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6-Quinolinylamine Condensation with Aldehydes and Methyl 2,2-Dimethyl-4,6-dioxocyclohexanecarboxylate

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Abstract—A condensation of methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate with 6-quinolinylamine and aldehydes of aromatic (heteroaromatic, alicyclic) series gave rise to new derivatives of 4,7-phenanthroline. The condensation in ethanol proceeded regioselectively and with a high extent of stereoselectivity leading to the formation of a mixture of *cis*- and *trans*- methyl 9,9-dimethyl-12-aryl (heteryl, cyclohexenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylates. In the more severe conditions both regio- and stereoselectivity of the process decreased resulting in the formation of a mixture of 8- and 10-methoxycarbonyl derivatives (~1:2), and somewhat grew the fraction of the *cis*-isomers in the mixture.

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Cyclic β-diketones owing to their high reactivity are extensively employed in the sysnthesis of fused nitrogen heterocycles [1–4]. In this study aiming at the preparation of new biologically active 4,7-phenanthroline derivatives, unsymmetrical and in particular chiral azaheterocyclic compounds, we investigated from the first time the reaction of methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**I**) with 6-quinolylamine (**II**), and aldehydes of aromatic, heteroaromatic, and cyclohexene series **IIIa–IIIl**.

The condensation of methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**I**) with 6-quinolylamine (**II**) and aldehydes **IIIa–IIIl** was carried out by boiling equimolar amounts of the reagents in ethanol or 1-butanol without catalyst. As a result we obtained in 32–76% yield methyl 9,9-dimethyl-12-aryl(heteryl, cyclohexenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phen-anthroline-10- (**IVa–IVl**, **Va–Vl**) and methyl 9,9-dimethyl-12-aryl(heteryl, cyclohexenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylates (**VIa–VIl, VIIa–VIII**) (Scheme 1).

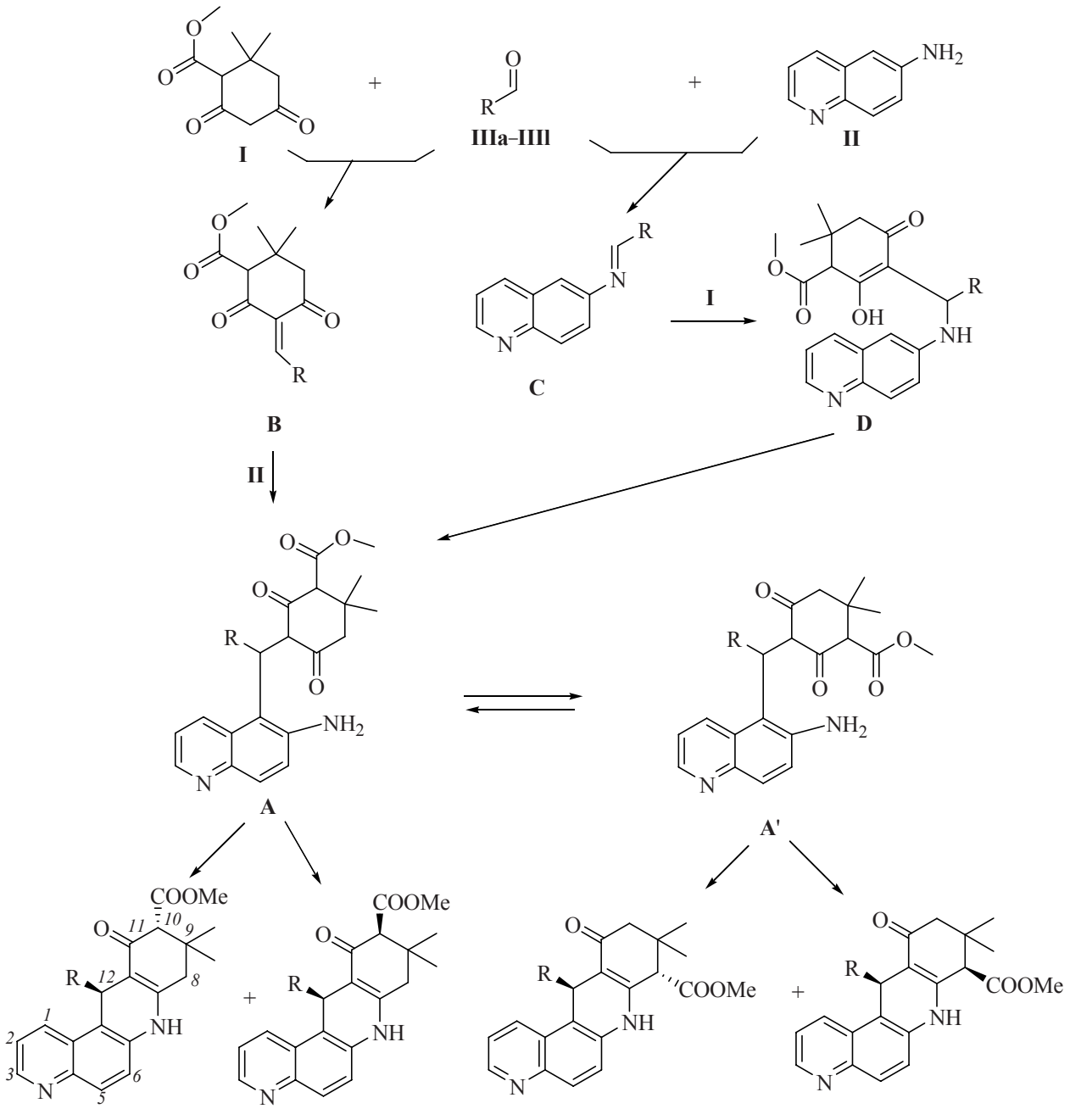
The formation of the benzo[*b*]fusion products suggests that in the three-component mixture 4-methoxycarbonyldimedone (**I**) first reacts with aldehyde **IIIa–IIIl** followed by the addition of the arising 2-aryl(heteryl, cyclohexenyl)methylene-4-methoxycarbonyldimedone **B** to 6-quinolinylamine (**II**) at the carbon atom possessing the highest electron density and located in the position *5* of the quinoline skeleton with the subsequent cyclization of the obtained aminodiketone **A**.

