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Dedicated to Full Member of the Russian Academy of Sciences V.A. Tartakovskii on the 75th anniversary of his birth

Synthesis of Photochromic Dithienylethenes Having Quinoline and Triazolo[4,3-*a*]quinoline Bridges

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Abstract—Convenient synthetic approaches to new photochromic dithienylethenes with quinoline and triazolo[4,3-*a*]quinoline bridging fragments have been developed.

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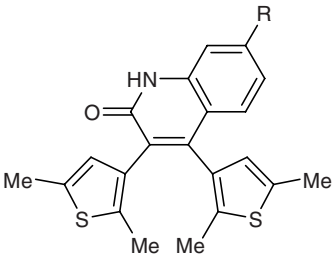
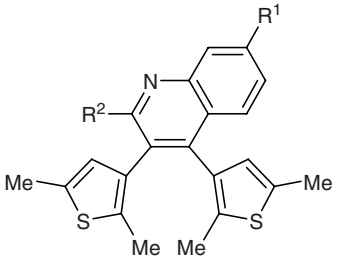
Most photochromic dihetarylethenes described previously include five-membered bridging fragments [1–6]. Obviously, the size of the bridge largely determines the dihedral and torsion angles between the heterocyclic fragments and hence photochromic properties of these compounds. The goal of the present study was to develop procedures for the synthesis of photochromic dithienylethenes **I** and **II** having quinoline bridging fragments and their subsequent transformation into dithienyl-substituted triazolo[4,3-*a*]-quinolines **III** and **IV**.

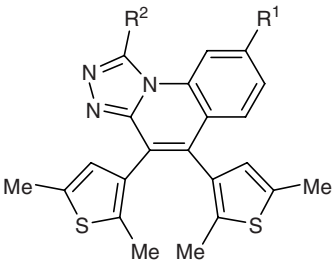
As reported in [7, 8], diaryl-substituted analogs of compounds **I** were synthesized by treatment of *o*-aminodiaryl ketones with arylacetyl chlorides and subsequent cyclization of the amides thus formed to the corresponding 3,4-diarylquinolin-2-ones in basic medium. This procedure was successfully extended to the synthesis of quinolinone derivatives **I** and **II** (Scheme 1). Initial compounds **Va** and **Vb** were prepared by tosylation of the corresponding anthranilic acids [9]. Treatment of **Va** and **Vb** with phosphorus pentachloride gave the corresponding benzoyl chlo-



