# Spiropyrans and spirooxazines 8.* 5′-(1,3-Benzothiazol-2-yl)-substituted spiro[indoline-2,3′-naphthopyrans]: synthesis and spectral and photochromic properties

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Novel photochromic 5′-(1,3-benzothiazol-2-yl)-substituted spiro[indoline-2,3′-naphthopyrans] possessing luminescence properties in both the cyclic and merocyanine forms were synthesized. Unlike the 8′-(1,3-benzothiazol-2-yl)-substituted benzopyran analogs, the synthesized compounds are characterized by the lower relative stability of the merocyanine isomers.

**Key words:** benzothiazole, spiropyran, merocyanine, photochromism, luminescence.

Photochromic spiroheterocyclic compounds are widely required objects of synthesis and investigation in modern chemistry due to interest in manufacturing related optical systems of information detection and imaging, molecular switches, transport systems, dynamic chemosensors and biosensors, systems of solar energy accumulation, and others.[2,3] Relatively easily synthesized spiropyrans make it possible to obtain numerous molecular structures with a widely varied range of spectral kinetic characteristics.[2—6]

The introduction of various functional fragments into spiropyran molecules provides a possibility to synthesize a series of polyfunctional photochromic molecular systems that demonstrate the fluorescence,[7—10] magnetic,[11] and complexation[7,12—14] properties controlled by optical radiation.

One of the methods for the functionalization of a molecule of the photochromic compound is the introduction of heterocyclic substituents into the side chain. The series of works was devoted to the synthesis[15] and study of the spectral and photochromic[16] properties and the processes of complexation of the spirooxazine derivatives containing the benzothiazole substituent in position 5′. The benzothiazole substituent was shown[17,18] to play the key role in the formation of stable complexes of the merocyanine isomers with metal ions.

We have earlier[19] reported the synthesis of photochromic 5′-(4,5-diphenyl-1,3-oxazol-2-yl)-substituted spironaphthopyrans (SNP), whose noncyclic isomers reversibly form complexes with divalent heavy metal cations. The present work continues these studies and is devoted to the synthesis and description of the spectral and photochromic properties of new SNP bearing the benzothiazole group in position 5 of the naphthopyran moiety.

## Results and Discussion

As shown in Scheme 1, 5′-benzothiazolyl-substituted spironaphthopyrans **4a—g** were synthesized by the reaction of 3*H*-indolium salts **3a—g** with 2-hydroxy-3-(1,3-benzothiazol-2-yl)-1-naphthaldehyde (**2**) in the presence of triethylamine as a base.

3*H*-Indolium iodides **3a—g** and 3-(1,3-benzothiazol-2-yl)-2-naphthol (**1**) were synthesized according to procedures described earlier.[15,20—22] The formylation of naphthol **1** in the Duff reaction afforded benzothiazolyl-substituted hydroxynaphthaldehyde **2**.

The structures of compounds **2** and **4a—g** were established by $^1$H NMR spectroscopy and confirmed by the elemental analysis data.

$^1$H NMR spectroscopy is a convenient method for the structural identification of spiropyrans of the indoline series and makes it possible to determine the structure of the synthesized compound by the characteristic values of chemical shifts and proton spin-spin coupling constants. The signals of such characteristics groups as the *gem*-dimethyl group, *N*-alkyl substituents, and protons at the double bond of the pyran ring are usually determined easily

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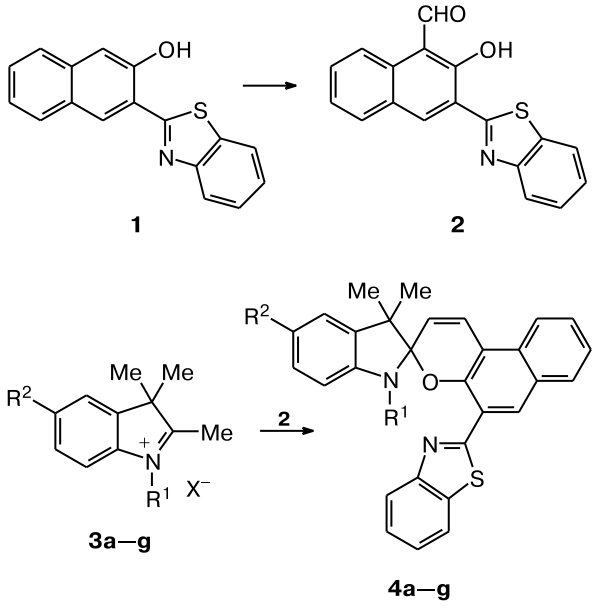
**Scheme 1**




