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Synthesis of 4,7-Phenanthroline Methyl Derivatives

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Abstract—6-Aminoquinaldine condensation with aromatic aldehydes and cyclic β-diketones (1,3-cyclohexanedione or dimedone) in butanol afforded new 12-aryl-3-methyl-8,9,10,12-tetrahydro-7H-benzo[*b*][4,7]phenanthrolin-11-ones and their 9,9-dimethyl derivatives.

Methyl derivatives of 4,7-phenanthroline are not yet sufficiently understood despite the published information on their possible application as respiration stimulators [1], bactericides [2], diagnostics for leucocytes and erythrocytes [3, 4], and initial compounds for synthesis of aldehydes, styryles, and dyes [5–8].

The known Debner–Miller procedure for preparation of methyl-substituted nitrogen-containing heterocycles involving reaction between an aromatic amine and α,β-unsaturated carbonyl compounds (methyl vinyl ketone, crotonaldehyde), or with their precursors (acetone, formaldehyde, paraldehyde) did not find appreciable application to the synthesis of 4,7-phenanthrolines proceeding from *p*-phenylenediamine or 6-quinolylamine due to the low yield of target product because the initial amines showed limited reactivity in this reaction, and thus prevailed condensation and polymerization of carbonyl compounds.

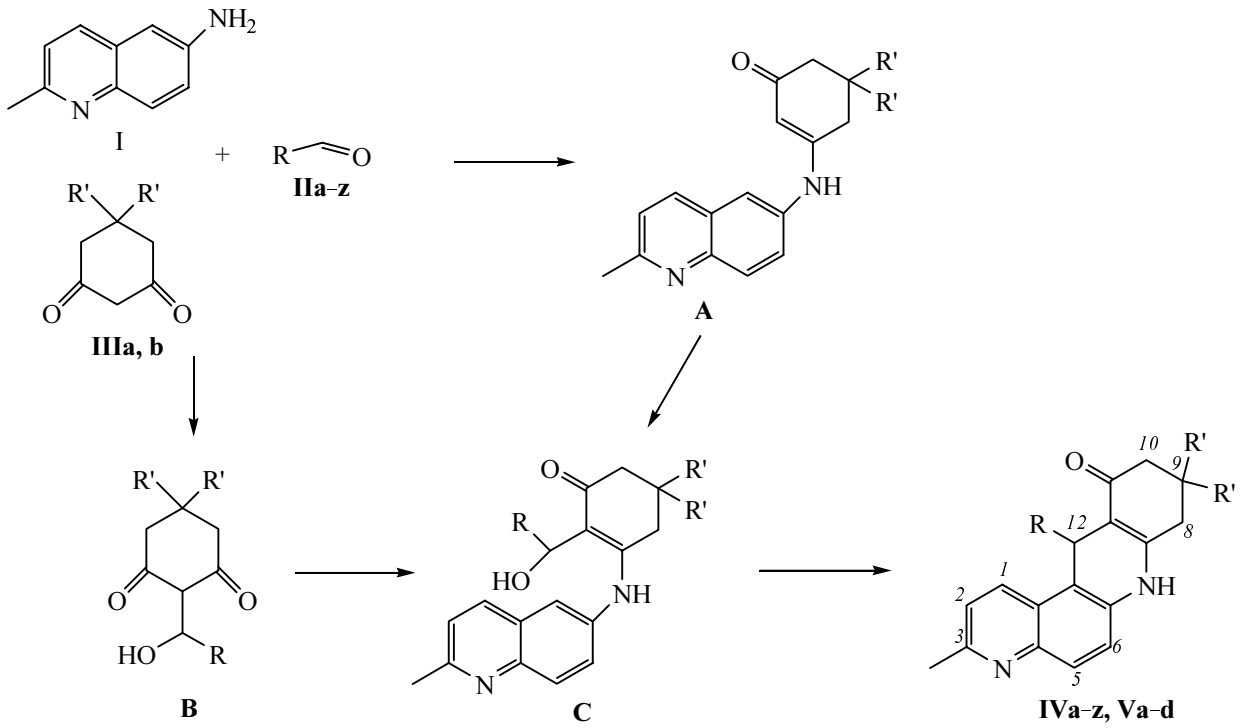
In this connection we developed a new approach to building up the methylphenanthroline structure based on introduction in the phenanthroline molecule of a methylquinoline fragment applying 6-aminoquinaldine as an initial compound. We formerly developed efficient synthetic methods for 4,7-phenanthroline derivatives by reacting 6-aminoquinoline with aromatic aldehydes and CH-acids of the aliphatic-aromatic and alicyclic series [9, 10]. In this study aiming at preparation methyl substituted 4,7-phenanthrolines we for the first time investigated a three-component condensation of 6-aminoquinaldine (**I**) with arylaldehydes **II** and cyclic β-diketones, 1,3-cyclo-hexanedione (**IIIa**) and dimedone (**IIIb**).