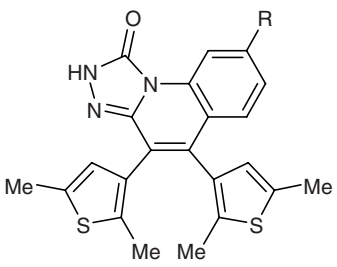
I



II

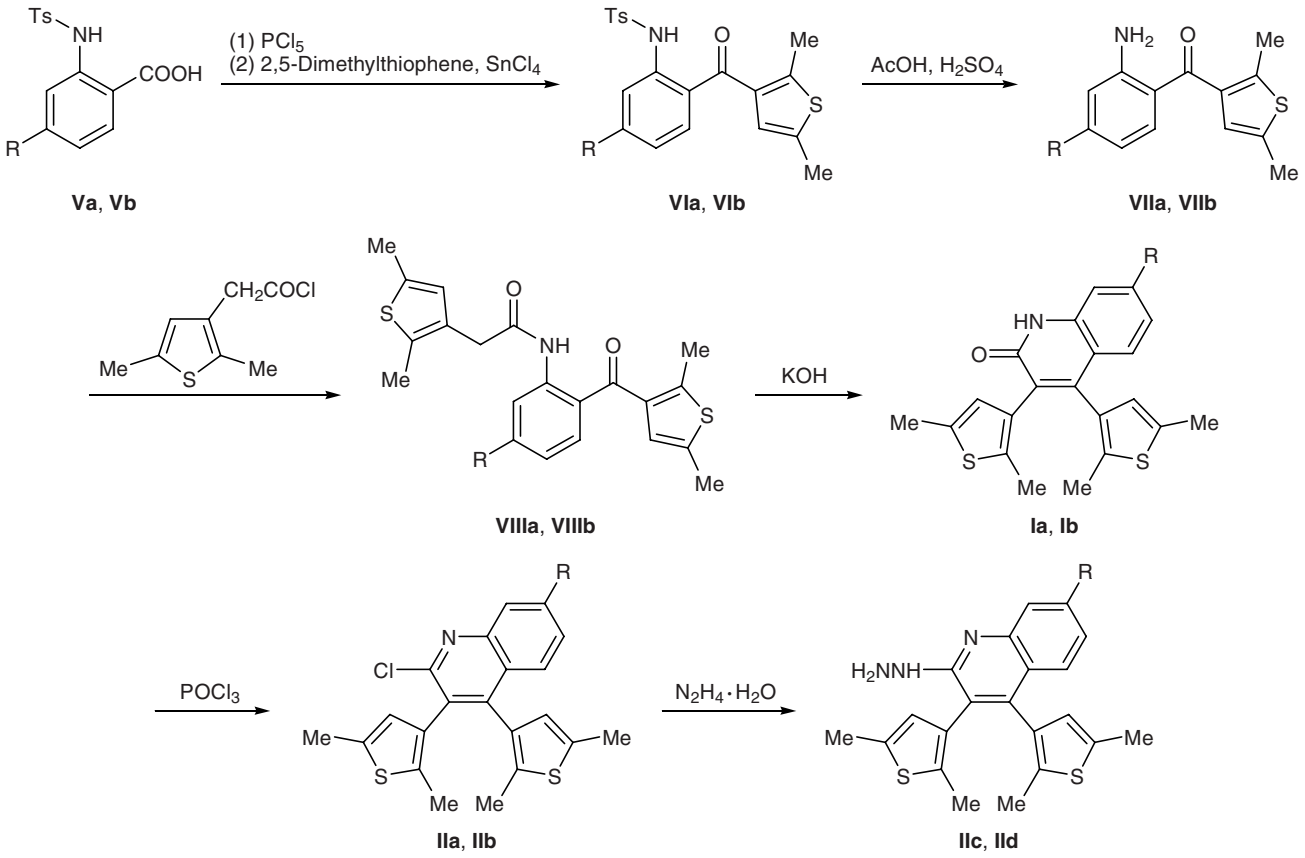


III



IV

Scheme 1.



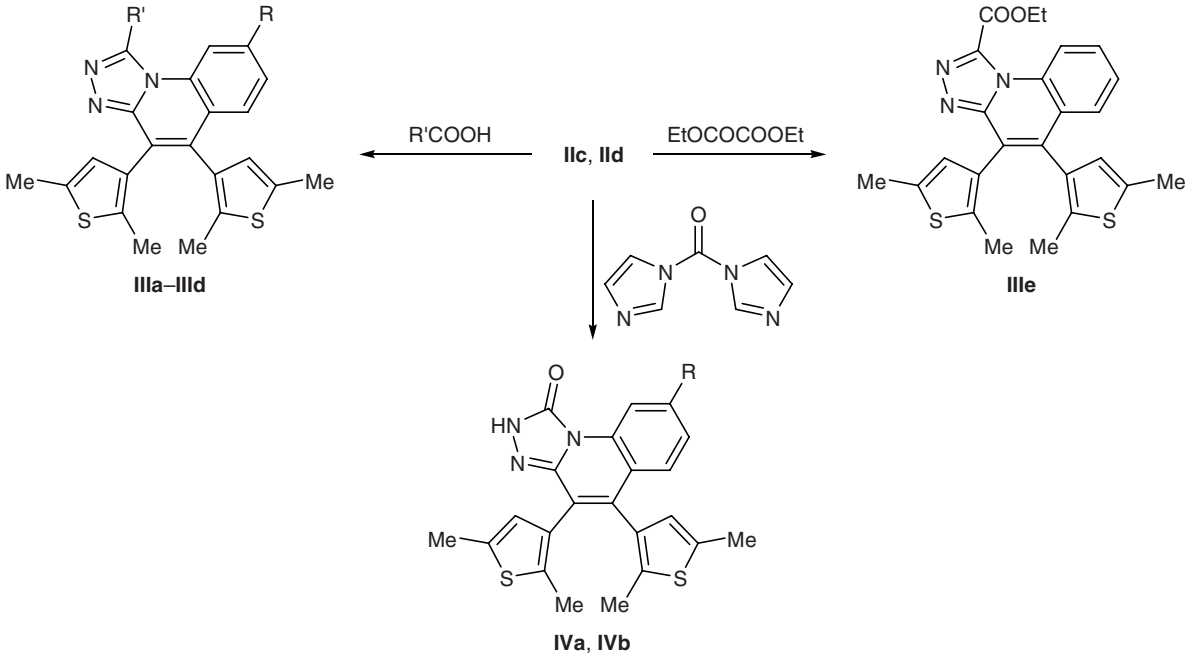
R = H (**a**, **c**), Cl (**b**, **d**).

