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Condensation of Quinolin-5-amine with Aromatic Aldehydes and Cyclohexane-1,3-dione

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Abstract—7-Aryl(hetaryl, cyclohexenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-ones were synthesized by three-component condensation of aromatic and heteroaromatic aldehydes and cyclohex-3-ene-1-carbaldehyde with quinolin-5-amine and cyclohexane-1,3-diones.

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Reactions of amines of the quinoline series with carbonyl-containing compounds are widely used in the synthesis of phenanthrolines. We previously [1–4] showed that quinolin-6-amine reacts with aromatic aldehydes and methyl or methylene ketones (as CH acids) to give various 4,7-phenanthrolines. Among the examined CH acids, the most efficient were cyclic 1,3-diketones [3, 4]. The resulting partially hydrogenated oxo derivatives of benzo[*b*][4,7]phenanthroline attract interest from the practical viewpoint as analogs of alkaloids, enzyme inhibitors, bactericide agents, and antibiotics [5–8].

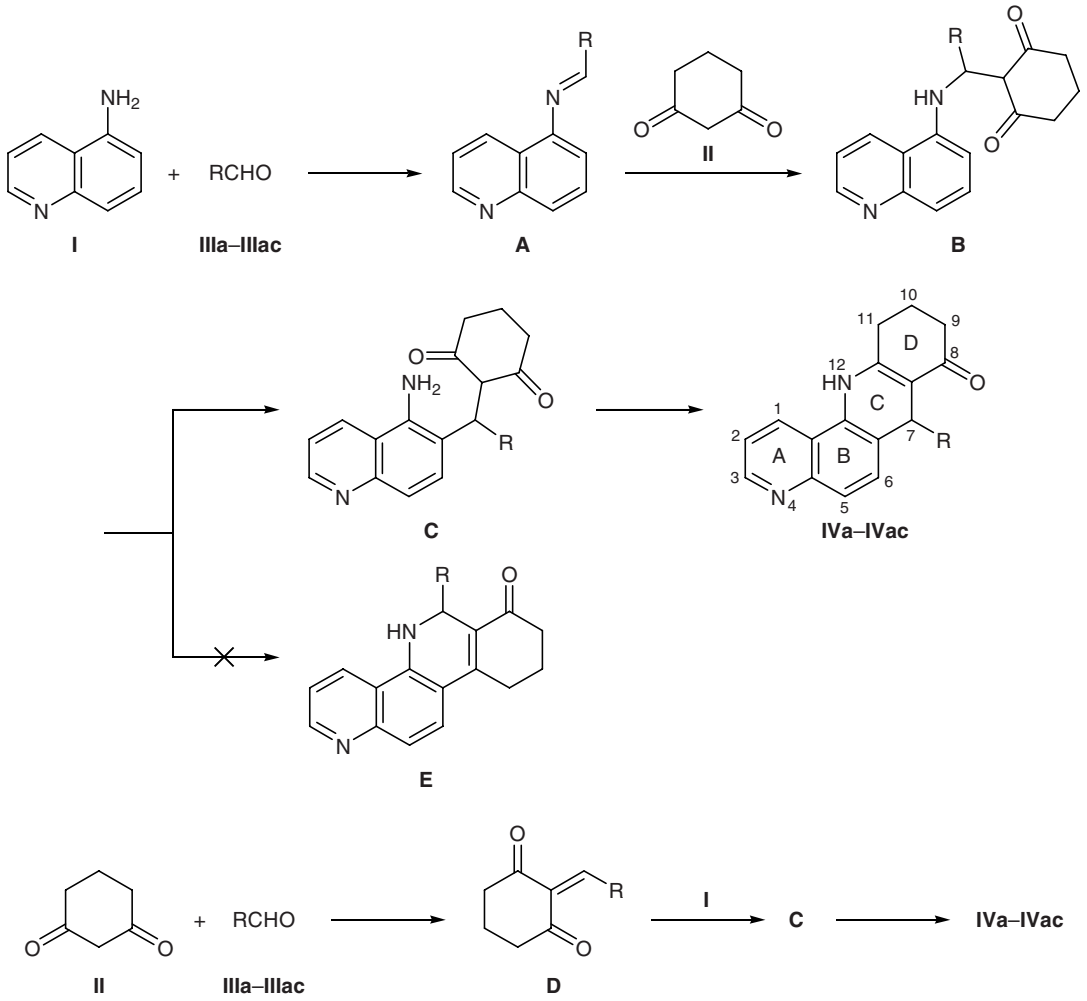
In the present work we tried to obtain previously unknown fused 1,7-phenanthroline derivatives that are isomeric to the above noted benzo[*b*][4,7]phenanthrolines and are potential biologically active substances [9, 10]. For this purpose, we studied three-component condensation of quinolin-5-amine (**I**) with cyclohexane-1,3-dione (**II**) and aromatic and heteroaromatic aldehydes **IIIa**–**IIIab** and cyclohex-3-ene-1-carbaldehyde (**IIIac**). The reactions were carried out by heating equimolar amounts of the reactants in boiling butanol. Due to high reactivity of the β-dicarbonyl component no addition of catalyst was necessary: the enol form of cyclohexane-1,3-dione acted as acid catalyst. As a result, we isolated in 37–80% yield the corresponding 7-substituted 7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-ones **IVa**–**IVac** (Scheme 1).

