Spiropyrans and spirooxazines
13.* Synthesis and photochromic properties of benzoxazolyl-substituted spirobenzopyrans

I. A. Rostovtseva, N. A. Voloshin, E. V. Solov'eva, A. V. Chernyshev, I. A. Metelitsa, and A. V. Metelitsa★

Institute of Physical and Organic Chemistry, Southern Federal University,
194/2 prosp. Stachki, 344090 Rostov on Don, Russian Federation.
Fax: +7 (863) 243 4667. E-mail: met@ipoc.sfedu.ru

New benzoxazolyl-substituted spiroindoline-benzopyrans with electron-withdrawing groups in the indoline fragment were obtained. These compounds exhibit positive P- and T-type photochromism. Structural correlations of the spectrokinetic properties depending on the variation of substituents in the indoline part of the spiropyran molecules were established. Electron-withdrawing groups were found to cause a bathochromic shift of the long-wavelength absorption maxima of the merocyanine isomers as compared to the unsubstituted spiropyran and decrease their lifetime. Conversely, an introduction of electron-donating groups results in a hypsochromic shift of the absorption maxima and an increase in the lifetime of the colored isomers of spiropyrans. Electron-withdrawing substituents at the position 5 of the indoline fragment cause the increase of the colorability of the spiropyrans.

Key words: spirocyclic compounds, spiropyrans, photochromism, merocyanines, colorability, molecular switches.

Photochromic spirocyclic compounds are unique molecular systems, which, due to the structural specificities, can dramatically change their physicochemical properties as a result of photoreaction.[2] This feature opens up wide possibilities for their use as molecular switches,[3—5] photodynamic chemosensors,[6—9] photoregulators of biological activity,[10—12], as well as for the use in subdifraction microscopy[13] and in the development of optical molecular memory devices.[14,15] Among spirocyclic compounds, spiropyrans are distinguished by a wide variability of their spectrokinetic properties and a relatively feasible structural modification.[16—19] These features make it possible to develop polyfunctional molecular systems with photoswitching fluorescent,[20—24] magnetic,[25] and chelating[26—29] properties on the basis of these compounds. In the latter case, it is important to have an additional coordinating group at *o*-position to the phenolate-type oxygen atom.

The purpose of the present work is to obtain a series of spiroindolinobenzopyrans with a benzoxazole fragment at position 8′ of the benzopyran moiety and a formyl group at position 6′, as well as to study their photochromic and spectrokinetic properties. Earlier, we synthesized a number of spiroindolinonaphthopyrans with a benzoxazole fragment at position 5′ of the naphthopyran part of the molecules.[30] The photochromic transformations of these spiropyrans was characterized by a low thermal stability of merocyanine isomers with the lifetimes of 0.03—1.0 s. For this reason, we planned to introduce an electron-withdrawing formyl group at position 6′ of the benzopyran fragment, which should cause a decrease in the electron density on the oxygen atom of the pyran fragment and, therefore, to slow down the rate of the reverse dark reaction, thus contributing to an increase in the thermal stability of the merocyanine form. The presence of a formyl group also opens the possibility of structural modification of these compounds, including the synthesis of polymer structures whose monomeric core possesses the properties of photo-controlled ionochrome.

The fundamental issue of this study is the establishment of structural correlations of the spectrokinetic properties and the efficiency of photo-coloration of spiropyrans caused by the variation of the electron-active properties of substituents in the indoline part of the molecule.

Results and Discussion

8′-Benzoxazolyl-6-formyl-substituted spirobenzopyrans **1a—f** were obtained by the reaction of 3*H*-indolium salts **2a—f** with 5-benzoxazolyl-substituted 4-hydroxyisophthalic aldehyde (**3**) in the presence of triethylamine as a base (Scheme 1).

