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Novel photochromic spiro compounds based on thieno[3,2-*b*]pyrroles

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ABSTRACT: Previously unknown spiro compounds of thienopyrroline series were synthesized by a convenient method starting from easily accessible 3-hydroxythiophene derivatives. The photochromic properties of spiro compounds of thienopyrroline series were studied. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: thienopyrrolenine; photochromism; spirooxazine; spiropyran

INTRODUCTION

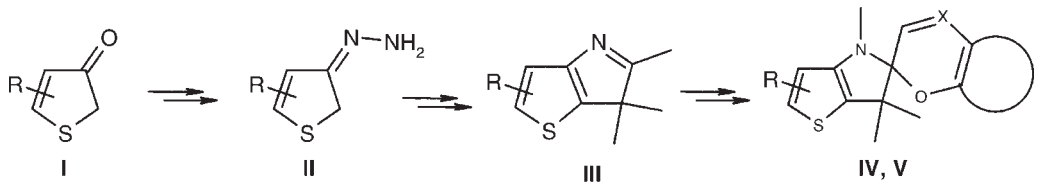
Most of the known photochromic spiro compounds are indole derivatives.[1–4] It seemed of interest to synthesize close analogs of these substances containing thieno[3,2-*b*]pyrrole fragments instead of indole ones. Such a replacement of the benzene ring in photochromic systems with electron rich thiophene cycle could give rise to new valuable properties and allows further chemical modification of products.

In this paper we summarize the results on the synthesis and some spectral and photochromic studies of spiro compounds based on thienopyrrole derivatives. A special emphasis is given to the methods of the preparation of the starting materials (thienopyrrolenines) and target spiro compounds. The studies on photochromic and spectral properties of spiro compounds of thienopyrroline series are presented.

RESULTS AND DISCUSSION

Synthesis of spiro compounds

As starting compounds for the synthesis of spiro compounds of thienopyrroline series **IV** and **V** easily accessible thiophen-3-ones (or 3-hydroxythiophenes) **I** were used. This synthetic route involves four simple stages, including the cyclization of hydrazones (thienylhydrazine derivatives) **II** with 3-methylbutan-2-one under Fischer reaction conditions (Scheme 1). It should be noted that although this reaction is widely used to prepare indolenine derivatives, it had not been used for the synthesis of thienopyrrolenines until now.[5–7] We have investigated this reaction using different solvents and acid catalysts and found that the better yields of thienopyrrolenines **III** were obtained when thiophen-3-one hydrazones **II** reacted with



Scheme 1.

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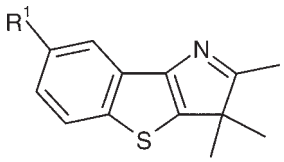
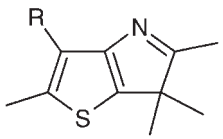
3-methylbutan-2-one in benzene in the presence of dry hydrogen chloride.

By this synthetic strategy previously unknown thienopyrrolenines **IIIa–d** were prepared in moderate yields. This method has been reported in detail recently.[8]



III a,b

IIIa, $R^1 = H$;
IIIb, $R^1 = NO_2$



IIIc-e

IIIc, R = H;
IIId, R = COOMe

Spiropyrans **IVa–h** of the thienopyrroline series were prepared via the classical route (Scheme 2) from the appropriate thienopyrrolenines **IIIa–d**. The scheme of the synthesis includes alkylation of thienopyrolenine by akyl triflates to afford salts **VI**. The reaction of **VI** with different derivatives of salicylic aldehyde yielded to desired spiropyrans, whose structures were proved by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and confirmed by elemental analyses. In the ^1H NMR spectra of spiropyrans, signals of the H-atoms of the pyran ring appeared as the AB-quartet with $J_{AB} = 10.0$ Hz.[5] The spin–spin coupling constants are in good accordance with the published data for spiropyrans of the indole series[9] so that the structures of the obtained spiro compounds were confirmed.