By analogy with our previous data [11] on the three-component condensation of naphthalen-1-amine (a carbocyclic analog of quinolin-5-amine) with aromatic aldehydes and dimedone (5,5-dimethylcyclohexane-1,3-dione), we believe that the scheme of formation of the benzo[*b*][1,7]phenanthroline system includes initial reaction of amine **I** with aldehyde **III** to give Schiff base **A**, addition of diketone **II** at the C=N bond of Schiff base **A**, rearrangement of adduct **B** thus formed in a way similar to the Hofmann–Martius rearrangement (migration of *N*-alkyl substituent in anilines to the aromatic ring [12]), and intramolecular ring closure of rearrangement product **C**.

The transformation of intermediate **B** could also involve its hydramine fission into initial amine **I** and α,β-unsaturated ketone **D**. The double C=C bond in the latter is strongly activated due to conjugation with two neighboring carbonyl groups; therefore, it is capable of reacting with amine **I** at the aromatic ring, namely at the carbon atom in the α-position with respect to the amino group, which possesses the largest electron density. The resulting amino diketone **C** undergoes dehydrocyclization to benzo[*b*][1,7]phenanthrolinone **IV**. Alternatively, diketone **II** can react first with aldehyde **III** to give 2-arylmethylidenecyclohexane-1,3-dione **D** which then attacks amine **I** at the aromatic ring (see above). Another theoretically possible reaction path including cyclization of adduct **B** (as in the condensation of arylmethylideneamines with cyclic ketones [1, 13]) is not observed, and benzo[*c*][1,7]-phenanthroline derivatives like **E** were not detected even as impurity.

The yield of products **IVa**–**IVac** depends to some extent on the nature of the R substituent in aldehyde **III**. Benzaldehydes **IIIi**–**IIIt** and **IIIv** having an ester, hydroxy, or alkoxy group (i.e., those exerting *–I* or *–I*

Scheme 1.



R = Ph (**a**), 2-MeC_6H_4 (**b**), 4-MeC_6H_4 (**c**), 4-*i*-PrC_6H_4 (**d**), 2-BrC_6H_4 (**e**), 4-BrC_6H_4 (**f**), 2-IC_6H_4 (**g**), 2-$CF_3C_6H_4$ (**h**), 3-HOC_6H_4 (**i**), 4-HOC_6H_4 (**j**), 3,4-$(HO)_2C_6H_3$ (**k**), 2-$MeOC_6H_4$ (**l**), 4-$MeOC_6H_4$ (**m**), 2,4-$(MeO)_2C_6H_3$ (**n**), 3,4-$(MeO)_2C_6H_3$ (**o**), 3,4,5-$(MeO)_3C_6H_2$ (**p**), 2-MeO-5-BrC_6H_3 (**q**), 3,4-$(OCH_2O)C_6H_3$ (**r**), 4-$EtOC_6H_4$ (**s**), 4-$PrOC_6H_4$ (**t**), 4-$MeSC_6H_4$ (**u**), 4-$MeOCOC_6H_4$ (**v**), 4-Ph-C_6H_4 (**w**), 4-$PhCH_2OC_6H_4$ (**x**), pyridin-3-yl (**y**), pyridin-4-yl (**z**), 2-thienyl (**aa**), 3-methyl-2-thienyl (**ab**), cyclohex-3-en-1-yl (**ac**).

and –*M* effects) give rise to phenanthrolines **IVi**–**IVt** and **IVv** in high yields (60–80%), the maximal yields (78–80%) being obtained from 2-methoxy-, 2,4-dimethoxy-, and 4-bromo-2-methoxybenzaldehydes **IIIl**, **IIIn**, and **IIIq**, despite negative steric effect of the *ortho*-substituent. Presumably, the carbonyl group in these aldehydes is activated most strongly by the methoxy group (negative inductive effect) located most closely to the reaction center. Steric hindrances created by the *ortho*-substituent in halogen derivatives **IIIe**, **IIIg**, and **IIIh** affect the reaction more strongly, for the negative inductive effect of halogen atoms is weaker than that of methoxy group; therefore, phenanthrolines **IVe**, **IVg**, and **IVh** were formed in a lower yield (37–43%). Negative steric effect on the product yield was also observed in the reactions with *o*-methylbenzaldehyde (**IIIb**) and 3-methylthiophene-2-carbaldehyde (**IIIab**); in these cases, additional deactivation of the carbonyl group is induced by the donor methyl group in the *ortho* position, and the yields of **IVb** and **IVab** were 38–46%. The yields of phenanthrolines **IVy** and **IVz** derived from pyridinecarbaldehydes **IIIy** and **IIIz** were fairly good (63–67%) due to –*I* effect of the pyridine nitrogen atom.