The second possible pathway of formation of 4,7-phenanthroline derivatives **IVa–l** consists in the reaction of 6-quinolinylamine (**II**) with aldehydes **IIIa–IIIl** yielding arylmethylene-6-quinolinylamines **C** with the subsequent addition of compound **I** to the C=N bond of the azomethine leading to intermediate aminodiketone **D**. The latter suffers a hydramine cleavage into 6-quinolinylamine and 2-arylmethylene-4-methoxycarbonyldimedone that further reacts with 6-quinolylamine (**II**) along the above described mechanism. Azomethines **C** were obtained in a preparative yield from 6-quinolinylamine (**II**) and aromatic, heteroaromatic, and cyclohexene aldehydes **IIIa–IIIl** [5, 6] by the reaction with 4-methoxycarbonyldimedone (**I**), and under the conditions used in the three-component condensation they cleanly formed the target 4,7-phenanthroline derivatives. Inasmuch as we failed to isolate intermediate reaction products **A**–**D**, we presumed that they participate in the suggested processes in situ.

It was established that the involvement into the cascade cyclization of an unsymmetrical β-diketone, 4-methoxycarbonyldimedone (methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate), led to the formation of a mixture of

regio- and stereoisomers. Under relatively mild conditions (e.g., at boiling the reagents in ethanol) the reaction proceeds regiospecifically and with a high degree of stereoselectivity: exclusively 10-methoxycarbonyl substituted phenanthrolines **IV, V** are formed, and the sterically and thermodynamically preferable 10,12-*trans*-isomer **IV** prevails in the reaction mixture (*trans/cis* ratio ~3:1). More severe conditions (boiling in 1-butanol) result in a decrease both in the regio- and stereoselectivity of the reaction: 8-methoxycarbonyl regioisomers **VI, VII** appear in the reaction mixture (~35%), and the ratio of *cis*- and *trans*-isomer both for 10- and 8-methoxy-

Scheme 1.