The structure of compounds **1d—f** was proved by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectra of spiropyrans **1d—f** exhibit two singlets of magnetically nonequivalent geminal methyl groups, the signals for the protons of the indoline *N*-methyl

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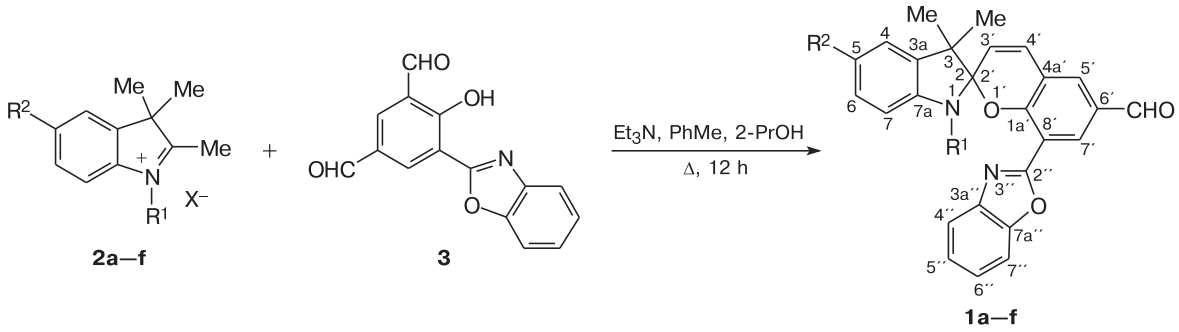
Scheme 1



1, 2: $R^1 = CH_2Ph$, $R^2 = H$ (**a**); $R^1 = Me$, $R^2 = Cl$ (**b**); $R^1 = Me$, $R^2 = Br$ (**c**); $R^1 = Me$, $R^2 = CF_3$ (**d**); $R^1 = Me$, $R^2 = CN$ (**e**); $R^1 = Me$, $R^2 = NO_2$ (**f**); X = I (**a**, **c—f**), ClO_4 (**b**)

group in the high field, as well as the signal for the formyl proton and several groups of mutually coupled proton signals in the low field region of the spectrum related to the indoline, benzopyran, and benzoxazole fragments.

The ^{1}H NMR spectroscopy data unambiguously confirm the structure of the obtained spiropyrans. The absence of the proton signals of the indoline and benzopyran fragments in the spectral region of the open merocyanine form[31—33] indicates that the obtained compounds exist in a spirocyclic form in the $CDCl_3$ solution.

We used 2D heteronuclear ^{1}H—^{1}H COSY, ^{1}H—^{13}C HSQC, ^{1}H—^{13}C HMBC, and ^{1}H—^{15}N HMBC correlation spectra to fully assign the signals for hydrogen, carbon, and nitrogen atoms in spiropyran **1d**. In the ^{13}C NMR spectrum, the signals for the carbon atoms of the geminal methyl groups at position 3 of the indoline fragment are found at δ 19.60 and 25.11. The signal for the carbon atom of the indoline *N*-methyl group is found at δ 29.07, while carbon atoms C(3′) and C(4′) of the pyran double bond resonate at δ 120.12 and 129.59. The quartet for the carbon atom of the indoline 5-trifluoromethyl group is at δ 121.78 with J = 32.1 Hz, while carbon atoms C(4) and C(6) resonate as quartets at δ 118.48 (J = 3.5 Hz) and 125.60 (J = 4.0 Hz), respectively.

The indicated signals completely coincide with the signals of the corresponding protons extrapolated in the ^{1}H—^{13}C HSQC spectrum. Heteronuclear methods ^{1}H—^{13}C HMBC and ^{1}H—^{15}N HMBC were used to determine the annulation pattern of the indoline, benzopyran, and benzoxazole aromatic rings and the chemical shifts for the hydrogen-free nitrogen and carbon atoms. The remote correlation spectra used to assign all the hydrogen-free spiropyran atoms completely confirm the structure of spiropyran **1d**. According to the ^{1}H—^{15}N HMBC correlation spectrum, the signals for the nitrogen atoms of the indoline and benzoxazole fragments are at δ 94.80 and 241.12, respectively.

