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Synthesis, Photochromic Properties, and Complex Formation with Metal Ions of Hydrazones Based on a Spiropyran of Oxaindane Series

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Abstract—A series of hydrazones based on a new spiropyran oxaindane series was synthesized. The compounds were found to possess photochromism and are characterized by a high rate of spontaneous decoloration of their photoinduced merocyanine form. Dark and photoinduced formation of complex compounds in the reaction of metal ions with molecules of the hydrazones in solution was observed.

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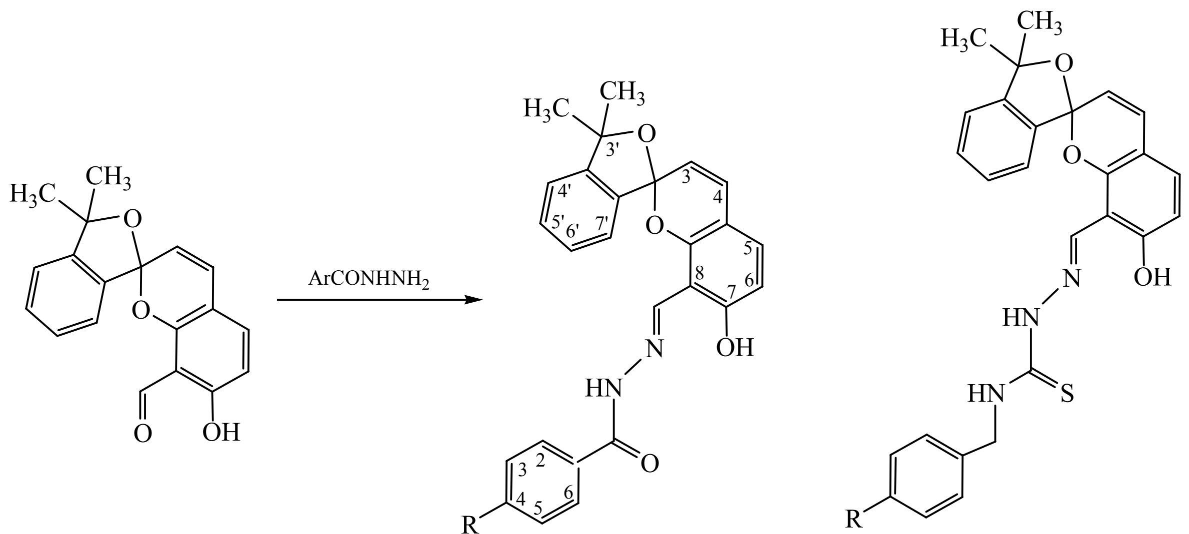
A promising area of application of photochromic spiro compounds is the development of a reversible photocontrolled chemosensors [1–4]. In continuation of our preceeding research in this area [5–7], we present in this paper the results of spectral and kinetic studies of photochromism and complexation with metal ions of a number of newly synthesized hydrazones based on spiropyranes of oxaindane series (**II–IX**). The synthesis scheme is shown below.

The composition and structure of compounds **II–IX** were established on the basis of elemental analysis (Table 1), IR and ^{1}H NMR spectroscopy. Methods of synthesis and spectral characteristics of the synthesized



I **II–VIII** **IX**

R = H (**II**), CH_3 (**III**), OCH_3 (**IV**), $N(CH_3)_2$ (**V**), F (**VI**), Br (**VII**), NO_2 (**VIII**).

Table 1. Yields and elemental analysis data of spiropyrans **I–IX**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
I	72	106	73.85	5.50	–	$C_{19}H_{16}O_4$	74.01	5.23	–
II	62	150	73.43	5.16	6.57	$C_{26}H_{22}N_2O_4$	73.23	5.20	6.57
III	87	172	73.70	5.61	6.45	$C_{27}H_{24}N_2O_4$	73.62	5.49	6.36
IV	70	173	70.90	5.25	6.34	$C_{27}H_{24}N_2O_5$	71.04	5.30	6.14
V	74	165	71.76	5.54	8.80	$C_{28}H_{27}N_3O_4$	71.62	5.80	8.95
VI	68	130	70.34	4.45	6.40	$C_{26}H_{21}FN_2O_4$	70.26	4.76	6.30
VII	59	138	61.73	4.34	5.43	$C_{26}H_{21}BrN_2O_4$	61.79	4.19	5.54
VIII	72	180	66.45	4.34	8.56	$C_{26}H_{21}N_3O_6$	66.24	4.49	8.91
IX	81	225	68.65	5.42	8.78	$C_{27}H_{25}N_3O_3S$	68.77	5.34	8.91

compounds are given in the experimental section. The results of the spectral-kinetic studies of photochromic properties of synthesized compounds are presented in Fig. 1 and Table 2.