R = 4-MeC_6H_4 (**a**), 4-*i*-PrC_6H_4 (**b**), 2-IC_6H_4 (**c**), 3-HOC_6H_4 (**d**), 3,4,5-$(MeO)_3C_6H_2$ (**e**), 3,4-$OCH_2OC_6H_3$ (**f**), 4-$EtOC_6H_4$ (**g**), 4-$PrOC_6H_4$ (**h**), 4-$PhCH_2OC_6H_4$ (**i**), 4-$MeSC_6H_4$ (**j**), 2-(3-methyl)thienyl (**k**), cyclohexen-4-yl (**l**).

carbonylphenanthrolines becomes ~1:2.

The structure of 10,12-*trans*-isomer was attributed to the compound prevailing in the reaction mixture basing on the fact that the proton signal from H^{10} in its ^1H NMR spectrum appeared more downfield (δ 3.50 ppm), indicating its location in the deshielding region of the aromatic ring. In the spectrum of 10,12-*cis*-isomer the signal of the respective proton was observed in a stronger field (δ 3.04 ppm), showing that it was situated over or under the plane of the aromatic ring (shielding region).

The difference in the chemical shifts of the protons attached to atom C^8 are also due to the difference in their spatial surrounding. The proton in compound **IVa** possessing a *cis*-orientation with respect to the methoxycarbonyl group (δ 2.70 ppm) is removed from the aromatic ring at the C^{12} atom and suffers deshilding only from the ester substituent. In the minor component the H^8-*cis* proton is deshielded both by the ester group and the aromatic ring resulting in a still more downfield shift (δ 2.80 ppm). Evidently the formation of 10-methoxycarbonyl isomers **IV, V** occurred by the cyclization of aminodiketone intermadiate **A** at the spatially more accessible (not shielded by the ester substituent) carbonyl group. The formation of 8-regioisomers **VI, VII** is sterically hindered and therefore requires more stringent reaction conditions (Scheme 2).

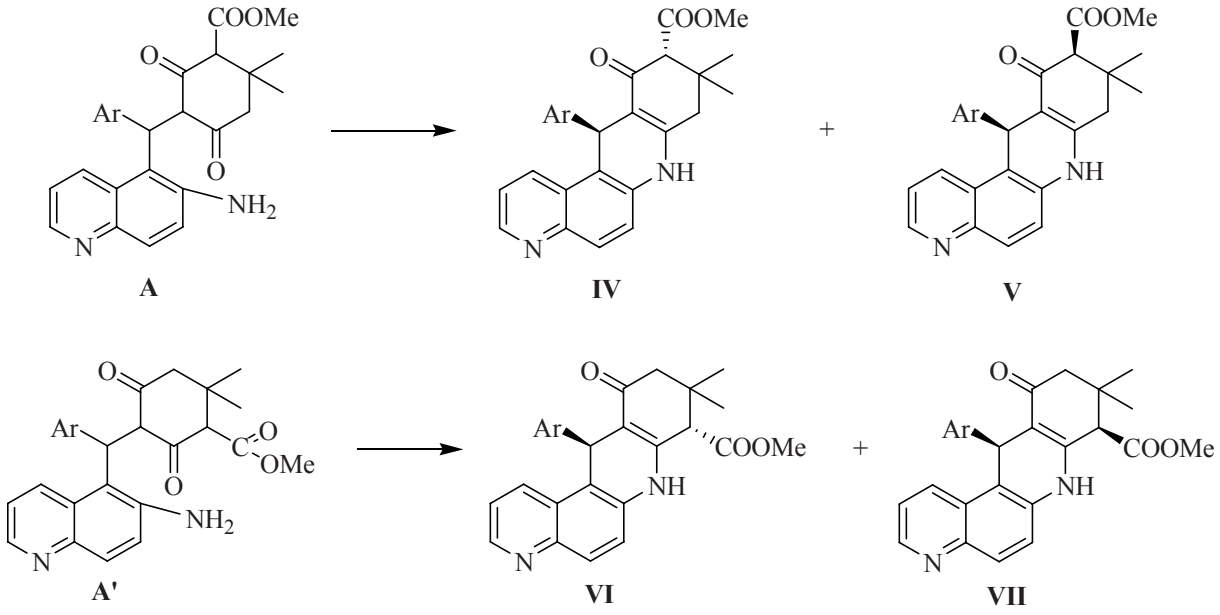
The sterical control that determined the predominant formation of the *trans*-isomers occurred at the earlier stage of the reaction, the addition of β-diketone to Schiff's base **C** resulting in the Mannich base **A** of the corresponding structure, or at the amination of arylidenediketone **B**.

