivity to irradiation. The efficiency of photodecomposition of these compounds depends on their structure, and introduction of a dimethylamino group leads to sharp weakening or disappearance of photochromic properties.

EXPERIMENTAL

Photochromic parameters were determined in toluene of ultrapure grade. The electronic absorption spectra were measured on a Varian Cary 50 Bio spectrophotometer, and the kinetic curves were obtained using a specially designed kinetic setup. Solutions were irradiated with a DRSh-250 high-pressure mercury lamp (with and without light filters). The ¹H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker WM-250 (250 MHz) spectrometers from solutions in DMSO-*d*₆. The melting points were deter-

mined on a Boetius melting point apparatus; uncorrected values are given. The reaction mixtures were analyzed, and the purity of the isolated compounds was checked, by TLC on silica gel 60 F254 (Merck) using ethyl acetate–hexane (1:3) as eluent.

3,4-Bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (I). A mixture of 1.89 g (0.01 mol) of ketone **II**, 1.90 g (0.011 mol) of acid **III**, and 2.07 g (0.015 mol) of potassium carbonate in 12 ml of DMF was stirred for 3 h at 80°C under argon. The mixture was poured into water, and the precipitate was filtered off and

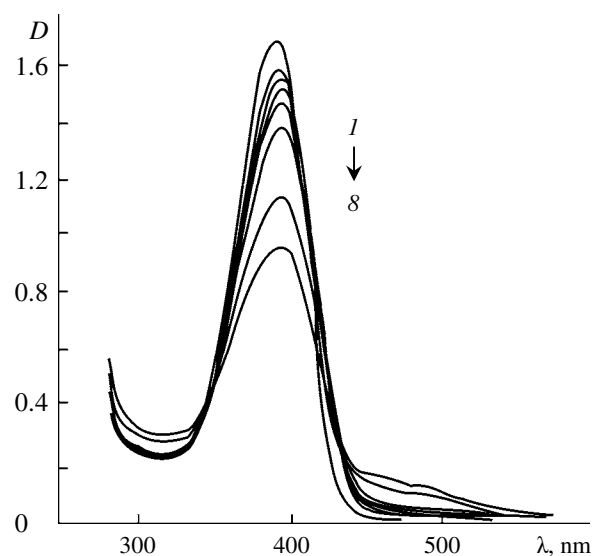


Fig. 4. Electronic absorption spectra of compound **VI** in toluene (**1**) before and (**2–8**) after irradiation at $\lambda = 365$ nm.

washed on a filter with a small amount of diethyl ether. Yield 2.31 g (76%), mp 153–155°C. ¹H NMR spectrum, δ, ppm: 1.88 s (3H, CH₃), 1.90 s (3H, CH₃), 2.30 s (3H, CH₃), 2.35 s (3H, CH₃), 5.20 s (2H, CH₂), 6.55 s (1H, 4'-H), 6.70 s (1H, 4''-H). Found, %: C 63.35; H 5.35; S 20.92. C₁₆H₁₆O₂S₂. Calculated, %: C 63.13; H 5.30; S 21.06.

2-(2,5-Dimethylthiophen-3-yl)-2-oxoethyl (2,5-dimethylthiophen-3-yl)acetate (IV). A mixture of 1.89 g (0.01 mol) of ketone **II**, 1.90 g (0.011 mol) of acid **III**, and 2.07 g (0.015 mol) of potassium carbonate in 12 ml of DMF was stirred for 30 min at room temperature. The mixture was diluted with water and extracted with diethyl ether, and the extract was washed with water, dried over MgSO₄, and evaporated. Yield 2.93 g (91%), oily substance. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.35 s (3H, CH₃), 2.39 s (3H, CH₃), 2.41 s (3H, CH₃), 2.65 s (3H, CH₃), 3.65 s (2H, CH₂), 5.10 s (2H, CH₂), 6.60 s (1H, 4'-H), 6.90 s (1H, 4''-H). Found, %: C 59.82; H 5.76; S 19.58. C₁₆H₁₈O₃S₂. Calculated, %: C 59.60; H 5.63; S 19.89.