**3:** $R^1$ = Me (**a**—**d**), Pr (**e**), All (**f**), $Bu^i$ (**g**); $R^2$ = H (**a**,**e**—**g**), Cl (**b**), Me (**c**), OMe (**d**); X = I (**a**,**c**—**g**), $ClO_4$ (**b**);
**4:** $R^1$ = Me (**a**—**d**), Pr (**e**), All (**f**), $Bu^i$ (**g**); $R^2$ = H (**a**,**e**—**g**), Cl (**b**), Me (**c**), OMe (**d**)

and have different chemical shifts for the open and closed forms.[23—25]

The $^1$H NMR spectra (two signals from the magnetically nonequivalent geminal methyl groups, diastereotopic splitting of the signals from the protons of the methylene group of the *N*-allyl substituent of spiropyran **4f**, which appear as two triplets of doublet of doublets; the methyl groups and protons of the methylene group of the *N*-isobutyl substituent of spiropyran **4g** manifested as two doublets and two doublets of doublets, respectively; and the values of chemical shifts and spin-spin coupling constants of protons of the double bond of the pyran moiety and protons of the indoline and pyran moieties) unambiguously confirm the structures of the synthesized spiropyrans. The absence of signals from the *N*-methyl and *gem*-dimethyl groups, *trans*-vinylic protons, and other protons of the indoline and pyran moieties in the spectral regions characteristic of the open merocyanine form without an asymmetric center indicates that the compounds synthesized exist in solution ($CDCl_3$) mainly in the spirocyclic form **A** (Scheme 2).

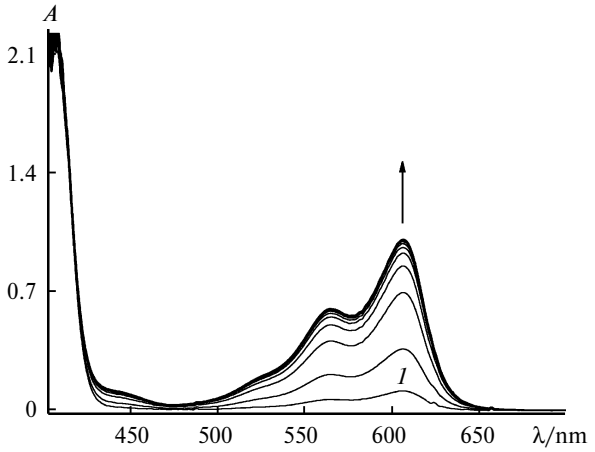



**Fig. 1.** Absorption spectra of SNP **4b** in acetone before (*1*) and during irradiation with λ =365 nm, the interval between the spectra being 2 s, $C$(**4b**) = $5.3 \cdot 10^{-4}$ mol $L^{-1}$, $T$ = 270 K.

The spectral properties of the SNP were studied in toluene and acetone. Unlike their 5′-(diphenyloxazolyl)-substituted analogs, toluenic solutions of the SNP under study are weakly colored, indicating an equilibrium between the spirocyclic **A** and merocyanine **B** isomers. On going to acetonic solutions, the color intensity increases (Fig. 1), which indicates an increase in the concentration of noncyclic isomers **B** due to the shift of equilibrium in a more polar solvent to the merocyanine form.

The absorption spectra of the studied SNP are similar to those of the earlier described[1,19] 5′-(diphenyloxazolyl)-substituted SNP. The cyclic form in toluene is characterized by the intense ($\varepsilon \approx 2.1 \cdot 10^4$—$3.1 \cdot 10^4$ L $mol^{-1}$ $cm^{-1}$) structured absorption band of the $\pi \rightarrow \pi^*$ type with maxima at 338 and 352 nm (Table 1) and a lee intense

**Scheme 2**

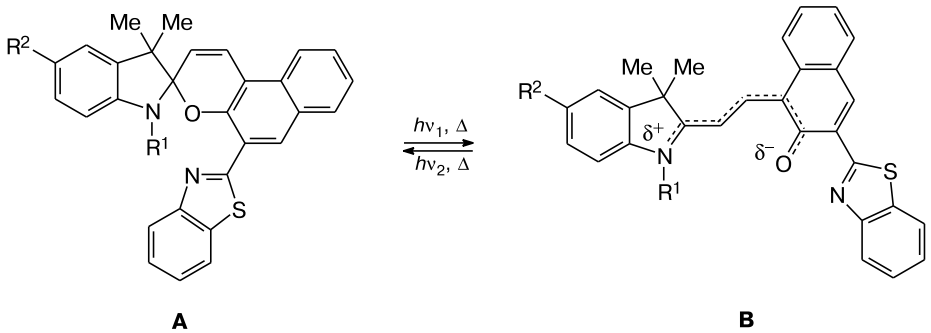


**Table 1.** Spectral properties of 3,3-dimethyl-5′-(1,3-benzothiazol-2-yl)spiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyrans]*