rides which were used without additional purification in Friedel–Crafts acylation of 2,5-dimethylthiophene. It should be noted that the use of thiophene derivatives instead of benzene analogs imposes some limitations on the reagent nature and reaction conditions because of electron-donor character of the thiophene ring and instability of thienyl derivatives in acid medium. In particular, the Friedel–Crafts acylation was performed in the presence of a relatively weak Lewis acid, tin(IV) chloride [10]. The use of concentrated sulfuric acid to remove the tosyl protection (as proposed for benzene analogs [11]) is inadmissible in reactions with thiophene derivatives, for it results in considerable decomposition of amino ketones **VII**. We found that a mixture of sulfuric and acetic acids ensures good yields of key intermediate compounds **VII**.

(2,5-Dimethylthiophen-3-yl)acetic acid was synthesized from 3-acetyl-2,5-dimethylthiophene according to Willgerodt–Kindler [12] and was treated with oxalyl chloride to obtain the corresponding acid chloride [13]; the latter was used without additional purification to acylate amino ketones **VII**. Intramolecular cyclization of amides **VIII** in ethanolic potassium hydroxide gave dithienyl-substituted quinolinones **I** in good yield. Compounds **I** were then converted into triazolo[4,3-*a*]-quinoline-bridged dithienylethenes. For this purpose, quinolinones **Ia** and **Ib** were treated with phosphoryl chloride, and 2-chloroquinolines **IIa** and **IIb** thus formed were heated with hydrazine hydrate in butanol to obtain hydrazinoquinolines **IIc** and **IId**. The latter reacted with formic or acetic acid on heating under reflux to afford triazolo[4,3-*a*]quinolines **IIIa**–**IIId**. The reaction of **IIc** and **IId** with carbonyldiimidazole in benzene gave triazoloquinolinones **IVa** and **IVb**, and hydrazine **IIc** reacted with excess diethyl oxalate to yield compound **IIIe** (Scheme 2).

The structure of the isolated compounds was studied by ^{1}H NMR spectroscopy. Most known dihetarylethenes are characterized by a low barrier to rotation of the thiophene rings about the bridging fragment, so that their rotation is fairly free [1]. Obviously, rotation of the thiophene rings in dithienylethenes with sterically overcrowded bridging moieties should be hindered, which should be reflected in their NMR

Scheme 2.



II, R = H (**c**), Cl (**d**); **III**, R = H (**a**, **c**), Cl (**b**, **d**), R′ = Me (**a**, **b**), H (**c**, **d**); **IV**, R = H (**a**), Cl (**b**).

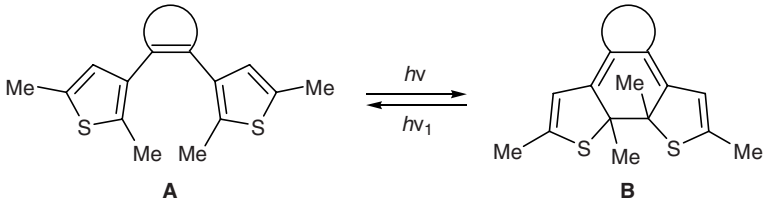
spectra. In particular, we presumed the occurrence of atropoisomerism for dithienylethenes having quinoline and triazoloquinoline bridging fragments. In fact, the ^{1}H NMR spectra of compounds **I**–**IV** at room temperature contained two sets of CH signals in the region δ 6.20–6.70 ppm and signals from the methyl groups in the thiophene rings in the region δ 1.90–2.50 ppm; the other proton signals were not doubled.