6-Aminoquinaldine (**I**)was prepared by reducing 6-nitro-quinaldine [11] with tin(II) chloride in a mixture of acetic and hydrochloric acids.

The condensation of amine **I** with aldehydes **II** and diones **IIIa, b** was carried out by boiling in butanol equimolar amounts of reagents. Due to the high reactivity of the β-dicarbonyl compound its reaction with amine and aldehyde in the alcohol environment did not require a catalyst, for the role of the latter played the proton of the dissociated enol form of the β-diketone. As a result the reaction afforded selectively in 43–92% yield previously unknown 12-aryl-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*]-[4,7]phenanthrolin-11-ones **IVa–z** and their 9-dimethyl derivatives **Va–d**.

We believe that the formation of benzo[*b*]-phenanthrolines **IV** and **V** occurs either through reaction of 6-aminoquinaldine (**I**) with diones **IIIa, b** giving enamine **A** that subsequently undergoes the condensation with aldehydes **II**, or by interaction of aminoquinaldine (**I**) with 2-arylmethylene-1,3-cyclohexanedione **B** arising from condensation of diketones **IIIa, b** with aldehyde **II**. Both processes involve formation of the same intermediate **C** that undergoes dehydrocyclization into the system of 3-methyl-substituted benzo[*b*][4,7]-phenanthroline.

The R substituent in aldehyde molecule exerts some influence on the yield of target reaction products **IVa–x**. Benzaldehydes **IIc, d, f, j–l, n, o, r** containing in the *ortho*- and *para*-positions of the phenyl ring halogen atoms, alkoxy and alkoxycarbonyl groups that activate the aldehyde molecule due to *–I*- or *–I*- and *–M*-effect afforded high yield of reaction products **IVc, d, f, j–l, n, o, r** and **Vb, c**). A fairly high yield of phenanthrolines **IVw–y** was obtained with pyridine- and thiophenecarbaldehydes **IIw–y**. Here the increase in polarization and reactivity of the C=O bond of the aldehyde molecule occurs due to the *–I*-effect of the nitrogen or sulfur in the heterocyclic ring. The replacement of a cyclohexene



R = Ph (**IIa, IVa**), 2-MeC_6H_4 (IIb, IVb), 4-FC_6H_4 (**IIc, IVc**), 4-ClC_6H_4 (**IId, IVd**), 2,3-$Cl_2C_6H_3$ (**IIe, IVe, Va**), 2,4-$Cl_2C_6H_3$ (**IIe, IVe, Vb**), 2-$CF_3C_6H_4$ (**IIg, IVg**), 4-HOC_6H_4 (**IIh, IVh**), 3,4-$(HO)_2C_6H_3$ (**IIi, IVi**), 4-$(MeO)C_6H_4$ (**IIj, IVj**), 2,4-$(MeO)_2C_6H_3$ (**IIk, IVk**), 2,5-$(MeO)_2C_6H_3$ (**IIl, IVl**), 3,4-$(MeO)_2C_6H_3$ (**IIm, IVm**), 3,4,5-$(MeO)_3C_6H_2$ (**IIn, IVn, Vc**), 4-$PrOC_6H_4$ (**IIo, IVo**), 3,4-$CM_2N_2C_6H_3$ (**IIp, IVp**), 4-$MeSC_6H_4$ (**IIq, IVq**), 4-$MeO_2CC_6H_4$ (**IIr, IVr**), 3-MeN-4-$MeNCNC_6H_3$ (**IIs, IVs**), 3-MeN-4-$PhCH_2OC_6H_3$ (**IIt, IVt**), 4-PhC_6H_4 (**IIu, IVu**), 4-$PhCH_2OC_6H_4$ (**IIv, IVv, Vd**), 2-pyridyl (**IIw, IVw**), 3-pyridyl (**IIx, IVx**), 3-methyl-2-thienyl (**IIy, IVy**), cyclohexen-4-yl (**IIz, IVz**); R^1 = H (**IIIa, IVa–z**), Me (**IIIb, Va–d**).

ring for the phenyl in the aldehyde molecule resulted in lower yield of phenanthroline **IVz** presumably caused by difficult separation of the reaction product from the tarry substances formed by polymerization of the initial aldehyde. The introduction of methyl groups into diketone **IIIb** molecule essentially did not affect the yield of methylphenanthrolines.

The synthesized methyl derivatives of 4,7-phenanthroline **IVa–z** and **Va–d** are high-melting crystalline colorless or light-yellow substances. Their IR spectra contain characteristic absorption bands of stretching vibrations of NH and CO groups at 3290–3195 and 1625–1580 cm^{-1} respectively. The stretching vibrations of alkyl groups and alicyclic C–H bonds give rise to absorption in the region of 2960–2870 cm^{-1}, those of the C–H bonds in the aromatic rings appear at 3060–3030 cm^{-1}. In the IR spectra of compounds **IVq–p, r–t, v, Vc, d** the bands of the fragment C–O–C are observed in the region 1240–1230 Cm^{-1}, in the spectrum of compound **IVq** the strong band of the stretching vibrations of C–S bond is seen at 1125 cm^{-1}, in the spectra of phenanthrolines **IVr, s** the band of C=O in the ester group appears at 1725–1720 cm^{-1}.

