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Synthesis of Hydrobenzo[*b*]phenanthrolinone Derivatives Proceeding from 8-Aminoquinoline, and Their Spectral and Luminescent Properties

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Abstract—By a three-component condensation of 8-aminoquinoline, aromatic aldehydes, and 1,3-diketones accompanied by the Hofmann–Martius rearrangement hydrobenzophenanthroline derivatives were synthesized. Their spectral and luminescence properties in ethanol solution were investigated at 293 and 77 K.

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The 8-aminoquinoline is the least studied among all the known aminoquinolines. It is known from published data that 8-aminoquinoline in reaction with *para*-substituted benzaldehyde does not provide Schiff bases and forms only aminals [1]. The influence of the unshared electron pair of the endocyclic nitrogen on the negative charge of the adjacent amino group likely prevents the formation of the azomethine bond in the reaction of 8-aminoquinoline with benzaldehyde. As a result of this effect the nucleophilic substitution with the second molecule of 8-aminoquinoline occurs at the carbon atom of benzaldehyde with the formation of aminals. It was formerly noted that in case the isolation of azomethines is difficult or impossible the preparation of heterocyclic products by three-component condensation of initial reagent would be efficient [2, 3].

In this work we performed by the first time the three-component condensation of aldehydes **Ia–Ie** and two 1,3-diketones [5,5-dimethyl-1,3-cyclohexanedione (dimedone) (**II**) and methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**III**)] with 8-aminoquinoline (**IV**).

The goal of our study was the synthesis of new hydrobenzophenanthroline derivatives with substituents providing intense fluorescence [4].

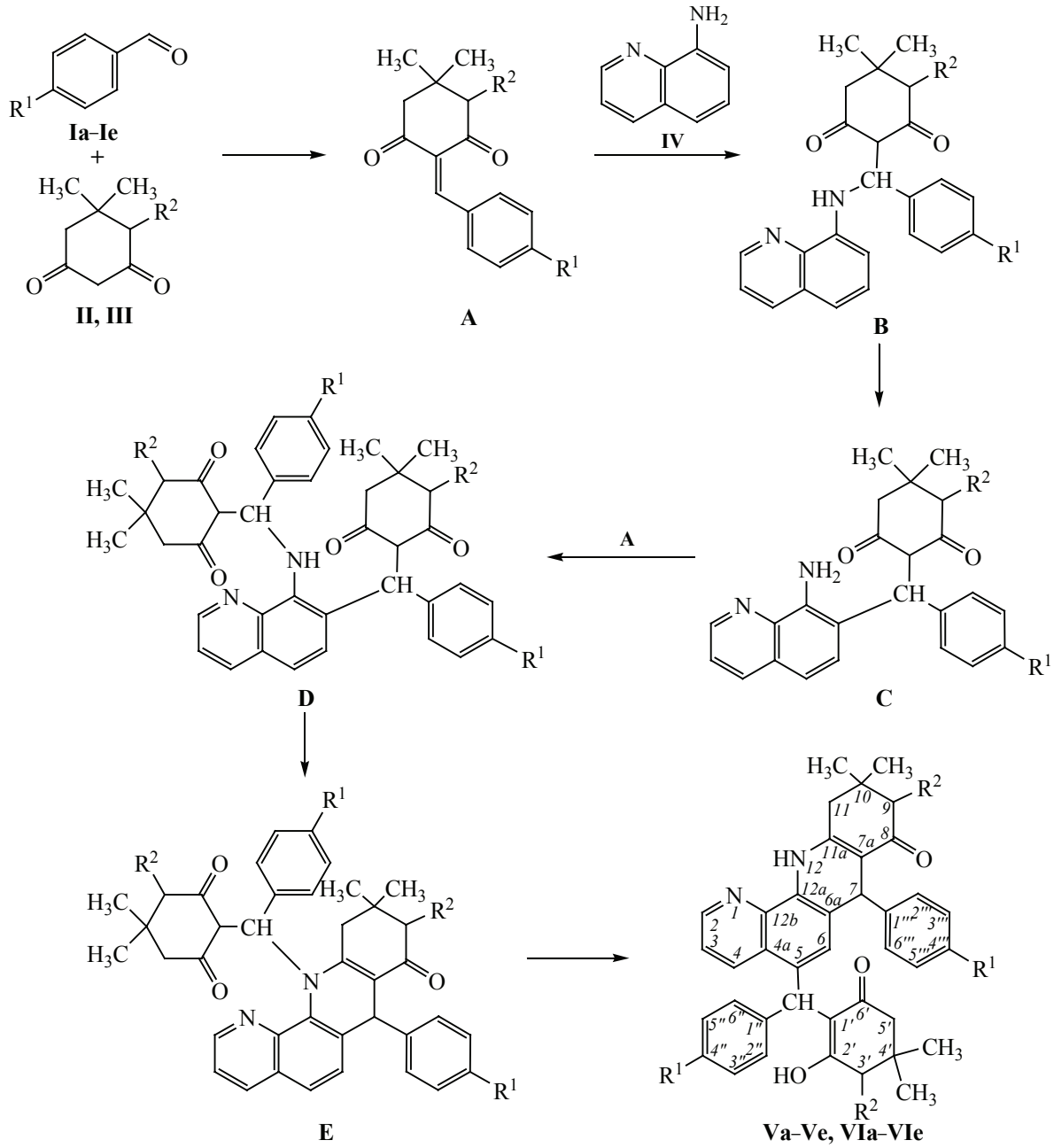
The condensation of aldehydes **Ia–Ie**, 1,3-diketones **II, III**, and 8-aminoquinoline (**IV**) was carried out by boiling equimolar amounts of reagents in ethanol. Formerly unknown 5-[(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(4-R-phenyl)methyl]-10,10-dimethyl-7-(4-R-phenyl)-10,11-dihydrobenzo[*b*][1,10]phenanthrolin-8(5*H*,7*H*,9*H*)-ones **Va–Ve** and methyl 5-[(2-hydroxy-5-(methoxycarbonyl)-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)(4-R-phenyl)methyl]-10,10-dimethyl-8-oxo-7-(4-R-phenyl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-[1,10]phenanthrolin-9-carboxylates **VIa–Ve** were obtained in 51–75% yields.

