

Photochromic spiro[indoline-pyridobenzopyrans]: fluorescent metal-ion sensors

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Dedicated to Prof. Oleg N. Chupakhin on the occasion of his 70th birthday in recognition of his outstanding contribution to the chemistry of heterocyclic compounds and investigation into reaction mechanisms

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Abstract

By coupling 5-bromo-(chloro)-7-formyl-8-hydroxyquinoline with 2-methylene-1,3,3-trimethylindoline, the 6'-halogeno-spiro[indoline-2,2'-[3,2-*h*]-pyrido[2*H*-1]benzopyrans] **3** have been prepared and their photochromic behaviors studied. The photoinduced merocyanine forms **4** of the spiropyran form fluorescent complexes with divalent metal ions (Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺).

Keywords: Formylquinolinols, spiropyran, synthesis, photochromism, chemosensors, fluorescence

Introduction

Thanks to the high quantum efficiency of the photoisomerization reaction and high molar extinction of the photoinduced merocyanine forms, spiropyran have been long recognized as one of the most important families of photochromic compounds possessing significant potential for diverse technical applications such as molecular switches and high-density photochemical erasable memories, variable density optical filters, and others.¹⁻⁵ In the recent time spiropyran

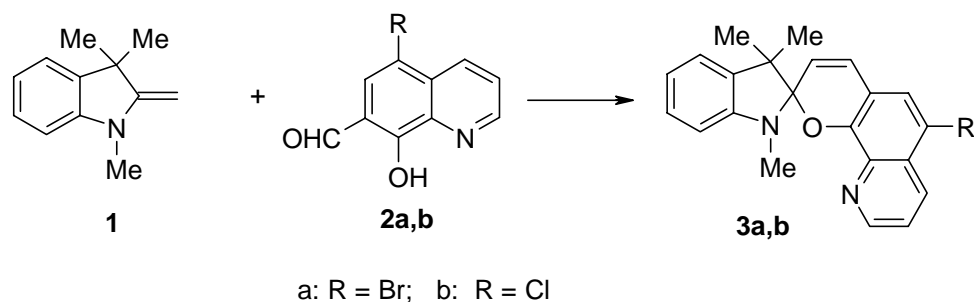
have also received much attention as efficient metal-ion-responsive photochromic materials for analytical applications and polyfunctional sensor systems containing various receptor and signal fragments.^{6,7} In particular, very efficient fluorescent sensors for some metal ions have been found within the class of spiro(indolinopyridobenzopyrans).⁸⁻¹⁰

Here we report on a new method for the synthesis of 5-halogeno-7-formyl-8-hydroxyquinolines and the synthesis of 6'-halogenospiro[indoline-2,2'-[3,2-*h*]-pyrido[2*H*-1]benzopyrans] **3a,b**, their photochromic behavior, and the metal-coordinating capacity of their photoinduced merocyanine forms.

Results and Discussion

Synthesis

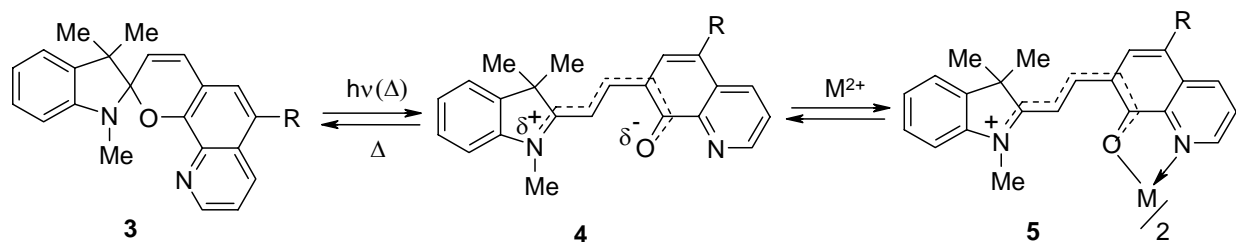
The previously described methods for the synthesis of spiropyrans **3a**¹¹ and **3b**¹² based on coupling Fisher's base **1** with 5-halogeno-7-formyl-8-hydroxyquinolines **2** (Scheme 1) have been modified slightly to obtain the products in better yields. The parent 7-formyl-8-hydroxyquinoline was prepared previously in low yield using a multistep method⁹ because direct formylation of 8-hydroxyquinoline leads to substitution not at the 7-, but at the 5-position.¹³ In the present work, for the formylation of 5-halogeno-8-hydroxyquinolines we employed the Duff reaction, affording the aldehydes **2** in one step, although in relatively low yields.