The structure of compounds **IVa**–**IVac** was determined on the basis of their IR, NMR, and mass spectra. In the IR spectra of these compounds we observed strong absorption bands at 1590 and 1525 cm^{-1}, which should be assigned to the vinylogous amide fragment (1580, 1520 cm^{-1} [14]). Strong bands at 3440 and

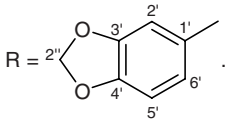
1620 cm^{-1} belong, respectively, to stretching and bending vibrations of the secondary NH group. Stretching vibrations of aliphatic C–H bonds appeared in the region 2960–2870 cm^{-1}, and aromatic C–H bonds gave rise to absorption bands at 3060–3030 cm^{-1}. In addition, compounds **IVk–IVt**, **IVv**, and **IVx** showed in the IR spectra absorption bands at 1240–1230 cm^{-1} due to the C–O–C fragment; the spectrum of **IVu** contained a strong C–S stretching vibration band at 1125 cm^{-1}, and the ester carbonyl band in the spectrum of **IVv** was located at 1725–1720 cm^{-1}.

The electron-impact mass spectra of benzophenanthrolinones **IVa–IVac** were characterized by the presence of molecular ion peaks $[M]^+$ with a relative intensity I_{rel} of 14–48%. The base peak in their mass spectra (I_{rel} 100%) was $[M - R]^+$ (m/z 249). The mass spectra of all compounds **IVa–IVac** contained a ion peak with m/z 193 (I_{rel} 8–28%), which corresponds to elimination of the CH_2CH_2CO fragment from the $[M - R]^+$ ion.

Signals in the ^1H NMR spectra of compounds **IVa–IVac** were assigned by analysis of the two-dimensional COSY spectra which revealed several closed spin systems in the resonance region of aromatic and aliphatic protons. Chemical shifts and multiplicities of signals belonging to each closed spin system were taken into account, and NOESY, HSQC, and HMC techniques were also used (see table). Likewise, signals in the ^{13}C NMR spectra (see Experimental) were assigned on the basis of joint analysis of two-dimensional NMR spectra.

The positions and multiplicities of signals from protons in the C and D rings were very similar for all compounds **IVa–IVac**, indicating that they belong to the same structural series. To distinguish between possible isomers, we examined the two-dimensional HSQC and HMBC spectra of compound **IVr** (see table). The choice of structure **IVr** rather than **D** was based on the presence of a fairly strong 12-H/C^{11} correlation peak. Structure **D** should be characterized by correlations between 12-H, on the one hand, and C^7 and $C^{1'}$ in the aryl substituent, on the other; however, no such correlations were observed. Therefore, structure **D** can be ruled out. It should be noted that the 7-H signal appears as a singlet at δ 5.13–5.78 ppm, i.e., it is displaced downfield relative to the corresponding

Intensities of correlation peaks[a] in the HMBC spectrum of compound (**IVr**)



Carbon atom	Proton													
	1-H	2-H	3-H	4-H	6-H	7-H	9-H	11-H_{ax}	11-H_{eq}	12-H	2′-H	5′-H	6′-H	2″-H
C^1			m											
C^{1a}		m		m										
C^{1b}	s				s	s				m				
C^7					m						m		m	
C^{7a}				s		s				s				
C^8						m	w							
C^{8a}						s								
C^9								w		s				
C^{10}							w		w					
C^{11}							w			m				
C^{12a}						s		m	m					
$C^{1'}$												m		
$C^{2'}$						s							s	
$C^{3'}$												s		s
$C^{4'}$											s		s	s
$C^{6'}$											s			

[a] Correlation peak intensities are denoted as "s" for strong, "m" for medium, and "w" for weak.

signal of 1,4-dihydropyridines [15] due to anisotropic effect of the neighboring aromatic ring.

We can conclude that the three-component condensation of quinolin-5-amine with cyclohexane-1,3-dione and aldehydes provides an effective and selective method for the synthesis of new fused heterocycles containing benzene and 1,7-phenanthroline fragments and pharmacophoric substituents, which attract interest as potential biologically active compounds with a broad spectrum of action.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protege-460 spectrometer with Fourier transform. The NMR spectra were measured on Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) instruments from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer and on a Hewlett–Packard HP 5890/HP 5972 GC–MS system (HP-5MS capillary column, 30 m×0.25 mm×0.25 μm, 5% of phenylmethylsilicone; injector temperature 250°C). The melting points were determined on a Kofler hot stage.