| SNP | Isomer | Toluene | | | | | Acetone | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}^{abs}$ ($\varepsilon \cdot 10^{-3}$/L mol$^{-1}$ cm$^{-1}$) | $\lambda_{max}^{ex,flu}$ | $\lambda_{max}^{flu}$ | $\lambda_{max}^{ex,ph}$ | $\lambda_{max}^{ph}$ | $\lambda_{max}^{abs}$ ($\varepsilon \cdot 10^{-3}$ /L mol$^{-1}$ cm$^{-1}$) | $\lambda_{max}^{ex,flu}$ | $\lambda_{max}^{flu}$ |
| **4a** | **A** | 338 (25.20), 351 (21.21), 385 (5.15), 405 (4.41) | 370, 408 | 428, 443, 465 | 385, 406 | 583, 637, 695 | 386 (5.48), 402 (5.09) | — | — |
| | **B** | 602 | — | — | — | — | 603 | 604 | 624 |
| **4b** | **A** | 338 (25.43), 351 (21.28), 382 (5.29), 403 (4.62) | 390, 406 | 416, 437, 460 | 385, 400 | 578, 630, 695 | 384 (4.47), 401 (4.15) | — | — |
| | **B** | 604 | — | — | — | — | 605 | 605 | 625 |
| **4c** | **A** | 338 (31.80), 353 (25.90), 385 (6.47), 406 (5.70) | 392, 405 | 420, 441, 469 | 385, 405 | 580, 633, 695 | 387 (4.95), 403 (4.55) | — | — |
| | **B** | 606 | — | — | — | — | 608 | 608 | 631 |
| **4d** | **A** | 337 (25.80), 352 (21.50), 386 (5.18), 406 (4.49) | 385, 400 | 460 | 400 | 580, 635, 690 | 386 (4.71), 404 (4.26) | — | — |
| | **B** | 612 | — | — | — | — | 614 | 615 | 641 |
| **4e** | **A** | 338 (26.60), 352 (22.76), 386 (5.84), 406 (5.10) | 390, 409 | 440 | 386, 404 | 580, 633, 695 | 386 (5.41), 405 (4.93) | — | — |
| | **B** | 604 | — | — | — | — | 613 | 614 | 643 |
| **4f** | **A** | 338 (27.24), 352 (23.18), 384 (5.63), 404 (4.90) | 392, 408 | 440 | 381, 402 | 582, 635, 700 | 387 (4.63), 405 (4.11) | — | — |
| | **B** | 602 | — | — | — | — | 607 | 607 | 633 |
| **4g** | **A** | 337 (25.91), 353 (22.13), 385 (5.25), 405 (4.68) | 395, 380 | 414, 430 | 395, 375 | 578, 628, 690 | 387 (4.68), 406 (4.19) | — | — |
| | **B** | 605 | — | — | — | — | 606 | 609 | 633 |

* Absorption at 293 K, luminescence at 77 K (vitrescent toluene—ethanol—diethyl ether). The wavelengths at the absorption ($\lambda_{max}^{abs}$/nm), fluorescence emission and excitation ($\lambda_{max}^{exc,flu}$ and $\lambda_{max}^{flu}$, respectively, nm), and phosphorescence emission and excitation ($\lambda_{max}^{exc,ph}$ and $\lambda_{max}^{ph}$, respectively) maxima.

($\varepsilon \approx 3.9 \cdot 10^3$—$6.1 \cdot 10^3$ L mol$^{-1}$ cm$^{-1}$) long-wavelength charge-transfer band with maxima at 382—406 nm. The substituents in the indoline moiety of the molecule and the replacement of the solvent exert almost no effect on the position and intensity of the absorption bands of the spirocyclic isomers. At 77 K spirocyclic SNP isomers **4a—g** demonstrate intense fluorescence and phosphorescence (Fig. 2, see Table 1). The fluorescence spectra lie at 400—500 nm. Phosphorescence is characterized by the structured band with maxima at 580, 635, and 690 nm. The fluorescence and phosphorescence excitation spectra are well consistent with the absorption spectra of the spirocyclic isomers, which allows one to assign the luminescence observed to these isomeric forms (see Table 1).

The colored forms of SNP **4a—g** are characterized by the long-wavelength absorption band with a maximum at 602—614 nm. The introduction of substituents into position 5′ of spiropyran and an increase in the solvent polarity result in the shift of the absorption band maximum to the long-wavelength spectral region (see Table 1).