Figure 1 shows the photoinduced changes in the absorption spectra of compound **II**. The absorption spectrum of the original form of the compound consists of several bands with a maximum at 310 nm. The photoinduced absorption band occupies the region from 400 to 550 nm. The hydrazone exhibits photochromic properties: after photo-coloration (Fig. 2, curve *2*) spontaneous decoloration occurs of the photoinduced form (Fig. 2, curve *3*). However, the magnitude of the photoinduced optical density at a wavelength of the absorption band maximum of the photoinduced form is insignificant.

The introduction of weak electron-donor substituents in the para-position of the phenyl ring (hydrazones **III** and **IV**) and electron-acceptor group (hydrazone **VII**), in some cases almost does not change the position and shape of the absorption band of the initial and photoinduced forms (Table 2). In other cases at the introduction of electron-donor (hydrazones **IV** and **V**) and electron-acceptor (hydrazone **VI**) substituents in the phenyl ring of the hydrazone fragment of the molecule there is an increase in the photoinduced changes in optical density (Table 2, Fig. 2). In these cases the absorption band of the original moiety undergoes a blue shift, while the absorption band of the photoinduced moiety suffers a red shift relative to that of the unsubstituted compound **II** (Table 2).

The nitro-substituted derivative **VIII** is characterized by a shift of the absorption band to the spectral region of longer wavelengths (Fig. 3). It is noteworthy that the photoinduced moiety of this compound does not undergo a spontaneous decoloration, but returns to the original colorless form under the action of visible light.

The replacement of the carbonyl group in the substituent of compound **II** by thiocarbonyl (compound **IX**) causes a red shift of the absorption bands of both the initial and photoinduced forms, although photo-coloration is weak (Table 2).

All investigated compounds are characterized by a high rate of spontaneous decoloration in comparison with the nitro-substituted spiropyrans [1], which largely determines the low photoinduced optical density under the conditions of steady-state photolysis.

The results of the spectral-kinetic studies of the synthesized compounds of the class of spiropyran derivatives indicate their photochromic trans-

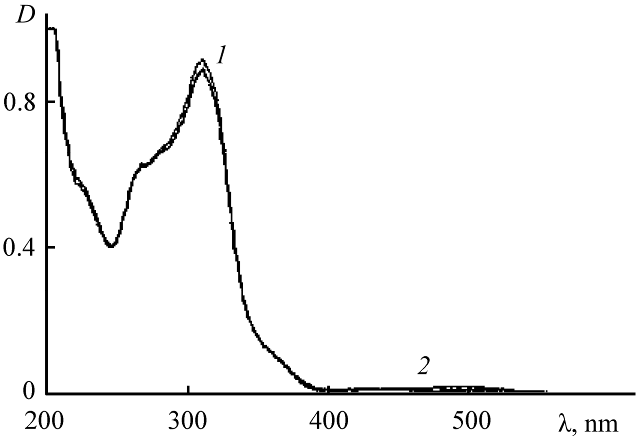


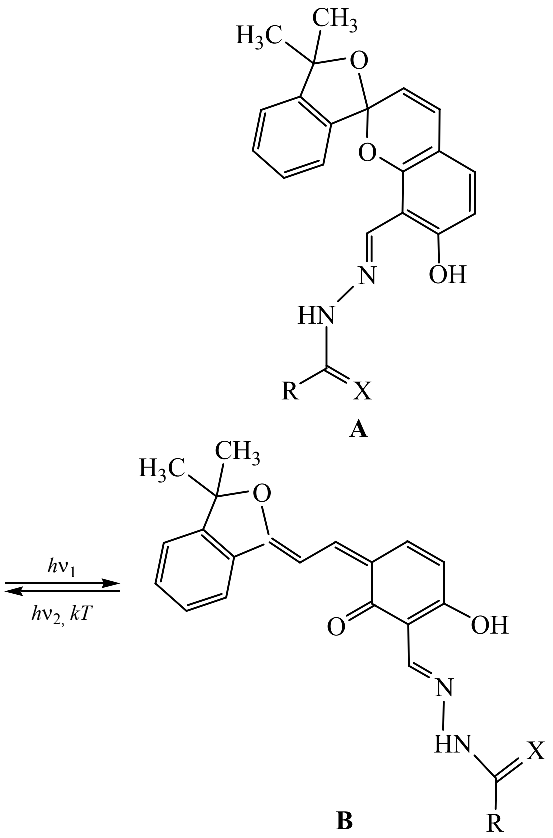
Fig. 1. The absorption spectra of solution of compound **II** in acetonitrile: (*1*) before irradiation, (*2*) after irradiation with UV light through an UVC-1 filter.