7-Substituted 7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-ones IVa–IVac (*general procedure*). A solution of 5 mmol of quinolin-5-amine (I), 5 mmol of cyclohexane-1,3-dione (**II**), and 5 mmol of aldehyde **IIIa–IIIac** in 20 ml of butanol was heated for 3–4 h under reflux. The precipitate was filtered off and washed with diethyl ether. Compounds **IVa**, **IVe–IVi**, **IVl–IVn**, **IVv**, and **IVy** were recrystallized from ethanol–benzene (1:4).

7-Phenyl-7,10,11,12-tetrahydrobenzo[*b*][1,7]-phenanthrolin-8(9H)-one (IVa). Yield 59%, mp 220–221°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.70 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.2 Hz), 2.90 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.55 s (1H, 7-H), 6.80–7.11 m (5H, Ph), 7.42 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.0 Hz), 7.56 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.58 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.72 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.81 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.20 s (NH). Found, %: C 80.84; H 5.37; N 8.30. $C_{22}H_{18}N_2O$. Calculated, %: C 80.98; H 5.52; N 8.59.

7-(2-Methylphenyl)-7,10,11,12-tetrahydrobenzo-[*b*][1,7]phenanthrolin-8(9*H*)-one (IVb). Yield 38%, mp 215–216°C. ^{1}H NMR spectrum, δ, ppm: 1.85 m (1H, 10-H$_{ax}$); 1.99 m (1H, 10-H$_{eq}$); 2.22 m (2H, 9-H); 2.68 s (Me); 2.72 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz); 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz); 5.46 s (1H, 7-H); 6.70 t, 6.88 d, 7.01 t, and 7.09 t (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.1, $J_{4',5'}$ = $J_{5',6'}$ = 8.5 Hz); 7.39 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz); 7.45 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz); 7.59 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.86 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz); 8.94 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz); 9.39 s (NH). Found, %: C 80.99; H 5.78; N 7.96. $C_{23}H_{20}N_2O$. Calculated, %: C 81.15; H 5.92; N 8.23.

7-(4-Methylphenyl)-7,10,11,12-tetrahydrobenzo-[*b*][1,7]phenanthrolin-8(9*H*)-one (IVc). Yield 49%, mp 218–219°C. ^{1}H NMR spectrum, δ, ppm: 1.88 m (1H, 10-H$_{ax}$), 2.00 m (1H, 10-H$_{eq}$), 2.24 m (2H, 9-H), 2.47 s (Me), 2.70 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.2 Hz), 2.86 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.28 s (1H, 7-H), 7.11 d (2H, 2′-H, 6′-H, $J_{2',3'}$ = $J_{6',5'}$ = 8.4 Hz), 7.28 d (2H, 3′-H, 5′-H, $J_{3',2'}$ = $J_{5',6'}$ = 8.4 Hz), 7.35 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.44 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.78 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz), 8.84 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.20 s (NH). Found, %: C 80.96; H 5.77; N 8.06. $C_{23}H_{20}N_2O$. Calculated, %: C 81.15; H 5.92; N 8.23.

7-(4-Isopropylphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVd). Yield 69%, mp 222–223°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H$_{ax}$), 2.05 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.65 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.3 Hz), 2.72 m (*i*-Pr), 2.85 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.28 s (1H, 7-H), 7.11 d (2H, 2′-H, 6′-H, $J_{2',3'}$ = $J_{6',5'}$ = 8.4 Hz), 7.28 d (2H, 3′-H, 5′-H, $J_{3',2'}$ = $J_{5',6'}$ = 8.4 Hz), 7.35 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.44 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.78 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz), 8.84 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.20 s (NH). Found, %: C 81.32; H 6.38; N 7.41. $C_{25}H_{24}N_2O$. Calculated, %: C 81.49; H 6.57; N 7.60.

7-(2-Bromophenyl)-7,10,11,12-tetrahydrobenzo-[*b*][1,7]phenanthrolin-8(9*H*)-one (IVe). Yield 43%, mp 275–276°C. ^{1}H NMR spectrum, δ, ppm: 1.85 m (1H, 10-H$_{ax}$); 1.99 m (1H, 10-H$_{eq}$); 2.22 m (2H, 9-H); 2.70 s (Me); 2.72 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz); 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz); 5.78 s (1H, 7-H); 6.95 t, 7.13 t, 7.26 d (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.1, $J_{4',5'}$ = $J_{5',6'}$ = 8.5 Hz); 7.43 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz); 7.48 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz); 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.78 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz);

8.84 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz); 9.13 s (NH). Found, %: C 65.02; H 4.06; Br 19.51; N 6.72. $C_{22}H_{17}BrN_2O$. Cal-culated, %: C 65.19; H 4.20; Br 19.75; N 6.91.