Scheme 1

Photochromic and spectral properties

The long-wavelength absorption of spiropyrans **3** is observed at λ_{max} 342–358 nm ($\epsilon = 4200\text{--}4600 \text{ mol L}^{-1} \text{ cm}^{-1}$), which is the spectral region characteristic of the ring-closed forms. In polar solvents, equilibrium is established between the ring-closed spirocyclic, **3**, and ring-opened merocyanine, **4**, forms (Scheme 2). The existence of small amounts of the latter is detected by the appearance of low intensity



Scheme 2

absorption bands in the spectral region of 522–605 nm, witnessing to the appearance of the merocyanine isomers of spiropyrans (Table 1).^{1,2} In polar solvents, the equilibrium amounts of more polar merocyanine forms of spiropyrans increase compared with that in toluene (Table 2).

Table 1. Spectral properties of the isomeric forms of spiropyrans **3**

	λ_{\max} , nm ($10^{-3} \epsilon_{\max}$, M ⁻¹ cm ⁻¹)		
	Toluene	Acetonitrile	Chloroform
3a	342 (4.3)	342	
	358 (4.2)	354	
4a	524sh	522sh	529sh (21.7*)
	559	562	566 (44.7*)
	598	597	605 (47.5*)
3b	342 (4.6)	342	
	358 (4.4)	355	
4b	524sh	522sh	529sh (23.4*)
	559	561	566 (46.5*)
	598	597	605 (47.6*)

* Molar extinctions of the merocyanine forms were calculated on the basis of ¹H NMR determinations of the contents of the latter in chloroform solutions.

Table 2. Thermodynamic parameters of the thermal equilibria (Scheme 2) in solutions of spiroopyrans **3** at 292 K*

	Solvent	$10^2 K_e$	ΔH° , kJ mol ⁻¹	ΔG° , kJ mol ⁻¹	ΔS° , J mol ⁻¹ K ⁻¹
3a	Toluene	1.7	–**	–**	–**
	Acetonitrile	8.4	6.2	6.0	0.7
	Chloroform	35.4			
3b	Toluene	0.5	14.2	12.9	4.5
	Acetonitrile	6.6	5.4	4.2	4.1
	Chloroform	33.4			

* Calculated from data on the temperature-dependence of the equilibrium constants K_e in the temperature interval of 283–323 K. ** The temperature dependence of K_e does not follow the van't Hoff relationship.

Under UV-irradiation of solutions of **3** (at λ_{\max}), the photoinitiated electrocyclic ring-opening reaction occurs (Scheme 2), giving rise to the formation of the colored merocyanine forms **4** with the long-wavelength absorption at $\lambda_{\max} = 561$ nm (R=Cl) and 598 nm (R=Br) and weak fluorescence ($\Phi \cong 0.001$ in acetone) at 620–630 nm (Figure 1).