In the reaction we have investigated it is reasonable to suggest that first aldehydes **Ia–Ie** with diketones **II, III** formed 2-arylidene-5,5-dimethylcyclohexane-1,3-dione **A** that interacts along Mannich reaction with 8-aminoquinoline (**IV**) resulting in an intermediate aminoarylidenediketone **B** which suffers the Hofmann–Martius rearrangement giving compound **C.** Compound **C** adds to the primary amino group the second molecule of arylidenedione **A** providing compound **D**. Further the heterocyclization of the initially added fragment occurs to afford compound **E** which undergoes the Hofmann–Martius rearrangement resulting in the hydrobenzophenanthrolinone derivatives **Va–Ve, VIa–VIe**. The driving force of Hofmann–Martius rearrangement is likely to be the electrostatic repulsion of the electronic cloud of the nitrogen heteroatom from the carbonyl group oxygen

in the arylidenediketone resulting in the decrease of the energy of the molecule and consequently in its more stable state as hydrobenzophenanthrolinone derivatives.

The three-component condensation of aromatic aldehydes **Ia–Ie**, methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**III**), and 8-aminoquinoline (**IV**) proceeded strictly regioselectively. The formation of regioisomers **VIa–VIe** corresponds to the intermediate formation through the reaction at the more accessible (unshielded by the ester substituent) carbonyl group of diketone **III**.

The structure and composition of compounds **Va–Ve, VIa–VIe** were established from the data of ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry, and elemental analysis. The structure of compounds synthesized was confirmed and the assignment of the signal in the NMR spectra was refined by the correlation 2D experiments COSY-45, NO-



R^1 = OH (**a**), OCH_3 (**b**), $N(CH_3)_2$ (**c**), $N(C_2H_5)_2$ (**d**), NO_2 (**e**); R^2 = H (**V**), $COOCH_3$ (**VI**).

ESY, HSQC, and HMCC performed on compound **IVb** which possessed the best solubility in DMSO-d_6 among the synthesized samples. All experimental data were obtained and processed using software XWIN-NMR 3.5.

The ^{1}H NMR spectra of compounds **Va–Ve, VIa–VIe** contain the signals from four methyl groups at 0.87–0.95 (2Me), 0.93–1.03, and 1.00–1.09 ppm; the methyl groups attached to C^{10} appear as one singlet, and at C$^{4'}$, as two singlets. Two doublets of the protons at the atom C^9 are observed at 2.03–2.08 and 2.17–2.21 ppm with the geminal coupling constant ^2J 17 Hz in the spectra of compounds **Va–Ve**. In the spectra of compounds **VIa–VIe** the proton at the atom C^9 gives rise to a singlet at 1.99–2.03 ppm for the *cis*-isomers and a singlet at 2.04–2.09 ppm for *trans*-isomers. Two doublets of protons at 2.56–2.67 and 2.74–2.82 ppm with the geminal constant ^2J 17 Hz belong to the protons at the atom C^{11} in compounds **Va–Ve**, and at signals 2.55–3.04 and 2.62–2.95 ppm correspond to the protons of the *cis*- and *trans*-isomers of compounds **VIa–VIe** respectively. The singlet of the proton linked to the atom C^7 that is characteristic of phenanthrolines spectra apears in the spectra of compounds **Va–Ve** at 4.87–5.30 ppm, and in the spectra of the *cis*- and *trans*-isomers of compounds **VIa–VIe** two singlets at 4.82–5.26 and 4.92–5.33 ppm are observed, respectively. In the spectra of all compounds synthesized also the signals of four protons characteristic of the quinoline ring appear 6.94–8.50, 7.44–7.52, 8.11–8.30 and 8.33–8.90 ppm.

In the mass spectra of obtained hydrobenzophenanthrolinones **Va–Ve, VIa–VIe** the peak of the molecular ion is the most abundant showing the stability of the compound against the electron impact. Also single-charged ions $[M + 1]^+$, $[M - 1]^+$ were detected, characteristic of the fused heteroaromatic compounds.

IR spectra of compounds **Va–Ve, VIa–VIe** contain absorption bands in the region 1612–1589 cm^{-1} characteristic of the stretching vibrations of the carbonyl group. Methylene groups of the cyclohexene rings give rise to two absorption bands at 2930–2910 and 2880–2856 cm^{-1}, the stretching vibrations of CH in aromatic rings appear at 3100–3000 cm^{-1}. The strong band belonging to vibrations of the OCH_3 group is observed in the spectra of compounds **Vb, VIb** in the region 2831 and 2834 cm^{-1}. Characteristic bands of compounds **Ve, VIe** at 1519 and 1430 cm^{-1} correspond respectively to symmetric and antisymmetric vibrations of N–O bond.

Electron absorption spectra in ethanol of compounds synthesized contain a characteristic set of the electronic-

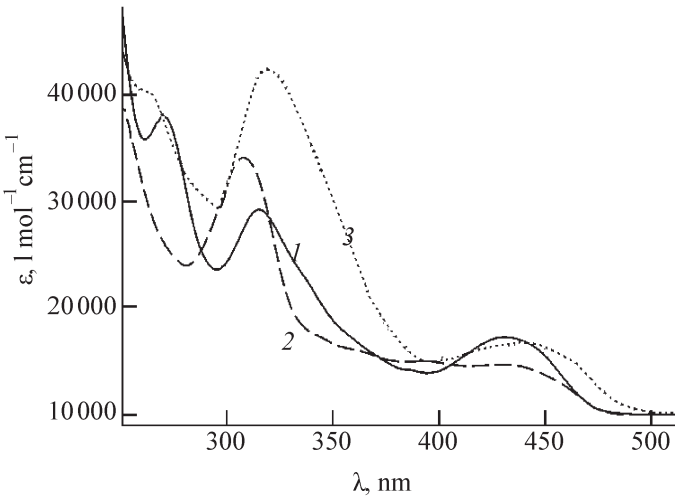


Fig. 1. Electron absorption spectra of compounds **Va** , *1*; **Vc**, *2*; **Ve**, *3* in ethanol, 293 K.