The electron absorption spectra of cyclic isomers **A** of spiropyrans (SPP) **1a—e** in acetone are characterized by a long-wavelength absorption maxima (as a shoulder) in the 341—357 nm region with the molar extinction coefficients of 4300—8100 L mol^{-1} cm^{-1} (Table. 1). The

Table 1. Spectral absorption characteristics of the isomeric forms, kinetic properties and colorability for a solution of SPP **1a—f** in acetone, T = 293 K

Compound	Form	λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1})	τ_B^{20} /s	E_a /kJ mol^{-1}	$\Phi_{AB}\varepsilon_{max}^{B}$ /mol^{-1} L cm^{-1}
1a	**A**	341* (8.1), 357* (5.8)	45.4	81.4	3452
	B	590			
1b	**A**	341* (5.8), 357* (4.3)	63.2	89.7	4082
	B	586			
1c	**A**	341* (7.4), 357* (5.2)	54.7	87.0	6375
	B	588			
1d	**A**	339* (5.9), 355* (4.4)	26.9	76.2	6300
	B	593			
1e	**A**	339* (8.1), 355* (5.0)	25.6	75.6	4964
	B	600			
1f	**A**	341* (14.3), 357 (16.7), 371* (14.5)	20.7	78.1	8554
	B	610			

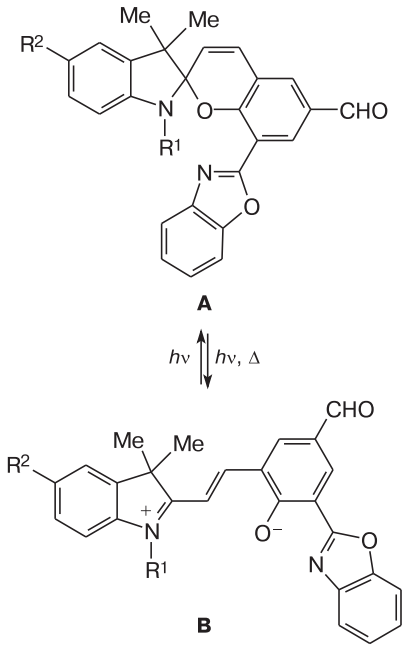
* Shoulder.

substituents in the indoline part of spiropyrans **1a**—**e** have little effect on the position of the long-wavelength absorption bands. As it was shown earlier, this is a consequence of the acoplanarity of the fragments composing the spiropyrans and the localization of the electronic transition responsible for the longest wavelength absorption band on the benzopyran part of the molecule.[34]

In the case of 5-NO_2-substituted spiropyran **1f**, the absorption spectrum has, along with the above-mentioned band, an additional long-wavelength band with a shoulder at 371 nm, with the intensity of the bands reaching 14300—16700 L mol^{-1} cm^{-1}. Such spectral changes, noted earlier for naphthopyran analogs,[30] appear to be due to the an additional electronic transition associated with the redistribution of the electron density between the nitro-substituted indoline and chromene fragments and its overlap with the absorption band of the chromene fragment.

Spiropyrans **1a**—**f** under irradiation in the region of the long-wavelength absorption of cyclic isomers exhibit coloration due to the appearance of merocyanine isomers **B** caused by the photoinduced cleavage of the pyran ring C—O bond and subsequent *cis*—*trans* isomerizations[16] (Scheme 2, Fig. 1).

Scheme 2



The absorption of acyclic isomeric forms **B** of spiropyrans **1a**—**f** is in the visible region of the spectrum with the band maxima at 586—610 nm (see Table 1). In this case, unlike in spirocyclic forms **A**, in merocyanine isomers **B** the substituents in the indoline part of the spiropyran molecules have a significant effect on the position of the long-wavelength absorption maxima, which results from

