Synthesis of spiropyrans and merocyanine dyes based on 1-benzothieno[3,2-*b*]pyrrole*

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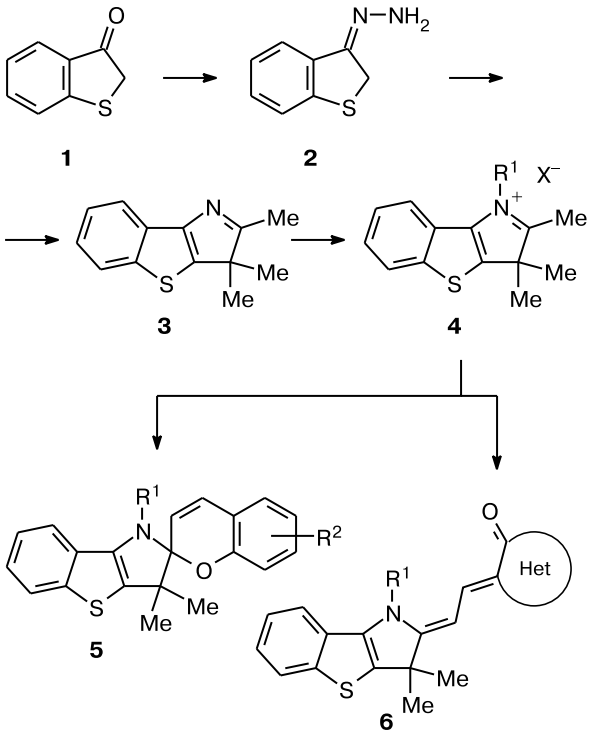
A convenient method was developed for the synthesis of photochromic spiropyrans and merocyanine dyes of the 1-benzothieno[3,2-*b*]pyrroline series based on the conventional condensation of the analog of Fischer's salt, *viz.*, 1,2,3,3-tetramethyl-3*H*-[1]benzothieno-[3,2-*b*]pyrrolium triflate, with aromatic 2-hydroxyaldehydes. Unlike Fischer's salt, benzothienopyrrolium salts readily undergo the [1,5]-sigmatropic rearrangement giving rise to 2*H*-[1]benzothieno[3,2-*b*]pyrrole derivatives. The latter compounds were used for the synthesis of the first representatives of the previously unknown spiro compounds and merocyanine dyes. The long-wavelength maxima of merocyanines of the 2*H*-benzothienopyrrole series are bathochromically shifted by more than 100 nm with respect to the absorption maxima of the "classical" 3*H*-benzothienopyrrole analogs.

Key words: spiropyrans, merocyanine dyes, benzothienopyrroles, Fischer's salt.

Photochromic spiropyrans have attracted interest as materials suitable for the use in optical memory devices and as molecular switches.[1] In addition, spiropyrans can be used for the extraction of ions from solutions,[2] in molecular optoelectronics,[3] and as sensors for metal ions.[4]

Previously, we have developed an approach to the synthesis of a new class of photochromic spiro compounds[5,6] and merocyanine dyes[7] based on the thienopyrrole moiety and studied the spectroscopic properties of the first representatives.[8,9] The aim of the present study was to synthesize new spiropyrans and merocyanine dyes based on 3*H*- and 2*H*-[1]benzothieno[3,2-*b*]pyrrole derivatives in four steps starting from readily available 1-benzothiophen-3(2*H*)-one (**1**). The synthesis of 3*H*-[1]benzothieno[3,2-*b*]pyrrole derivatives involving the preparation of hydrazone **2** and its Fischer reaction with various ketones has been described in detail.[10] In the present study, we investigated the alkylation of benzothienopyrrolenine **3** and examined the possibility of using salts **4** for the synthesis of spiropyrans **5** and merocyanine dyes **6** (Scheme 1).

Scheme 1



Results and Discussion

Recently, we have shown[7] that the reaction of benzothienopyrrolenine **3** with alkylating agents can afford both salts **4** and their 2*H*-isomers **7** (Scheme 2). The latter are generated from compounds **4** *via* the [1,5]-sigmatropic

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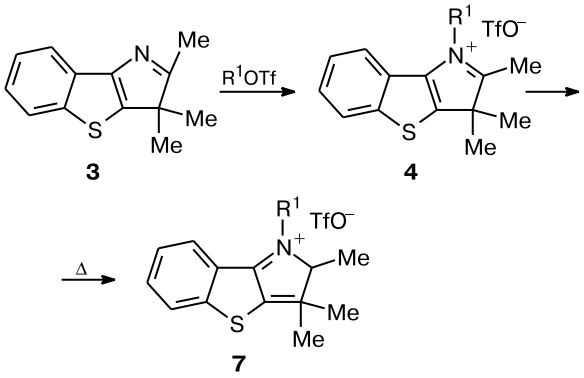
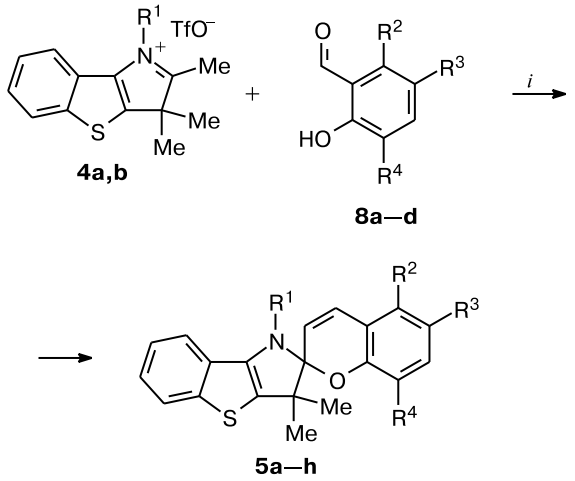
Scheme 2