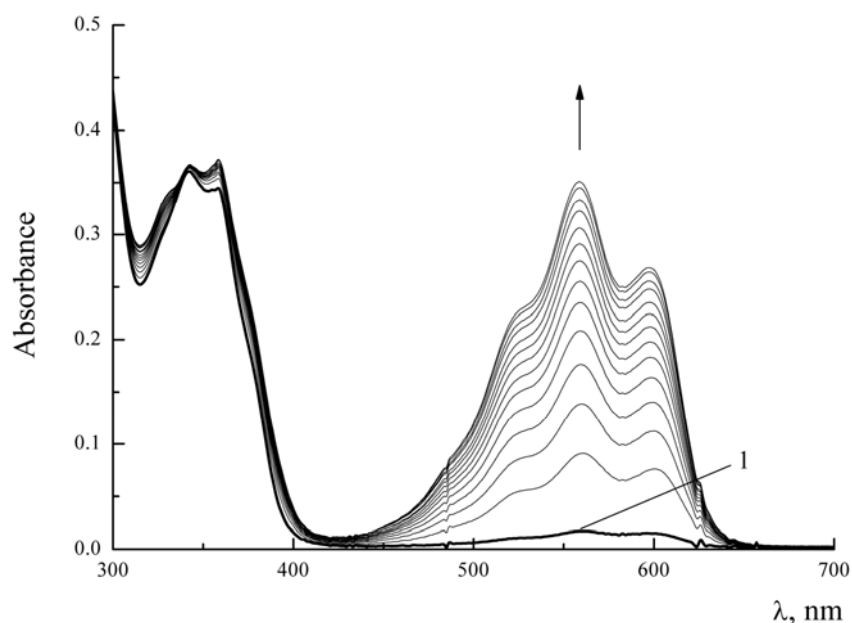


Figure 1. Absorption spectra of spiroopyran **3b** in toluene solution ($c=7.9 \cdot 10^{-5}$ M; $T=293$ K): before irradiation (**1**) and after irradiation with the filtered light of a mercury lamp 365 nm (the absorption at the longest wavelength band gradually increases with increase in duration of the irradiation).

The kinetics of the dark reactions $3 \rightarrow 4$ and $4 \rightarrow 3$ are well described by mono-exponential functions. Activation energies of the thermal reactions were determined from the Arrhenius relationship. Table 3 contains the data on kinetic properties of the dark reactions.

Table 3. Kinetic parameters of the dark $3 \rightarrow 4$ and $4 \rightarrow 3$ reactions of spiropyrans at 292 K

	Solvent	$10^2 k_{3,4} \text{ s}^{-1}$	$E_a^{3,4} \text{ kJ mol}^{-1}$	$10^2 k_{4,3} \text{ s}^{-1}$	$E_a^{4,3} \text{ kJ mol}^{-1}$
3a	Toluene	0.6	-*	35.3	-*
	Acetonitrile	1.4	90.6	16.4	86.4
3b	Toluene	0.02	53.2	4.9	40.1
	Acetonitrile	1.4	92.2	20.4	87.2

* The temperature-dependence of rate constants does not follow the Arrhenius relationship.

Complexation properties

The addition of salts of Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} to the colorless or weakly colored solutions of spiropyrans **3** results in the appearance in the absorption spectra of new intense bands at 533–573 nm, which are assigned to the absorption of metal complexes of merocyanine forms of spiropyrans **5** (Scheme 2).⁹ The complexes **5** with metal ions Mg^{2+} , Zn^{2+} and, Cd^{2+} exhibit sufficiently intense fluorescence with maxima at 610–625 nm (Figure 2).