vibration bands in the UV range (Fig. 1, Table 1), which may be divided in three groups. The first group consists of the bands in the range 200–240 nm possessing a high molar extinction factor (ε ~35000 l mol^{-1} cm^{-1}), the bands in the region 240–330 nm (ε 18000–32000 l·mol^{-1}·cm^{-1}) belong to the second group, and weak bands in the region 330–450 nm (ε 5000–8000 l mol^{-1} cm^{-1}) belong to the third group.

The electronic spectra of compounds **Vb, Vd, VIa–VIe** are similar to the EAS of **Va, Vc, Ve**, therefore they are not shown in the figure.

Each of these groups is corresponding to the electron transition $S_n \leftarrow S_0$ (n = 1–3) possessing the respective oscillator strength f calculated by formula (1) [5].

$$f = \frac{4.39\times10^{-9}}{n}\int\varepsilon(\tilde{\nu})\,d\tilde{\nu}. \qquad (1)$$

Here n is the refraction index of the solvent, ν is the wave number. It is clear from the data of f in Table 1 corresponding to the long-wave absorption band (330–450 nm) that the oscillator strengths vary in the range 0.05–0.10. The oscillator strength of the longwave transition $S_1 \leftarrow S_0$ is approximately tenfold less than that of the $S_3 \leftarrow S_0$ transition, and it is proportional to the rate constant (k_f^{calc}) of the radiation transition $S_1 \rightarrow S_0$ calculated from the absorption and fluorescence spectra [6] by formula (2).

$$k_f^{calc} = (2.88\times10^{-9})n^2\int\frac{\varepsilon(\tilde{\nu})(2\tilde{\nu}_0-\tilde{\nu})^3}{\tilde{\nu}}\,d\tilde{\nu}. \qquad (2)$$

Table 1 Spectral and luminescence properties of compounds **Va–Ve, VIa–VIe** in ethanol solution at room temperature

Compound no	Absorption maximum, λ	*f*	$k_f^{calc} \times 10^{-8}$, s^{-1}	Fluorescence maximum, λ	Φ_f
Va	380 (3.9)	0.09	0.70	440	0.0020
Vb	387 (3.7)	0.06	0.45	450	0.0021
Vc	380 (3.4)	0.07	0.52	447	0.0010
Vd	386 (3.8)	0.09	0.65	448	0.0011
Ve	389 (3.8)	0.09	0.65	453	0.0001
VIa	381 (3.7)	0.06	0.45	442	0.0037
VIb	380 (3.6)	0.05	0.40	443	0.0044
VIc	381 (3.6)	0.05	0.39	441	0.0011
VId	379 (3.9)	0.10	0.78	435	0.0007
VIe	368 (3.65)	0.06	0.45	448	0.0001

Here ν is the wave number of the 0-0-transition determined from the crossing of absorption and fluorescence spectra. The k_f^{calc} values given in the table indicate that their variations agree well with the changes in *f* of the long wave $S_1 \leftarrow S_0$ transition. The relatively large values of *f* and k_f^{calc} show that S_1 S_0 is an allowed transition.

It is necessary to note the difference in the EAS of compounds (Fig. 1): At going from **Va** to **Vc,Ve** the absorption spectra broaden. This effect is due to the charge transfer from the dimethylamino group of compound **Vc** to the conjugation system of the molecule in the ground state S_0 and to the electron-withdrawing nitro group from the conjugation system of compound **Ve**.

Fluorescence spectra in ethanol originating from the radiation transition $S_1 \rightarrow S_0$ are characterized by a wide electronic-vibration band with the maxima in the region 430–480 nm (Table 1, Fig. 2). The absorption (*1*) and fluorescence excitation (*2*) spectra coincide (Fig. 2), indicating that the luminescence originates from just the compound possessing the absorption spectrum *1*. Quantum yields of the fluorescence Φ_f listed in the table are very small (10^{-4}–10^{-3}). Consequently, the fluorescence duration is also small τ_f (≤0.1 ns).

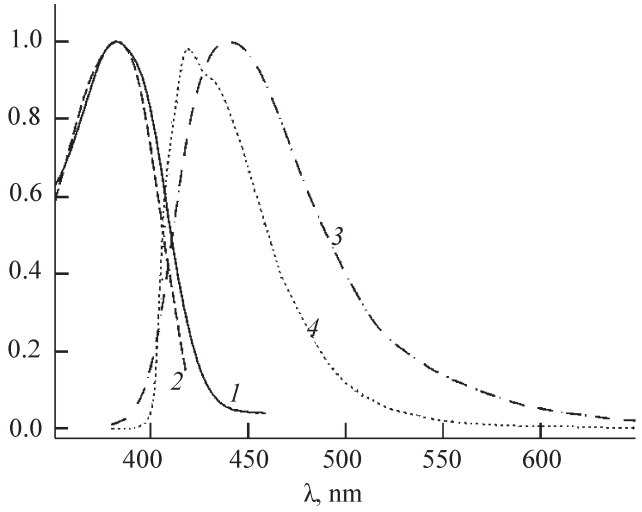


Fig. 2. Absorption (*1*), fluorescence (*3*, *4*, λ_{excit} 380 nm), and fluorescence excitation (*2*, λ_{reg} 450 nm) spectra of compound **Va** in ethanol at 293 K (*1–3*) and 77 K (*4*)

Φ_f of compounds under study in toluene is larger by an order of magnitude and more as compared with Φ_f in ethanol (Table 2). Still the spectral properties of the compounds in ethanol and toluene have close values. The measured values of τ_f made it possible to calculate $k_f = \Phi_f/\tau_f$ (Table 2). The comparison of two last columns of Table 2 shows that the k_f values obtained experimentally and those resulting from the calculation using the absorption and fluorescence spectra are in good agreement. This fact indicates that the fluorescence occurs from the lower singlet-excited state S_1.