Spirooxazines **V** based on thienopyrrole were prepared by the condensation of salts **VI** with *o*-nitrosonaphthol or phenanthrene-9,10-dione oxime in the presence of a base (Scheme 3).

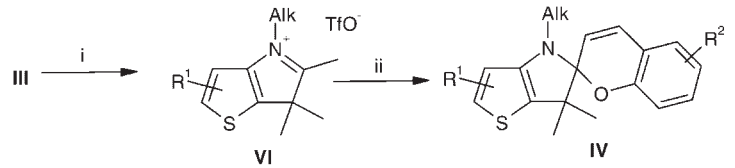
Photochromic studies

We have studied the photochromic properties of novel spiro compounds of thienopyrroline series. UV-irradiation of solutions of spiropyrans **IV** and spirooxazines **V** results in coloration due to the photoinitiated ring-opening reaction leading to the formation of the merocyanine isomers **B** (Scheme 4).

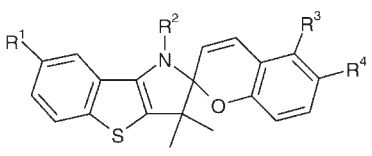
In Fig. 1, the spectral changes of the photochromic spiropyran **IVg** in ethanol solution under UV-irradiation ($\lambda_{ir} = 365$ nm) at 203 K are presented. The spectral pattern closely resembles that reported for other photochromic spiropyrans.[10,11]

This spectrum is typical for the compounds **IV** and **V**. The long wavelength absorption bands of the merocyanine forms **B** of spiro compounds **IV** and **V** in ethanol solutions have maxima at 525–626 nm. Our investigation shows that, unlike the indoline analogs, the thermal back reaction (**B** to **A**) of these compounds were very fast at room temperature, so the absorption spectra were recorded at 203 K.

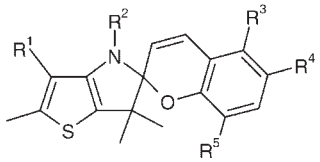
Some spectral and kinetic data for spiropyran **IVf** and spirooxazines **Vc,d** are reported in Table 1. As expected, the absorption maxima of ring-opened form **B**, the rate constants of ring-opening reaction and activation energy for the thermal decoloration of these spiro compounds depend on solvent polarity. The absorption maximum of the ring-opened form **B** of spiropyran **IVf** in ethanol



i - AlkOTf, MeCN, Δ; ii - hydroxyaldehydes, pyperidine, EtOH, Δ



IVa-d



IVe-g

IVa, $R^1 = H$, $R^2 = Me$, $R^3 + R^4 = C_4H_4$
IVb, $R^1 = H$, $R^2 = Me$, $R^3 = H$, $R^4 = NO_2$;
IVc, $R^1 = NO_2$, $R^2 = Me$, $R^3 + R^4 = C_4H_4$,
IVd, $R^1 = H$, $R^2 = C_{18}H_{37}$, $R^3 = H$, $R^4 = NO_2$;

IVe, $R^1 = H$, $R^2 = Et$, $R^3 = R^4 = R^5 = H$;
IVf, $R^1 = H$, $R^2 = Et$, $R^3 = R^5 = H$, $R^4 = NO_2$;
IVg, $R^1 = COO_2Me$, $R^2 = Me$, $R^3 + R^4 = C_4H_4$, $R^5 = H$;

Scheme 2.