Compounds **4a—g** are photochromic. The UV irradiation of solutions of SNP at $T = 293$ K induces an insignificant equilibrium shift to the merocyanine form. A decrease in the temperature of the solutions below 280 K results in a more pronounced photochromic effect due to the retardation of the backward thermal reaction **B** → **A** (see Fig. 1). Under these conditions, the merocyanine forms exhibit lowly intense fluorescence in the red spec-

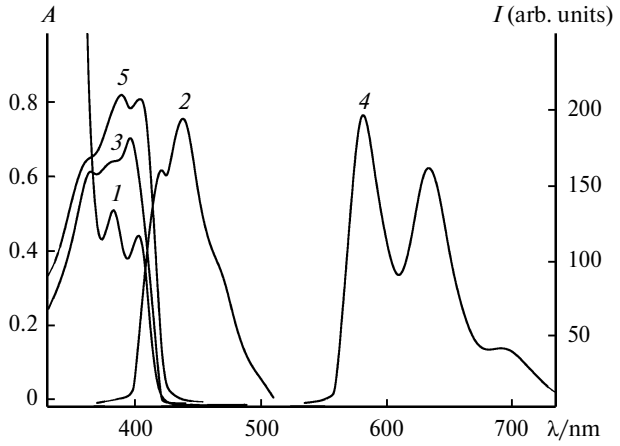



**Fig. 2.** Absorption spectrum (*1*), fluorescence emission (*2*) and excitation (*3*) spectra, and phosphorescence emission (*4*) and excitation (*5*) spectra of a solution of SNP **4b** in a vitrescent toluene—ethanol—diethyl ether mixture, $T = 77$ K.

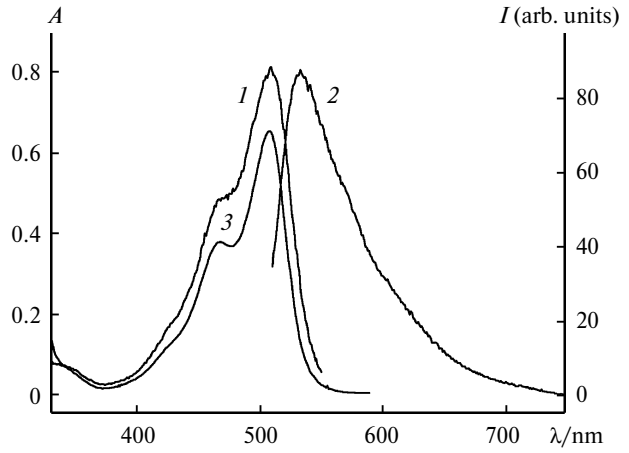



**Fig. 3.** Fluorescence excitation (*1*) and emission (*2*) spectra and absorption spectrum (*3*) of SNP merocyanine isomer **4b** in acetone at $T = 270$ K (a solution of SNP was pre-irradiated with $\lambda = 365$ nm).

tral region with band maxima at 624—643 nm and quantum yields lower than 0.001 (Fig. 3, see Table 1). The fluorescence excitation spectra coincide with the absorption spectra of the merocyanine forms. After the end of irradiation, the primary equilibrium state is recovered. The kinetic curves of the dark relaxation processes are satisfactorily described by a monoexponential function, which is indicated by the linear dependences of the logarithm of the relative change in the absorbance of the long-wavelength absorption band maxima of merocyanine SNP isomers **4a**—**g** on the thermal bleaching duration presented in Fig. 4.

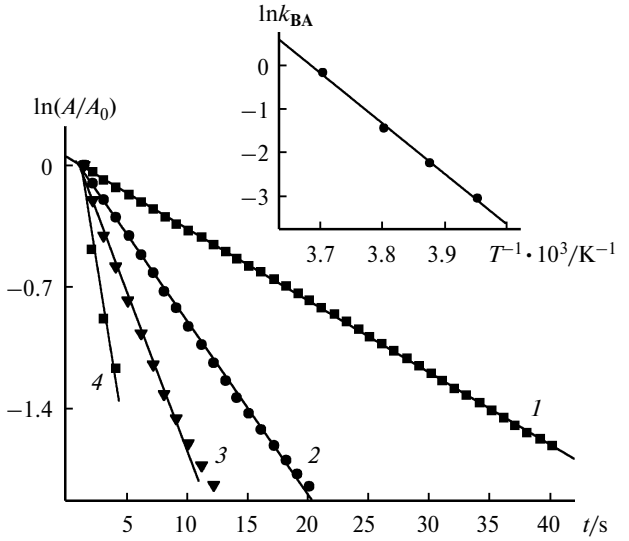



**Fig. 4.** Logarithm of the relative change in the absorbance of a solution of SNP **4b** *vs* duration of thermal relaxation at $T = 253$ (*1*), 258 (*2*), 263 (*3*), and 270 K (*4*). Inset: logarithm of the rate constant of thermal bleaching *vs* inverse temperature.