The large difference in quantum yield of compounds fluorescence in ethanol and toluene may originate from the existence of an additional electronic excitation state near the singlet excited state S_1 and the quenching of the fluorescence occurs through this additional state. In the polar ethanol this additional state is located nearer to S_1 than in nonpolar toluene. This reasoning is well consistent with Marcus theory [7] that regarded this additional state as the state with the charge transfer. This is supported by the additional quenching of the fluorescence in compounds **Ve, VIe** containing electron-withdrawing group NO_2. This assumption is also consistent with the strong growth of Φ_f at cooling the solution to 77 K. The quantum yield in ethanol increased, e.g., for compounds **Va, VIa** 200-fold and it is estimated at 0.40 and 0.74, respectively. The fluorescence spectrum at 77 K is narrower and displaced to the shortwave region (maximum

Table 2. Spectral and luminescence properties of compounds **Va–Ve, VIa–VIe** in toluene solution at room temperature

Compound no	Absorption maximum, λ, nm	Fluorescence maximum, λ	Φ_f	τ_f, ns	$k_f^{exp} \times 10^{-8}$, s^{-1}	$k_f^{calc} \times 10^{-8}$, s^{-1}
Va	380	452	0.0230	0.42	0.54	0.70
Vb	388	458	0.0210	0.49	0.43	0.45
Vc	380	459	0.0180	0.38	0.47	0.52
Vd	383	459	0.0270	0.57	0.47	0.65
Ve	389	455	0.0092	0.20	0.46	0.65
VIa	381	442	0.0240	0.50	0.48	0.45
VIb	376	442	0.0250	0.53	0.47	0.40
VIc	378	455	0.0200	0.50	0.40	0.39
VId	379	457	0.0260	0.55	0.47	0.78
VIe	369	453	0.0049	0.12	0.41	0.45

of fluorescence at 420 nm).

Thus the spectral and luminescence investigation of compounds **Va–Ve, VIa–VIe** showed that they possess strong oscillators *f* of the allowed electron transitions $S_n \leftarrow S_0$ (n = 1–3). The low quantum yields of the fluorescence of the compounds under study ($\Phi_f \sim 10^{-4}$–10^{-3}) in ethanol, their growth in toluene ($\sim 10^{-2}$) at room temperature and at cooling to 77 K ($\sim 10^{-1}$) are fairly rationalized proceeding from Marcus theory [7], which suggests that the fluorescence quenching occurs through an additional state with the charge transfer. The position of the state with the charge transfer depends on the electronic donor-acceptor properties of the molecule and from the characteristics of the medium (polarity and viscosity). Therefore it seems advisable to explore the luminescence properties of the compounds in rigid polymer matrices at room temperature aiming at making therefrom large flexible fine-film panels suitable for photovoltaic elements, optical filters, and electroluminescence displays.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Avance-500 Bruker–Biospin (operating frequencies 500.13 and 125.77 MHz respectively) from 2–5% solutions in deuterodimethyl sulfoxide, chemical shifts were measured according to the internal TMS standard.

Mass spectra of compounds synthesized were obtained on an instrument Agilent 6890N equipped with a mass-selective detector Agilent 5975 Inert operating in electron impact ionization mode, ionizing electrons energy 70 eV, adjusted to the highest sensitivity to the substances under study. Capillary column HP-5MS (30 m × 0.25 mm × 0.25 μm) was attached directly to the ion source of the spectrometer, the samples were introduced dissolved in dichloromethane.

IR spectra were recorded on an IR Fourier spectrometer Protege-460 Nicolet.

Electron absorption spectra were registered at room temperature on a spectrophotometer Cary-500 (Varian, USA). Fluorescence spectra were measured on an installation described in [8], the concentration of the substance in the solution (in ethanol or toluene) did not exceed 2×10^{-5} mol l^{-1}. Quantum yields of the fluorescence were measured by a relative method using as a standard quinine sulfate dissolved in 1N H_2SO_4 (Φ_f 0.55 [9]). The measurements of the fluorescence duration was performed in the Division of the automation of spectral research of the Physical Institute of the Belarusian National Academy of Sciences on a pulse fluorimeter PRA-3000 operating in the mode of time-correlated photon counting. The error in the measurement of molar extinction factors was ε 20%, fluorescence quantum yields Φ_f, 15%, fluorescence duration τ_f, 10%.

Compounds Va–Ve were prepared by boiling in alcoholic solution a mixture of 0.01 mol of an appropriate aromatic aldehyde **Ia–Ie**, 2.1 g (0.015 mol) of dimedone (**II**), and 1.44 g (0.01 mol) of 8-aminoquinoline (**IV**) till crystals started to separate (30–60 min). On cooling the separated precipitate was filtered off, washed with ether from tar, and recrystallized from the mixture alcohol–benzene, 1:1.