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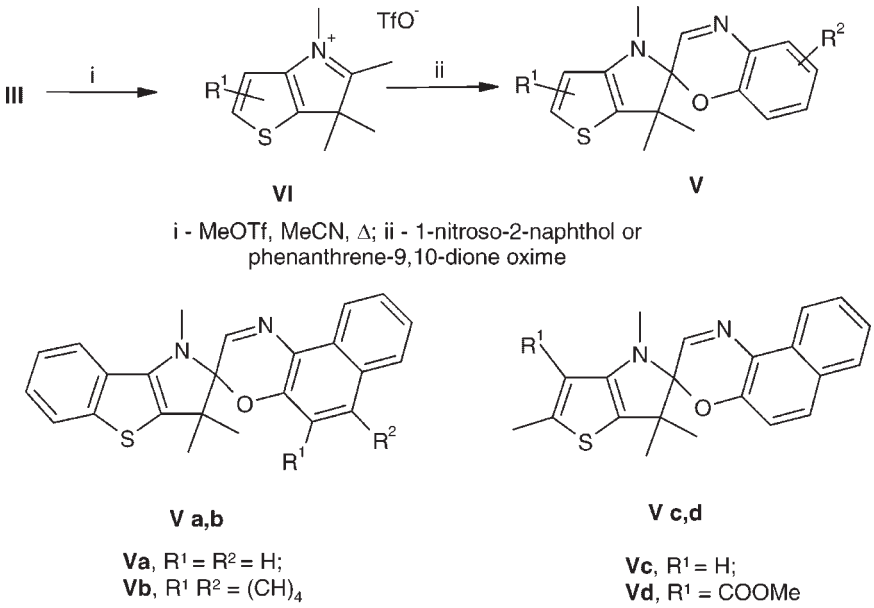
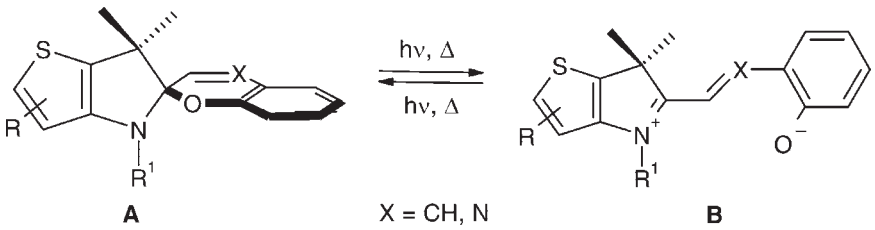


Scheme 3.



Scheme 4.

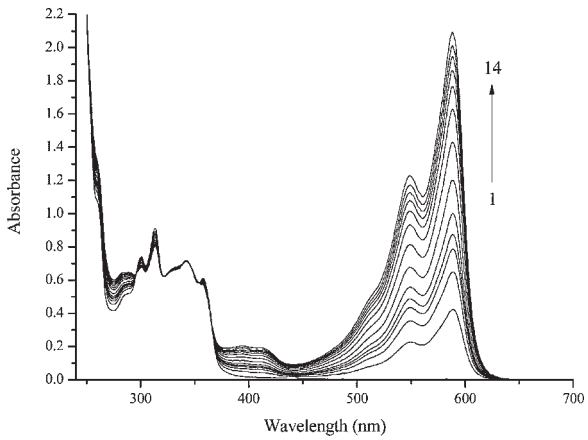


Figure 1. Absorption spectra of the compound **IVg** ($C = 1.0.10^{-4}\,mol \cdot L^{-1}$) in EtOH at $T = 203\,K$ under UV irradiation ($\lambda_{ir} = 365\,nm$, $\Delta t = 30\,s$)

solution is blue shifted as compared with that in toluene. On the contrary, the absorption bands of merocyanine form **B** of spirooxazines **Vc**,**d** in ethanol solutions are bathochromically shifted in comparison with those in toluene solution. The lifetimes of ring-opened forms of these compounds in ethanol solution are longer than in toluene that may be explained by the increasing of activation energy for the thermal decay in ethanol.

Table 2 presents spectral data of closed (**A**) and colored (**B**) isomers of spiropyrans **IV** and spirooxazines **V** in toluene solutions. The absorption maxima of ring-closed forms **A** are observed at 296–333 nm except that of spiropyran **IVc** that absorbs at 436 nm. This effect is obviously caused by the presence of the nitro group on the 1-benzothieno[3,2-*b*]pyrrole system. The merocyanine forms **B** obtained after irradiation of the solutions with UV light absorb at 610–630 nm.