In the IR spectra of compounds **IVa–IVl** strong absorption bands are observed at 1605 and 1515 cm^{-1} characteristic of the vinylog amide fragment (1580, 1520 cm^{-1}) [7]. The strong bands at 3260 and 1630 cm^{-1} belong respectively to the stretching and bending vibrations of the secondary amino group. The stretching vibrations of alkyl groups and the cycloaliphatic C-H bonds appear in the region 2960–2870 cm^{-1}, those of the C–H bonds of the aromatic rings, at 3060–3030 cm^{-1}. In the IR spectra of the compounds synthesized the ester group C=O band is observed at 1740–1730 cm^{-1}.

The spatial arrangement of the obtained benzacridones was established from the data of ^1H NMR spectroscopy. The NMR spectra were registered from the samples enriched with the corresponding stereoisomer to 80% or more.

We showed formerly that in the structural analogs of these compounds synthesized from dimedone the two methyl groups in the cyclohexene fragment possessed different geminal coupling constants, 18 and 16 Hz. The oximation of the corresponding derivatives resulted in the downfield shift in the ^1H NMR spectrum for the pair of protons with the larger coupling constant (δ ~0.6–0.7 for pseudoequatorial and ~0.2–0.3 ppm for pseudoaxial

Scheme2.



protons). From this fact we drew a conclusion that the pair of geminal protons with the coupling constant of 18 Hz was linked to C^{10}. Whereas in the spectra of phenanthrolines **IV** and **V** formed under mild conditions pairs of doublet signals were present with the geminal coupling constant 16 Hz (δ ~2.45 and 2.7 ppm) characteristic of the methylene group C^8H_2, these compounds were assigned the structure of 10-methoxycarbonyl regioisomers. The predominant in the reaction mixture compound **IV** was considered to be the *trans*-isomer because the signal of its methine proton attached to atom C^{10} appeared downfield (δ ~3.4 ppm) with respect to that of compound **V** (δ ~3.1 ppm) indicating the location of this proton in isomer **IV** in the deshielding region, its *cis*-position to the aryl substituent at the atom C^{12}, and consequently the *trans*-position to the methoxycarbonyl group.

In the spectra of the second pair of isomeric phenanthrolines **VI** and **VII** obtained under more severe conditions doublet signals appeared with the geminal coupling constant 18 Hz characteristic of $C^{10}H_2$ group (δ ~2 and 2.4 ppm) evidencing the structure of 8-methoxycarbonyl regioisomers. The strong downfield shift of one among the signals (~2 ppm) corresponds to the occurrence of the C^{10}H-*trans* proton in the shielding region of the aromatic substituent at the atom C^{12}. The methine protons C^8H of compounds **VI** and **VII** appeared at δ 3.37 and 3.06 ppm respectively that indicated as mentioned above the *trans*- and *cis*-position of the aryl and methoxycarbonyl groups in these compounds.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer Nicolet Protégé-460. ^{1}H NMR spectra were registered on a spectrometer Bruker Avance (500 MHz) from solutions in DMSO-d_6, internal reference TMS. The reaction progress was monitored and the purity of compounds was checked by GLC on a chromatograph Chrom-5 equipped with a glass column (2000 × 2 mm) packed with Chromaton-N-AW-DMCS (0.16–0.20), liquid phase Apiezon L.

4-Methoxycarbonyldimedone (I) was obtained by procedure [8] from mesityl oxide and dimethyl malonate. 6-Quinolylamine (**II**) was prepared by procedure [9].