Photochromic and fluorescent properties of dithienyl-substituted quinolines and triazoloquinolines **I**–**IV**

Comp. no.	R	R′	λ^{A},[a] nm	λ^{B},[a] nm	D^{B}_{max} [b]	Irradiation time, min	λ_{excit},[c] nm	λ^{A}_{fl},[d] nm	I^{A}_{fl}, arb. units
Ia	H		330	535	0.238	7	340	435	0.80
Ib	Cl		335	540	0.162	5	342	450	0.69
IIa	H		315	590	0.245	5	325	445	0.27
IIb	Cl		325	602	0.269	5	330	465	0.37
IIc	H		342	530	0.016	9	350	400	0.122
IId	Cl		350	~520	0.003	9	357	400	0.033
IIIa	H	Me	315	520	0.235	5	325	415	0.35
IIIb	Cl	Me	318	530	0.096	5	335	415	0.52
IIIc	H	H	310	523	0.196	5	330	420	0.28
IIId	Cl	H	320	528	0.189	5	343	425	0.82
IIIe	H		325	530	0.35	8	335	440	0.62
IVa	H		340	515	0.26	5	350	425	8.48[e]
IVb	Cl		350	520	0.147	3	354	425	13.10

[a] λ^{A} and λ^{B} are the long-wave absorption maxima of the initial (open) and colored (cyclic) forms, respectively.
[b] D^{B}_{max} is the optical density of solution (cell path length 1 cm) after irradiation with filtered light (λ 321 nm) of mercury lamp for indicated time.
[c] λ_{excit} stands for the excitation wavelength at which the fluorescence emission band has the maximal intensity I^{A}_{fl}.
[d] λ^{B}_{fl} is the fluorescence maximum of the initial (open) form.
[e] Concentration 5×10^{-5} M.

Scheme 3.



A **B**

All the synthesized quinoline and triazoloquinoline derivatives were found to possess photochromic properties in acetonitrile solution at a concentration of 1×10^{-4} M. Their photoinduced transformations are thermally irreversible. The initial (open) forms **A** are characterized by absorption maxima in the λ range from 310 to 350 nm (see table). Irradiation of solutions of these compounds with UV light at λ 321 nm gives rise to new broad absorption bands in the visible region with their maxima at λ 515–600 nm, indicating formation of cyclic structures **B** [14] (Scheme 3). A small red shift (Δλ = 5–10 nm) was observed for the absorption maxima of open and cyclic forms of 7-chloroquinoline and 8-chlorotriazoloquinoline derivatives as compared to their unsubstituted analogs. In addition, the optical densities of solutions of cyclic forms of chloro-substituted compounds (except for **IIb**) at the absorption maximum (D^{B}_{max}) were lower than those for the corresponding unsubstituted derivatives (see table).

The open forms exhibit a weak fluorescence with the emission maxima located in the λ range from 400 to 465 nm. The fluorescence spectra were measured both before and after UV irradiation (λ_{excit} 325–360 nm). UV irradiation resulted in reduced fluorescence intensity, the shape and position of the fluorescence bands remaining almost unchanged. These findings suggest that the cyclic forms show no fluorescence. The fluorescence intensity of 7-chloroquinoline derivatives (except for **IIb**) are lower, while the fluorescence intensity of 8-chlorotriazoloquinoline derivatives is considerably higher, than the corresponding parameters of their unsubstituted analogs. It should also be noted that the fluorescence intensity of triazoloquinolinones **IVa** and **IVb** is higher by more than order of magnitude than the fluorescence intensity of the other compounds.

Thus we have developed convenient synthetic approaches to new photochromic dithienylethenes **I–IV** having quinoline and triazoloquinoline bridging fragments. The proposed procedures are characterized by mild conditions and good yields, and they seem to be quite acceptable from the preparative viewpoint.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker WM-250 (250 MHz) spectrometers from solutions in DMSO-d_6 and $CDCl_3$. The melting points were determined on a Boetius hot stage and were not corrected. The progress of reactions and the purity of products were monitored by TLC on Silica gel 60 F254 plates (Merck) using ethyl acetate–hexane as eluent. The electronic absorption and fluorescence spectra were measured on an SF-256 UVI two-channel spectrophotometer (LOMO) and Flyuorat-02 Panorama spectrofluorimeter (Lyumeks). Solutions were irradiated using an OI-18A luminescent lighter (LOMO) equipped with a DRK-120 mercury lamp and a composite optical filter; acetonitrile was used as solvent; concentration 1×10^{-4} M. Samples were placed in 10-mm quartz cells; and measurements were performed under the following conditions: monochromator step 1 nm, split width 3 nm, averaging by 3–5 points at each step.

2-(4-Methylphenylsulfonylamino)benzoic acid (Va) was synthesized according to the procedure described in [10]. Yield 60%, mp 227–229°C; published data [11]: mp 230°C.

4-Chloro-2-(4-methylphenylsulfonylamino)benzoic acid (Vb) was prepared according to [14]. Yield 56%, mp 204–206°C; published data [15]: mp 203°C.