Table 1. Spectral and kinetic data of spiropyran **IVf** and spirooxazines **Vc,d** in ethanol and toluene solutions at 203 K

	λ_{max}(A) nm		λ_{max}(B) nm		k_0(AB) s^{-1}		E_a(BA) kJ/mol	
Compounds	Toluene	EtOH	Toluene	EtOH	Toluene	EtOH	Toluene	EtOH
IVf	333	335	613	541	$1.08 \cdot 10^{16}$	—	98.5	—
Vc	351	350	620	633	$1.34 \cdot 10^{11}$	$1.92 \cdot 10^{18}$	65.5	108.6
Vd	346	344	610	626	$9.11 \cdot 10^{12}$	$9.08 \cdot 10^{17}$	75.5	100.8

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Table 2. Spectral data of spiropyrans and spirooxazines in toluene

Compounds	λ_{max}(A) nm	λ_{max}(B) nm
IVa	336	—
IVb	325	620
IVc	436	—
IVd	326	628
IVf	333	613
Va	296	626
Vc	351	620
Vd	346	610

Table 3. Wavelengths (λ_{max}, nm) of the absorption maxima (abs), excitation fluorescence (ex), and fluorescence (flu) of the ring-opened forms **B** of spiropyrans **IVf,g** in ethanol solutions at 203 K

Compounds	**IVf**	**IVg**
λ_{max} (abs)	541	588
λ_{max} (ex)	522	585
λ_{max} (flu)	584	603

In ethanol solutions at $T = 203$ K, the merocyanine forms **B** of spiropyrans **IVf** and **IVg** exhibit fluorescence with maxima at 584 and 603 nm, respectively (Table 3). The fluorescence excitation spectra conform to the absorption spectra (Table 2). The fluorescent maxima of **IVf** are blue shifted relative to those of **IVg** that may be explained by the effect of an electron withdrawing substituent on the thiophene ring of spiropyran **IVg**.

CONCLUSION

In conclusion, we have developed a convenient synthetic route to the synthesis of spiro compounds of thienopyrroline series. A large set of new spiropyrans and spirooxazines, have been reported and their photochromic properties were studied.

EXPERIMENTAL

General methods

^{1}H and ^{13}C NMR spectra were performed on Bruker WM-250 or AC-200 spectrometers. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. Column chromatography was performed using silica gel 60 (70–230 mesh). TLC analysis was conducted on silica gel 60 F254 plates. Commercially available (Acros, Merck) reagents (2-hydroxysalicylic aldehyde, 2-hydroxy-1-nitrozonaphthol, phenanthrene-9,10-dione, trifluoromethanesulfonic anhydride, piperidine) and solvents (acetonitrile, light petroleum ether (45–70°C), ethanol, ethyl acetate) were used. Chromatography products were purchased from Merck. Thienopyrrolenines **III** were synthesized as described elsewhwere.[6,12]

Spectroscopic studies

Absorption spectra were recorded with Agilent 8453 diode array spectrophotometer. Irradiation light was brought into the temperature-controlled cell compartment at 90° from a 250 W high-pressure mercury lamp equipped with glass filters for allocation of mercury lines. The solutions were stirred with a magnetic bar driven by a speed controlled motor. Low temperature absorption spectra were recorded using a home-made quartz cryostat with working temperature range of 77–293 K. Luminescence emission and excitation spectra were recorded with a Varian Cary Eclipse spectrofluorimeter. The solvents were ethanol and toluene of the spectroscopic grade (Acros Organics).

Synthesis of spiropyrans and spirooxazines

Methyl- or octadecyltryflate (1.1 mmol) was added to the solution of thienopyrrolenine **III** (1.0 mmol) in acetonitrile (5 ml). The reaction mixture was refluxed for 1.5 h. After cooling the solvent was removed *in vacuo*. Ethanol (5 ml), 2-hydroxysalicylic aldehyde, 2-hydroxy-1-nitrozonaphthol or phenanthrene-9,10-dione oxime (1.0 mmol), and piperidine (0.1 ml, 1.0 mmol) were added to the residue and the reaction mixture was refluxed until starting materials disappeared (TLC control, eluent light petroleum/ethyl acetate 5:1). The solvent was removed and the residue was purified by column chromatography (eluent light petroleum/ethyl acetate 5:1 or 12:1) or recrystallization.