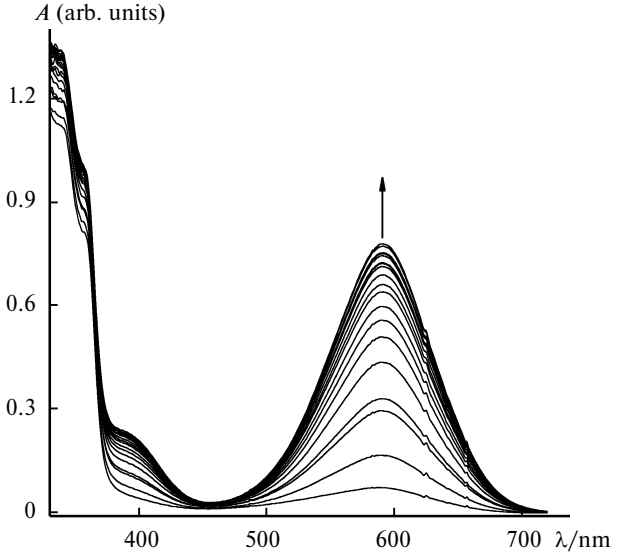


Fig. 1. The changes in the absorption spectrum of the solution of SPP **1a** in acetone under continuous irradiation with UV light (λ_{irr} = 365 nm), T = 293 K.

the conjugation of the indoline fragment with the rest of the molecule arising upon opening of the pyran ring. The enhancement of the electron-withdrawing properties of substituents at position 5 of the indoline part of spiropyrans results in a long-wavelength shift of the absorption bands of merocyanine isomers as compared to SPP **1a**. Thus, the long-wave absorption maxima in acetone in the series of SPPs **1a**,**d**—**f** with substituents R^2 = H, CF_3, CN, NO_2 are observed at 590, 593, 600, and 610 nm (see Table 1). Conversely, the weak electron-donating properties of substituents R^2 = Cl, Br due to the positive mesomeric effect lead to a small short-wavelength shift of the long-wavelength absorption maxima, 586 and 588 nm, respectively (see Table 1).

To evaluate the effect of substituents in the indoline fragment on the **A**→**B** photoconversion efficiency, the colorability values ($\Phi_{AB} \cdot \varepsilon_{max}^{B}$) were determined in the series of spiropyrans under consideration. The data given in Table 1 demonstrate a tendency of increasing colorability upon introduction of electron-withdrawing substituents at position 5 of the indoline fragment.

After the irradiation is stopped, discoloration of the SPP solutions associated with the thermal recyclization reactions is observed. The kinetics of the **B**→**A** dark relaxation processes in solutions of spiropyrans **1a**—**f** is well described by the monoexponential function, which allows one to determine the lifetimes (τ_B) of acyclic forms **B** (see Table 1, Fig. 2).

Analysis of the data in Table 1 shows that the lifetime of photoinduced forms **B** depends on the properties of substituents R^2 in the indoline part of spiropyrans. Thus, on going from spiropyrans **1a**,**b** with electron-donating substituents to unsubstituted spiropyran **1c** and further to

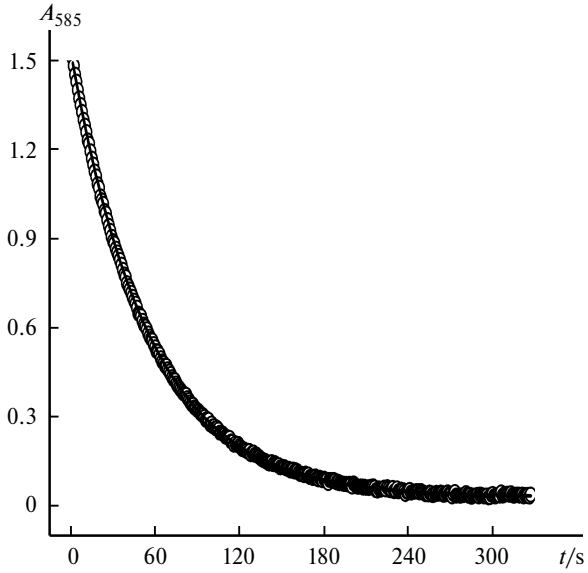


Fig. 2. The kinetic curve of the thermal recyclization reaction of SPP **1c** in acetone obtained by recording the optical density at the long-wave absorption maximum (585 nm) of the open form, T = 293 K. The dots are the experimental data, the line is the result of approximation by the monoexponential function.