The electron absorption bands in the spectra of compounds **IVa–z** and **Va–d** are located in the UV region and possess a pronounced vibronic structure. The molecules of benzo[*b*]phenanthrolinones **IVa–z** and **Va–d** contain three independent chromophore fragments: an aryl substituent, a carbonyl group, and a quinoline ring. The latter provides the main contribution into the system of π–π*-electron transitions. In this connection the bands of λ_{max} 212–220, 240–255, 292–296 nm may be assigned to the system of 6-quinolylamine [UV spectrum, λ_{max} nm (log ε): 206(4.08), 247 (4.35), 279 (3.59)]. The notable red shift and the increased intensity of the first and third bands in the spectra of phenanthrolinones **IVa–z** and **Va–d** are likely to originate from superposition of absorption bands of the phenyl, heteroaromatic, or cyclohexenyl substituent R. The appearance of absorp-tion bands in the long-wave spectral region (331–340, 370–388 nm) is due according to [12] to the presence of a carbonyl group. The substituents in the phenyl ring of compounds **IVa–v**

and **Va–d** almost do not affect the position and intensity of the spectral bands.

The mass spectra of benzophenanthrolineones **IVa–x** contain molecular ion peaks $[M]^+$ (I_{rel} 14–48%). The most abundant (100%) in the spectra is the peak of ion $[M-R]^+$ (*m/z* 263 for compounds **IVa–z** and *m/z* 291 for phenanthrolines **Va–d**). In the spectra of all phenanthrolines a peak of ion with *m/z* 207 (8–28%) is present corresponding to elimination from the ion $[M-R]^+$ of a fragment CH_2CH_2CO for compounds **IVa–z** and $(CH_3)_2CHCH_2CO$ for dimethyl derivatives **Va–d**.

The ^{1}H NMR spectra of compounds **IVa–z** and **Va–d** with respect to positions and multiplicity of signals from the aromatic protons of the phenanthroline skeleton are identical to the previously published spectra of the 4,7- phenanthrolines [9, 10]. The methine proton (H^{12}) of the dihydropyridine ring gives rise to a singlet at 5.46–6.06 ppm. The downfield shift of this signal compared to the usual position of the methine protons signals in the cyclic compounds [13] is due to the anisotropic effect of the contiguous aromatic ring. This effect is confirmed by the fact that in the spectrum of phenanthroline **IVz** with a cyclohexenyl and not an aromatic substituent the signal of H^{12} atom suffers the smallest downfield shift and in the phenanthroline series **IVa–z** is located in the most upfied position (5.46 ppm). Anisotropic influence of fragments attached to the phenyl ring of the R substituent affects mainly the aromatic protons of the latter. However in the spectra of compounds **IVe, f, k, l, Va, b** containing in the *ortho*-position of the phenyl ring a chlorine atom or a methoxy group, and also in the spectrum of 2-pyridyl-substituted 4,7- phenanthroline **IVw** a downfield shift of signals of protons H^1 and H^{12} belonging to the phenanthroline skeleton is observed originating from the reduced shielding of these atoms due to the strong *–I*-effect of the above substituents and the nitrogen in the position *2* of the pyridine ring. The substituents containing electronegative atoms similarly affected the position of the H^2 proton from the phenanthroline skeleton in the spectra of 1,3-diaryl-4,7-phenanthrolines [9].

Hence the three-component condensation of 6-aminoquinaldine, aromatic aldehyde, and cyclic β-diketone provides a convenient one-stage synthetic procedure leading to a wide range of difficultly available methyl derivatives of 4,7-phenanthroline. According to this procedure in some cases the methyl groups are introduces into the phenanthroline molecule via dimedone and aldehyde synthons. However the most interesting methyl group in the structure of 4,7-phenanthroline is that in the quinaldine fragment which is present in all condensation products obtained. This group possesses a high synthetic potential for preparation of new compounds with practically useful properties.

EXPERIMENTAL

Mass spectra were measured on Finnigan MAT. INCOS-50 instrument at the ionizing electrons energy 70 eV. IR spectra were recorded of Fourier spectrometer Nicolet Protege-460. ^{1}H NMR spectra were registered on spectrometers AC-500 (500 MHz, Bruker) and Tesla BS-567 (100 MHz) in DMSO-d_6; internal reference TMS. UV spectra were taken from solutions of compounds in ethanol (C 10^{-4} mol l^{-1}) on spectrometer Specord UV-Vis. The melting points were measured on a Koeffler heating block.