Table 2. Spectral and kinetic characteristics of photochromic transformations of spiropyran in acetonitrile[a]

Comp. no.	λ_A^{max}, nm	D_A	λ_B^{max}, nm	ΔD_B^{phot}	$\Delta D_B^{phot}/D_A$	k_{BA}, s^{-1}
II	310	0.98	450	0.02	0.02	0.004
III	307	0.85	450	0.02	0.02	0.025
IV	310	1.27	453	0.18	0.14	0.038
V	333	1.25	445	0.15	0.12	0.016
VI	305	1.13	467	0.10	0.09	0.016
VII	310	0.79	438	0.03	0.04	0.038
VIII	257/320	0.90/0.70	485	0.08	0.10	–
IX	325	0.93	486	0.03	0.03	0.040

[a] λ_A^{max} and λ_B^{max} are the maxima of absorption bands of the initial and photoinduced forms of photochromic compounds, respectively; D_A is optical density at the maximum of absorption band of the initial form; ΔD_B^{phot} is the photoinduced change in optical density at the maximum of the absorption band of the photoinduced forms in the state of photo-equilibrium; k_{BA} is the spontaneous decoloration constant at 250°C.

formations, like those established for the other types of spiro compounds [1], namely, mutual photoinduced transformations between spiropyran and merocyanine forms (**A** and **B**, respectively).



In the course of study the properties were examined of all new compounds toward ability of complexation of the molecules of synthesized hydrazones with metal cations. Table 3 lists the results of comparative spectral and kinetic studies.

Table 3 shows that all investigated hydrazones react with metal ions. The introduction of bivalent Mg^{+2} or trivalent La^{+3} ions into the solution of photochromic hydrazones **II** and **VIII** leads to the coloration of the solution in the absence of light. The absorption spectra of these products shows a structurized absorption band of the complex with Mg^{+2} with two pronounced maxima or La^{+3}, with three maxima.

Similar absorption spectra with minor changes in the position of the maxima of the absorption bands, depending on the structure of the compounds, are observed for the products of interaction of the carbonyl-containing spiropyran hydrazones molecules

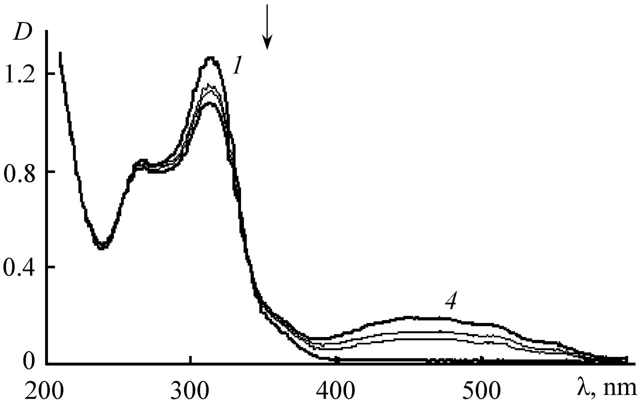


Fig. 2. Absorption spectra of solution of compound **IV** in acetonitrile: (*1*) before irradiation, (*2–4*) after consecutive irradiation through the filter UVC-1.

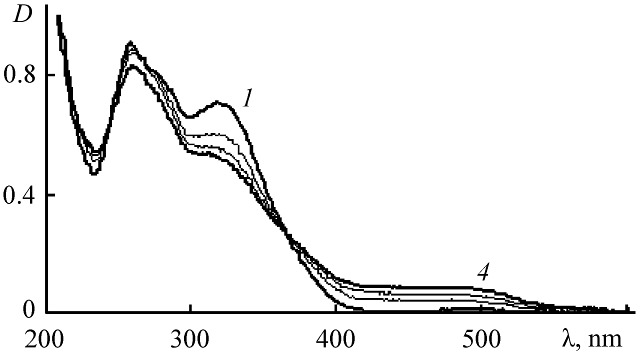


Fig. 3. The absorption spectra of solution of compound **VIII**: (*1*) before irradiation, (*2–4*) after consecutive irradiation through the filter UVC-1.