1,3,3-Trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrol-2,3′-3*H*-benzo[f]chromen] (IVa)

Yield 68%, m.p. 243–245°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.32 (s, 3H, ½CMe_2), 1.40 (s, 3H, ½CMe_2), 3.07 (s, 3H, NMe), 5.90 (d, $J = 10.5$ Hz, 1H, CH), 7.08 (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.20–7.40 (m, 3H, H^{arom}), 7.53 (t, $J = 7.2$, 7.9 Hz, 1H, H^{arom}), 7.62 (d, $J = 10.5$ Hz, 1H, CH), 7.67 (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.72–7.87 (m, 3H, H^{arom}), 8.06 (d, $J = 8.5$ Hz, 1H, H^{arom}). MS: *m/z* (%) = 383 (100) $[M]^+$, 368 (85) $[M-Me]^+$, 215 (41). Elemental analysis: Calcd. for $C_{25}H_{21}NOS$: C, 78.30; H, 5.52; N, 3.65. Found: C, 77.68; H, 5.37; N, 3.79%.

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1,3,3-Trimetyl-6′-nitrospiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromen] (IVb)

Yield 47%, m.p. 184–186°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (s, 3H, ½CMe_2), 1.35 (s, 3H, ½CMe_2), 3.06 (s, 3H, NMe), 5.95 (d, $J = 10.5$ Hz, 1H, CH), 6.86 (d, $J = 8.5$ Hz, 1H, H^{arom}), 6.93 (d, $J = 10.5$ Hz, 1H, CH), 7.21–7.37 (m, 2H, H^{arom}), 7.76–7.85 (m, 2H, H^{arom}), 8.01–8.11 (m, 2H, H^{arom}). MS: *m/z* (%) = 378 (88) $[M]^+$, 363 (100) $[M-Me]^+$. Elemental analysis: Calcd. for $C_{21}H_{18}N_2O_3S$: C, 66.65; H, 4.79; N, 7.40. Found: C, 66.45; H, 4.84; N, 7.34%.

1,3,3-Trimethyl-7-nitrospiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,3′-3*H*-benzo[f]chromen] (IVc)

Yield 53%, m.p. 204–205°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 3H, ½CMe_2), 1.42 (s, 3H, ½CMe_2), 3.12 (s, 3H, NMe), 5.89 (d, $J = 10.5$ Hz, 1H, CH), 7.06 (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.37 (t, $J = 7.2$, 7.9 Hz, 1H, H^{arom}), 7.55 (t, $J = 7.2$, 7.9 Hz, 1H, H^{arom}), 7.61–7.72 (m, 2H, H^{arom}), 7.76 (d, $J = 8.5$ Hz, 1H, H^{arom}), 7.87 (d, $J = 9.2$ Hz, 1H, H^{arom}), 8.03–8.13 (m, 2H, H^{arom}), 8.70 (d, $J = 2.0$ Hz, 1H, H^{arom}). MS: *m/z* (%) = 428 (100) $[M]^+$, 413 (99) $[M-Me]^+$, 398 (99) $[M-2Me]^+$, 383 (78) $[M-3Me]^+$. Elemental analysis: Calcd. for $C_{25}H_{20}N_2O_3S$: C, 70.07; H, 4.70; N, 6.54. Found: C, 70.12; H, 4.81; N, 6.69%.