6-Aminoquinaldine (I). A solution of 70 g of tin(II) chloride dihydrate in 200 ml of concn. hydrochloric acid was added at stirring to a solution of 20 g of 6-nitroquinaldine in 200 ml of glacial acetic acid. The mixture self-heated to 60–70°C. After stirring at this temperature for 10 min the reaction mixture was cooled to room temperature, the separated precipitate was filtered off, washed with 40–50 ml of glacial acetic acid, dried, and thereto was added at stirring 25% solution of NaOH till neutral reaction. The precipitate was filtered off and dried. The reaction product was extracted from the precipitate by toluene. We obtained 49.3 g (85%) of 6-aminoquinaldine (**I**), mp 190.5–191°C (publ.: mp 190–191°C [14]).

12-Aryl(heteryl-,cyclohexen-4-yl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin -11-ones (IVa–z) and 12-aryl-3,9,9-trimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones (Va–d). A solution of 5 mmol of 6-aminoquinaldine (**I**), 5 mmol of an appropriate aldehyde **IIa–z**, and 5 mmol of 1,3-diketone **IIIa, b** in 20 ml of 1-butanol was heated at reflux for 3–4 h. The separated precipitate was filtered off, compounds (**IVa, b, e–h, k–q, u, v, x–z, Va–d** were recrystallized from a mixture ethanol–benzene, 2:1, phenanthrolines **IVc, d, j, w** were recrystallized from ethanol, substances **IVi, r–t** from DMF.

3-Methyl-12-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVa). Yield 70%, mp 293–294°C. ^{1}H NMR spectrum, δ, ppm: 1.89 m ($2H^9$), 2.22 m ($2H^8$), 2.54 s (Me), 2.61 m ($2H^{10}$), 5.80 s (H^{12}), 6.97 t, 7.10 m, 7.19 d (5H arom, ^3J 7.2 Hz), 7.22 d (H^2, ^3J

8.2 Hz), 7.47 d, 7.71 d ($H^{5,6}$, ^3J 8.5 Hz), 8.18 d (H^1, ^3J 4.6 Hz), 9.60 s (NH). Found, %: C 81.10; H 5.74; N 8.03. $C_{23}H_{20}N_2O_3$. Calculated, %: C 81.18; H 5.88; N 8.23.

3-Methyl-12-(2-methylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVb). Yield 71%, mp 299–300°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m ($2H^9$), 2.15 (Me), 2.23 m ($2H^8$), 2.55 s (Me), 2.62 m ($2H^{10}$), 5.77 s (H^{12}), 6.72–7.01 m (4H arom), 7.22 d (H^2, ^3J 8.0 Hz), 7.45 d, 7.74 ($H^{5,6}$, ^3J 8.6 Hz), 8.20 (H^1, ^3J 4.7 Hz), 9.58 s (NH). Found, %: C 81.24; H 5.97; N 7.64. $C_{24}H_{22}N_2O$. Calculated, %: C 81.35; H 6.21; N 7.91.

3-Methyl-12-(4-fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVc). Yield 78%, mp 306–307°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m ($2H^9$), 2.21 m ($2H^8$), 2.55 s (Me), 2.61 m ($2H^{10}$), 5.82 s (H^{12}), 6.95 t, 7.21 m, (4H arom, ^3J 9.1 Hz), 7.23 d (H^2, ^3J 8.1 Hz), 7.45 d, 7.72 d ($H^{5,6}$, ^3J 8.5 Hz), 8.16 d (H^1, ^3J 4.8 Hz), 9.76 s (NH). Found, %: N 7.59. $C_{23}H_{19}FN_2O_3$. Calculated, %: N 7.82.

3-Methyl-12-(4-chlorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVd). Yield 78%, mp 311–312°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m ($2H^9$), 2.21 m ($2H^8$), 2.56 s (Me), 2.60 m ($2H^{10}$), 5.81 s (H^{12}), 7.10 m, 7.18 d (4H arom, ^3J 7.8 Hz), 7.24 d (H^2, ^3J 7.9 Hz), 7.46 d, 7.73 d ($H^{5,6}$, ^3J 8.6 Hz), 8.12 d (H^1, ^3J 4.9 Hz), 9.69 s (NH). Found, %: C 73.80; H 4.11; Cl 9.10; N 7.28. $C_{23}H_{19}ClN_2O$. Calculated, %: C 73.79; H 4.28; Cl 9.36; N 7.49.

12-(2,3-Dichlorophenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVe). Yield 79%, mp 342–343°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m ($2H^9$), 2.22 m ($2H^8$), 2.55 s (Me), 2.62 m ($2H^{10}$), 5.92 s (H^{12}), 7.06 t, 7.20 d, 7.28 d (3H arom, ^3J 7.4 Hz), 7.24 d (H^2, ^3J 7.7 Hz), 7.44 d, 7.71 d ($H^{5,6}$, ^3J 8.8 Hz), 8.34 d (H^1, ^3J 4.7 Hz), 9.63 s (NH). Found, %: C 67.23; H 4.69; Cl 16.98; N 6.61. $C_{23}H_{18}Cl_2N_2O$. Calculated, %: C 67.51; H 4.65; Cl 17.32; N 6.85.