Table 3. The spectral-kinetic characteristics of the complexes of spiropyran with metal ions in acetonitrile[a]

Comp. no.	Ion	λ_A^{max}, nm	D_A	λ_B^{max} (ΔD_B^{orig}), nm	ΔD_B^{phot}
II	Li^+	310	0.86	445	0.03
	Ag^+	310	1.01	500	0.17
	Mg^{+2}	320	0.87	450(0.94)/545(1.39)	–
	La^{+3}	330	0.71	460(1.00)/540(1.53)	–
III	Li^+	305	0.85	435(0.05)	0.03
	Ag^+	307	0.86	505	0.33
	Mg^{+2}	320	0.75	445(0/82)/540(1.10)	–
	La^{+3}	325	0.58	460(0.98)/533(1.27)	–
IV	Li^+	310	1.28	440	0.03
	Ag^+	310	1.27	500	0.16
	Mg^{+2}	323	1.19	450(1.05)/545(1.46)	–
	La^{+3}	330	0.94	463(1.10)/535(1.58)	–
V	Li^+	338	1.23	435	0.01
	Ag^+	337	1.45	450(0.06)/542(0.05)	0.01/0.01
	Mg^{+2}	366	1.25	465(0.88)/545(0/98)	–
	La^{+3}	370	1.09	495(1.17)/525(1.18)	Photoindced changes in the band shape
VI	Li^+	307	1.15	439	0.04
	Mg^{+2}	317/343	0.93/0.49	444(1/04)/540(1/40)	–
	La^{+3}	273/325	0.57/0.74	460(1/26)/498(1/50)/530(1/60)	–
VII	Li^+	308	0.83	436	0.04
	Ag^+	308	0.79	436(0.05)	<0.01
	Mg^{+2}	308	0.83	448(0.75)/536(0.95)	0.02/0.03
	La^{+3}	328	0.55	495(1.08)/526(1.18)	Photoindced changes in the band shape
VIII	Li^+	260/320	0.94/0.73	487	0.08
	Ag^+	260/320	0.92/0.73	500(0.14)	<0.01
	Mg^{+2}	260/328	0.66/0.67	445(0.83)/545(1.40)	–
	La^{+3}	263/340	0.78/0.55	464(0.95)/538(1.57)	–
IX	Li^+	323	0.90	440	0.01
	Ag^+	320	0.97	490	<0.01
	Mg^{+2}	325	0.92	460	0.05
	La^{+3}	325	0.90	475(0.25)/493(0.28)/526(0.20)	0.16/0.14

[a] $\Delta D_B^{orig.}$ is the optical density at the maximum of the absorption band of the colored product, which arises directly after the addition of the metal salt to the acetonitrile solution prior to irradiation.

with metal ions (Table 3). Some changes were also observed in the absorption bands in the UV region. The irradiation of colored solutions with UV or visible filtered radiation has no significant effect on the absorption spectra, except for the colored products of interaction of compounds **V** and **VII** with lanthanum ions.

We believe that the latter fact shows the formation of stable products of chemical interaction between the molecules of photochromic derivatives of spiro compounds with metal ions. The closeness of the spectral characteristics of these products for all investigated hydrazones apparently indicates the similarity of their nature and structure, practically independent of the nature of the substituents at the phenyl ring of the hydrazone fragment (Table 3).

In the case of univalent ions Li^+ and Ag^+ photoinduced changes of absorption spectra are observed where after UV irradiation a new absorption band appears in the visible spectrum. Similar photoinduced spectral changes are observed in the case of the photochromic hydrazones in solution containing Li^+ ions (Table 3).

Comparing the spectral data for the hydrazones in the absence (Table 3) and in the presence of Li^+ or Ag^+ ions one can see that for most compounds a blue shift of the absorption band of photoinduced form in the case of the Li^+ ions and a red shift with the Ag^+ ions is observed. It should be noted that spontaneous relaxation of the photoinduced bands does not lead to the full return of the molecules to the initial form **A**. In some cases (compounds with strong electron-donor substituents **V** and electron-acceptor substituents **VII** and **VIII**) colored products are formed even before the UV irradiation, including those displaying the absorption bands observed for the products of interaction with the ions Mg^{+2} and La^{+3} (compound **V**).