7-(4-Bromophenyl)-7,10,11,12-tetrahydrobenzo-[*b*][1,7]phenanthrolin-8(9*H*)-one (IVf). Yield 62%, mp 255–256°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H$_{ax}$), 2.05 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.65 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.2 Hz), 2.80 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.28 s (1H, 7-H), 7.11 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.4 Hz), 7.28 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 7.35 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.44 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.78 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz), 8.84 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.20 s (NH). Found, %: C 64.96; H 4.19; Br 19.41; N 6.73. $C_{22}H_{17}BrN_2O$. Calculated, %: C 65.19; H 4.20; Br 19.75; N 6.91.

7-(2-Iodophenyl)-7,10,11,12-tetrahydrobenzo[*b*]-[1,7]phenanthrolin-8(9*H*)-one (IVg). Yield 39%, mp 247–248°C. ^{1}H NMR spectrum, δ, ppm: 1.85 m (1H, 10-H$_{ax}$); 1.99 m (1H, 10-H$_{eq}$); 2.22 m (2H, 9-H); 2.70 s (Me); 2.72 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz); 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz); 5.78 s (1H, 7-H); 6.95 t, 7.13 t, 7.26 d (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.1, $J_{4',5'} = J_{5',6'}$ = 8.5 Hz); 7.43 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz); 7.48 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz); 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.78 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz); 8.84 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz); 9.21 s (NH). Found, %: C 58.25; H 3.63; I 27.81; N 5.87. $C_{22}H_{17}IN_2O$. Calculated, %: C 58.42; H 3.79; I 28.06; N 6.19.

7-(2-Trifluoromethylphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVh). Yield 37%, mp 192–193°C. ^{1}H NMR spectrum, δ, ppm: 1.85 m (1H, 10-H$_{ax}$); 1.99 m (1H, 10-H$_{eq}$); 2.22 m (2H, 9-H); 2.70 s (Me); 2.72 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz); 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz); 5.78 s (1H, 7-H); 6.95 t, 7.13 t, 7.26 d (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.1, $J_{4',5'} = J_{5',6'}$ = 8.5 Hz); 7.43 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz); 7.48 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.78 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz); 8.84 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz); 9.18 s (NH). Found, %: N 6.89. $C_{23}H_{17}F_3N_2O$. Calculated, %: N 7.10.

7-(3-Hydroxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVi). Yield 61%, mp 271–272°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (1H, 10-H$_{ax}$), 2.05 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.73 m (1H, 11-H$_{ax}$), 2.88 m (1H, 11-H$_{eq}$), 5.31 s (1H, 7-H), 7.19 d (2H, 5′-H, 6′-H, $J_{5',6'} = J_{5',4'}$ = 8.8 Hz), 7.42 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.20 d (1H, 4′-H, $J_{4',5'}$ = 8.8 Hz), 8.50 s (1H, 2′-H), 8.64 s (OH), 8.74 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.81 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.15 s (NH). Found, %: C 76.92; H 5.13; N 7.97. $C_{22}H_{18}N_2O_2$. Calculated, %: C 77.17; H 5.30; N 8.18.

7-(4-Hydroxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVj). Yield 61%, mp 281–282°C. ^{1}H NMR spectrum, δ, ppm: 1.97 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.27 m (2H, 9-H), 2.81 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.2 Hz), 2.85 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.13 s (1H, 7-H), 6.50 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.4 Hz), 6.44 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 7.37 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.42 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 3.9 Hz), 7.50 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.62 s (1H, OH), 8.75 d (1H, 3-H, $J_{3,2}$ = 3.9 Hz), 8.83 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.12 s (NH). Found, %: C 76.95; H 4.97; N 7.88. $C_{22}H_{18}N_2O_2$. Calculated, %: C 77.17; H 5.30; N 8.18.

7-(3,4-Dihydroxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVk). Yield 60%, mp 266–267°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.73 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.6 Hz), 2.81 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.6 Hz), 5.18 s (1H, 7-H), 6.58 d (1H, 6′-H, $J_{6',5'}$ = 8.7 Hz), 6.64 d (1H, 5′-H, $J_{5',6'}$ = 8.7 Hz), 6.71 s (1H, 2′-H), 7.48 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz), 7.52 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.58 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.60 s (1H, OH), 8.63 s (1H, OH), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz), 8.89 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.31 s (NH). Found, %: C 73.51; H 4.94; N 7.71. $C_{22}H_{18}N_2O_3$. Calculated, %: C 73.74; H 5.03; N 7.82.