5-Arylmethylidene-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-ones Va–Vk (general procedure). Piperidine, 0.085 g (0.001 mol), was added to a mixture of 0.31 g (0.001 mol) of furanone (**I**) and 0.001 mol of aromatic aldehyde in 3 ml of ethanol, and the mixture was heated for 5 h under reflux in an argon atmosphere. The mixture was then cooled, and the precipitate was filtered off and washed with ethanol on a filter.

5-Benzylidene-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Va). Yield 0.27 g (69%), mp 155–157°C. ¹H NMR spectrum, δ, ppm: 1.88 s (3H, CH₃), 1.90 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 6.10 s (1H, CH), 6.55 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.50 m (3H, H_{arom}), 7.80 m (2H, H_{arom}). Found, %: C 70.07; H 5.25; S 16.52. C₂₃H₂₀O₂S₂. Calculated, %: C 70.38; H 5.14; S 16.34.

3,4-Bis(2,5-dimethylthiophen-3-yl)-5-(4-methylbenzylidene)furan-2(5H)-one (Vb). Yield 0.29 g (72%), mp 145–148°C. ¹H NMR spectrum, δ, ppm: 1.89 s (3H, CH₃), 1.90 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 6.10 s (1H, CH), 6.55 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.75 d (2H, H_{arom}, *J* = 8 Hz), 7.70 d (2H, H_{arom}, *J* = 8 Hz). Found, %: C 70.63; H 5.37; S 15.54. C₂₄H₂₂O₂S₂. Calculated, %: C 70.90; H 5.45; S 15.77.

5-(4-Bromobenzylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Vc). Yield 0.35 g

(75%), mp 193–195°C. ¹H NMR spectrum, δ, ppm: 1.89 s (3H, CH₃), 1.91 s (3H, CH₃), 2.33 s (3H, CH₃), 2.40 s (3H, CH₃), 6.10 s (1H, CH), 6.55 s (1H, 4'-H), 6.78 s (1H, 4''-H), 7.65 d (2H, H_{arom}, *J* = 8 Hz), 7.75 d (2H, H_{arom}, *J* = 8 Hz). Found, %: C 58.94; H 4.25; Br 16.73; S 13.38. C₂₃H₁₉BrO₂S₂. Calculated, %: C 58.60; H 4.06; Br 16.95; S 13.60.

5-(3-Chlorobenzylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Vd). Yield 0.32 g (75%), mp 139–141°C. ¹H NMR spectrum, δ, ppm: 1.90 s (3H, CH₃), 1.92 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 6.15 s (1H, CH), 6.55 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.40 m (2H, H_{arom}), 7.88 m (1H, H_{arom}), 7.98 m (1H, H_{arom}). Found, %: C 64.82; H 4.57; Cl 8.41; S 14.94. C₂₃H₁₉ClO₂S₂. Calculated, %: C 64.70; H 4.49; Cl 8.30; S 15.02.

5-(2-Chlorobenzylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Ve). Yield 0.30 g (70%), mp 153–155°C. ¹H NMR spectrum, δ, ppm: 1.88 s (3H, CH₃), 1.90 s (3H, CH₃), 2.35 s (3H, CH₃), 2.40 s (3H, CH₃), 6.40 s (1H, CH), 6.60 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.35–7.60 m (3H, H_{arom}), 8.15 m (1H, H_{arom}). Found, %: C 64.56; H 4.36; Cl 8.54; S 15.23. C₂₃H₁₉ClO₂S₂. Calculated, %: C 64.70; H 4.49; Cl 8.30; S 15.02.

3,4-Bis(2,5-dimethylthiophen-3-yl)-5-(4-methoxybenzylidene)furan-2(5H)-one (Vf). Yield 0.31 g (73%), mp 186–188°C. ¹H NMR spectrum, δ, ppm: 1.90 s (3H, CH₃), 1.91 s (3H, CH₃), 2.32 s (3H, CH₃), 2.40 s (3H, CH₃), 3.80 s (3H, OCH₃), 6.10 s (1H, CH), 6.55 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.05 d (2H, H_{arom}, *J* = 8 Hz), 7.80 d (2H, H_{arom}, *J* = 8 Hz). Found, %: C 68.44; H 5.36; S 15.33. C₂₄H₂₂O₃S₂. Calculated, %: C 68.22; H 5.25; S 15.18.