The results of the study of the interaction between molecules of synthesized spiropyran hydrazones and metal ions suggest the formation of complexes of different types. Under the influence of light, when the spiropyran hydrazone molecules interact with univalent ions Li^+ or Ag^+, apparently complexes are formed between the ions and the phenoxide oxygen of the merocyanine form (complexes of 1:1 composition, LM). These complexes are characterized by the induvidual absorption bands at 430–500 nm. The appearance of structurized absorption band in the visible spectrum at the interaction of spiropyran hydrazone molecules with bivalent and trivalent metal ions in the absence of light may be due to the formation of complexes of the LM and L_2M type [4].

Based on these data, it is difficult to formulate definit conclusions on the structure of the obtained complex compounds in solutions. The results of additional studies on this subject will be published later.

EXPERIMENTAL

The IR spectra were recorded on a Varian Scimitar instrument in the range of 400–4000 cm^{-1}, ^1H NMR spectra of solutions in DMSO-d_6 were obtained on a Varian Unity 300 spectrometer (300 MHz), internal reference HMDS. Spectrophotometric measurements (photostationary spectra) of compounds in solution, the kinetic curves of the processes of photocoloration and spontaneous decoloration of the photoinduced forms were carried out using a Cary 50 bio spectrophotometer. As the solvent acetonitrile from Aldrich was used, working concentration was 2×10^{-4} M. Measurements were carried out in a quartz cell of 0.2 cm thickness. For the study of the processes of complex formation were used solutions of metal salts $LiClO_4$, $AgClO_4$, $Mg(ClO_4)_2$, and $La(NO_3)_3$ in acetonitrile at a ratio of the concentrations of the photochromic compounds and metal ions 1:100.

Irradiation of solutions was performed with filtered light of a lamp Hamamatsu LC-4.

The objects of study were hydrazones based on spiropyrans **II–IX,** obtained in the reaction of 7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromen-2,1'-isobenzofuran]-8-aldehyde (**I**) with the acids hydrazides and *N*-benzylthiosemicarbazide along the procedure [8].

Hydrazones (II–IX): To a solution of 0.001 mol of aldehyde **I** [9] in 5 ml of ethanol was added a solution of the corresponding hydrazide in a minimum amount of ethanol. The mixture was refluxed for 15–30 min. After cooling to room temperature the formed precipitate was filtered off, washed with minimum amount of ethanol, and twice recrystallized from acetonitrile.

Hydrazone (II). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.50 s, 1.67 s (6H, 3',3'-Me), 7.30–7.55 m (4H, 4',5',6',7'-Ar), 5.61 d (1H, 3-Ar, $J_{3,4}$ 9.50 Hz), 6.79 d (1H, 4-Ar), 7.17 d (1H, 5-Ar, $J_{5,6}$ 8.30 Hz), 6.54 d (1,6-Ar, 12.23 (1H, 6-Ar), 12.23 br.s, 12.05 br.s 7.88 (2H, 2,6-Ar, $J_{2,3}$ = $J_{6,5}$ = 7.54, 12.05 br.s (1H, NH, OH), 8.76 s (1H, CH=), 7.88 d (2H, $H^{2,6}$, Ph, $J_{2,3}$ = $J_{6,5}$ 7.54), 7.30–7.55 m (2H, $H^{3,5}$, Ph), 7.30–7.55 m (1H, H^4, Ph).

Hydrazone (III). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s, 1.64 s (6H, 3',3'-Me), 7.30–7.55 m (4H, 4',5',6',7'-Ar), 5.75 d (1H, 3-Ar, $J_{3,4}$ 9.60 Hz), 6.89 d (1H, 4-Ar), 7.30 d (1H, 5-Ar, $J_{5,6}$ 8.40 Hz), 6.60 d(1H, 6-Ar12.37 br.s, (1H, H^6, Ph), 12.37 br.s, 12.18 br.s (1H, NH, OH), 8.77 s (1H, CH=), 7.78 d (2H, $H^{2,6}$, Ph, $J_{2,3}$ = $J_{6,5}$ 8.10), 7.30 d (2H, $H^{3,5}$, Ph), 2.35 s (3H, Me).