7-(2-Methoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVl). Yield 79%, mp 231–232°C. ^{1}H NMR spectrum, δ, ppm: 1.99 m (1H, 10-H$_{ax}$); 2.06 m (1H, 10-H$_{eq}$); 2.28 m (2H, 9-H); 2.71 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz); 2.82 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz); 3.89 s (3H, MeO); 5.65 s (1H, 7-H); 6.72 t, 6.83 d, 7.01 t, 7.09 t (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.0, $J_{4',5'} = J_{5',6'}$ = 8.6 Hz); 7.32 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.1 Hz); 7.50 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz); 7.59 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.86 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz); 8.95 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz); 9.39 s (NH). Found, %: C 77.29; H 5.51; N 7.65. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.53; H 5.51; N 7.65.

7-(4-Methoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVm). Yield 76%, mp 216–217°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (1H, 10-H$_{ax}$), 2.01 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.72 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.1, $J_{11\text{-}ax,10\text{-}eq}$ = 4.3 Hz), 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.3 Hz), 3.65 s (3H, MeO), 5.21 s (1H, 7-H), 6.75 d (2H, 2′-H, 6′-H, $J_{2',3'}$ = $J_{6',5'}$ = 8.5 Hz), 7.12 d (2H, 3′-H, 5′-H, $J_{3',2'}$ = $J_{5',6'}$ = 8.5 Hz), 7.50 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.58 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.84 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.91 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.42 s (NH). Found, %: C 77.33; H 5.47; N 7.54. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.53; H 5.51; N 7.65.

7-(2,4-Dimethoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVn). Yield 80%, mp 215–216°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (1H, 10-H$_{ax}$), 2.02 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.75 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.4, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz), 2.86 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz), 3.68 s (3H, MeO), 3.73 s (3H, MeO), 5.49 s (1H, 7-H), 6.69 d (2H, 5′-H, 6′-H, $J_{5',6'}$ = 8.8 Hz), 6.80 s (1H, 3′-H), 7.43 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.1 Hz), 7.50 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.54 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.82 d (1H, 3-H, $J_{3,2}$ = 4.1 Hz), 8.89 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.36 s (NH). Found, %: C 74.42; H 5.65; N 7.15. $C_{24}H_{22}N_2O_3$. Calculated, %: C 74.61; H 5.70; N 7.25.

7-(3,4-Dimethoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVo). Yield 72%, mp 248–249°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.26 m (2H, 9-H), 2.77 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.5 Hz), 2.83 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.6 Hz), 3.70 s (3H, MeO), 3.76 s (3H, MeO), 5.44 s (1H, 7-H), 6.68 d (1H, 6′-H, $J_{6',5'}$ = 8.7 Hz), 6.73 d (1H, 5′-H, $J_{5',6'}$ = 8.7 Hz), 6.81 s (1H, 2′-H), 7.42 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.0 Hz), 7.51 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.56 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.80 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.88 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.37 s (NH). Found, %: C 74.60; H 5.61; N 7.18. $C_{24}H_{22}N_2O_3$. Calculated, %: C 74.61; H 5.70; N 7.25.

7-(3,4,5-Trimethoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVp). Yield 67%, mp 215–216°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.76 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz), 2.84 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz), 3.60 s (6H, MeO), 3.72 s (3H, MeO), 5.36 s (1H, 7-H), 6.76 s (1H, 2′-H), 6.90 s (1H, 6′-H), 7.44 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.2 Hz), 7.50 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.56 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.2 Hz), 8.90 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.27 s (NH). Found, %: C 71.84; H 5.67; N 6.57. $C_{25}H_{24}N_2O_4$. Calculated, %: C 72.10; H 5.81; N 6.73.

7-(5-Bromo-2-methoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVq). Yield 78%, mp 229–230°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.76 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz), 2.84 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz), 3.72 s (3H, MeO), 5.34 s (1H, 7-H), 6.69 d (2H, 3′-H, 4′-H, $J_{3',4'}$ = 8.8 Hz), 6.90 s (1H, 6′-H), 7.44 d.d (1H, 2-H, $J_{2,1}$ = 8.9, $J_{2,3}$ = 4.2 Hz), 7.50 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.56 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.2 Hz), 8.90 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.27 s (NH). Found, %: C 63.29; H 4.30; Br 18.22; N 6.28. $C_{23}H_{19}BrN_2O_2$. Calculated, %: C 63.45; H 4.37; Br 18.22; N 6.44.