3,4-Bis(2,5-dimethylthiophen-3-yl)-5-(3-methoxybenzylidene)furan-2(5H)-one (Vg). Yield 0.34 g (82%), mp 160–162°C. ¹H NMR spectrum, δ, ppm: 1.89 s (3H, CH₃), 1.90 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 3.80 s (3H, OCH₃), 6.10 s (1H, CH), 6.55 s (1H, 4'-H), 6.75 s (1H, 4''-H), 6.95 m (1H, H_{arom}), 7.40 m (3H, H_{arom}). Found, %: C 68.53; H 5.31; S 15.30. C₂₄H₂₂O₃S₂. Calculated, %: C 68.22; H 5.25; S 15.18.

3,4-Bis(2,5-dimethylthiophen-3-yl)-5-(2-methoxybenzylidene)furan-2(5H)-one (Vh). Yield 0.35 g (83%), mp 141–143°C. ¹H NMR spectrum, δ, ppm: 1.89 s (3H, CH₃), 1.92 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 3.80 s (3H, OCH₃), 6.45 s (1H, CH), 6.55 s (1H, 4'-H), 6.72 s (1H, 4''-H), 7.05 m (2H,

H_{arom}), 7.35 m (1H, H_{arom}), 8.05 m (1H, H_{arom}). Found, %: C 68.44; H 5.37; S 15.06. C₂₄H₂₂O₃S₂. Calculated, %: C 68.22; H 5.25; S 15.18.

5-(1,3-Benzodioxol-5-ylmethylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Vi). Yield 0.32 g (74%), mp 176–178°C. ¹H NMR spectrum, δ, ppm: 1.89 s (3H, CH₃), 1.90 s (3H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 6.10 m (3H, CH, CH₂), 6.52 s (1H, 4'-H), 6.72 s (1H, 4''-H), 7.00 m (1H, H_{arom}), 7.30 m (1H, H_{arom}), 7.45 m (1H, H_{arom}). Found, %: C 65.87; H 4.51; S 14.40. C₂₄H₂₀O₄S₂. Calculated, %: C 66.03; H 4.62; S 14.69.

5-(2-Chloro-6-fluorobenzylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Vj). Yield 0.29 g (65%), mp 171–173°C. ¹H NMR spectrum, δ, ppm: 1.90 s (3H, CH₃), 2.00 s (3H, CH₃), 2.33 s (3H, CH₃), 2.40 s (3H, CH₃), 6.10 s (1H, CH), 6.60 s (1H, 4'-H), 6.75 s (1H, 4''-H), 7.30–7.50 m (3H, H_{arom}). Found, %: C 62.31; H 4.15. C₂₃H₁₈ClFO₂S₂. Calculated, %: C 62.08; H 4.08.

5-(4-Dimethylaminobenzylidene)-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (Vk). Yield 0.32 g (73%), mp 212–213°C. ¹H NMR spectrum, δ, ppm: 1.90 s (6H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 3.00 s (6H, NCH₃), 6.00 s (1H, CH), 6.50 s (1H, 4'-H), 6.75 m (3H, 4''-H, H_{arom}), 7.65 d (2H, H_{arom}, *J* = 8 Hz). Found, %: C 69.15; H 5.92; N 3.14; S 14.65. C₂₅H₂₅NO₂S₂. Calculated, %: C 68.93; H 5.78; N 3.22; S 14.72.

5-Dimethylaminomethylidene-3,4-bis(2,5-dimethylthiophen-3-yl)furan-2(5H)-one (VI). A mix-

ture of 0.31 g (0.001 mol) of furanone **I** and 0.12 g (0.001 mol) of *N,N*-dimethyl(dimethoxy)methanamine in 4 ml of toluene was heated for 8 h under reflux in an argon atmosphere. The mixture was cooled and evaporated, and the residue was recrystallized from ethanol. Yield 0.28 g (78%), mp 184–186°C. ¹H NMR spectrum, δ, ppm: 1.90 s (6H, CH₃), 2.30 s (3H, CH₃), 2.40 s (3H, CH₃), 3.15 s (6H, NCH₃), 6.05 s (1H, CH), 6.35 s (1H, 4'-H), 6.60 s (4''-H). Found, %: C 63.62; H 5.97; N 3.83; S 17.71. C₁₉H₂₁NO₂S₂. Calculated, %: C 63.48; H 5.89; N 3.90; S 17.84.

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