***N*-[2-(2,5-Dimethylthiophen-3-ylcarbonyl)phenyl]-4-methylbenzenesulfonamide (VIa).** 2-(4-Methylphenylsulfonylamino)benzoic acid (**Va**), 0.29 g (1 mmol), was added to a suspension of 0.24 g (1.15 mmol) of phosphorus pentachloride in 3 ml of methylene chloride, and the mixture was heated for 30 min under reflux. 2,5-Dimethylthiophene, 0.112 g (1 mmol), was then added, a solution of 1.15 g (4.4 mmol) of tin(IV) chloride in 3 ml of methylene chloride was added dropwise, and the mixture was heated for 6 h under reflux, cooled, and poured into 50 ml of water. The organic layer was separated, the aqueous layer was extracted with methylene chloride (2×10 ml), the extracts were combined with the organ-

ic phase, washed with a solution of sodium hydrogen carbonate (3×20 ml) and water, and dried over sodium sulfate, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol. Yield 299 mg (62%), mp 123–125°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.2–2.4 s (9H, CH_3), 6.45 s (1H, 4′-H), 7.2–7.6 m (8H, H_{arom}), 9.95 s (1H, NH). Found, %: C 62.41; H 5.02; N 3.85; S 16.52. $C_{20}H_{19}NO_3S_2$. Calculated, %: C 62.31; H 4.97; N 3.63; S 16.63.

***N*-[5-Chloro-2-(2,5-dimethylthiophen-3-ylcarbonyl)phenyl]-4-methylbenzenesulfonamide (VIb)** was synthesized in a similar way. Yield 260 mg (62%), mp 108–110°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.2–2.4 s (9H, CH_3), 6.45 s (1H, 4′-H), 7.15–7.6 m (7H, H_{arom}), 10.15 s (1H, NH). Found, %: C 57.41; H 4.30; Cl 8.56; N 3.45; S 15.55. $C_{20}H_{18}ClNO_3S_2$. Calculated, %: C 57.20; H 4.32; Cl 8.44; N 3.34; S 15.27.

(2-Aminophenyl)(2,5-dimethylthiophen-3-yl)-methanone (VIIa). Compound **VIa**, 0.03 g (0.078 mmol), was dissolved in 0.5 g of acetic acid, 0.5 g of sulfuric acid was added, and the mixture was stirred for 6 h at 50–60°C. The mixture was then poured into 5 ml of water and extracted with diethyl ether (2×5 ml), and the extracts were washed with water (2×5 ml) and evaporated. Yield 140 mg (77%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.4–2.45 s (6H, CH_3), 6.05 br.s (2H), 6.55 m (1H, H_{arom}), 6.65 s (1H, H_{arom}), 6.65 m (1H, H_{arom}) 6.70 s (1H, 4′-H), 7,25 m (1H, H_{arom}) 7.5 m (1H, H_{arom}). Found, %: C 67.59; H 5.70; N 6.15; S 13.99. $C_{13}H_{13}NOS$. Calculated, %: C 67.50; H 5.66; N 6.06; S 13.86.

(2-Amino-4-chlorophenyl)(2,5-dimethylthiophen-3-yl)methanone (VIIb) was synthesized in a similar way. Yield 80%, oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35–2.45 s (6H, CH_3), 6.0 br.s (2H), 6.55 d (1H, 6-H, $J_{6,5}$ = 8 Hz), 6.65 s (1H, H_{arom}), 6.70 s (1H, 4′-H), 7.4 d (1H, 5-H, $J_{5,6}$ = 8 Hz). Found, %: C 58.88; H 4.48; Cl 13.25; N 5.45; S 12.17. $C_{13}H_{12}ClNOS$. Calculated, %: C 58.75; H 4.55; Cl 13.34; N 5.27; S 12.06.