7-(1,3-Benzodioxol-5-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVr). Yield 70%, mp 266–267°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m (1H, 10-H$_{ax}$), 2.00 m (1H, 10-H$_{eq}$), 2.27 m (2H, 9-H), 2.70 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.3, $J_{11\text{-}ax,10\text{-}eq}$ = 4.5 Hz), 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.20 s (1H, 7-H), 5.81 s and 5.88 s (2H, OCH$_2$O), 6.66 d (1H, 6′-H, $J_{6',5'}$ = 8.8 Hz), 6.70 d (1H, 5′-H, $J_{5',6'}$ = 8.8 Hz), 6.77 s (1H, 2′-H), 7.54 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz), 7.55 d (1H, 5-H, $J_{5,6}$ = 8.8 Hz), 7.56 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 8.85 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.92 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.42 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 21.0 (C^3), 26.9 (C^{11}), 36.7 (C^9), 39.5 (C^7), 100.6 (C$^{2''}$), 107.7 (C$^{2'}$), 107.8 (C$^{5'}$), 108.7 (C^{8a}), 117.3 (C^{1a}), 119.9 (C$^{6'}$), 120.5 (C^2), 121.2 (C^{7a}), 123.4 (C^5), 129.9 (C^1), 130.7 (C^{1b}), 131.3 (C^6), 142.5 (C$^{1'}$), 145.3 (C$^{4'}$), 146.9 (C^{5a}), 147.1 (C$^{3'}$), 149.8 (C^3), 153.3 (C^{12a}), 194.0 (C^8). Found, %: C 74.42; H 4.73; N 7.38. $C_{23}H_{18}N_2O_3$. Calculated, %: C 74.58; H 4.90; N 7.56.

7-(4-Ethoxyphenyl)-7,10,11,12-tetrahydrobenzo-[*b*][1,7]phenanthrolin-8(9*H*)-one (IVs). Yield 79%, mp 237–238°C. ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H), 3.89 q (2H, OEt), 2.02 m (1H, 10-H$_{ax}$), 2.22 m (1H, 10-H$_{eq}$), 2.47 m (2H, 9-H), 2.75 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.2 Hz), 2.89 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax}$ = $J_{11\text{-}eq,10\text{-}eq}$ = 4.3 Hz), 5.20 s

(1H, 7-H), 6.77 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.5 Hz), 7.14 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.5 Hz), 7.51 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.0 Hz), 7.52 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.59 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.84 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.90 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.30 s (NH). Found, %: C 77.64; H 5.78; N 7.41. $C_{24}H_{22}N_2O_2$. Calculated, %: C 77.81; H 5.99; N 7.56.

7-(4-Propoxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVt). Yield 75%, mp 302–303°C. ^{1}H NMR spectrum, δ, ppm: 0.95 t, 1.63 q, 3.75 t (OPr); 1.91 m (1H, 10-H$_{ax}$); 2.00 m (1H, 10-H$_{eq}$); 2.26 m (2H, 9-H); 2.71 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.1, $J_{11\text{-}ax,10\text{-}eq}$ = 4.3 Hz); 2.87 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.2 Hz); 5.24 s (1H, 7-H); 6.76 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.5 Hz); 7.14 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz); 7.51 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz); 7.54 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz); 7.59 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz); 8.83 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz); 8.91 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz); 9.41 s (NH). Found, %: C 77.93; H 6.12; N 7.14. $C_{25}H_{24}N_2O_2$. Calculated, %: C 78.10; H 6.29; N 7.29.

7-(4-Methylsulfanylphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVu). Yield 50%, mp 223–224°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (1H, 10-H$_{ax}$), 2.01 m (1H, 10-H$_{eq}$), 2.27 m (2H, 9-H), 2.35 s (SMe), 2.71 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz), 2.88 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.2 Hz), 5.28 s (1H, 7-H), 6.75 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.5 Hz), 7.14 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 7.52 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.1 Hz), 7.54 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz), 7.59 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.91 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.41 s (NH). Found, %: C 73.94; H 5.22; N 6.07; S 7.29. $C_{23}H_{20}N_2OS$. Calculated, %: C 74.16; H 5.41; N 6.25; S 7.52.

Methyl 4-(8-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*][1,7]phenanthrolin-7-yl)benzoate (IVv). Yield 74%, mp 245–246°C. ^{1}H NMR spectrum, δ, ppm: 1.97 m (1H, 10-H$_{ax}$), 2.08 m (1H, 10-H$_{eq}$), 2.30 m (2H, 9-H), 2.70 m (1H, 11-H$_{ax}$), 2.83 m (1H, 11-H$_{eq}$), 3.80 s (3H, MeO), 5.38 s (1H, 7-H), 7.30 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.7 Hz), 7.38 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.46 d.d (1H, 2-H, $J_{2,1}$ = 8.8, $J_{2,3}$ = 4.0 Hz), 7.54 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 7.79 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.7 Hz), 8.80 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.86 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.24 s (NH). Found, %: C 74.82; H 5.07; N 7.11. $C_{24}H_{20}N_2O_3$. Calculated, %: C 75.00; H 5.21; N 7.29.

7-(Biphenyl-4-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVw). Yield 52%, mp 330–331°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H$_{ax}$), 2.05 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.67 m (1H, 11-H$_{ax}$), 2.89 m (1H, 11-H$_{eq}$), 5.18 s (1H, 7-H), 7.19 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.4 Hz), 7.30 m (4H, H$_{arom}$), 7.47 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.49 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 7.60 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 8.85 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 8.92 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 9.43 s (NH). Found, %: C 83.39; H 5.37; N 6.73. $C_{28}H_{22}N_2O$. Calculated, %: C 83.56; H 5.51; N 6.96.