**Table 2.** Rate constants at $T = 293$ K ($k_{BA}$) and the activation energies of the thermal cyclization reaction ($E_a$) for some SNP in an acetone solution

| SNP | $k_{BA}/s^{-1}$ | $E_a$/kJ mol$^{-1}$ |
|---|---|---|
| **4a** | 8.65 | 98.3 |
| **4b** | 30.88 | 96.3 |
| **4c** | 5.60 | 101.5 |
| **4d** | 1.08 | 99.7 |

The small equilibrium content of the merocyanine form in solution indicates the low value of the tautomeric equilibrium constant between the cyclic and colored isomers. In this case, it can be accepted that $k_{app} = k_{BA} + k_{AB} \approx k_{BA}$, where $k_{app}$ is the apparent rate constant obtained from the kinetic curves, and $k_{BA}$ and $k_{AB}$ are the rate constants of the forward and backward thermal reactions, respectively.

The temperature dependence of the thermal bleaching rate constant $k_{BA}$ is of the Arrhenius type (see Fig. 4, inset), which made it possible to estimate the activation energy of this process (Table 2).

As can be seen from Table 2, the rate constants $k_{BA}$ depend on the nature of the substituent in position 5′. The electron-releasing group in position 5′ retards the thermal bleaching process. For instance, on going from 5′-chloro-substituted SNP derivative **4b** to SNP **4a** unsubstituted in position 5′ and further to SNP **4c** and **4d** including the electron-releasing substituents, the rate constant of reaction **B** → **A** decreases noticeably. As mentioned earlier,[26] annulation in the pyran moiety exerts a substantial effect on the kinetic properties of spiropyrans, For example, compared to 8′-(1,3-benzothiazol-2-yl)-substituted spiro[indoline-2,3′-benzopyrans][27] characterized by $k_{BA} = (1.9—7.0) \cdot 10^{-2}$ s$^{-1}$, studied compounds **4a**—**d** representing their naphthopyran analogs exhibit a substantially lower thermal stability of the merocyanine isomers and demonstrate the values of $k_{BA}$ higher by two orders of magnitude (see Table 2).

Thus, novel photochromic 5′-(1,3-benzothiazol-2-yl)-substituted spiro[indoline-2,3′-naphthopyrans] possessing fluorescence and phosphorescence in the cyclic form were synthesized. Unlike the 8′-(1,3-benzothiazol-2-yl)-substituted benzopyran analogs, the compounds synthesized are characterized by a lower stability of the merocyanine isomers.

## Experimental

$^1$H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) at 20 °C (the values of δ were measured with the accuracy to 0.01, and those of SSCC were measured with the accuracy to 0.1 Hz).

Electronic absorption spectra and kinetic curves of thermal recyclization of the studied compounds were detected on an

Agilent 8453 spectrophotometer with an attachment for temperature maintenance of the samples.

Fluorescence and fluorescence excitation spectra were measured on a Varian Cary Eclipse instrument. Phosphorescence and phosphorescence excitation spectra were measured on an Elyumin-2M spectrofluorimeter at 77 K.

Solutions were irradiated with the filtered light from a high-pressure mercury lamp on an Newport 66902 setup. Interferential light filters (λ = 365 nm) were used to pick out monochromatic radiation.

Toluene and acetone (Aldrich) of spectral purity grade were used for the preparation of solutions.

**3-(1,3-Benzothiazol-2-yl)-2-hydroxy-1-naphthaldehyde (2).** A mixture of naphthol **1** (2.77 g, 10 mmol), hexamethylenetetramine (2.80 g, 20 mmol), and acetic acid (40 mL) was stirred for 5.5 h at 95—100 °C. A mixture of concentrated hydrochloric acid (12 mL) and water (14 mL) were added, and the mixture was stirred for 1 h at 95—100 °C. The reaction mixture was poured to water (130 mL), and the precipitate was filtered off, washed with water, and dried. The resulting naphthaldehyde was recrystallized from chlorobenzene. The yield was 46%, m.p. 226.5—228 °C. Found (%): C, 70.92; H, 3.79; N, 4.41. $C_{18}H_{11}NO_2S$. Calculated (%): C, 70.80; H, 3.63; N, 4.59. $^1$H NMR, δ: 7.45—7.51 (m, 2 H, H(6), H(5(6), thiazole); 7.57 (m, 1 H, H(5(6), thiazole); 7.70 (ddd, 1 H, H(7), *J* = 8.6 Hz, *J* = 6.9 Hz, *J* = 1.5 Hz); 7.94 (d, 1 H, H(5), *J* = 8.2 Hz); 7.99 (m, 1 H, H(7), thiazole); 8.11 (m, 1 H, H(4), thiazole); 8.80—8.92 (m, 2 H, H(4), H(8)); 11.00 (s, 1 H, 1-CHO); 14.03 (s, 1 H, 2-OH).