3,3-Dimethyl-6′-nitro-1-octadecylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-2*H*-chromen] (IVd)

Yield 29%, m.p. 61–63°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (t, $J = 6.6$ Hz, 3H, Me), 1.20–1.31 (m, 33H, ½CMe_2 + $(CH_2)_{15}$), 1.34 (s, 3H, ½CMe_2), 1.69–1.83 (m, 2H, CH_2), 3.23–3.59 (m, 2H, NCH_2), 5.95 (d, $J = 10.5$ Hz, 1H, CH), 6.83 (d, $J = 8.5$ Hz, 1H, H^{arom}), 6.90 (d, $J = 10.5$ Hz, 1H, CH), 7.20–7.40 (m, 2H, H^{arom}), 7.69 (d, $J = 7.8$ Hz, 1H, H^{arom}), 7.80 (d, $J = 7.8$ Hz, 1H, H^{arom}), 8.00–8.10 (m, 2H, H^{arom}). MS: *m/z* (%) = 616 (18) $[M]^+$, 600 (20) $[M-Me]^+$, 570 (52) $[M-NO_2]^+$, 364 (100) $[M-C_{18}H_{36}]^+$. Elemental analysis: Calcd. for $C_{38}H_{52}N_2O_3S$: C, 73.98; H, 8.50; N, 4.54. Found: C, 73.44; H, 8.80; N, 4.45%.

4′-Ethyl-2′,6′,6′-trimethylspiro[2*H*-1-benzopyran-2,5′-2,3-dihydrothieno[3,2-*b*]pyrrol] (IVe)

Yield 40%, m.p. 72–74°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.19 (t, $J = 7.2$ Hz, 3H, CH_3CH_2), 1.19 (s, 3H, ½CMe_2), 1.28 (s, 3H, ½CMe_2), 2.49 (s, 3H, Me), 3.10 (dq, $J = 7.2$, 12.5 Hz, CH_2CH_3), 5.71 (d, $J = 10.5$ Hz, 1H, CH), 6.35 (s, 1H, H^{thioph}), 6.75 (d, $J = 10.5$ Hz, 1H, CH), 6.87–7.17 (m, 4H, H^{arom}). MS, *m/z* (%): 311 (32) $[M]^+$, 296 (9) $[M-Me]^+$, 282 (100) $[M-Et]^+$, 210 (15), 138 (30). Elemental analysis: Calcd. for $C_{25}H_{25}NO_2S$: C, 74.41; H, 6.24; S, 7.95. Found: C, 74.32; H, 6.13; S, 7.77%.

4′-Ethyl-2′,6′,6′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,5′-2,3-dihydrothieno[3,2-*b*]pyrrol] (IVf)

Yield 25%, m.p. 110–112°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.18 (t, $J = 7.2$ Hz, 3H, CH_3CH_2), 1.19 (s, 3H, ½CMe_2), 1.24 (s, 3H, ½CMe_2), 2.49 (s, 3H, Me), 3.08 (dq, $J = 7.2$, 12.5 Hz, CH_2CH_3), 5.87 (d, $J = 10.5$ Hz, 1H, CH), 6.34 (s, 1H, H^{thioph}), 6.82 (d, $J = 10.5$ Hz, 1H, CH), 6.87 (d, $J = 8.5$ Hz, 1H, H^{arom}), 8.06 (s, 1H, H^{arom}), 8.04 (d, $J = 8.5$ Hz, 1H, H^{arom}). MS, *m/z* (%): 356 (12) $[M]^+$, 341 (4) $[M-Me]^+$, 328 (28), 57 (100). Elemental analysis: Calcd. for $C_{19}H_{20}N_2O_3S$: N, 7.87. Found: N, 7.33%.

2′,4′,6′,6′-Tetramethyl-3′-carbmethoxyspiro[2*H*-naphtho[2,1-*b*][1,4]pyran-2,5′-2,3-dihydrothieno[3,2-*b*]pyrrol] (IVg)