5-[(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-hydroxyphenyl)methyl]-10,10-dimethyl-7-(4-hydroxyphenyl)-10,11-dihydrobenzo[*b*][1,10]phenanthrolin-8(5*H*,7*H*,9*H*)-one (Va). Yield 72%,

yellow crystals, mp 263–264°C. IR spectrum, cm^{-1}: 2950, 1589, 1566, 1509, 1476, 1387, 1315, 1244, 1169, 1148, 1122, 830, 676. ^{1}H NMR spectrum, δ, ppm: 0.91 s [6H, C$^{4'}$(Me)$_2$], 0.96 s (3H, 10-CH$_3$), 1.02 s (3H, 10-CH$_3$), 2.03 d, 2.17 d (2H, C^{9}H$_2$), 1.80–2.50 m (4H, C$^{3'}$H$_2$, C$^{5'}$H$_2$), 2.57 d, 2.77 d (1H, C^{11}H$_2$), 4.87 s (1H, C^{7}H), 5.91 s (1H, CH), 6.49 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.60 d (2H, C$^{3''}$H, C$^{5''}$H), 6.75 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.85 d (2H, C$^{2''}$H, C$^{6''}$H), 6.92 s (1H, C^{6}H), 7.45 s (1H, C^{3}H), 8.11 s (1H, C^{4}H), 8.82 s (1H, C^{2}H), 9.08 s (1H, OH), 9.16 s (1H, OH), 9.49 s (1H, NH), 10.41 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): [*M* + 1]$^+$ 615 (44), [*M*]$^+$ 614(100), [*M* – 1]$^+$ 613 (27), [*M* – OH]$^+$ 597 (16), [*M* – C$_6$H$_4$OH]$^+$ 521 (11). Found, %: C 76.25; H 6.19; N 4.62. $C_{39}H_{38}N_2O_5$. Calculated, %: C 76.20; H 6.23; N 4.56. m 614.28.

5-[(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-methoxyphenyl)methyl]-10,10-dimethyl-7-(4-methoxyphenyl)-10,11-dihydrobenzo[*b*][1,10]phenanthrolin-8(5*H*,7*H*,9*H*)-one (Vb). Yield 64%, yellow crystals, mp 250–251°C. IR spectrum, cm^{-1}: 3302, 2947, 2831, 1608, 1582, 1563, 1508, 1483, 1406, 1386, 1365, 1328, 1300, 1251, 1174, 1147, 1123, 1037, 831, 786. ^{1}H NMR spectrum, δ, ppm: 0.91 s [6H, C$^{4'}$(Me)$_2$], 0.96 s (3H, 10-CH$_3$), 1.02 s (3H, 10-CH$_3$), 2.03 d, 2.17 d (2H, C^{9}H$_2$), 1.90–2.60 m (4H, C$^{3'}$H$_2$, C$^{5'}$H$_2$), 2.56 d, 2.74 d (2H, C^{11}H$_2$), 3.62 s (3H, OCH$_3$), 3.71 s (3H, OCH$_3$), 4.93 s (1H, C^{7}H), 5.97 s (1H, CH), 6.67 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.76 d (2H, C$^{3''}$H, C$^{5''}$H), 6.89 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.92 s (1H, C^{6}H), 6.94 d (2H, C$^{2''}$H, C$^{6''}$H), 7.47 s (1H, C^{3}H), 8.13 s (1H, C^{4}H), 8.82 s (1H, C^{2}H), 9.54 s (1H, NH), 10.52 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 196.19 (C$^{6'}$), 193.59 (C^8), 171.82 (C$^{2'}$), 157.38 (C$^{4''}$), 157.32 (C$^{4'''}$), 151.94 (C^{11a}), 148.09 (C^2), 140.02 (C$^{1'''}$), 137.13 (C^{12b}), 134.86 (C^5), 134.58 (C$^{1''}$), 132.49 (C^4), 129.99 (C$^{2'',6''}$), 129.62 (C^{6a}), 129.23 (C^6), 127.66 (C$^{2''',6'''}$), 125.26 (C^{4a}), 122.35 (C^{12a}), 120.99 (C^3), 115.97 (C$^{1'}$), 113.51 (C$^{3''',5'''}$), 113.23 (C$^{3'',5''}$), 106.88 (C^{7a}), 54.96, 55.02 (OCH$_3$), 50.44 (C^9), 43.38, 50.19 (C$^{3',5'}$), 40.30 (C^{11}), 39.66 (CH), 39.34 (C^7), 32.11 (C^{10}), 31.59 (C$^{4'}$), 26.96, 29.26 (10-CH$_3$), 27.60, 28.18 (4′-CH$_3$). Mass spectrum, *m/z* (I_{rel}, %): [*M* + 1]$^+$ 643 (45), [*M*]$^+$ 642 (100), [*M* – 1]$^+$ 641 (75), [*M* – CH$_3$O]$^+$ 611 (14), [*M* – C$_6$H$_4$OCH$_3$]$^+$ 535 (21). Found, %: C 76.65; H 6.54; N 4.39. $C_{41}H_{42}N_2O_5$. Calculated, %: C 76.61; H 6.59; N 4.36. m 642.31.

5-[(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-(4-dimethylaminophenyl)methyl]-10,10-dimethyl-7-(4-dimethylaminophenyl)-10,11-dihydrobenzo[*b*][1,10]-phenanthrolin-8(5*H*,7*H*,9*H*)-one (Vc). Yield 58%, brown crystals, mp 180–182°C. IR spectrum, cm^{-1}: 3381, 3254, 2953, 2924, 2869, 2800, 1612, 1563, 1517, 1478, 1400, 1385, 1365, 1328, 1247, 1223, 1146, 1124, 1062, 820, 789. ^{1}H NMR spectrum, δ, ppm: 0.93 s (6H, C$^{4'}$Me$_2$), 0.99 s (3H, 10-CH$_3$), 1.04 s (3H, 10-CH$_3$), 2.08 d, 2.19 d (2H, C^{9}H$_2$), 1.90–2.50 m (4H, C$^{3'}$H$_2$, C$^{5'}$H$_2$), 2.61 d (1H, C^{11}H$_2$), 2.73 s (12H, 2NMe$_2$), 2.78 d (1H, C^{11}H$_2$), 4.85 s (1H, C^{7}H), 5.90 s (1H, CH), 6.39 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.54 d (2H, C$^{3''}$H, C$^{5''}$H), 6.75 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.89 d (2H, C$^{2''}$H, C$^{6''}$H), 7.02 s (1H, C^{6}H), 7.46 s (1H, C^{3}H), 8.18 s (1H, C^{4}H), 8.82 s (1H, C^{2}H), 9.40 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): [*M* + 1]$^+$ 669 (33), [*M*]$^+$ 668 (100), [*M* – 1]$^+$ 667 (62), [*M* – N(CH$_3$)$_2$]$^+$ 624 (18), [*M* – C$_6$H$_4$N(CH$_3$)$_2$]$^+$ 548 (11). Found, %: C 77.19; H 7.28; N 8.42. $C_{43}H_{48}N_4O_3$. Calculated, %: C 77.21; H 7.23; N 8.38. m 668.37.