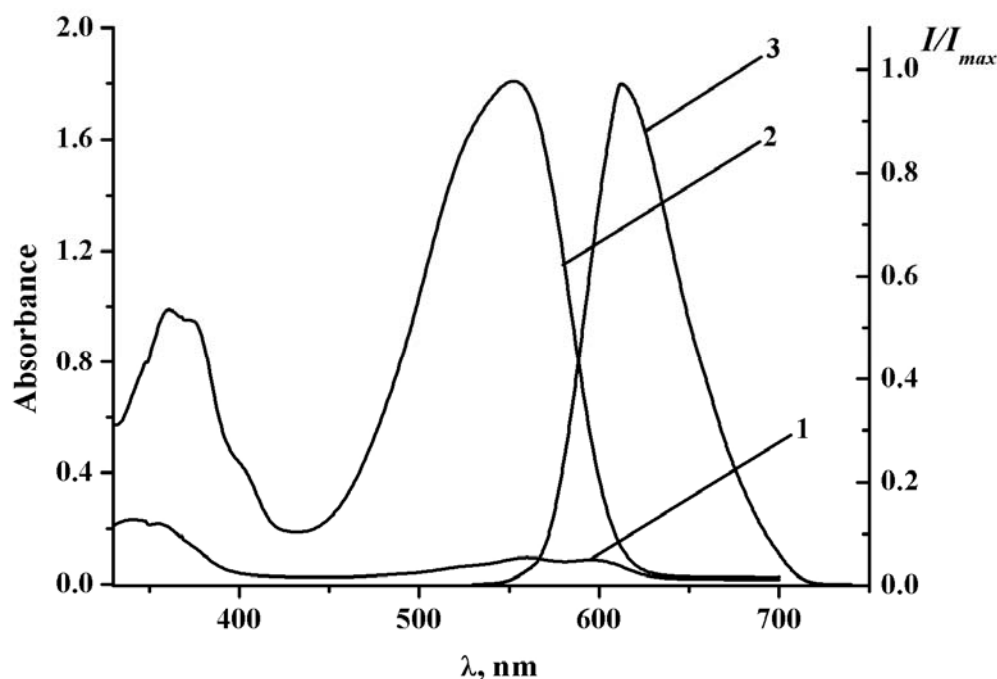


Figure 2. 1 - Absorption spectrum of spiropyran **3a** (solvent, acetone, $C = 3 \cdot 10^{-5} \text{ M}$); 2 - absorption spectrum of its Zn^{2+} complex **5a** (as formed on addition of an equivalent amount of zinc perchlorate to an acetone solution of **3a**); 3 - fluorescence of **5a** (solvent, acetone).

The quantum efficiency of the fluorescence ($\Phi = 0.007$ – 0.011) is an order of magnitude higher than that for the merocyanine ligands. Figure 3 depicts the metal-ion influence on the fluorescent contrast as occurs on complexation of merocyanines with metal ions.

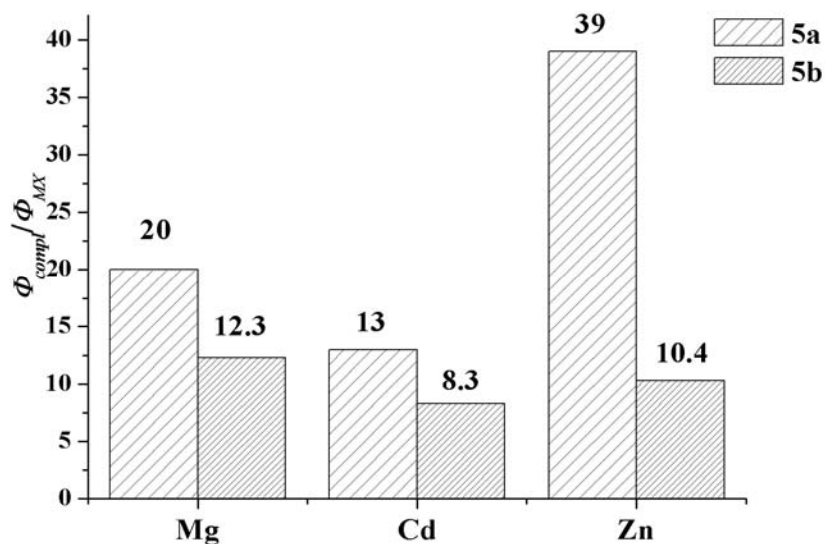


Figure 3. Metal-ion influence on the fluorescent contrast (Φ_{compl}/Φ_{Mc}) at complexation of a merocyanine with metal ions.

Table 4 contains some data on the spectral properties of the spiropyran complexes **5**. The composition of the complexes of the spiropyrans with metal ions was determined using the spectrophotometric methods of isomolar solutions (Job method) and molar ratio absorbance, which were previously employed for the analysis of the ionic equilibria of spiropyrans and chromenes.^{14,15} For all complexes **5**, a distinct maximum appears in the plot of absorption vs. composition of the isomolar solutions at the point where the metal-ion to merocyanine ratio is 1:2 (Figure 4). This finding is in accord with the results obtained for a complex of spiropyran **3** ($R = NO_2$) with Zn^{2+} .¹⁶

Table 4. Spectral properties of the complexes **5**

Ion	5a			5b		
	λ_{max}^{abs} , nm	λ_{max}^{flu} , nm	$\Phi \times 10^3$	λ_{max}^{abs} , nm	λ_{max}^{flu} , nm	$\Phi \times 10^3$
Mg^{2+}	570	612	10	578	618	11
Cd^{2+}	573	620	7	575	626	7.6
Zn^{2+}	551	612	20	578	618	9.2
Co^{2+}	556			556		
Ni^{2+}	571			572		
Cu^{2+}	533			526		