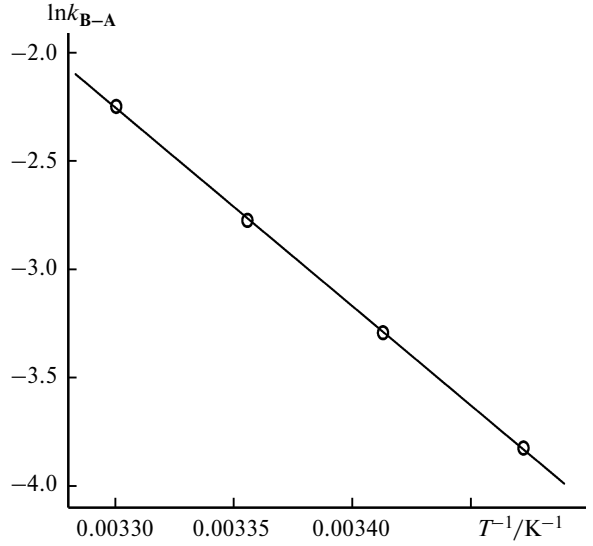


Fig. 3. The dependence of the logarithm of the thermal reaction rate constant on the reciprocal temperature for the solution of SPP **1e** in acetone.

spiropyrans **1d—f** with electron-withdrawing groups at position 5, the lifetime of merocyanine isomers decreases monotonically from 63.2 to 20.7 s in accordance with the change in the electronic activity of the substituents. The observed regularity is probably due to the fact that the electron-withdrawing substituents in the indoline part of spiropyran increase the positive charge on the nitrogen atom and thus destabilize the merocyanine isomers, while the electron-donating substituents increase their thermal stability through the delocalization of the positive charge.

As the temperature increases, the rate constants of the reverse dark reactions of spiropyrans **1a—f** increase. Using the Arrhenius dependence of the rate constants of **B→A** thermal recyclization of spiropyrans **1a—f** on temperature, the activation energy values were determined and found to be equal to 75.6—89.7 kJ mol^{-1} (see Table 1, Fig. 3).

According to the data in Table 1, for spiropyrans the inverse values of the rate constants (lifetimes) at 273 K correlate with the activation energies of recyclization reactions: the slower the reaction, the higher the activation energy, which confirms the correctness of the data obtained.

In addition to the reverse thermal reaction, spiropyrans **1a—f** undergo a photoinduced recyclization reaction **B→A**. After the UV irradiation is stopped, the colored solutions of spiropyrans demonstrate a thermal discoloration reaction. If during the thermal relaxation process the irradiation in the long-wavelength absorption of merocyanine isomers is applied, in particular at a wavelength of 546 nm, the decoloration reaction kinetics significantly accelerate (Fig. 4).

In conclusion, a series of new benzoxazolyl-substituted spiroindoline-benzopyrans with electron-withdrawing substituents in the indoline fragment exhibiting positive T- and P-type photochromism was obtained. The nature of substituents in the indoline part of spiropyrans significantly influences the spectrokinetic properties. Thus, the introduction of electron-withdrawing substituents at position 5 of the indoline part of spiropyran molecules leads to a long-wavelength shift of the absorption bands of merocyanine isomers, while electron-donating substituents cause a short-wavelength shift of the absorption

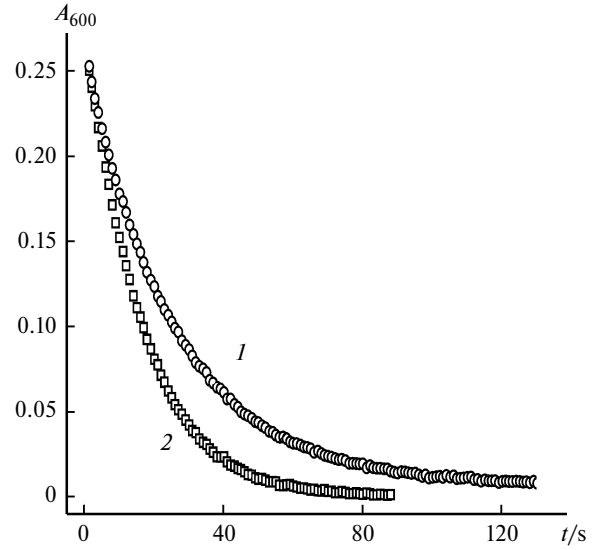


Fig. 4. The kinetic curves of the thermal reaction (*1*) and the photobleaching reaction (*2*) (λ_{irr} = 546 nm) of a pre-colored solution of SPP **1d** in acetone, T = 293 K.

maxima. It was found that the colorability of spiropyrans increases when electron-withdrawing substituents are introduced into the indoline fragment. It was shown that the lifetime of merocyanine isomers decreases on going from spiropyrans with electron-donating substituents to the unsubstituted spiropyran and further to spiropyrans with electron-withdrawing groups at position 5.