Three-component condensation (see procedure [10]). Equimolar amounts (5 mmol) of methyl 2,2-dimethyl-4,6-dioxocyclohexanecarboxylate (**I**), 6-quinolinylamine (**II**), and aldehyde of aromatic, heteroaromatic, or cyclohexene series **IIIa–IIIl** were boiled in 20 ml of ethanol (butanol) without catalyst till the completion of the reaction (3–4 h, GLC monitoring). Then the reaction mixture was evaporated to ~1/4 of the initial volume, and the reaction product was precipitated by adding excess ether. The precipitated crystals were filtered off and recrystallized. On crystallization from ethanol the precipitated product was enriched with the prevailing in the reaction mixture 10-methoxycarbonyl isomer (stereoisomers mixture). The mixture of products obtained on evaporation of the mother liquor and containing mainly 8-methoxycarbonyl isomers was recrystallized from anhydrous acetone. Many times repeated dissolution-crystallization provided samples enriched with the corresponding isomers to 80% and more. The separation of stereoisomers was performed by crystallization from a mixture ethanol–benzene. The samples used in registering the spectra contained no less than 80% of the corresponding stereoisomer.

Compounds IVa–VIIa were obtained in an overall yield 51%. After 6 crystallizations from the mixture of regioisomeric from ethanol a sample was obtained contain-ing ~90% of the mixture of 10-methoxycarbonyl isomer **IVa** and **IVb**. The mixture containing ~85% of 8-methoxycarbonyl isomers **VIa** and **VIIa** was obtained from 7 crystallizations from acetone of the mother residue from the evaporation of the solution. *cis*- and *trans*-Isomers were separated by multiple crystallization from the mixture ethanol–benzene, 1:2. The samples used in registering the spectra contained no less than 80% of the corresponding stereoisomer.

Methyl 9,9-dimethyl-12-(4-methylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVa). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.12 s (3H, $ArCH_3$), 2.43 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.70 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.50 s (1H, H^{10}), 3.56 s (3H, OCH_3), 5.63 s (1H, H^{12}); 6.92 d (2H), 7.12 d (2H) (C_6H_4); 7.41 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.54 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.80 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.63 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.90 s (NH).

10,12-*cis*-Isomer (Va). ^{1}H NMR spectrum, δ, ppm: 0.91 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 2.12 s (3H, $ArCH_3$), 2.40 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.80 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.04 C (1H, H^{10}), 3.58 s (3H, OCH_3), 5.70 s (1H, H^{12}); 6.92 d (2H), 7.12 d (2H) (C_6H_4); 7.40 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.39 d (1H, H^1, $J_{1,2}$ 8.0 Hz),

8.63 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.05 s (NH).

Methyl 9,9-dimethyl-12-(4-methylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIa). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.03 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.12 c (3H, $ArCH_3$), 2.40 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.45 s (1H, H^8), 3.56 s (3H, OCH_3), 5.63 s (1H, H^{12}); 6.92 d (2H), 7.12 d (2H) (C_6H_4); 7.41 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.54 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.80 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.64 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.90 s (NH).

10,12-*cis*-Isomer (VIIa). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 1.97 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.12 s (3H, $ArCH_3$), 2.42 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.02 s (1H, H^8), 3.56 s (3H, OCH_3), 5.63 s (1H, H^{12}); 6.92 d (2H), 7.12 d (2H) (C_6H_4); 7.40 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.53 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.81 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.64 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 s (NH).

Compounds (IVb–VIIb) were obtained in an overall yield 84%.

Methyl 9,9-dimethyl-12-(4-isopropylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVb). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 0.99 s (3H) [$C^9CH_3)_2$], 1.07 d [6H, $CH(CH_3)_2$], 2.46 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.67 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 2.72 m [1H, $CH(CH_3)_2$], 3.42 s (1H, H^{10}), 3.59 s (3H, OCH_3), 5.69 s (1H, H^{12}); 7.01 d (2H, *J* 7.0 Hz), 7.16 d (2H, *J* 7.0 Hz) (C_6H_4), 7.43 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.54 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.91 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.96 (NH).