5-[(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-(4-diethylaminophenyl)methyl]-10,10-dimethyl-7-(4-diethylaminophenyl)-10,11-dihydrobenzo-[*b*]-[1,10]phenanthrolin-8(5*H*,7*H*,9*H*)-one (Vd). Yield 53%, brown crystals, mp 227°C. IR spectrum, cm^{-1}: 3385, 3256, 2963, 2927, 2889, 2869, 1610, 1584, 1564, 1516, 1481, 1366, 1327, 1262, 1196, 1170, 1148, 1122, 1068, 1024, 1012, 783. ^{1}H NMR spectrum, δ, ppm: 0.93 s (6H, C$^{4'}$Me$_2$), 0.99 s (3H, 10-Me), 1.04 s (3H, 10-Me), 1.07 t [6H, N(CH$_2$<u>Me</u>)$_2$], 2.08 d, 2.19 d (2H, C^{9}H$_2$), 2.05–2.60 m (4H, C$^{3'}$H$_2$, C$^{5'}$H$_2$), 2.61 d, 2.78 d (2H, C^{11}H$_2$), 3.32 q [4H, N(<u>CH$_2$</u>Me)$_2$], 4.85 s (1H, C^{7}H), 5.90 s (1H, CH), 6.39 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.54 d (2H, C$^{3''}$H, C$^{5''}$H), 6.75 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.89 d (2H, C$^{2''}$H, C$^{6''}$H), 7.02 (1H, C^{6}H), 7.46 s (1H, C^{3}H), 8.18 s (1H, C^{4}H), 8.82 s (1H, C^{2}H), 9.40 s (1H, NH), 10.39 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): [*M* + 1]$^+$ 723 (55), [*M*]$^+$ 724 (100), [*M* – 1]$^+$ 723 (59), [*M* – N(C$_2$H$_5$)$_2$]$^+$ 652 (11), [*M* – C$_6$H$_4$N(C$_2$H$_5$)$_2$]$^+$ 576 (48). Found, %: C 77.90; H 7.75; N 7.78. $C_{47}H_{56}N_4O_3$. Calculated, %: C 77.87; H 7.79; N 7.73. m 724.44.

5-[(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-nitrophenyl)methyl]-10,10-dimethyl-7-(4-nitrophenyl)-10,11-dihydrobenzo[*b*][1,10]phenanthrolin-8(5*H*,7*H*,9*H*)-one (Ve). Yield 75%, yellow crystals, mp 258–259°C. IR spectrum, cm^{-1}: 3381, 3249, 3067, 2957, 2928, 2888, 2869, 1624, 1582, 1564, 1519, 1482, 1405, 1386, 1346, 1253, 1225, 1150, 1109, 1016, 855, 790. ^{1}H NMR spectrum, δ, ppm: 0.98 s [6H, 4′-Me$_2$], 1.03 s (3H, 10-Me), 1.04 s (3H, 10-Me), 2.08 d, 2.21 d (2H, C^{9}H$_2$), 2.05–2.60 m (2H, C$^{3'}$H$_2$, C$^{5'}$H$_2$), 2.67 d, 2.82 d (1H, C^{11}H$_2$), 5.30 s (1H, C^{7}H), 6.19 s (1H, CH), 6.97 s (1H, C^{6}H), 7.99 d (2H, C$^{3'''}$H, C$^{5'''}$H), 8.05 d (2H,

C$^{3''}$H, C$^{5''}$H), 7.12 d (2H, C$^{2'''}$H, C$^{6'''}$H), 7.35 d (2H, C$^{2''}$H, C$^{6''}$H), 7.52 s (1H, C^{3}H), 8.12 s (1H, C^{4}H), 8.90 s (1H, C^{2}H), 9.74 s (1H, NH), 10.76 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 673 (65), $[M]^+$ 672 (100), $[M - 1]^+$ 671 (58), $[M - NO_2]^+$ 626 (23), $[M - C_6H_4NO_2]^+$ 550 (53). Found, %: C 69.60; H 5.44; N 8.38. $C_{39}H_{36}N_4O_7$. Calculated, %: C 69.63; H 5.39; N 8.33. m 672.26.

Compounds VIa–VIe were obtained analogously using methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**III**).

Methyl 5-[(2-hydroxy-4,4-dimethyl-5-methoxycarbonyl-6-oxocyclohex-1-enyl)(4-hydroxyphenyl) methyl]-7-(4-hydroxyphenyl)-10,10-dimethyl-8-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*][1,10]phenanthrolin-9-carboxylate (VIa). Yield 62%, yellow crystals, mp 195–196°C. IR spectrum, cm^{-1}: 3460, 3358, 3000, 2947, 2928, 2850, 2836, 1734, 1610, 1512, 1482, 1437, 1389, 1371, 1320, 1246, 1178, 1150, 1102, 1032, 934, 825, 793. ^{1}H NMR spectrum, δ, ppm: 0.87 s (6H, C$^{4'}$Me$_2$), 0.93 s (3H, 10-Me), 1.00 s (3H, 10-Me), 2.03 s (1H, C^{9}H, *cis*-isomer), 2.08 s (1H, C^{9}H, *trans*-isomer), 2.15 d (2H, C$^{5'}$H$_2$), 2.42 s (1H, C$^{3'}$H, *cis*-isomer), 2.46 s (1H, C$^{3'}$H, *trans*-isomer), 2.77 d (1H, C^{11}H$_2$, *cis*-isomer), 2.84 d (1H, C^{11}H$_2$, *trans*-isomer), 2.95 d (1H, C^{11}H$_2$, *trans*-isomer), 3.04 d (1H, C^{11}H$_2$, *cis*-isomer), 4.86 s (1H, C^{7}H, *cis*-isomer), 4.93 s (1H, C^{7}H, *trans*-isomer), 5.97 s (1H, CH), 6.60 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.75 d (2H, C$^{3''}$H, C$^{5''}$H), 6.79 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.85 d (2H, C$^{2''}$H, C$^{6''}$H), 6.94 s (1H, C^{6}H), 7.45 s (1H, C^{3}H), 8.25 s (1H, C^{4}H), 8.45 s (1H, C^{2}H), 9.08 s (1H, OH), 9.16 s (1H, OH), 9.46 s (1H,NH, *cis*-isomer), 9.48 s (1H, NH, *trans*-isomer), 10.41 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 730 (32), $[M]^+$ 730 (100), $[M - 1]^+$ 729 (43), $[M - OH]^+$ 713 (22), $[M - C_6H_4OH]^+$ 637 (18). Found, %: C 70.70; H 5.73; N 3.78. $C_{43}H_{42}N_2O_9$. Calculated, %: C 70.67; H 5.79; N 3.83. m 730.29.