12-(2,4-Dichlorophenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVf). Yield 93%, mp 316–317°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m ($2H^9$), 2.24 m ($2H^8$), 2.55 s (Me), 2.69 m $2H^{10}$), 5.90 s (H^{12}), 7.11 d, 7.25 d (3H arom, ^3J 7.2 Hz), 7.31 d (H^2, ^3J 7.9 Hz), 7.43 d, 7.72 d ($H^{5,6}$, ^3J 8.6 Hz), 8.36 d (H^1, ^3J 4.5 Hz), 9.72 s (NH). Found, %: C 67.33; H 4.24; Cl 17.20; N 6.74. $C_{23}H_{18}Cl_2N_2O$. Calculated, %: C 67.51; H 4.65; Cl 17.32; N 6.85.

3-Methyl-12-[2-(trifluoromethyl)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (IVg). Yield 73%, mp 317–318°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m ($2H^9$), 2.21 m ($2H^8$), 2.56 s (Me), 2.62 m ($2H^{10}$), 5.94 s (H^{12}), 7.26 d (H^2, ^3J 7.9 Hz), 7.42 m, 8.10 m (4H arom), 7.45 d, 7.74 d ($H^{5,6}$, ^3J 9.0 Hz), 8.24 d (H^1, ^3J 4.4 Hz), 9.58 s (NH). Found, %: N 6.79. $C_{24}H_{19}F_3N_2O$. Calculated, %: N 6.81.

12-(4-Hydroxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVh). Yield 72%, mp 332–333°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m ($2H^9$), 2.25 m ($2H^8$), 2.54 s (Me), 2.61 m ($2H^{10}$), 5.70 s (H^{12}), 6.48 d, 6.96 d (4H arom, ^3J 7.2 Hz), 7.27 d (H^2, ^3J 7.8 Hz), 7.45 d, 7.77 d ($H^{5,6}$, ^3J 8.7 Hz), 8.22 d (H^1, ^3J 4.7 Hz), 8.50 s (OH), 9.58 s (NH). Found, %: C 77.39; H 5.51; N 7.63. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.53; H 5.62; N 7.86.

12-(3,4-Dihydroxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVi). Yield 73%, mp 336–337°C. ^{1}H NMR spectrum, δ, ppm: 1.97 m ($2H^9$), 2.26 m ($2H^8$), 2.53 s (Me), 2.60 m ($2H^{10}$), 5.68 s (H^{12}), 6.41 s, 6.58 s (3H arom), 7.28 d (H^2, ^3J 8.0 Hz), 7.44 d, 7.78 d ($H^{5,6}$, ^3J 8.5 Hz), 8.11 s (OH), 8.21 d (H^1, ^3J 4.6 Hz), 8.61 s (OH), 9.61 s (NH). Found, %: C 73.85; H 5.29; N 7.26. $C_{23}H_{20}N_2O_3$. Calculated, %: C 74.19; H 5.39; N 7.53.

3-Methyl-12-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVj). Yield 78%, mp 288–289°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m ($2H^9$), 2.22 m ($2H^8$), 2.54 s (Me), 2.60 m ($2H^{10}$), 3.80 C (OMe), 5.77 C (H^{12}), 6.60 d, 6.78 d (4H arom, ^3J 7.9 Hz), 7.22 d (H^2, ^3J 7.8 Hz), 7.43 d, 7.75 d ($H^{5,6}$, ^3J 8.8 Hz), 8.19 d (H^1, ^3J 4.8 Hz), 9.60 s (NH). Found, %: C 77.64; H 5.90; N 7.41. $C_{24}H_{22}N_2O_2$. Calculated, %: C 77.84; H 5.94; N 7.57.

12-(2,4-Dimethoxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVk). Yield 85%, mp 272–273°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m ($2H^9$), 2.23 m ($2H^8$), 2.56 s (Me), 2.63 m ($2H^{10}$), 3.65 (OMe), 3.98 s (OMe), 5.98 s (H^{12}), 6.28 d, 6.34 s, 7.04 d (3H arom, ^3J 7.6 Hz), 7.26 d (H^2, ^3J 7.9 Hz), 7.42 d, 7.73 d ($H^{5,6}$, ^3J 8.8 Hz), 8.58 d (H^1) (^3J 4.4 Hz), 9.70 s (NH). Found, %: C 74.79; H 5.82; N 6.81. $C_{25}H_{24}Cl_2N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

12-(2,5-Dimethoxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVl). Yield 92%, mp 263–264°C. ^{1}H NMR spectrum, δ,

ppm: 1.90 m (2H^{9}), 2.24 m (2H^{8}), 2.55 s (Me), 2.60 m (2H^{10}), 3.14 s (OMe), 3.26 s (OMe), 5.97 s (H^{12}), 6.48 m, 7.00 s (3H arom), 7.29 d (H^{2}, ^{3}J 7.9 Hz), 7.43 d, 7.75 d (H^{5,6}, ^{3}J 8.2 Hz), 8.56 d (H^{1}, ^{3}J 4.4 Hz), 9.70 s (NH). Found, %: C 74.90; H 5.81; N 6.69. $C_{25}H_{24}N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