Scheme 3



rearrangement. It was found that the most active alkylating agents, such as triflates, are reagents of choice for the synthesis of salts **4**. The reactions of benzothienopyrrolenine **3** with less active alkyl tosylates and alkyl iodides require prolonged heating, resulting in the formation of a mixture of 3*H*- and 2*H*-benzothienopyrroles **4** and **7**. Compounds **7** can be prepared in the pure form by heating salts **4** in a high-boiling point solvent (*p*-xylene). In this case, triflates are also reagents of choice, because they are easier to isolate.

The condensation of salts **4a,b** with various *o*-hydroxyaldehydes **8a—d** in ethanol in the presence of piperidine afforded a broad range of spiropyrans of the benzothienopyrrole series **5a—g** containing both the methyl and octadecyl groups at the nitrogen atom of the benzothienopyrrole moiety (Scheme 3). The latter compounds are of interest for studying the aggregation in solution and at the air—water interface.[11] The yields of spiropyrans vary from moderate to high.

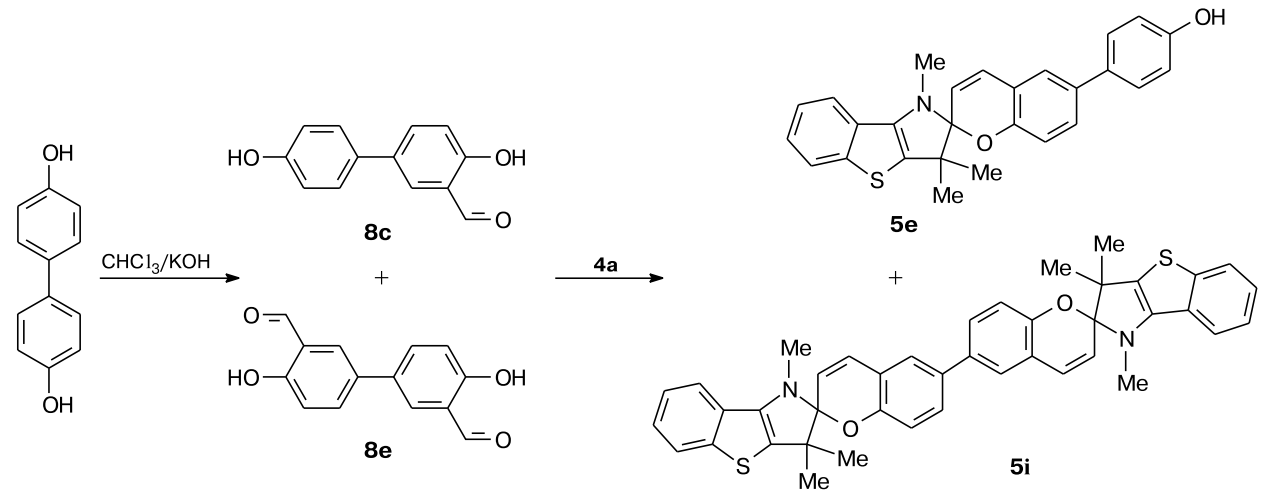
The formylation of 4,4′-dihydroxybiphenyl (biphenol) affords both mono- and diformylation products (compounds **8c** and **8e)**, which were not separated. Hence,

Reagents and conditions: *i*, piperidine, EtOH, Δ.