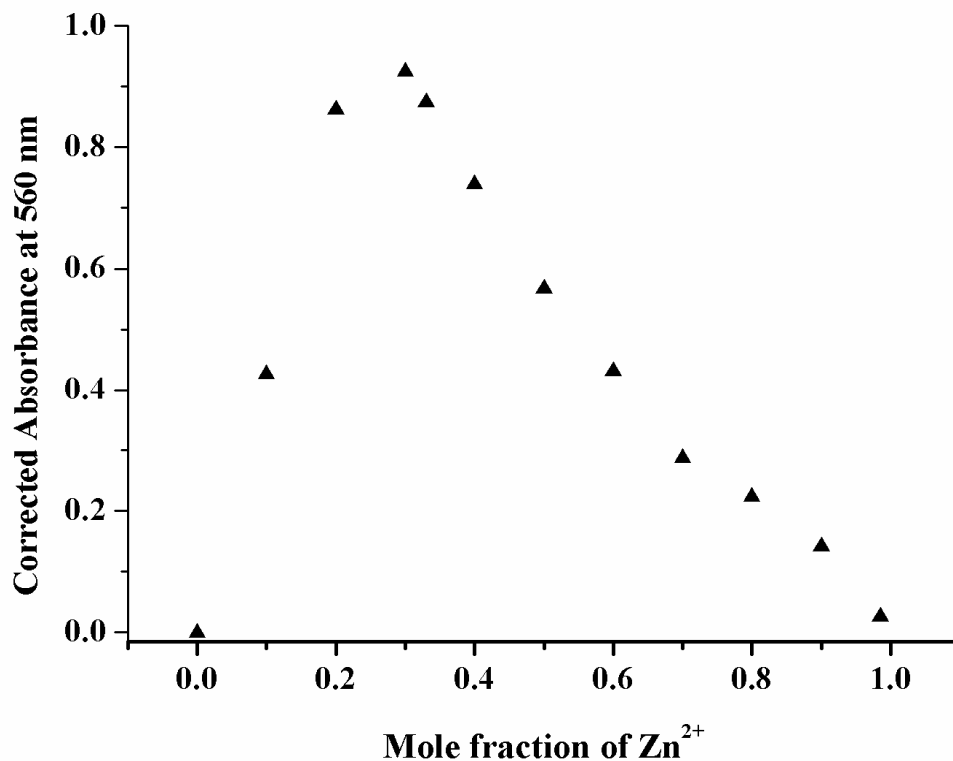


Figure 4. Job plots of $3 \cdot 10^{-5}$ M acetone solutions of Zn^{2+} and **3b** containing 0.01 M Bu_4NClO_4 .

Conclusions

A one-step procedure has been developed for the preparation of 5-bromo-(chloro)-7-formyl-8-hydroxyquinolines by the Duff formylation of 5-halogeno-8-hydroxyquinolines. The photochromic behavior of 6'-halogenospiro[indoline-pyridobenzopyrans] has been studied, and their properties as fluorescent sensors for metal ions (Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}) have been explored.

Experimental Section

General Procedures. NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) using $CDCl_3$ as solvent. Electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer, and fluorescence was measured using a Shimadzu RF 5001 PC spectrofluorimeter. The irradiation of solutions was carried out with the light of a high-pressure mercury lamp DRSh-250 equipped with a set of interference filters. The highest grade solvents (Fluka) were used for spectroscopic measurements. Metal perchlorates were used as ion salts.

General procedure for the preparation of formylquinolinols 2a,b

A mixture of 5-halogeno-8-hydroxyquinoline (0.015 mol), hexamethylenetetramine (4.2 g, 0.030 mol) and trifluoroacetic acid (25 ml) was heated under reflux for 6 h under an argon atmosphere. After cooling, the reaction mixture was poured onto a solution of conc. hydrochloric acid (20 ml) in water (220 ml), stirred for 30 min and neutralized with NaOH solution to pH ~ 5. The precipitate was filtered off, washed with water, dried, and extracted with boiling benzene (3x20 ml). After evaporation of the solvent, the resulting crude product was recrystallized from ethanol.