***N*-[2-(2,5-Dimethylthiophen-3-ylcarbonyl)phenyl](2,5-dimethylthiophen-3-yl)acetamide (VIIIa).** A solution of 0.55 g (3 mmol) of (2,5-dimethylthiophen-3-yl)acetyl chloride in 5 ml of methylene chloride was added to a solution of 0.66 g (2.87 mmol) of compound **VIIa** in 15 ml of methylene chloride. The mixture was stirred for 3 h at room temperature, poured into 50 ml of water, and extracted with methylene chloride (2×15 ml), the extracts were combined, washed with a saturated solution of sodium hydrogen carbonate (4×15 ml) and water (2×20 ml), and dried over sodium sulfate, and the solvent was removed under reduced pressure. Yield 0.96 g (87%). Oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.3–2.5 s (12H, CH_3), 3.6 s (2H, CH_2), 6.6 s (1H, 4′-H), 6.7 s (1H, 4″-H), 7.1 m (1H, H_{arom}), 7.55 m (2H, H_{arom}), 8.75 s (1H, H_{arom}), 10.7 s (1H, NH). Found, %: C 65.92; H 5.58; N 3.80; S 16.85. $C_{21}H_{21}NO_2S_2$. Calculated, %: C 65.77; H 5.52; N 3.65; S 16.72.

***N*-[5-Chloro-2-(2,5-dimethylthiophen-3-ylcarbonyl)phenyl](2,5-dimethylthiophen-3-yl)acetamide (VIIIb)** was synthesized in a similar way. Yield 84%, mp 120–122°C (from ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.3–2.55 s (12H, CH_3), 3.6 s (2H, CH_2), 6.55 s (1H, 4′-H), 6.65 s (1H, 4″-H), 7.05 d (1H, 6-H, $J_{6,5}$ = 8 Hz), 7.05 d (1H, H_{arom}, $J_{5,6}$ = 8 Hz), 8.75 s (1H, 5-H), 10.85 s (1H, NH). Found, %: C 60.48; H 4.90; Cl 8.65; N 3.45; S 15.37. $C_{21}H_{20}ClNO_2S_2$. Calculated, %: S 60.35; H 4.82; Cl 8.48; N 3.35; S 15.34.

3,4-Bis(2,5-dimethylthiophen-3-yl)-1*H*-quinolin-2-one (Ia). A solution of 0.96 g (2.5 mmol) of compound **VIIIa** in 10 ml of a 1 N alcoholic solution of potassium hydroxide was heated for 1 h under reflux. The mixture was cooled, 0.65 g of acetic acid and 10 ml of water were added, and the precipitate was filtered off and dried. Yield 0.737 g (80%), mp 248–249°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85 s (3H, CH_3), 1.85–1.95 s (6H, CH_3), 2.0 s (3H, CH_3), 2.15–2.25 s (6H, CH_3), 2.35 s (6H, CH_3), 6.15–6.55 m (2H, 4′-H), 7.05–7.65 m (4H, H_{arom}), 11.95 s (1H, NH). Found, %: C 69.12; H 5.28; N 3.90; S 17.75. $C_{21}H_{19}NOS_2$. Calculated, %: C 69.01; H 5.24; N 3.83; S 17.54.

7-Chloro-3,4-bis(2,5-dimethylthiophen-3-yl)-1*H*-quinolin-2-one (Ib) was synthesized in a similar way. Yield 84%, mp 130–132°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.8–2.0 s (6H, CH_3), 2.07 s (3H, CH_3), 2.35 s (3H, CH_3), 2.45 s (3H, CH_3), 2.55 s (3H, CH_3), 6.1–6.5 m (2H, 4′-H), 7.0–7.5 m (3H, H_{arom}), 12.5 s (1H, NH). Found, %: C 63.18; H 4.60; Cl 8.95; N 3.45; S 16.17. $C_{21}H_{18}ClNOS_2$. Calculated, %: C 63.06; H 4.54; Cl 8.86; N 3.50; S 16.03.

2-Chloro-3,4-bis(2,5-dimethylthiophen-3-yl)-quinoline (IIa). A mixture of 0.43 g (1.18 mmol) of compound **Ia** and 6 g (39 mmol) of phosphoryl chloride was heated for 12 h under reflux. Excess $POCl_3$ was removed under reduced pressure, 15 ml of water

was added to the residue, and the mixture was kept for 12 h. The precipitate was filtered off and thoroughly washed with water. Yield 0.275 g (61%), mp 103–105°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85–2.1 s (6H, CH_3), 2.3–2.4 s (6H, CH_3), 6.4–6.5 br.s (2H, 4′-H), 7.45 m (1H, H_{arom}), 7.65 m (1H, H_{arom}), 7.85 m (1H, H_{arom}), 8.05 m (1H, H_{arom}). Found, %: C 65.88; H 4.80; Cl 9.35; N 3.55; S 16.85. $C_{21}H_{18}ClNS_2$. Calculated, %: C 65.69; H 4.73; Cl 9.23; N 3.65; S 16.70.