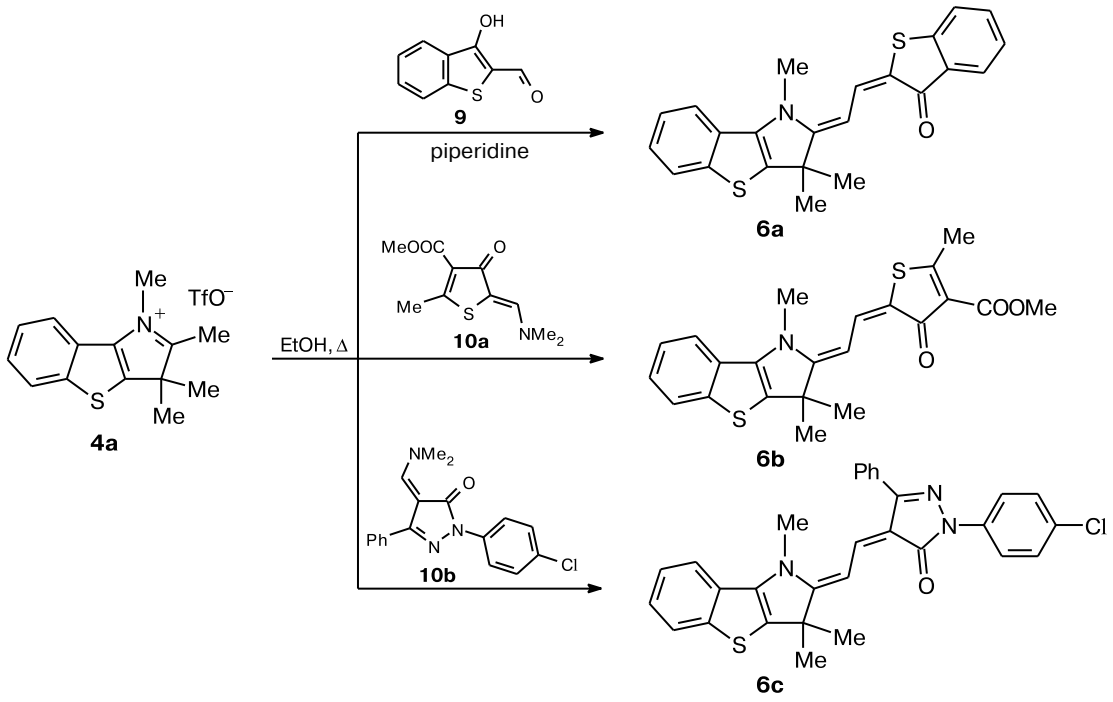
Compound	R^1	R^2	R^3	R^4
5a	Me	H	NO_2	H
5b	$C_{18}H_{37}$	H	NO_2	H
5c	Me	$(CH)_4$		H
5d	$C_{18}H_{37}$	$(CH)_4$		H
5e	Me	H	4-HOC_6H_4	H
5f	$C_{18}H_{37}$	H	4-HOC_6H_4	H
5g	Me	H	H	MeO
5h	$C_{18}H_{37}$	H	H	H
8a		H	NO_2	H
8b		$(CH)_4$		H
8c		H	H	4-HOC_6H_4
8d		H	H	MeO

when synthesizing spiropyran **5e**, we also isolated bisspiropyran **5i** in low yield (Scheme 4). After the recrystallization from ethanol, this compound contains an ethanol molecule. Even the drying over P_2O_5 with heating (50—55 °C) for a long time did not allow us to completely

Scheme 4



Scheme 5



remove the ethanol. There are four bis-spiropyran molecules **5i** per ethanol molecule. This is clearly seen in the ^{1}H NMR spectrum and is confirmed by elemental analysis.

Merocyanine dyes of the benzothienopyrrole series **6** were synthesized by the condensation of salt **4a** with heterocyclic analogs of salicylic aldehyde **9** or, if these compounds are difficult to synthesize, with dimethylaminomethylidene derivatives **10** (Scheme 5). The latter compounds were synthesized by the reactions of methylene-active heterocyclic compounds with dimethylformamide dimethylacetal[12] and have not been previously used for the synthesis of merocyanines. However, these compounds proved to be very convenient synthons due both to the ease of preparation and high activity. Merocyanine dyes **6** were synthesized by refluxing the reagents in ethanol in the presence of piperidine. The reactions of compounds **10** do not require the addition of bases because dimethylamine that is eliminated in the course of the reaction acts as the base.

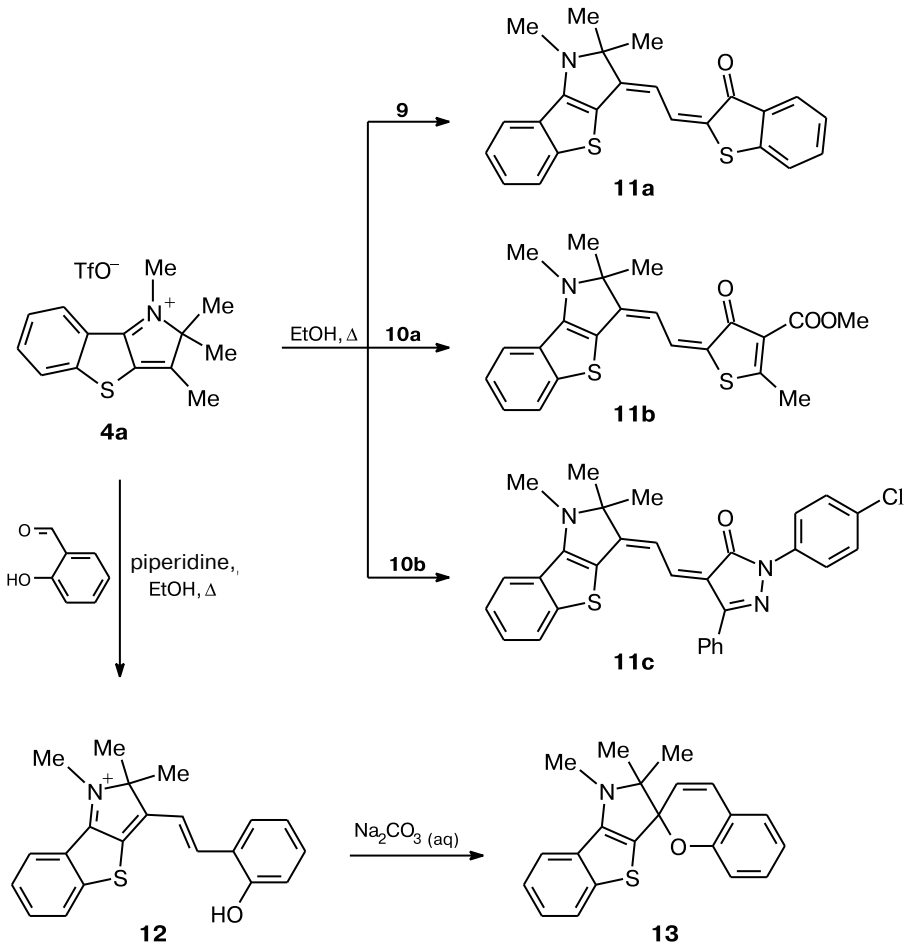
The analogous reactions of 2*H*-benzothienopyrrolium salt **7** with 2-hydroxyaldehydes **9** or dimethylaminomethylidene derivatives of heterocycles **10** give isomeric merocyanines **11** (Scheme 6). Under the analogous conditions, the reaction of salt **7** with salicylic aldehyde produces triflate **12**, which is stable in the presence of a weak base, such as piperidine. The treatment of salt **12** with an aqueous sodium carbonate solution affords compound **13**, which is the first representative of the previously unknown spiropyrans of the 2*H*-[1]benzothieno-[3,2-*b*]pyrrole series.