5-Bromo-8-hydroxyquinoline-7-carboxaldehyde (2a). Yield 14%, m.p. 209–210 °C. ¹H NMR (δ, ppm, J/Hz): 7.68 (1H, dd, J = 4.3 and 8.6, 3-H), 8.06 (1H, s, 6-H), 8.51 (1H, dd, J = 1.5 and 8.6, 4-H), 8.93 (1H, dd, J = 1.5 and 4.3, 2-H), 10.38 (1H, s, 7-CHO). Anal. Calc. for C₁₀H₆BrNO₂ (252.07): C, 47.65; H, 2.40; N, 5.56. Found: C, 47.80; H, 2.49; N, 5.43%.

5-Chloro-8-hydroxyquinoline-7-carboxaldehyde (2b). Yield 15%, m.p. 211–212 °C. ¹H NMR (δ, ppm, J/Hz): 7.69 (1H, dd, J = 4.2 and 8.5, 3-H), 7.85 (1H, s, 6-H), 8.54 (1H, dd, J = 1.4 and 8.5, 4-H); 8.92 (1H, dd, J = 1.4 and 4.2, 2-H), 10.37 (1H, s, 7-CHO). Anal. Calc. for C₁₀H₆ClNO₂ (207.62): C, 57.85; H, 2.91; N, 6.75. Found: C, 57.97; H, 3.15; N, 6.86%.

General Procedure for the Preparation of Spiropyrans 3a,b

To a boiling mixture of the formylquinolinol **2a,b** (1.05 mmol) and 2-butanone (15 ml) was added a solution of methyleneindoline **1** (0.17 g, 1 mmol) in 2-butanone (2 ml), over a period of 30 min. After heating at reflux for 16 h under Ar, the reaction mixture was cooled and the solvent removed under reduced pressure. The residue was purified by column chromatography on Al₂O₃ using CHCl₃ as eluent.

6'-Bromo-1,3,3-trimethylspiro[indoline-2,2'-[3,2-h]pyrido[2H-1]benzopyran] (3a). Yield 67 %, m.p. 186–187.5 °C (from heptane) (Lit.¹¹ mp 195 °C). ¹H NMR (δ, ppm, J/Hz): 1.19 (3H, s, 3-Me), 1.34 (3H, s, 3-Me), 2.79 (3H, s, 1-Me), 5.78 (1H, d, J = 10.2, 3'-H), 6.52 (1H, d, J = 7.7, 7-H), 6.82 (1H, td, J = 7.4 and 0.9, 5-H), 6.87 (1H, d, J = 10.2, 4'-H), 7.06 (1H, dd, J = 7.3 and J = 1.1, 4-H), 7.15 (1H, td, J = 7.7 and 1.2, 6-H), 7.37 (1H, dd, J = 8.6 and 4.2, 8'-H), 7.52 (1H, s, 5'-H), 8.35 (1H, dd, J = 8.6 and 1.6, 7'-H), 8.77 (1H, dd, J = 4.2 and 1.7, 9'-H). Anal. Calc. for C₂₂H₁₉BrN₂O (407.31): C, 64.88; H, 4.70; N, 6.88. Found: C, 65.05; H, 4.62; N, 7.03%.

6'-Chloro-1,3,3-trimethylspiro[indoline-2,2'-[3,2-h]pyrido[2H-1]benzopyran] (3b). Yield 72 %, m.p. 177–178 °C (from heptane) (Lit.¹² m.p. 137–141 °C). ¹H NMR (δ, ppm, J/Hz): 1.19 (3H, s, 3-Me), 1.34 (3H, s, 3-Me), 2.79 (3H, s, 1-Me), 5.79 (1H, d, J = 10.2, 3'-H), 6.52 (1H, d, J = 7.7, 7-H), 6.82 (1H, td, J = 7.4 and 0.9, 5-H), 6.87 (1H, d, J = 10.2, 4'-H), 7.06 (1H, dd, J = 7.3 and 0.9, 4-H), 7.15 (1H, td, J = 7.7 and 1.2, 6-H), 7.33 (1H, s, 5'-H), 7.43 (1H, dd, J = 8.6 and 4.2, 8'-H), 8.39 (1H, dd, J = 8.6 and 1.7, 7'-H), 8.80 (1H, dd, J = 4.2 and 1.7, 9'-H). Anal. Calc. for C₂₂H₁₉ClN₂O (362.86): C, 72.82; H, 5.28; N, 7.72. Found: C, 72.90; H, 5.45; N, 7.83%.

Acknowledgments

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