Methyl 5-[(2-hydroxy-5-methoxycarbonyl-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-methoxyphenyl) methyl]-7-(4-methoxyphenyl)-10,10-dimethyl-8-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-[1,10]phenanthrolin-9-carboxylate (VIb). Yield 60%, yellow crystals, mp 250–251°C. IR spectrum, cm^{-1}: 3463, 3363, 2949, 2923, 2834, 1737, 1607, 1508, 1479, 1441, 1369, 1315, 1301, 1248, 1174, 1157, 1107, 1034, 929, 820, 791. ^{1}H NMR spectrum, δ, ppm: 0.94 s (6H, C$^{4'}$Me$_2$), 0.98 s (3H, 10-Me), 1.02 s (3H, 10-Me), 2.03 s (1H, C^{9}H, *cis*-isomer), 2.09 s (2H, C^{9}H, *trans*-isomer), 2.18 d (2H, C$^{5'}$H$_2$), 2.48 s (1H, C$^{3'}$H, *cis*-isomer), 2.54 s (1H, C$^{3'}$H, *trans*-isomer), 2.69 d (1H, C^{11}H$_2$, *cis*-isomer), 2.74 d (1H, C^{11}H$_2$, *trans*-isomer), 2.78 d (1H, C^{11}H$_2$, *trans*-isomer), 2.95 d (1H, C^{11}H$_2$, *cis*-isomer), 3.61 s (3H, OCH$_3$), 3.69 s (3H, OCH$_3$), 4.92 s (1H, C^{7}H, *cis*-isomer), 4.98 s (1H, C^{7}H, *trans*-isomer), 5.99 s (1H, CH), 6.63 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.68 d (2H, C$^{3''}$H, C$^{5''}$H), 6.84 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.97 d (2H, C$^{2''}$H, C$^{6''}$H), 7.48 s (1H, C^{3}H), 8.13 s (1H, C^{4}H), 8.33 s (1H, C^{2}H), 8.50 s (1H, C^{6}H), 10.46 s (1H, OH), 11.71 s (1H, NH, *cis*-isomer), 11.73 s (1H, NH, *trans*-isomer). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 759 (42), $[M]^+$ 758 (100), $[M - 1]^+$ 757 (75), $[M - CH_3O]^+$ 727(23), $[M - C_6H_4OCH_3]^+$ 651 (10). Found, %: C 71.28; H 6.07; N 3.66. $C_{45}H_{46}N_2O_9$. Calculated, %: C 71.22; H 6.11; N 3.69. m 758.32.

Methyl 5-[(2-hydroxy-5-methoxycarbonyl-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-dimethylaminophenyl) methyl]-7-(4-dimethylaminophenyl)-10,10-dimethyl-8-oxo-7,8,9,10,11,12-hexahydro-benzo[*b*][1,10]phenanthrolin-9-carboxylate (VIc). Yield 51%, dark brown crystals, mp 168–169°C. IR spectrum, cm^{-1}: 3372, 2950, 2924, 2871, 2798, 1731, 1610, 1518, 1506, 1477, 1427, 1367, 1317, 1267, 1248, 1156, 1127, 1059, 1027, 947, 820, 789. ^{1}H NMR spectrum, δ, ppm: 0.93 s (6H, C$^{4'}$Me$_2$), 0.98 s (3H, 10-Me), 1.09 s (3H, 10-Me), 1.99 s (1H, C^{9}H, *cis*-isomer), 2.04 s (1H, C^{9} H, *trans*-isomer), 2.15 d (2H, C$^{5'}$H$_2$), 2.43 s (1H, C$^{3'}$H, *cis*-isomer), 2.46 s (1H, C$^{3'}$H, *trans*-isomer), 2.55 d (1H, C^{11}H$_2$, *cis*-isomer), 2.62 d (1H, C^{11}H$_2$, *trans*-isomer), 2.65 d (1H, C^{11}H$_2$, *trans*-isomer), 2.70 d (1H, C^{11}H$_2$, *cis*-isomer), 2.73 s [12H, N(CH$_3$)$_2$], 4.82 s (1H, C^{7}H, *cis*-isomer), 4.88 s (1H, C^{7}H, *trans*-isomer), 5.81 s (1H, CH), 6.49 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.64 d (2H, C$^{3''}$H, C$^{5''}$H), 6.81 d (2H, C$^{2'''}$H, C$^{6'''}$H), 7.02 d (2H, C$^{2''}$H, C$^{6''}$H), 7.09 s (1H, C^{6}H), 7.51 s (1H, C^{3}H), 8.23 s (1H, C^{4}H), 8.35 s (1H, C^{2}H), 10.12 s (1H, OH), 10.37 s (1H, NH, *cis*-isomer), 10.43 s (1H, NH, *trans*-isomer). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 785 (22), $[M]^+$ 784 (100), $[M - 1]^+$ 783 (53), $[M - N(CH_3)_2]^+$ 740 (18), $[M - C_6H_4N(CH_3)_2]^+$ 664 (23). Found, %: C 71.89; H 6.63; N 7.09. $C_{47}H_{52}N_4O_7$. Calculated, %: C 71.92; H 6.68; N 7.14. m 784.38.