Experimental

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on Varian Unity-300 (300 MHz, ^{1}H) and Bruker AVANCE-600 (600 MHz, ^{1}H; 150 MHz, ^{13}C; 60 MHz, ^{15}N) spectrometers in $CDCl_3$ at 20 °C. Signals were assigned relative to the residual signals of the deuterated solvent (^{1}H, δ 7.26; ^{13}C, δ 77.2), the δ values and spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. Elemental analysis was carried out on a Kovo CHN-analyzer. Melting points were measured on a Boetius hot stage. Electrospray ionization high resolution mass spectra were recorded on a Bruker MicroTOF instrument.

Electronic absorption spectra and kinetic curves of thermal recyclization reactions of the test compounds were recorded on an Agilent 8453 spectrophotometer with a console for thermostating the samples. Photolysis of solutions (a concentration of $2 \cdot 10^{-5}$ mol L^{-1}) was carried out using the Newport system based on a 200 W mercury lamp with a set of interference filters. The solutions were prepared in acetone (Aldrich, spectrophotometric grade).

A Newport 2935 optical radiation power meter was used to measure the optical radiation intensity, which was $2.18 \cdot 10^{16}$ photon s^{-1} on a 365 nm wavelength. Colorability ($\Phi_{AB} \cdot \varepsilon_{max}^{B}$) was measured according to the procedure described earlier in the work.[35]

3*H*-Indolium salts **2d—f** were obtained according to the procedures described earlier.[36,37]

The synthesis of spiropyrans **1a—c** was described earlier.[38] 8-Benzoxazolyl-6-formyl-substituted spirobenzopyrans **1d—f** were obtained according to the procedure described earlier.[38]

8′-(1,3-Benzoxazol-2-yl)-1,3,3-trimethyl-5-(trifluoromethyl) spiro[indoline-2,2′-chromene]-6′-carbaldehyde (1d). The yield was 46%. M.p. 195—196 °C (toluene—heptane, 1 : 3). Found (%): C, 68.69; H, 4.25; N, 5.78. $C_{28}H_{21}F_3N_2O_3$. Calculated (%): C, 68.57; H, 4.32; N, 5.71. ^{1}H NMR ($CDCl_3$), δ: 1.26 (s, 3 H, C(3)Me); 1.39 (s, 3 H, C(3)Me); 2.77 (s, 3 H, N(1)Me); 5.95 (d, 1 H, H(3′), J = 10.4 Hz); 6.59 (d, 1 H, H(7), J = 8.1 Hz); 6.80—6.83 (m, 1 H, H(7′′)); 7.06 (d, 1 H, H(4′), J = 10.4 Hz); 7.19—7.29 (m, 2 H, H(5′′), H(6′′)); 7.35 (d, 1 H, H(4), J = 1.7 Hz); 7.51 (dd, 1 H, H(6), J = 8.1 Hz, J = 1.7 Hz); 7.61—7.64 (m, 1 H, H(4′′)); 7.80 (d, 1 H, H(5′), J = 2.0 Hz); 8.58 (d, 1 H, H(7′), J = 2.0 Hz); 9.93 (s, 1 H, 6′-CHO). ^{13}C NMR ($CDCl_3$, 150 Hz), δ: 19.60 (3-Me); 25.11 (3-Me); 29.07 (1-Me); 52.01 (C(3)); 106.79 (C(7)); 107.16 (C(2)); 110.33 (C(7′′)); 114.49 (C(4a′)); 118.48 (q, C(4), J = 3.5 Hz); 119.68 (C(4′′)); 120.12 (C(3′)); 120.56 (C(8′)); 121.78 (q, CF_3, J = 32.1 Hz); 124.20 (C(5)); 124.48 (C(5′′)); 125.21 (C(6′′)); 125.60 (q, C(6), J = 4.0 Hz); 128.83 (C(5′)); 129.59 (C(4′)); 129.68 (C(6′)); 135.17 (C(7′)); 137.57 (C(3a)); 140.94 (C(3a′′)); 150.73 (C(7a)); 150.88 (C(7a′′)); 157.59 (C(1a′)); 160.55 (C(2′′)); 189.88 (6-CHO). ^{15}N NMR ($CDCl_3$, 60 Hz), δ: 94.80 (N(1)), 241.12 (N(3′′)). MS (ESI-TOF) m/z:. found 491.1577 $[M + H]^+$. $C_{28}H_{21}F_3N_2O_3$. Calculated: 491.1577.