In spite of the fact that this compound is intensely colored in the solid state, it exists in the spiro form in chloroform solutions, as evidenced by the spin-spin coupling constants ($J \approx 10$ Hz) of the signals for the methine protons in the ^{1}H NMR spectrum. Therefore, compound **13** is the first example of spiropyrans containing the 2*H*-pyrrole fragment. However, this spiropyran appeared to be very unstable and it was characterized only by ^{1}H NMR spectroscopy. This compound can be stored only as the salt.

The structures of the resulting compounds were established by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The absorption bands of solutions of merocyanines **6** in acetonitrile are in the 503—540 nm range and are shifted to longer wavelengths by ~20 nm compared to indoline analogs. The absorption bands of isomeric dyes **11** are red-shifted by more than 110 nm. This is a consequence of the presence of an additional double bond between the nitrogen atom and the carbonyl group in these compounds.

To sum up, we developed a convenient method for the synthesis of photochromic spiropyrans and merocyanine dyes of the 1-benzothieno[3,2-*b*]pyrroline series based on the condensation of quaternary benzothienopyrrolium salts with aromatic 2-hydroxyaldehydes. Unlike Fischer's

Scheme 6



salt, benzothienopyrrolium salts readily undergo the [1,5]-sigmatropic rearrangement to give 2*H*-[1]benzothieno-[3,2-*b*]pyrrole derivatives. The condensation of the latter compounds with various hydroxyaldehydes afforded first representatives of the previously unknown spiro compounds and merocyanine dyes containing the 2*H*-pyrrole fragment.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300, Bruker WM-250, and Bruker AC-200 spectrometers. The mass spectra were obtained on a Kratos instrument (70 eV) using a direct inlet system. The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. The electronic spectra were measured on a LOMO SF-256U spectrophotometer. The completion of the reactions was controlled by TLC (Silufol UV-254). The column chromatography was carried out with the use of Merck silica gel (0.060—0.200). Commercially available (Acros, Merck) reagents and solvents were used. Aldehydes **8c,e** based on 4,4′-biphenol were synthesized according to a known procedure.[13]

Synthesis of spiropyrans 5 (general procedure). Methyl or octadecyl triflate (1.1 mmol) was added to a solution of 3*H*-benzothienopyrrole **3** (0.22 g, 1.0 mmol) in anhydrous acetonitrile (5 mL). The reaction solution was refluxed until compound **3** was consumed (0.5—3 h) and then cooled and concentrated. Anhydrous ethanol (5 mL), the corresponding *o*-hydroxyaldehyde **8** (1.0 mmol), and piperidine (0.1 mL, 1 mmol) were added to the residue. The reaction mixture was refluxed for 3—12 h. The course of the reactions was monitored by TLC (petroleum ether—ethyl acetate, 5 : 1, as the eluent). The product was isolated by column chromatography or recrystallization from an appropriate solvent.

1,3,3-Trimethyl-6′-nitrospiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5a). The yield was 47%, m.p. 184—186 °C (hexane). ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 3 H, 0.5 CMe_2); 1.35 (s, 3 H, 0.5 CMe_2); 3.06 (s, 3 H, NMe); 5.95 (d, 1 H, CH, J = 10.5 Hz); 6.86 (d, 1 H, H_{arom}, J = 8.5 Hz); 6.93 (d, 1 H, CH, J = 10.5 Hz); 7.21—7.37 (m, 2 H, 2 H_{arom}); 7.76—7.85 (m, 2 H, 2 H_{arom}); 8.01—8.11 (m, 2 H, 2 H_{arom}). MS (EI, 70 eV), m/z (I_{rel} (%)): 378 $[M]^+$ (88), 363 $[M - Me]^+$

(100). Found (%): C, 66.45; H, 4.84; N, 7.34. $C_{21}H_{18}N_2O_3S$. Calculated (%): C, 66.65; H, 4.79; N, 7.40.