Methyl 5-[(2-hydroxy-5-methoxycarbonyl-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-diethylaminophenyl) methyl]-7-(4-diethylaminophenyl)-10,10-dimethyl-8-oxo-7,8,9,10,11,12-hexahydro-benzo[*b*][1,10]phenanthrolin-9-carboxylate (VId). Yield 52%, dark brown crystals, mp 238–239°C. IR spectrum, cm^{-1}: 3380, 3248, 2957, 2931, 2889, 1613, 1586, 1561, 1522, 1493, 1488, 1366, 1329, 1265, 1196, 1177, 1156, 1123, 1064, 1011,

793. ^{1}H NMR spectrum, δ, ppm: 0.95 s (6H, C$^{4'}$Me$_2$), 1.00 s (3H, 10-Me), 1.04 s (3H, 10-Me), 1.11 t [6H, N(CH$_2$CH$_3$)$_2$], 2.01 s (2H, C^{9}H, *cis*-isomer), 2.09 s (2H, C^{9}H, *trans*-isomer), 2.21 d (2H, C$^{5'}$H$_2$), 2.42 s (1H, C$^{3'}$H, *cis*-isomer), 2.47 s (1H, C$^{3'}$H, *trans*-isomer), 2.64 d (1H, C^{11}H$_2$, *cis*-isomer), 2.70 d (1H, C^{11} H$_2$, *trans*-isomer), 2.75 d (1H, C^{11} H$_2$, *trans*-isomer), 2.90 d (1H, C^{11}H$_2$, *cis*-isomer), 3.35 q [4H, N(CH$_2$CH$_3$)$_2$], 4.83 s (1H, C^{7}H, *cis*-isomer), 4.92 s (1H, C^{7}H, *trans*-isomer), 5.90 s (1H, CH), 6.54 d (2H, C$^{3'''}$H, C$^{5'''}$H), 6.78 d (2H, C$^{3''}$H, C$^{5''}$H), 6.84 d (2H, C$^{2'''}$H, C$^{6'''}$H), 6.97 d (2H, C$^{2''}$H, C$^{6''}$H), 7.05 s (1H, C^{6}H), 7.44 s (1H, C^{3}H), 8.30 s (1H, C^{4}H), 8.38 s (1H, C^{2}H), 10.37 s (1H, OH), 10.42 s (1H, NH, *cis*-isomer), 10.45 s (1H, NH, *trans*-isomer). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 841 (30), $[M]^+$ 40(100), $[M - 1]^+$ 839 (47), $[M - N(C_2H_5)_2]^+$ 768 (25), $[M - C_6H_4N(C_2H_5)_2]^+$ 706 (42). Found, %: C 72.86; H 7.15; N 6.64. $C_{51}H_{60}N_4O_7$. Calculated, %: C 72.83; H 7.19; N 6.66. m 840.45.

Methyl 5-[(2-hydroxy-5-methoxycarbonyl-4,4-dimethyl-6-oxocyclohex-1-enyl)(4-nitrophenyl) methyl]-7-(4-nitrophenyl)-10,10-dimethyl-8-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*][1,10]phenanthrolin-9-carboxylate (VIe). Yield 71%, brown crystals, mp 273–275°C. IR spectrum, cm^{-1}: 3469, 3372, 3067, 2955, 2872, 1731, 1605, 1594, 1514, 1479, 1430, 1370, 1344, 1263, 1190, 1157, 1108, 1014, 854, 824, 788. ^{1}H NMR spectrum, δ, ppm: 0.92 s (6H, C$^{4'}$Me$_2$), 0.96 s (3H, 10-Me), 1.07 s (3H, 10-Me), 2.01 s (1H, C^{9}H, *cis*-isomer), 2.07 s (1H, C^{9}H, *trans*-isomer), 2.22 d (2H, C$^{5'}$H$_2$), 2.35 s (1H, C$^{3'}$H, *cis*-andзO-mep), 2.41 s (1H, C$^{3'}$H, *trans*-isomer), 2.57 d (1H, C^{11}H$_2$, *cis*-isomer), 2.64 d (1H, C^{11}H$_2$, *trans*-isomer), 2.70 d (1H, C^{11}H$_2$, *trans*-isomer), 2.76 d (1H, C^{11}H$_2$, *cis*-isomer), 5.26 s (1H, C^{7}H, *cis*-isomer), 5.33 s (1H, C^{7}H, *trans*-isomer), 6.18 s (1H, CH), 7.03 s (1H, C^{6}H), 7.12 d (2H, C$^{2'''}$H, C$^{6'''}$H), 7.30 d (2H, C$^{2''}$H, C$^{6''}$H), 7.51 C (1H, C^{3}H), 7.89 d (2H, C$^{3'''}$H, C$^{5'''}$H), 8.10 d (2H, C$^{3''}$H, C$^{5''}$H), 8.30 s (1H, C^{4}H), 8.52 s (1H, C^{2}H), 9.76 s (1H, OH), 10.73 s (1H, NH, *cis*-isomer), 10.75 s (1H, NH, *trans*-isomer). Mass spectrum, *m/z* (I_{rel}, %): $[M + 1]^+$ 789 (72), $[M]^+$ 788 (100), $[M - 1]^+$ 787 (44), $[M - NO_2]^+$ 742 (11), $[M - C_6H_4NO_2]^+$ 666 (49). Found, %: C 65.43; H 5.15; N 7.06. $C_{43}H_{40}N_4O_{11}$. Calculated, %: C 65.47; H 5.11; N 7.10. m 788.27.

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