**5′-(1,3-Benzothiazol-2-yl)-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyrans] 4a—g (general procedure).** A mixture of 3*H*-indolinium salt **5a—g** (1 mmol), triethylamine (0.14 mL, 1 mmol), and aldehyde **4** (0.31 g, 1 mmol) in toluene (10 mL) and propan-2-ol (2 mL) were refluxed for 5.5 h and evaporated. The residue was purified by column chromatography on $Al_2O_3$ (benzene as an eluent). Spiropyrans **6a—d** were recrystallized from an isooctane—toluene (1 : 1) mixture, and compounds **6e—g** were recrystallized from isooctane.

**5′-(1,3-Benzothiazol-2-yl)-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4a).** The yield was 75%, m.p. 244.5—245.5 °C. Found (%): C, 78.40; H, 5.11; N, 6.01. $C_{30}H_{24}N_2OS$. Calculated (%): C, 78.23; H, 5.25; N, 6.08. $^1$H NMR, δ: 1.34 (s, 3 H, 3-Me); 1.39 (s, 3 H, 3-Me); 2.76 (s, 3 H, 1-Me); 6.02 (d, 1 H, H(2′), *J* = 10.6 Hz); 6.62 (d, 1 H, H(7), *J* = 7.7 Hz); 6.99 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.19 (dd, 1 H, H(4), *J* = 7.3 Hz, *J* = 1.0 Hz); 7.28 (dt, 1 H, H(6), *J* = 7.6 Hz, *J* = 1.3 Hz); 7.29 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.1 Hz); 7.41 (ddd, 1 H, H(8′), *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.1 Hz); 7.44 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz); 7.58 (ddd, 1 H, H(7), thiazole, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 7.59 (ddd, 1 H, H(9′), *J* = 8.3 Hz, *J* = 6.9 Hz, *J* = 1.3 Hz); 7.73 (d, 1 H, H(1′), *J* = 10.6 Hz); 7.96 (ddd, 1 H, H(7′), *J* = 8.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 8.05 (ddd, 1 H, H(4), thiazole, *J* = 8.2 Hz, *J* = 1.0 Hz, *J* = 0.7 Hz); 8.07 (d, 1 H, H(10′), *J* = 8.5 Hz); 9.00 (s, 1 H, H(6′)).

**5′-(1,3-Benzothiazol-2-yl)-5-chloromethyl-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4b).** The yield was 71%, m.p. 234—235 °C. Found (%): C, 72.65; H, 4.84; N, 5.75. $C_{30}H_{23}ClN_2OS$. Calculated (%): C, 72.79; H, 4.68; N, 5.66. $^1$H NMR, δ: 1.34 (s, 3 H, 3-Me); 1.39 (s, 3 H, 3-Me); 2.72 (s, 3 H, 1-Me); 5.99 (d, 1 H, H(2′), *J* = 10.6 Hz); 6.51 (d, 1 H, H(7), *J* = 8.2 Hz); 7.16 (d, 1 H, H(4), *J* = 2.1 Hz); 7.24 (dd, 1 H, H(6), *J* = 8.2 Hz, *J* = 2.1 Hz); 7.33 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.1 Hz); 7.41 (ddd, 1 H, H(8′), *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.1 Hz); 7.46 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz); 7.59 (ddd, 1 H, H(9′), *J* = 8.4 Hz, *J* = 6.8 Hz, *J* = 1.3 Hz); 7.66 (ddd, 1 H, H(7), thiazole, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 7.74 (d, 1 H, H(1′), *J* = 10.6 Hz); 7.96 (ddd, 1 H, H(7′), *J* = 8.1 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 8.04—8.08 (m, 2 H, H(10′), H(4), thiazole); 9.01 (s, 1 H, H(6′)).

**5′-(1,3-Benzothiazol-2-yl)-1,3,3,5-tetramethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4c).** The yield was 69%, m.p. 222—223 °C. Found (%): C, 78.61; H, 5.65; N, 5.97. $C_{31}H_{26}N_2OS$. Calculated (%): C, 78.45; H, 5.52; N, 5.90. $^1$H NMR, δ: 1.34 (s, 3 H, 3-Me); 1.37 (s, 3 H, 3-Me); 2.44 (s, 3 H, 5-Me); 2.73 (s, 3 H, 1-Me); 6.01 (d, 1 H, H(2′), *J* = 10.6 Hz); 6.51 (d, 1 H, H(7), *J* = 7.8 Hz); 7.02 (d, 1 H, H(4), *J* = 1.7 Hz); 7.09 (dd, 1 H, H(6), *J* = 7.8 Hz, *J* = 1.7 Hz); 7.31 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.1 Hz); 7.40 (ddd, 1 H, H(8′), *J* = 8.2 Hz, *J* = 6.9 Hz, *J* = 1.0 Hz); 7.45 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz); 7.54—7.61 (m, 2 H, H(9′), H(7), thiazole); 7.71 (d, 1 H, H(1′), *J* = 10.6 Hz); 7.95 (ddd, 1 H, H(7′), *J* = 8.2, *J* = 1.3 Hz, *J* = 0.7 Hz); 8.04—8.08 (m, 2 H, H(10′), H(4), thiazole); 9.00 (s, 1 H, H(6′)).