3,3-Dimethyl-6′-nitro-1-octadecylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5b). The yield was 20%, amorphous powder. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me, J = 6.6 Hz); 1.20—1.31 (m, 33 H, 0.5 CMe_2 + $(CH_2)_{15}$); 1.34 (s, 3 H, 0.5 CMe_2); 1.69—1.83 (m, 2 H, CH_2); 3.23—3.59 (m, 2 H, NCH_2); 5.95 (d, 1 H, CH, J = 10.5 Hz); 6.83 (d, 1 H, H_{arom}, J = 8.5 Hz); 6.90 (d, 1 H, CH, J = 10.5 Hz); 7.20—7.40 (m, 2 H, 2 H_{arom}); 7.69 (d, 1 H, H_{arom}, J = 7.8 Hz); 7.80 (d, 1 H, H_{arom}, J = 7.8 Hz); 8.00—8.10 (m, 2 H, 2 H_{arom}). MS (EI, 70 eV), m/z (I_{rel} (%)): 616 $[M]^+$ (18), 600 $[M - Me]^+$ (20), 570 $[M - NO_2]^+$ (52), 364 $[M - C_{18}H_{36}]^+$ (100). Found (%): C, 73.44; H, 8.80; N, 4.45. $C_{38}H_{52}N_2O_3S$. Calculated (%): C, 73.98; H, 8.50; N, 4.54.

1,3,3-Trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno-[3,2-*b*]pyrrole-2,3′-3*H*-benzo[*f*]chromene] (5c). The yield was 68%, m.p. 243—245 °C (petroleum ether—benzene). ^{1}H NMR ($CDCl_3$), δ: 1.32 (s, 3 H, 0.5 CMe_2); 1.40 (s, 3 H, 0.5 CMe_2); 3.07 (s, 3 H, NMe); 5.90 (d, 1 H, CH, J = 10.5 Hz); 7.08 (d, 1 H, H_{arom}, J = 9.2 Hz); 7.20—7.40 (m, 3 H, H_{arom}); 7.53 (t, 1 H, H_{arom}, J = 7.2 Hz, J = 7.9 Hz); 7.62 (d, 1 H, CH, J = 10.5 Hz); 7.67 (d, 1 H, H_{arom}, J = 9.2 Hz); 7.72—7.87 (m, 3 H, 3H_{arom}); 8.06 (d, 1 H, H_{arom}, J = 8.5 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 383 $[M]^+$ (100), 368 $[M - Me]^+$ (85), 215 (41). Found (%): C, 77.68; H, 5.37; N, 3.79. $C_{25}H_{21}NOS$. Calculated (%): C, 78.30; H, 5.52; N, 3.65.

3,3-Dimethyl-1-octadecylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,3′-3*H*-benzo[*f*]chromene] (5d). The yield was 69%, viscous oil. ^{1}H NMR ($CDCl_3$), δ: 0.91 (t, 3 H, Me, J = 6.6 Hz); 1.17—1.35 (m, 33 H, 0.5 CMe_2 + $(CH_2)_{15}$); 1.39 (s, 3 H, 0.5 CMe_2); 1.72—1.84 (m, 2 H, CH_2); 3.35—3.55 (m, 2 H, NCH_2); 5.90 (d, 1 H, CH, J = 10.3); 7.05 (d, 1 H, H_{arom}, J = 8.8 Hz); 7.20—7.40 (m, 3 H, H_{arom}); 7.49—7.60 (m, 2 H, CH + H_{arom}); 7.66 (d, 1 H, H_{arom}, J = 8.8 Hz); 7.69—7.83 (m, 3 H, 3 H_{arom}); 8.06 (d, 1 H, H_{arom}, J = 8.1 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 621 $[M]^+$ (73), 606 $[M - Me]^+$ (18), 454 (100), 370 (64). Found (%): N, 2.19. $C_{42}H_{55}NOS$. Calculated (%): N, 2.25.

6′-(4-Hydroxyphenyl)-1,3,3-trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5e). The yield was 67%, m.p. 114—116 °C (hexane). ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3 H, 0.5 CMe_2); 1.41 (s, 3 H, 0.5 CMe_2); 3.10 (s, 3 H, NMe); 4.81 (br.s, 1 H, OH); 5.84 (d, 1 H, CH, J = 10.2 Hz), 6.82—6.97 (m, 4 H, CH + 3 CH_{arom}); 7.22—7.37 (m, 4 H, 4 H_{arom}); 7.43 (d, 2 H, 2 H_{arom}, J = 8.8 Hz); 7.76—7.88 (m, 2 H, 2 H_{arom}). MS (EI, 70 eV), m/z (I_{rel} (%)): 425 $[M]^+$ (100), 410 $[M - Me]^+$ (99). Found (%): C, 76.22; H, 6.50; N, 3.17. $C_{27}H_{23}NO_2S$. Calculated (%): C, 76.21; H, 6.45; N, 3.29.