Hydrazone (IV). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.51 s, 1.67 s (6H, 3',3'-Me), 7.30–7.50 m (4H, 4',5',6',7'-Ar), 5.61 d (1H, 3-Ar, $J_{3,4}$ 9.60 Hz), 6.79 d (1H, 4-Ar), 7.16 d (1H, 5-Ar, $J_{5,6}$ 8.45 Hz), 6.53 d (1H, H^6, Ph), 12.29 br.s, 11.91 br.s (1H, NH, OH), 8.73 s

(1H, CH=), 7.85 d (2H, $H^{2,6}$, Ph, $J_{2,3} = J_{6,5}$ 8.65), 6.93 d (2H, $H^{3,5}$, Ph), 3.83 s (3H, OMe).

Hydrazone (V). ^{1}H NMR (DMSO-d_6), δ, ppm: 1.48 s, 1.65 s (6H, 3',3'-Me), 7.38–7.55 m (4H, 4',5',6',7'-Ar), 5.74 d (1H, 3-Ar,, $J_{3,4}$ 9.60 Hz), 6.88 d (1H, 4-Ar), 7.26 d (1H, 5-Ar,, $J_{5,6}$ 8.40 Hz), 6.58 d (1, 6-Ar 12.51 (1H, H^6, Ph), 12.51 br.s, 11.96 br.s (1H, NH, OH), 8.73 s (1H, CH=), 7.75 d (2H, $H^{2,6}$, Ph, $J_{2,3} = J_{6,5}$ 9.00), 6.71 d (2H, $H^{3,5}$, Ph), 2.97 s (6H, NMe_2).

Hydrazone (VI). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s, 1.64 s (6H, 3',3'-Me), 7.30–7.50 m (4H, 4',5',6',7'-Ar), 5.74 d (1H, 3-Ar,, $J_{3,4}$ 9.60 Hz), 6.88 d (1H, 4-Ar), 7.30 d (1H, 5-Ar, $J_{5,6}$ 8.40 Hz), 6.59 d (1H, 6-Ar (1H, H^6, Ph), 12.28 br.s, 12.23 br.s (1H, NH, OH), 8.75 s (1H, CH=), 7.90–7.95 m (2H, $H^{2,6}$, Ph), 7.28–7.40 m (2H, $H^{3,5}$, Ph).

Hydrazone (VII). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s, 1.64 s (6H, 3',3'-Me), 7.30–7.50 m (4H, 4',5',6',7'-Ar), 5.76 d (1H, 3-Ar, $J_{3,4}$ 9.60 Hz), 6.90 d (1H, 4-Ar), 7.30 d (1H, 5-Ar, $J_{5,6}$ 8.40 Hz), 6.60 d (1H, H^6, Ph), 12.28 br.s, 12.23 br.s (1H, NH, OH), 8.75 s (1H, CH=), 7.90–7.95 m (2H, $H^{2,6}$, Ph), 7.28–7.40 m (2H, $H^{3,5}$, Ph).

Hydrazone (VIII). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.51 s, 1.67 s (6H, 3',3'-Me), 7.30–7.50 m (4H, 4',5',6',7'-Ar), 5.63 d (1H, 3-Ar, $J_{3,4}$ 9.60 Hz), 6.80 d (1H, 4-Ar), 7.20 d (1H, 5-Ar, $J_{5,6}$ 8.40 Hz), 6.55 d (1H, 6-Ar (1H, H^6, Ph), 12.33 br.s, 12.08 br.s (1H, NH, OH), 8.78 s (1H, CH=), 8.13 d (2H, $H^{2,6}$, Ph, $J_{2,3} = J_{6,5}$ 8.80), 8.29 d (2H, $H^{3,5}$, Ph).

Hydrazone (IX). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.49 s, 1.66 s (6H, 3',3'-Me), 7.20-7.50 m (4H, 4',5',6',7'-Ar), 5.59 d (1H, 3-Ar, $J_{3,4}$ 9.60 Hz), 6.76 d (1H, 4-Ar), 7.13 d (1H, 5-Ar, $J_{5,6}$ 8.40 Hz), 6.49 d (1H, H^6, Ph), 11.51 br.s, 9.98 br.s, 8.70 br.s (1H, NH, OH), 8.33 s (1H, CH=), 4.77 d (2H, CH_2, J_{HH} 6.00), 7.20–7.50 m (5H, Ph).

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