12-(3,4-Dimethoxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVm). Yield 78%, mp 281–282°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (2H^{9}), 2.26 m (2H^{8}), 2.57 s (Me), 2.61 m (2H^{10}), 3.62 s (OMe), 3.70 s (OMe), 5.74 s (H^{12}), 6.54 d, 6.97 s (3H arom, ^{3}J 7.2 Hz), 7.27 d (H^{2}, ^{3}J 7.6 Hz), 7.44 d, 7.76 d (H^{5,6}, ^{3}J 8.5 Hz), 8.28 d (H^{1}, ^{3}J 4.7 Hz), 9.61 s (NH). Found, %: C 75.03; H 5.98; N 6.88. $C_{25}H_{24}N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

3-Methyl-(3,4,5-trimethoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVn). Yield 85%, mp 256–257°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (2H^{9}), 2.25 m (2H^{8}), 2.55 s (Me), 2.62 m (2H^{10}), 3.50 s (OMe), 3.62 s (2OMe), 5.78 s (H^{12}), 6.56 s (2H arom), 7.27 d (H^{2}, ^{3}J 8.0 Hz), 7.43 d, 7.75 d (H^{5,6}, ^{3}J 8.8 Hz), 8.22 d (H^{1}, ^{3}J 4.6 Hz), 9.63 s (NH). Found, %: C 72.51; H 5.84; N 6.42. $C_{26}H_{26}N_2O_4$. Calculated, %: C 72.56; H 6.05; N 6.51.

3-Methyl-(4-propoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVo). Yield 78%, mp 291–292°C. ^{1}H NMR spectrum, δ, ppm: 0.98 t, 1.41 q, 3.75 t (OPr), 1.90 m (2H^{9}), 2.24 m (2H^{8}), 2.56 s (Me), 2.60 m (2H^{10}), 5.79 s (H^{12}), 6.57 d, 7.04 d (4H arom, ^{3}J 7.6 Hz), 7.21 d (H^{2}, ^{3}J 7.8 Hz), 7.42 d, 7.71 d (H^{5,6}, ^{3}J 8.9 Hz), 8.20 d (H^{1}, ^{3}J 4.3 Hz), 9.61 s (NH). Found, %: C 78.24; H 6.21; N 6.73. $C_{26}H_{26}N_2O_2$. Calculated, %: C 78.39; H 6.53; N 7.03.

3-Methyl-(3,4-methylenedioxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (IVp). Yield 71%, mp 346–347°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m (2H^{9}), 2.26 m (2H^{8}), 2.57 s (Me), 2.61 m (2H^{10}), 5.73 s (H^{12}), 5.81 d (CH_2), 6.60 d, 6.70 s (3H arom, ^{3}J 7.3 Hz), 7.32 d (H^{2}, ^{3}J 7.9 Hz), 7.46 d, 7.72 d (H^{5,6}, ^{3}J 8.7 Hz), 8.18 d (H^{1}, ^{3}J 4.6 Hz), 9.62 s (NH). Found, %: C 74.69; H 5.08; N 7.31. $C_{24}H_{20}N_2O_3$. Calculated, %: C 75.00; H 5.21; N 7.29.

3-Methyl-(4-methylthiophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVq). Yield 71%, mp 313–314°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (2H^{9}), 2.23 m (2H^{8}), 2.55 s (Me), 2.60 m 2H^{10}), 3.28 s (SMe), 5.76 s (H^{12}), 6.69 d, 7.12 d (4H arom, ^{3}J 7.9 Hz), 7.23 d (H^{2}, ^{3}J 7.2 Hz), 7.41 d, 7.70 d (H^{5,6}, ^{3}J 9.0 Hz), 8.20 d (H^{1}, ^{3}J 4.5 Hz), 9.61 s (NH). Found, %: C 74.56; H 5.53; N 7.01; S 8.38. $C_{24}H_{22}N_2OS$. Calculated, %: C 74.61; H 5.70; N 7.25; S 8.29.

3-Methyl-[4-(methoxycarbonyl)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (IVr). Yield 82%, mp 319–320°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (2H^{9}), 2.27 m (2H^{8}), 2.55 s (Me), 2.62 m (2H^{10}), 3.80 s (CO_2Me), 5.90 s (H^{12}), 7.29 d (H^{2}, ^{3}J 7.8 Hz), 7.31 d, 7.70 d (4H arom, ^{3}J 7.7 Hz), 7.49 d, 7.80 d (H^{5,6}, ^{3}J 8.9 Hz), 8.21 d (H^{1}, ^{3}J 4.7 Hz), 9.70 s (NH). Found, %: C 75.15; H 5.42; N 6.74. $C_{25}H_{22}N_2O_3$. Calculated, %: C 75.38; H 5.53; N 7.04.