6′-(4-Hydroxyphenyl)-3,3-dimethyl-1-octadecylspiro-[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5f). The yield was 23%, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.92 (t, 3 H, Me, J = 6.6 Hz); 1.24—1.36 (m, 33 H, 0.5 CMe_2 + $(CH_2)_{15}$); 1.40 (s, 3 H, 0.5 CMe_2); 1.74—1.87 (m, 2 H, CH_2); 3.33—3.59 (m, 2 H, NCH_2); 5.84 (d, 1 H, CH, J = 10.3 Hz); 6.81—6.93 (m, 4 H, CH + 3 H_{arom}); 7.23—7.28 (m, 2 H, 2 H_{arom}); 7.30—7.38 (m, 2 H, 2 H_{arom}); 7.43 (d, 2 H, 2 H_{arom}, J = 8.8 Hz); 7.73 (d, 1 H, H_{arom}, J = 8.1 Hz); 7.80 (d, 1 H, H_{arom}, J = 8.1 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 663 $[M]^+$ (100), 453 (56), 410 $[M - C_{18}H_{37}]^+$ (37). A sample suitable for elemental analysis was not obtained.

8′-Methoxy-1,3,3-trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5g). The yield was 41%, m.p. 173—175 °C (petroleum ether—benzene). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 3 H, 0.5 CMe_2); 1.38 (s, 3 H, 0.5 CMe_2); 3.07 (s, 3 H, NMe); 3.74 (s, 3 H, OMe); 5.79 (d, 1 H, CH, J = 10.5 Hz); 6.68—6.76 (m, 1 H, H_{arom}); 6.77—6.86 (m, 3 H, CH + 2 H_{arom}); 7.23 (t, 1 H, H_{arom}, J = 7.2 Hz, J = 7.9 Hz); 7.31 (t, 1 H, H_{arom}, J = 7.2 Hz, J = 7.9 Hz); 7.75—7.85 (m, 2 H, 2 H_{arom}). MS (EI, 70 eV), m/z (I_{rel} (%)): 363 $[M]^+$ (100), 348 $[M - Me]^+$ (38). Found (%): C, 72.25; H, 6.56; N, 3.48. $C_{22}H_{21}NO_2S$. Calculated (%): C, 72.70; H, 5.82; N, 3.85.

8′-Methoxy-3,3-dimethyl-1-octadecylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromene] (5h). The yield was 47%, amorphous powder. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 6.6 Hz); 1.21—1.31 (m, 33 H, 0.5 CMe_2 + $(CH_2)_{15}$); 1.36 (s, 3 H, 0.5 CMe_2); 1.68—1.84 (m, 2 H, CH_2); 3.36—3.50 (m, 2 H, NCH_2); 3.73 (s, 3 H, OMe); 5.77 (d, 1 H, CH, J = 10.3); 6.68—6.73 (m, 1 H, H_{arom}); 6.75—6.82 (m, 3 H, CH + 2 H_{arom}); 7.22 (t, 1 H, H_{arom}, J = 7.3 Hz, J = 7.7 Hz); 7.31 (t, 1 H, H_{arom}, J = 7.3 Hz, J = 7.7 Hz); 7.69 (d, 1 H, H_{arom}, J = 7.7 Hz); 7.78 (d, 1 H, H_{arom}, J = 7.7 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 601 (100) $[M]^+$, 586 (40) $[M - Me]^+$. Found (%): C, 77.01; H, 9.24; N, 2.36. $C_{39}H_{55}NO_2S$. Calculated (%): C, 77.82; H, 9.21; N, 2.33.

8′,8″-Bis(1,3,3-trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-b]pyrrole-2,2′-2H-chromene]) (5i). The yield was 30 mg (9%), m.p. 261—263 °C (ethanol). ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.26 (t, 0.75 H, CH_3, J = 7.2 Hz); 1.28 (s, 6 H, 0.5 CMe_2); 1.39 (s, 6 H, 0.5 CMe_2); 3.08 (s, 6 H, NMe); 3,74 (m, 0.5 H, CH_2); (d, 2 H, CH, J = 10.5 Hz); 6.85 (d, 2 H, H_{arom}, J = 8.5 Hz); 6.91 (d, 2 H, CH, J = 10.5 Hz); 7.18—7.37 (m, 8 H, H_{arom}); 7.75—7.88 (m, 4 H, H_{arom}). MS (EI, 70 eV), m/z (I_{rel} (%)): 664 $[M]^+$ (1), 652 (34), 214 (100). Found (%): C, 74.51; H, 5.94; N, 4.03. $C_{42}H_{36}N_2O_2S_2 \cdot 0.25EtOH$. Calculated (%): C, 74.33; H, 5.95; N, 3.94.

Synthesis of dimethylaminomethylidene derivatives of heterocycles 10 (general procedure). A solution of dimethylformamide dimethylacetal (1.5 mL, 11 mmol) in petroleum ether (10 mL) was added with stirring and cooling (10 °C) to a suspension of the corresponding heterocyclic ketone (10 mmol) in petroleum ether (20 mL) for 40 min. Then the cooling was stopped, and the reaction mixture was kept with stirring at room temperature. After 3 h, the precipitate was filtered off. The mother liquor was concentrated to 5 mL. The precipitate that formed was filtered off and combined with the precipitate obtained previously. The compounds were used without purification.