7-(4-Benzyloxyphenyl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVx). Yield 61%, mp 165–166°C. ^{1}H NMR spectrum, δ, ppm: 1.97 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.68 m (1H, 11-H$_{ax}$), 2.88 m (1H, 11-H$_{eq}$), 5.00 s (2H, OCH$_2$), 5.20 s (1H, 7-H), 7.20 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.4 Hz), 7.32 m (4H, H$_{arom}$), 7.47 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.49 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 7.60 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 8.85 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 8.92 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 9.43 s (NH). Found, %: C 80.39; H 5.44; N 6.30. $C_{29}H_{24}N_2O_2$. Calculated, %: C 80.53; H 5.59; N 6.48.

7-(Pyridin-3-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVy). Yield 67%, mp 240–241°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (1H, 10-H$_{ax}$), 2.05 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.73 m (1H, 11-H$_{ax}$), 2.88 m (1H, 11-H$_{eq}$), 5.31 s (1H, 7-H), 7.19 d (2H, 5′-H, 6′-H, $J_{5',6'} = J_{5',4'}$ = 8.8 Hz), 7.42 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.20 d (1H, 4′-H, $J_{4',5'}$ = 8.8 Hz), 8.50 s (1H, 2′-H), 8.75 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.83 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.50 s (NH). Found, %: C 76.93; H 5.08; N 12.67. $C_{21}H_{17}N_3O$. Calculated, %: C 77.06; H 5.20; N 12.84.

7-(Pyridin-4-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVz). Yield 63%, mp 222–223°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (1H, 10-H$_{ax}$), 2.04 m (1H, 10-H$_{eq}$), 2.30 m (2H, 9-H), 2.70 m (1H, 11-H$_{ax}$), 2.82 m (1H, 11-H$_{eq}$), 5.30 s (1H, 7-H), 7.20 d (2H, 2′-H, 6′-H, $J_{2',3'} = J_{6',5'}$ = 8.4 Hz), 7.47 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.49 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.30 d (2H, 3′-H, 5′-H, $J_{3',2'} = J_{5',6'}$ = 8.4 Hz), 8.80 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 9.52 s (NH). Found, %: C 76.80; H 4.95; N 12.59. $C_{21}H_{17}N_3O$. Calculated, %: C 77.06; H 5.20; N 12.84.

7-(2-Thienyl)-7,10,11,12-tetrahydrobenzo[*b*]-[1,7]phenanthrolin-8(9*H*)-one (IVaa). Yield 57%, mp 257–258°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (1H, 10-H$_{ax}$), 2.02 m (1H, 10-H$_{eq}$), 2.26 m (2H, 9-H), 2.72 m (1H, 11-H$_{ax}$), 2.88 m (1H, 11-H$_{eq}$), 5.60 s (1H, 7-H), 7.15 m (3H, thienyl), 7.48 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.50 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.86 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.92 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.56 s (NH). Found, %: C 72.05; H 4.71; N 8.28; S 9.41. $C_{20}H_{16}N_2OS$. Calculated, %: C 72.26; H 4.85; N 8.43; S 9.65.

7-(3-Methylthiophen-2-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVab). Yield 46%, mp 283–284°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.73 m (1H, 11-H$_{ax}$), 2.88 m (1H, 11-H$_{eq}$), 5.58 s (1H, 7-H), 6.67 d (1H, 4′-H, $J_{4',5'}$ = 5.0 Hz), 7.05 d (1H, 5′-H, $J_{5',4'}$ = 5.0 Hz), 7.47 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.51 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.87 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 8.93 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.59 s (NH). Found, %: C 72.59; H 5.07; N 7.83; S 9.01. $C_{21}H_{18}N_2OS$. Calculated, %: C 72.80; H 5.24; N 8.09; S 9.26.

7-(Cyclohex-3-en-1-yl)-7,10,11,12-tetrahydrobenzo[*b*][1,7]phenanthrolin-8(9*H*)-one (IVac). Yield 51%, mp 195–196°C. ^{1}H NMR spectrum, δ, ppm: 0.94–2.05 m (7H, CH_2, 10-H$_{ax}$, 10-H$_{eq}$), 2.30 m (2H, 9-H), 2.70 m (1H, 11-H$_{ax}$), 2.82 m (1H, 11-H$_{eq}$), 5.32 s (1H, 7-H), 7.47 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.49 d.d (1H, 2-H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 4.0 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.80 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 8.83 d (1H, 3-H, $J_{3,2}$ = 4.0 Hz), 9.50 s (NH). Found, %: C 79.82; H 6.61; N 8.33. $C_{22}H_{22}N_2O$. Calculated, %: C 79.97; H 6.71; N 8.48.

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