2,7-Dichloro-3,4-bis(2,5-dimethylthiophen-3-yl)-quinoline (IIb) was synthesized in a similar way. Yield 59%, mp 95–97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.9–2.2 s (6H, CH_3), 2.3–2.5 s (6H, CH_3), 6.25–6.35 m (2H, 4′-H), 7.4–7.55 m (2H, H_{arom}), 8.1 s (1H, H_{arom}). Found, %: C 60.38; H 4.25; Cl 16.75; N 3.45; S 15.38. $C_{21}H_{17}Cl_2NS_2$. Calculated, %: C 60.28; H 4.10; Cl 16.95; N 3.35; S 15.33.

[3,4-Bis(2,5-dimethylthiophen-3-yl)quinolin-2-yl]hydrazine (IIc). A mixture of 0.46 g (1.2 mmol) of compound **IIa**, 4 ml of hydrazine hydrate, and 6 ml of butanol was heated for 48 h under reflux. The mixture was evaporated to dryness on a rotary evaporator, and the residue was recrystallized from 2 ml of ethanol. Yield 0.220 g (50%), mp 164–166°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.9 s (3H, CH_3), 2.0 s (3H, CH_3), 2.3 s (6H, CH_3), 4.5 br.s (2H, NH_2), 6.3–6.5 m (2H, 4′-H), 6.6–6.8 br.s (1H, NH_2), 7.1–7.2 m (2H, H_{arom}), 7.65 s (1H, H_{arom}). Found, %: C 66.58; H 5.65; N 11.22; S 16.73. $C_{21}H_{21}N_3S_2$. Calculated, %: C 66.46; H 5.58; N 11.07; S 16.90.

[7-Chloro-3,4-bis(2,5-dimethylthiophen-3-yl)-quinolin-2-yl]hydrazine (IId) was synthesized in a similar way. Yield 76%, mp 175–177°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.9–2.05 s (12H, CH_3), 2.25–2.35 s (12H, CH_3), 4.5 br.s (2H, NH_2), 6.25–6.4 m (2H, 4′-H), 6.6–6.8 br.s (1H, NH), 7.1–7.2 m (2H, H_{arom}), 7.65 s (1H, H_{arom}). Found, %: C 60.82; H 4.70; Cl 8.75; N 10.25; S 15.28. $C_{21}H_{20}ClN_3S_2$. Calculated, %: C 60.93; H 4.87; Cl 8.56; N 10.15; S 15.49.

4,5-Bis(2,5-dimethylthiophen-3-yl)-1-methyl-[1,2,4]triazolo[4,3-*a*]quinoline (IIIa). A mixture of 152 mg (0.4 mmol) of compound **IIc** and 2 ml of acetic acid was heated for 7 h under reflux. The mixture was then evaporated, 5 ml of water was added to the residue, the mixture was extracted with benzene (2× 5 ml), the extracts were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 96 mg (58%), mp 236–238°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85 s (3H, CH_3), 1.9 s (3H, CH_3), 1.95 s (3H, CH_3), 2.1 s (3H, CH_3), 2.25 s (3H, CH_3), 2.3 s (3H, CH_3), 2.35 s (6H, CH_3), 3.1 s (3H, CH_3), 6.25–6.6 m (2H, 4′-H), 7.35–7.6 m (2H, H_{arom}), 7.75 s (1H, H_{arom}), 8.4 m (1H, H_{arom}). Found, %: C 68.78; H 5.12; N 10.48; S 15.83. $C_{23}H_{21}N_3S_2$. Calculated, %: C 68.45; H 5.25; N 10.41; S 15.89.

8-Chloro-4,5-bis(2,5-dimethylthiophen-3-yl)-1-methyl[1,2,4]triazolo[4,3-*a*]quinoline (IIIb) was synthesized in a similar way. Yield 65%, mp 173–175°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.9–2.1 s (6H, CH_3), 2.3–2.5 s (6H, CH_3), 3.3 s (3H, CH_3), 6.2–6.6 m (2H, 4′-H), 7.2–7.65 m (2H, H_{arom}), 8.25 s (1H, H_{arom}). Found, %: C 63.12; H 4.72; Cl 8.15; N 9.38; S 14.42. $C_{23}H_{20}ClN_3S_2$. Calculated, %: C 63.07; H 4.60; Cl 8.09; N 9.59; S 14.64.