Methyl 5-[(dimethylamino)methylidene]-2-methyl-4-oxo-3(4*H*)-thiophenecarboxylate (10a). The yield was 87%, m.p. 157—160 °C. ^{1}H NMR ($CDCl_3$), δ: 2.60 (s, 3 H, Me); 3.21 (s, 6 H, NMe_2); 3.83 (s, 3 H, OMe); 7.76 (s, 1 H, CH). MS (EI, 70 eV), m/z (I_{rel} (%)): 227 $[M]^+$ (76), 167 $[M - HCOOMe]^+$ (100).

2-(4-Chlorophenyl)-4-[(dimethylamino)methylidene]-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (10b). The yield was 93%, m.p. 180—182 °C. ^{1}H NMR ($CDCl_3$), δ: 3.26 (s, 3 H, 0.5 NMe_2); 3.89 (s, 3 H, 0.5 NMe_2); 7.16 (s, 1 H, CH); 7.33 (d, 2 H, H_{arom}, J = 8.5 Hz); 7.41—7.57 (m, 5 H, H_{arom}); 8.06 (d, 2 H, H_{arom}, J = 8.5 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 325 $[M]^+$ (100), 281 $[M - NMe_2]^+$ (43).

Synthesis of merocyanines (general procedure). Merocyanines were synthesized analogously to spiropyrans **5**. The reactions of

dimethylaminomethylidene derivatives **10** were carried out in the absence of piperidine. The product was isolated by column chromatography (chloroform—ethyl acetate, 3 : 1, as the eluent) or recrystallization from ethanol. Merocyanines **6a** and **11a** have been synthesized and characterized earlier.[7]

Methyl 2-methyl-4-oxo-5-[2-(1,3,3-trimethyl-1,3-dihydro-2*H*-[1]benzothieno[3,2-*b*]pyrrol-2-ylidene)ethylidene]-3(4*H*)-thiophenecarboxylate (6b). The yield was 57%, m.p. 216—218 °C (ethanol), λ_{max} = 520 nm (acetonitrile). ^{1}H NMR (DMSO-d_6 + CF_3COOH), δ: 1.82 (s, 6 H, CMe_2); 2.69 (s, 3 H, Me); 3.85 (s, 3 H, NMe); 4.19 (s, 3 H, COOMe); 6.76 (d, 1 H, CH, *J* = 15.3 Hz); 7.51 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 7.58 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 8.17 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 8.22—8.32 (m, 2 H, 2 H_{arom}). ^{13}C NMR (DMSO-d_6 + CF_3COOH), δ: 18.00 (Me), 27.49 ($C\underline{Me}_2$), 35.01 (NMe), 51.11 (COO<u>Me</u>), 51.66 ($\underline{C}Me_2$), 101.92, 116.18, 120.79, 122.04, 124.95, 125.20, 125.65, 126.14, 137.08, 137.96, 141.49, 142.61, 161.05, 163.00, 169.49, 179.03 (<u>C</u>OOMe). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 411 $[M]^+$ (100), 396 $[M - Me]^+$ (20), 264 (66), 215 (50). Found (%): C, 63.73; H, 5.33; N, 3.38. $C_{22}H_{21}NO_3S_2$. Calculated (%): C, 64.21; H, 5.14; N, 3.40.

1-(4-Chlorophenyl)-3-phenyl-4-[2-(1,3,3-trimethyl-1,3-dihydro-2*H*-[1]benzothieno[3,2-*b*]pyrrol-2-ylidene)ethylidene]-1*H*-pyrazol-5-one (6c). The yield was 49%, m.p. 241—243 °C (ethanol), λ_{max} = 525 nm (acetonitrile). ^{1}H NMR ($CDCl_3$), δ: 1.71 (s, 6 H, CMe_2); 3.89 (s, 3 H, NMe); 7.29—7.59 (m, 7 H, 7 H_{arom}); 7.60—7.76 (m, 3 H, 3 H_{arom}); 7.85 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 7.90—8.06 (m, 2 H, 2 H_{arom}); 8.15 (d, 2 H, 2 H_{arom}, *J* = 7.9 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 509 $[M]^+$ (100), 494 $[M - Me]^+$ (54), 228 (52). Found (%): C, 70.32; H, 5.01; N, 8.42. $C_{30}H_{24}ClN_3OS$. Calculated (%): C, 70.64; H, 4.74; N, 8.24.