12-(4-Acetoxy-3-methoxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVs). Yield 81%, mp 310–311°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (2H^{9}), 2.25 m (2H^{8}), 2.53 s (Me), 2.61 m (2H^{10}), 3.70 s (OMe), 3.85 s (OCOMe), 5.87 s (H^{12}), 7.06 s, 7.15 m (3H arom), 7.26 d (H^{2}, ^{3}J 7.5 Hz), 7.45 d, 7.74 d (H^{5,6}, ^{3}J 8.7 Hz), 8.23 d (H^{1}, ^{3}J 4.5 Hz), 9.62 s (NH). Found, %: C 72.64; H 5.49; N 6.39. $C_{26}H_{24}N_2O_4$. Calculated, %: C 72.90; H 5.61; N 6.54.

12-(4-Benzyloxy-3-methoxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (IVt). Yield 71%, mp 299–300°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (2H^{9}), 2.25 (2H^{8}), 2.54 s (Me), 2.60 m (2H^{10}), 3.80 s (OMe), 4.85 s (OCH_2Ph), 5.81 s (H^{12}), 6.68 m, 7.07 s (3H arom), 7.23 d (H^{2}, ^{3}J 7.3 Hz), 7.44 d, 7.72 d (H^{5,6}, ^{3}J 8.5 Hz), 8.22 d (H^{1}, ^{3}J 4.6 Hz), 9.63 s (NH). Found, %: C 77.95; H 5.57; N 5.62. $C_{31}H_{28}N_2O_3$. Calculated, %: C 78.15; H 5.88; N 5.88.

12-(4,4'-Biphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVu). Yield 67%, mp 322–323°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (2H^{9}), 2.21 m (2H^{8}), 2.55 s (Me), 2.61 m (2H^{10}), 5.80 s (H^{12}), 6.88 d, 7.10 d, 7.30 m (9H arom, ^{3}J 7.2 Hz), 7.22 d (H^{2}, ^{3}J 7.6 Hz), 7.41 d, 7.70 d (H^{5,6}, ^{3}J 8.6 Hz), 8.19 d (H^{1}, ^{3}J 4.8 Hz), 9.61 s (NH). Found, %: C 83.44; H 5.69; N 6.76. $C_{29}H_{24}N_2O$. Calculated, %: C 83.65; H 5.77; N 6.73.

12-(4-Benzyloxyphenyl)-3-methyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVv). Yield 71%, mp 314–315°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m (2H^{9}), 2.22 m (2H^{8}), 2.57 s (Me), 2.62 m (2H^{10}), 4.88 s (OCH_2Ph), 5.82 s (H^{12}), 6.73 d, 7.08 d,

7.32 m (10H arom, ^3J 7.0 Hz), 7.23 d (H^2, ^3J 7.9 Hz), 7.40 d, 7.72 d ($H^{5,6}$, ^3J 8.9 Hz), 8.20 d (H^1, ^3J 4.9 Hz), 9.62 s (NH). Found, %: C 80.36; H 5.74; N 6.04. $C_{30}H_{26}N_2O_2$. Calculated, %: C 80.72; H 5.83; N 6.28.

3-Methyl-12-(2-pyridyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVw). Yield 77%, mp 297–298°C. ^{1}H NMR spectrum, δ, ppm: 1.96 m ($2H^9$), 2.26 m ($2H^8$), 2.58 s (Me), 2.65 m ($2H^{10}$), 5.93 s (H^{12}), 6.97 m, 7.46 m, 7.53 m, 8.26 d (4H arom, ^3J 4.9 Hz), 7.22 d (H^2, ^3J 8.0 Hz), 7.42 d, 7.69 d ($H^{5,6}$, ^3J 9.0 Hz), 8.50 d (H^1, ^3J 4.4 Hz), 9.60 s (NH). Found, %: C 77.19; H 5.60; N 12.01. $C_{22}H_{19}N_3O$. Calculated, %: C 77.42; H 5.57; N 12.32.

3-Methyl-12-(3-pyridyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVx). Yield 76%, mp 302–303°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m ($2H^9$), 2.23 m ($2H^8$), 2.55 s (Me), 2.62 m ($2H^{10}$), 5.84 C (H^{12}), 6.96 m, 8.32 s (4H arom), 7.26 d (H^2, ^3J 8.1 Hz), 7.41 d, 7.70 d ($H^{5,6}$, ^3J 9.0 Hz), 8.24 d (H^1, ^3J 4.8 Hz), 9.61 s (NH). Found, %: C 77.25; H 5.53; N 12.14. $C_{22}H_{19}N_3O$. Calculated, %: C 77.42; H 5.57; N 12.32.