**5′-(1,3-Benzothiazol-2-yl)-5-methoxy-1,3,3-trimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4d).** The yield was 73%, m.p. 243—244 °C. Found (%): C, 75.82; H, 5.51; N, 5.63. $C_{31}H_{26}N_2O_2S$. Calculated (%): C, 75.89; H, 5.34; N, 5.71. $^1$H NMR, δ: 1.34 (s, 3 H, 3-Me); 1.38 (s, 3 H, 3-Me); 2.70 (s, 3 H, 1-Me); 3.88 (s, 3 H, 5-OMe); 6.01 (d, 1 H, H(2′), *J* = 10.6 Hz); 6.52 (d, 1 H, H(7), *J* = 8.1 Hz); 6.82 (dd, 1 H, H(6), *J* = 8.1 Hz, *J* = 2.6 Hz); 6.85 (d, 1 H, H(4), *J* = 2.6 Hz); 7.30 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.1 Hz); 7.40 (ddd, 1 H, H(8′), *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.1 Hz); 7.45 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz); 7.55—7.61 (m, 2 H, H(9′), H(7), thiazole); 7.71 (d, 1 H, H(1′), *J* = 10.6 Hz); 7.95 (ddd, 1 H, H(7′), *J* = 8.2 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 8.03—8.07 (m, 2 H, H(10′), H(4), thiazole); 9.00 (s, 1 H, H(6′)).

**5′-(1,3-Benzothiazol-2-yl)-3,3-dimethyl-1-propylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4e).** The yield was 70%, m.p. 156—157 °C. Found (%): C, 78.51; H, 5.90; N, 5.79. $C_{32}H_{28}N_2OS$. Calculated (%): C, 78.66; H, 5.78; N, 5.73. $^1$H NMR, δ: 0.89 (t, 3 H, 1-$CH_2CH_2C\underline{H}_3$, *J* = 7.4 Hz); 1.33 (s, 3 H, 3-Me); 1.36 (s, 3 H, 3-Me); 1.66 (m, 2 H, 1-$CH_2C\underline{H}_2CH_3$); 3.16 (m, 2 H, 1-$C\underline{H}_2CH_2CH_3$); 6.02 (d, 1 H, H(2′), *J* = 10.6 Hz); 6.65 (d, 1 H, H(7), *J* = 7.7 Hz); 6.96 (dt, 1 H, H(5), *J* = 7.4 Hz, *J* = 0.9 Hz); 7.17 (dd, 1 H, H(4) *J* = 7.3 Hz, *J* = 1.0 Hz); 7.23—7.32 (m, 2 H, H(6), H(5(6)), thiazole); 7.40 (ddd, 1 H, H(8′), *J* = 8.1 Hz, *J* = 6.9 Hz, *J* = 1.1 Hz); 7.44 (ddd, 1 H, H(5(6)), thiazole, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz); 7.58 (ddd, 1 H, H(7), thiazole, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz); 7.58 (ddd, 1 H, H(9′), *J* = 8.4 Hz, *J* = 6.9 Hz, *J* = 1.4 Hz); 7.69 (d, 1 H, H(1′), *J* = 10.6 Hz); 7.95 (ddd, 1 H, H(7′), *J* = 8.2 Hz, *J* = 1.4 Hz, *J* = 0.7 Hz); 8.03—8.07 (m, 2 H, H(10′), H(4), thiazole); 8.99 (s, 1 H, H(6′)).