Yield 79%, m.p. 126–128°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.25 (s, 3H, ½CMe_2), 1.30 (s, 3H, ½CMe_2), 2.63 (s, 3H, Me), 2.83 (s, 3H, NMe), 3.86 (s, 3H, COOMe), 5.85 (d, $J = 10.3$ Hz, 1H, CH), 7.08 (d, $J = 8.8$ Hz, 1H, H^{arom}), 7.31–7.77 (m, 4H, H^{arom}), 7.56 (d, $J = 10.3$ Hz, 1H, CH), 8.03 (d, $J = 8.8$ Hz, 1H, H^{arom}). MS, *m/z* (%): 405 (100) $[M]^+$, 390 (25) $[M-Me]^+$, 358 (58), 340 (31), 237 (78), 222 (24). Elemental analysis: Calcd for $C_{24}H_{23}NO_3S$: C, 71.09; H, 5.79; N, 3.45. Found: C, 71.02; H, 6.01; N, 3.66%.

1,3,3-Trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,3′-[3*H*]-naphtho[2,1-*b*][1,4]oxazine] (Va)

Yield 25%, m.p. 225–227°C.[7]

1,3,3-Trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,2′-[2*H*]-phenanthro[9,10-*b*][1,4]oxazine] (Vb)

Yield 46%, m.p. 212–214°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 3H, ½CMe_2), 1.51 (s, 3H, ½CMe_2), 3.12 (s, 3H, NMe), 7.25–7.41 (m, 2H, H^{arom}), 7.50–7.76 (m, 4H, H^{arom}), 7.84 (d, $J = 8.1$ Hz, 2H, H^{arom}), 7.93 (s, 1H, CH═N), 8.26 (d, $J = 8.1$ Hz, 1H, H^{arom}), 8.64 (t, $J = 8.8$ Hz, 2H, H^{arom}), 8.74 (d, $J = 8.1$ Hz, 1H, H^{arom}). MS, *m/z* (%): 434 (15) $[M]^+$, 419 (22) $[M-Me]^+$, 215

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(100). Elemental analysis: Calcd. for $C_{28}H_{22}N_2OS$: C, 77.39; H, 5.10; N, 6.45. Found: C, 77.29; H, 5.31; N, 6.43%.

2,4,6,6-Tetramethylspiro[2,3-dihydrothieno [3,2-*b*]pyrrole-5,3′-[3*H*]naphtho[2,1-*b*] [1,4]oxazine] (Vc)

Yield 18%, m.p. 138–140°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35 (s, 3H, ½CMe_2), 1.39 (s, 3H, ½CMe_2), 2.50 (s, 3H, Me), 2.71 (s, 3H, NMe), 6.31 (s, 1H, H^{thioph}), 7.15 (d, $J = 8.5$ Hz, 1H, H^{arom}), 7.37–7.82 (m, 4H, H^{arom}), 7.77 (s, 1H, CH═N), 8.59 (d, $J = 8.5$ Hz, 1H, H^{arom}). MS, *m/z* (%): 348 (57) $[M]^+$, 333 (67) $[M-Me]^+$, 179 (76), 165 (31), 57 (100). Elemental analysis: Calcd. for $C_{21}H_{20}N_2OS$: C, 72.38; H, 5.79; N, 8.04. Found: C, 72.07; H, 5.96; N, 7.99%.

2,4,6,6-Tetramethyl-3-carbmethoxyspiro [2,3-dihydrothieno[3,2-*b*]pyrrole-5,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (Vd)

Yield 40%, m.p. 140–142°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.31 (s, 3H, ½CMe_2), 1.37 (s, 3H, ½CMe_2), 2.62 (s, 3H, Me), 2.85 (s, 3H, NMe), 3.87 (s, 3H, COOMe), 7.09 (d, $J = 8.5$ Hz, 1H, H^{arom}), 7.35–7.75 (m, 4H, H^{arom}), 7.77 (s, 1H, CH═N), 8.56 (d, $J = 8.5$ Hz, 1H, H^{arom}). MS, *m/z* (%): 406 (22) $[M]^+$, 391 (38) $[M-Me]^+$, 237 (100). Elemental analysis: Calcd. for $C_{23}H_{22}N_2O_3S$: C, 67.96; H, 5.46; N, 6.89. Found: C, 68.05; H, 5.58; N, 7.09%.

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