Methyl 2-methyl-4-oxo-5-[3-(1,2,2-trimethyl-1,2-dihydro-3*H*-[1]benzothieno[3,2-*b*]pyrrol-3-ylidene)ethylidene]-3(4*H*)-thiophenecarboxylate (11b). The yield was 49%, m.p. > 350 °C (ethanol), λ_{max} = 645 nm (acetonitrile). ^{1}H NMR (DMSO-d_6 + CF_3COOH), δ: 1.66 (s, 6 H, CMe_2); 2.67 (s, 3 H, Me); 3.83—3.93 (m, 6 H, NMe + COOMe); 6.81 (d, 1 H, CH, *J* = 15.9 Hz); 7.46 (d, 1 H, CH, *J* = 15.9 Hz); 7.65 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 7.90 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 8.16 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 8.49 (d, 1 H, H_{arom}, *J* = 7.9 Hz). ^{13}C NMR (DMSO-d_6 + CF_3COOH), δ: 17.40 (Me), 21.20 ($C\underline{Me}_2$), 31.76 (NMe), 52.02 (COO<u>Me</u>), 84.39 ($\underline{C}Me_2$), 111.70, 114.33, 119.22, 122.06, 124.20, 125.95, 126.80, 128.80, 132.58, 135.40, 152.38, 153.65, 158.93, 161.66, 163.64, 168.71. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 411 $[M]^+$ (61), 396 $[M - Me]^+$ (23), 264 (100). Found (%): N, 3.38. $C_{22}H_{21}NO_3S_2$. Calculated (%): N, 3.40.

1-(4-Chlorophenyl)-3-phenyl-4-[2-(1,2,2-trimethyl-1,2-dihydro-3*H*-[1]benzothieno[3,2-*b*]pyrrol-3-ylidene)ethylidene]-1*H*-pyrazol-5-one (11c). The yield was 45%, m.p. 271—273 °C (ethanol), λ_{max} = 648 nm (acetonitrile). ^{1}H NMR ($CDCl_3$), δ: 1.56 (s, 6 H, CMe_2); 3.52 (s, 3 H, NMe); 7.36 (d, 2 H, H_{arom}, *J* = 8.5 Hz); 7.38—7.65 (m, 6 H, H_{arom}); 7.70—7.82 (m, 4 H, H_{arom}); 7.01 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 8.17 (d, 2 H, H_{arom}, *J* = 8.5 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 509 $[M]^+$ (100), 494 $[M - Me]^+$ (56), 227 (45). Found (%): C, 69.95; H, 4.59; N, 7.89. $C_{30}H_{24}ClN_3OS$. Calculated (%): C, 70.64; H, 4.74; N, 8.24.

1′,2′,2′-Trimethylspiro-2*H*-1-benzopyran-2,3′-[1]benzothieno[3,2-*b*]pyrrolidine (13). Methyl triflate (0.37 mL, 3.3 mmol) was added to a solution of 3*H*-benzothienopyrrole **3** (0.65 g, 3.0 mmol) in anhydrous acetonitrile (6 mL). The reaction solution was refluxed for 32 h, cooled, and concentrated. Anhydrous ethanol (6 mL), salicylaldehyde (0.32 mL, 3.0 mmol), and piperidine (0.33 mL, 3.3 mmol) were added to the residue. The reaction mixture was refluxed for 1 h. The precipitate that formed was filtered off and washed with ethanol (2×5 mL). The mother liquor was concentrated and washed with petroleum ether. Then ethanol (10 mL) was added, and the precipitate was again filtered off.

The yield was 0.38 g (26%), red needle-like crystals (triflate **12**), m.p. 290—292 °C (ethanol). ^{1}H NMR (DMSO-d_6 + CF_3COOH), δ: 1.70 (s, 6 H, CMe_2); 3.93 (s, 3 H, NMe); 6.92 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 6.99 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 7.31 (t, 1 H, H_{arom}, *J* = 7.3 Hz, *J* = 7.9 Hz); 7.45 (d, 1 H, CH, *J* = 16.5 Hz); 7.63—7.73 (m, 2 H, CH + H_{arom}); 7.91—7.98 (m, 2 H, 2 H_{arom}); 8.19 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 8.53 (d, 1 H, H_{arom}, *J* = 7.9 Hz). ^{13}C NMR (DMSO-d_6 + CF_3COOH), δ: 20.67 ($C\underline{Me}_2$), 32.20 (NMe), 85.51 ($\underline{C}Me_2$), 116.18, 116.42, 119.76, 122.15, 122.27, 126.23, 126.48, 127.18, 127.47, 129.60, 132.74, 136.26, 138.74, 153.15, 157.03, 161.72, 170.29. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 333 $[M]^+$ (36), 318 $[M - Me]^+$ (100), 217 (28). Found (%): C, 54.56; H, 4.17; N, 2.89. $C_{21}H_{19}NOS \cdot CF_3SO_3H$. Calculated (%): C, 54.65; H, 4.17; N, 2.90.

Triflate **12** (30 mg) was treated with an aqueous Na_2CO_3 solution and extracted with chloroform. The greenish solution was concentrated, and dark-blue solid substance **13** was obtained. ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 3 H, 0.5 CMe_2); 1.42 (s, 3 H, 0.5 CMe_2); 3.10 (s, 3 H, NMe); 5.82 (d, 1 H, CH, *J* = 9.9 Hz); 6.63 (d, 1 H, CH, *J* = 9.9 Hz); 6.76—6.89 (m, 2 H, 2 H_{arom}); 7.03 (d, 1 H, H_{arom}, *J* = 7.9 Hz); 7.10 (t, 1 H, H_{arom}, *J* = 7.2 Hz, *J* = 7.9 Hz); 7.26—7.33 (m, 2 H, 2 H_{arom}); 7.61—7.75 (m, 1 H, H_{arom}); 7.85—7.94 (m, 1 H, H_{arom}).

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