3-Methyl-12-[2-(3-methyl)thienyl]-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVy). Yield 76%, mp 292–293°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m ($2H^9$), 2.22 m ($2H^8$), 2.45 s (Me), 2.56 s (Me), 2.63 m ($2H^{10}$), 5.86 s (H^{12}), 6.58 d, 6.96 d (2H arom, ^3J 7.0 Hz), 7.23 d (H^2, ^3J 8.2 Hz), 7.40 d, 7.72 d ($H^{5,6}$, ^3J 8.8 Hz), 8.24 d (H^1, ^3J 4.9 Hz), 9.68 s (NH). Found, %: C 73.26; H 5.60; N 7.54; S 8.65. $C_{22}H_{20}N_2OS$. Calculated, %: C 73.33; H 5.56; N 7.78; S 8.89.

3-Methyl-12-(cyclohexenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVz). Yield 43%, mp 290–291°C. ^{1}H NMR spectrum, δ, ppm: 1.20–1.76 (7H alicyclic), 1.92 m ($2H^9$), 2.21 m ($2H^8$), 2.55 s (Me), 2.62 m ($2H^{10}$), 4.86 s (CH=CH), 5.46 s (H^{12}), 7.24 d (H^2, ^3J 8.2 Hz), 7.43 d, 7.70 d ($H^{5,6}$, ^3J 8.8 Hz), 8.21 d (H^1, ^3J 4.7 Hz), 9.60 s (NH). Found, %: C 79.97; H 7.01; N 7.84. $C_{23}H_{24}N_2O$. Calculated, %: C 80.23; H 6.98; N 8.14.

12-(2,3-Dichlorophenyl)-3,9,9-trimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (Va). Yield 80%, mp 320–321°C. ^{1}H NMR spectrum, δ, ppm: 0.94 s (Me), 1.10 s (Me), 2.10 d.d ($2H^8$, ^2J 16.0 Hz), 2.41 m ($2H^{10}$), 2.53 s (Me), 6.06 s (H^{12}), 7.08 t, 7.21 d, 7.32 d (3H arom, ^3J 7.5 Hz), 7.28 d (H^2, ^3J 7.9 Hz), 7.41 d, 7.71 d ($H^{5,6}$, ^3J 8.9 Hz), 8.36 d (H^1, ^3J 4.5 Hz), 9.70 s (NH). Found, %: C 68.29; H 4.93; Cl 16.03; N 6.28. $C_{25}H_{22}Cl_2N_2O$. Calculated, %: C 68.67; H 5.04; Cl 16.23; N 6.41.

12-(2,4-Dichlorophenyl)-3,9,9-trimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (Vb). Yield 88%, mp 230–231°C. ^{1}H NMR spectrum, δ, ppm: 0.91 s (Me), 1.08 s (Me), 2.12 d.d ($2H^8$, ^2J 16.2 Hz), 2.45 m ($2H^{10}$), 2.55 s (Me), 5.91 s (H^{12}), 7.02–7.12 m, 7.18 s (3H arom), 7.29 d (H^2, ^3J 7.8 Hz), 7.44 d, 7.73 d ($H^{5,6}$, ^3J 8.7 Hz), 8.35 d (H^1, ^3J 4.6 Hz), 9.63 s (NH). Found, %: C 68.50; H 4.99; Cl 15.87; N 6.19. $C_{25}H_{22}Cl_2N_2O$. Calculated, %: C 68.67; H 5.04; Cl 16.23; N 6.41.

3,9,9-Trimethyl-12-(3,4,5-trimethoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin -11-one (Vc). Yield 82%, mp 242–243°C. ^{1}H NMR spectrum, δ, ppm: 0.93 s (Me), 1.09 s (Me), 2.10 d.d ($2H^8$, ^2J 16.1 Hz), 2.46 m ($2H^{10}$), 2.54 s (Me), 3.55 s (OMe), 3.61 s (2OMe), 5.79 s (H^{12}), 6.44 s (2H arom), 7.30 d (H^2, ^3J 7.6 Hz), 7.42 d, 7.70 d ($H^{5,6}$, ^3J 8.8 Hz), 8.20 d (H^1, ^3J 4.8 Hz), 9.62 s (NH). Found, %: C 73.12; H 6.48; N 5.74. $C_{28}H_{30}N_2O_2$. Calculated, %: C 73.36; H 6.55; N 6.11.

12-(4-Benzyloxyphenyl)-3,9,9-trimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin -11-one (Vd). Yield 70%, mp 296–297°C. ^{1}H NMR spectrum, δ, ppm: 0.94 s (Me), 1.10 s (Me), 2.11 d.d ($2H^8$, ^2J 16.2 Hz), 2.44 m ($2H^{10}$), 2.55 C (Me), 4.90 s (OCH_2Ph), 5.78 s (H^{12}), 6.71 d, 7.12 d, 7.31 m (10H arom), 7.27 d (H^2, ^3J 7.3 Hz), 7.40 d, 7.71 d ($H^{5,6}$, ^3J 8.7 Hz), 8.19 d (H^1, ^3J 4.5 Hz), 9.60 s (NH). Found, %: C 80.73; H 6.28; N 5.76. $C_{32}H_{30}N_2O_2$. Calculated, %: C 81.01; H 6.33; N 5.91.

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