8′-(1,3-Benzoxazol-2-yl)-5-cyano-1,3,3-trimethylspiro[indoline-2,2′-chromene]-6′-carbaldehyde (1e). The yield was 41%. M.p. 228—229 °C (toluene—heptane, 1 : 3). Found (%): C, 75.22; H, 4.62; N, 9.46. $C_{28}H_{21}N_3O_3$. Calculated (%): C, 75.15; H, 4.73; N, 9.39. ^{1}H NMR ($CDCl_3$), δ: 1.26 (s, 3 H, C(3)Me); 1.40 (s, 3 H, C(3)Me); 2.82 (s, 3 H, N(1)Me); 5.95 (d, 1 H, H(3′), J = 10.4 Hz); 6.60 (d, 1 H, H(7), J = 8.2 Hz); 6.91—6.94 (m, 1 H, H(7′′)); 7.09 (d, 1 H, H(4′), J = 10.4 Hz); 7.29—7.32 (m, 2 H, H(5′′), H(6′′)); 7.37 (d, 1 H, H(4), J = 1.7 Hz); 7.59 (dd, 1 H, H(6), J = 8.1 Hz, J = 1.7 Hz); 7.64—7.67 (m, 1 H, H(4′′)); 7.83 (d, 1 H, H(5′), J = 2.1 Hz); 8.60 (d, 1 H, H(7′), J = 2.1 Hz); 9.95 (s, 1 H, 6′-CHO). MS (ESI-TOF) m/z: found 448.1656 $[M + H]^+$. $C_{28}H_{21}N_3O_3$. Calculated: 448.1655.

8′-(1,3-Benzoxazol-2-yl)-1,3,3-trimethyl-5-nitrospiro[indoline-2,2′-chromene]-6′-carbaldehyde (1f). The yield was 39%. M.p. 232—233 °C (toluene—heptane, 1 : 3). Found (%): C, 69.24; H, 4.59; N, 8.82. $C_{27}H_{21}N_3O_5$. Calculated (%): C, 69.37; H, 4.53; N, 8.99. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 3 H, C(3)Me); 1.45 (s, 3 H, C(3)Me); 2.88 (s, 3 H, N(1)Me); 5.96 (d, 1 H, H(3′), J = 10.4 Hz); 6.59 (d, 1 H, H(7), J = 8.7 Hz); 6.88—6.91 (m, 1 H, H(7′′)); 7.11 (d, 1 H, H(4′), J = 10.4 Hz); 7.22—7.32 (m, 2 H, H(5′′), H(6′′)); 7.62—7.66 (m, 1 H, H(4′′)); 7.84 (d, 1 H, H(5′), J = 2.1 Hz); 8.04 (d, 1 H, H(4), J = 2.3 Hz); 8.26 (dd, 1 H, H(6), J = 8.7 Hz, J = 2.3 Hz); 8.60 (d, 1 H, H(7′), J = 2.1 Hz); 9.96 (s, 1 H, 6′-CHO). MS (ESI-TOF) m/z: found 468.1554 $[M + H]^+$. $C_{27}H_{21}N_3O_5$. Calculated: 468.1553.

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