4,5-Bis(2,5-dimethylthiophen-3-yl)[1,2,4]triazolo-[4,3-*a*]quinoline (IIIc). A mixture of 100 mg (0.26 mmol) of compound **IIc** and 2 ml of formic acid was heated for 7 h under reflux. The mixture was evaporated, 5 ml of water was added to the residue, and the mixture was extracted with benzene. The extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 105 mg (65%), mp 167–169°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85–2.4 s (24H, CH_3), 6.3–6.6 m (2H, 4′-H), 7.3–7.85 m (3H, H_{arom}), 8.5 s (1H, H_{arom}), 10.0 s (1H, CH). Found, %: C 62.22; H 4.30; Cl 8.25; N 9.78; S 15.42. $C_{22}H_{18}ClN_3S_2$. Calculated, %: C 62.32; H 4.28; Cl 8.36; N 9.91; S 15.12.

8-Chloro-4,5-bis(2,5-dimethylthiophen-3-yl)-[1,2,4]triazolo[4,3-*a*]quinoline (IIId) was synthesized in a similar way. Yield 60%, mp 173–175°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.9–2.5 s (24H, CH_3), 6.25–6.6 m (2H, 4′-H), 7.25–7.65 m (2H, H_{arom}), 8.05 s (1H, H_{arom}), 9.3 s (1H, CH). Found, %: C 67.72; H 4.90; N 10.70; S 16.42. $C_{22}H_{19}N_3S_2$. Calculated, %: C 67.83; H 4.92; N 10.79; S 16.46.

Ethyl 4,5-bis(2,5-dimethylthiophen-3-yl)[1,2,4]-triazolo[4,3-*a*]quinoline-1-carboxylate (IIIe). A mixture of 190 mg (0.5 mmol) of compound **IIc** and 3 ml of diethyl oxalate was heated for 20 h under reflux. The mixture was evaporated, and the residue was recrystallized from 2 ml of ethanol. Yield 74 mg (35%), mp 142–144°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.9–2.15 s (12H, CH_3), 2.3–2.45 s (12H, CH_3), 6.3–6.65 m (2H, 4′-H), 7.5 m (1H, H_{arom}), 7.65 m (1H, H_{arom}), 7.8 m (1H, H_{arom}), 8.55 m (1H, H_{arom}). Found, %: C 65.21; H 5.14; N 8.85; S 14.03. $C_{25}H_{23}N_3O_2S_2$. Calculated, %: C 65.05; H 5.02; N 9.10; S 13.89.

4,5-Bis(2,5-dimethylthiophen-3-yl)[1,2,4]triazolo-[4,3-*a*]quinolin-1(2*H*)-one (IVa). A solution of

130 mg (0.8 mmol) of 1,1′-carbonyldiimidazole in 2 ml of benzene was added to 30 mg (0.08 mmol) of compound **IIc**, and the mixture was heated for 6 h under reflux and evaporated. The residue was dissolved in chloroform, the solution was thoroughly washed with water (3×10 ml) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Yield 19 mg (59%), mp >300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.9 s (3H, CH_3), 1.95 s (3H, CH_3), 2.0 s (3H, CH_3), 2.1 s (3H, CH_3), 2.25 s (3H, CH_3), 2.3 s (3H, CH_3), 2.35 s (6H, CH_3), 6.2–6.6 m (2H, 4′-H), 7.15–7.4 m (2H, H_{arom}), 7.6 m (1H, H_{arom}), 9.05 m (1H, H_{arom}), 12.5 s (1H, NH). Found, %: C 67.92; H 4.79; N 10.58; S 16.63. $C_{22}H_{19}N_3S_2$. Calculated, %: C 67.83; H 4.92; N 10.79; S 16.46.

8-Chloro-4,5-bis(2,5-dimethylthiophen-3-yl)-[1,2,4]triazolo[4,3-*a*]quinolin-1(2*H*)-one (IVb) was synthesized in a similar way. Yield 65%, mp 305–307°C (sublimes). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.9–2.15 s (6H, CH_3), 2.2–2.5 s (6H, CH_3), 6.2–6.6 m (2H, 4′-H), 7.1–7.5 m (2H, H_{arom}), 9.05 s (1H, H_{arom}), 12.6 s (1H, NH). Found, %: C 62.52; H 4.47; Cl 8.57; N 9.77; S 15.42. $C_{22}H_{18}ClN_3S_2$. Calculated, %: C 62.32; H 4.28; Cl 8.36; N 9.91; S 15.12.

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