**1-Allyl-5′-(1,3-benzothiazol-2-yl)-3,3-dimethylspiro[indoline-2,3′-[3*H*]naphtho[2,1-*b*]pyran] (4f).** The yield was 72%, m.p. 185.5—187 °C. Found (%): C, 79.15; H, 5.27; N, 5.68. $C_{32}H_{26}N_2OS$. Calculated (%): C, 78.98; H, 5.39; N, 5.76. $^1$H NMR, δ: 1.37 (s, 3 H, 3-Me); 1.39 (s, 3 H, 3-Me); 3.63 (tdd,

1 H, 1-C$\underline{H}_2$CH=CH$_2$, $J$ = 17.1 Hz, $J$ = 5.7 Hz, $J$ = 1.5 Hz, $J$ = 1.5 Hz); 4.00 (tdd, 1 H, 1-C$\underline{H}_2$CH=CH$_2$, $J$ = 17.1 Hz, $J$ = 4.2 Hz, $J$ = 2.1 Hz, $J$ = 2.1 Hz); 5.03 (qd, 1 H, 1-CH$_2$CH=C$\underline{H}_2$, $J$ = 10.3 Hz, $J$ = 1.7 Hz, $J$ = 1.7 Hz, $J$ = 1.7 Hz); 5.19 (qd, 1 H, 1-CH$_2$CH=C$\underline{H}_2$, $J$ = 17.3 Hz, $J$ = 1.8 Hz, $J$ = 1.8 Hz, $J$ = 1.8 Hz); 5.89 (m, 1 H, 1-CH$_2$C$\underline{H}$=CH$_2$); 6.02 (d, 1 H, H(2´), $J$ = 10.6 Hz); 6.65 (d, 1 H, H(7), $J$ = 7.7 Hz); 6.97 (dt, 1 H, 5-H, $J$ = 7.4 Hz, $J$ = 0.9 Hz); 7.19 (dd, 1 H, H(4), $J$ = 7.3 Hz, $J$ = 1.2 Hz); 7.24 (dt, 1 H, H(6), $J$ = 7.6 Hz, $J$ = 1.3 Hz); 7.29 (ddd, 1 H, H(5(6)), thiazole, $J$ = 8.1 Hz, $J$ = 7.2 Hz, $J$ = 1.1 Hz); 7.40 (ddd, 1 H, H(8´), $J$ = 8.0 Hz, $J$ = 6.8 Hz, $J$ = 1.1 Hz); 7.44 (ddd, 1 H, H(5(6)), thiazole, $J$ = 8.3 Hz, $J$ = 7.2 Hz, $J$ = 1.3 Hz); 7.58 (d, 1 H, H(7), thiazole, $J$ = 7.9 Hz); 7.58 (ddd, 1 H, H(9´), $J$ = 8.4 Hz, $J$ = 6.9 Hz, $J$ = 1.4 Hz); 7.70 (d, 1 H, H(1´), $J$ = 10.6 Hz); 7.95 (d, 1 H, H(7´), $J$ = 8.2 Hz); 8.03—8.07 (m, 2 H, H(10´), H(4), thiazole); 9.00 (s, 1 H, H(6´)).

**1-Isobutyl-5´-(1,3-benzothiazol-2-yl)-3,3-dimethylspiro-[indoline-2,3´-[3*H*]naphtho[2,1-*b*]pyran] (4g).** The yield was 64%, m.p. 162.5—164 °C. Found (%): C, 78.79; H, 6.14; N, 5.50. $C_{33}H_{30}N_2OS$. Calculated (%): C, 78.85; H, 6.02; N, 5.57. $^1$H NMR, δ: 0.88 (d, 3 H, 1-CH$_2$CH(C$\underline{H}_3$)$_2$, $J$ = 6.7 Hz); 0.97 (d, 3 H, 1-CH$_2$CH(C$\underline{H}_3$)$_2$, $J$ = 6.5 Hz); 1.35 (s, 3 H, 3-Me); 1.36 (s, 3 H, 3-Me); 2.07 (m, 1 H, 1-CH$_2$C$\underline{H}$(CH$_3$)$_2$); 2.90 (dd, 1 H, 1-C$\underline{H}_2$CH(CH$_3$)$_2$, $J$ = 14.0 Hz, $J$ = 9.1 Hz); 2.96 (dd, 1 H, 1-C$\underline{H}_2$CH(CH$_3$)$_2$, $J$ = 14.0 Hz, $J$ = 5.7 Hz); 6.03 (d, 1 H, H(2´), $J$ = 10.6 Hz); 6.64 (d, 1 H, H(7), $J$ = 7.8 Hz); 6.97 (dt, 1 H, H(5), $J$ = 7.4 Hz, $J$ = 0.9 Hz); 7.18 (dd, 1 H, H(4), $J$ = 7.3 Hz, $J$ = 1.0 Hz); 7.24—7.32 (m, 2 H, H(6), H(5(6)), thiazole); 7.37 (m, 2 H, H(8´), H(5(6)), thiazole); 7.55—7.61 (m, 2 H, H(9´), H(7), thiazole); 7.68 (d, 1 H, H(1´), $J$ = 10.6 Hz); 7.95 (d, 1 H, H(7´), $J$ = 8.2 Hz); 8.03—8.07 (m, 2 H, H(10´), H(4), thiazole); 8.99 (s, 1 H, H(6´)).

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