10,12-*cis*-Isomer (Vb). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 0.98 C (3H) [$C^9(CH_3)_2$], 1.07 d [6H, $CH(CH_3)_2$], 2.44 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.76 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 2.72 m [1H, $CH(CH_3)_2$], 3.10 s (1H, H^{10}), 3.58 s (3H, OCH_3), 5.71 s (1H, H^{12}); 7.01 d (2H, *J* 7.0 Hz), 7.16 d (2H, *J* 7.0 Hz) (C_6H_4); 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.88 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.93 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.03 (NH).

Methyl 9,9-dimethyl-12-(4-isopropylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIb). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.10 s (3H) [$C^9(CH_3)_2$], 1.07 d [6H, $CH(CH_3)_2$], 2.04 d (1H, H^{10a}, $^2J_{10a,10\varepsilon}$ 18.0 Hz), 2.41 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 2.72 m [1H, $CH(CH_3)_2$], 3.37 s (1H, H^8), 3.70 s (3H, OCH_3), 5.75 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.18 d (2H, *J* 7.0 Hz) (C_6H_4); 7.43 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.84 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.93 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.65 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.92 (NH).

10,12-*cis*-Isomer (VIIb). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.02 s [3H, $C^9(CH_3)_2$], 1.07 d [6H, $CH(CH_3)_2$], 1.96 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.43 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 2.72 m [1H, $CH(CH_3)_2$], 3.06 s (1H, H^8), 3.69 s (3H, OCH_3), 5.81 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.17 d (2H, *J* 7.0 Hz) (C_6H_4); 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.93 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.97 (NH).

Compounds (IVc–VIIc) were obtained in an overall yield 62%.

Methyl 9,9-dimethyl-12-(2-iodophenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVc). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 2.43 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.82 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.43 s (1H, H^{10}), 3.60 s (3H, OCH_3), 5.72 s (1H, H^{12}), 6.76 t ($1H_{arom}$), 7.18 m ($3H_{arom}$), 7.46 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.57 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.72 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.92 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.67 m (2H, H^3), 10.15 (NH).

10,12-*cis*-Isomer (Vc). ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H), 1.04 s (3H) [$C^9(CH_3)_2$], 2.46 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.73 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.05 s (1H, H^{10}), 3.56 s (3H, OCH_3), 5.70 s (1H, H^{12}), 6.76 t ($1H_{arom}$), 7.18 m ($3H_{arom}$), 7.45 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.71 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.89 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.67 m (1H, H^3), 10.08 (NH).

Methyl 9,9-dimethyl-12-(2-iodophenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthro-line-8-carboxylate. 10,12-*trans*-Isomer (VIc). ^{1}H NMR spectrum, δ, ppm: 1.00 s (3H), 1.05 s (3H) [$C^9(CH_3)_2$], 1.92 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.46 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.37 s (1H, H^8), 3.64 s (3H, OCH_3), 5.82 s (1H, H^{12}), 6.76 t ($1H_{arom}$), 7.18 m ($3H_{arom}$), 7.45 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.72 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.87 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.67 m (1H, H^3), 10.13 (NH).

10,12-*cis*-Isomer (VIIc). ^{1}H NMR spectrum, δ, ppm: 0.99 s (3H), 1.11 s (3H) [$C^9(CH_3)_2$], 2.04 d (1H,

H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.40 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.02 s (1H, H^8), 3.62 s (3H, OCH_3), 5.77 s (1H, H^{12}), 6.76 t ($1H_{arom}$), 7.18 m ($3H_{arom}$), 7.45 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.71 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.66 m (1H, H^3), 10.05 (NH).

Compounds (IVd–VIId) were obtained in an overall yield 74%.

Methyl 12-(3-hydroxyphenyl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVd). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.68 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.47 s (1H, H^{10}), 3.51 s (3H, OCH_3), 5.67 s (1H, H^{12}), 6.60 d (^3J 7.3 Hz), 6.92 d (^3J 7.3 Hz), 7.30–7.50 m (5H, H^2, C_6H_4), 7.59 d (1H, H^5, $J_{5,6}$ 7.8 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 9.1 Hz), 8.34 d (1H, H^6, $J_{6,5}$ 7.8 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 9.12 s (1H, OH), 10.06 s (NH).

10,12-*cis*-Isomer (Vd). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 1.06 s (3H) [$C^9(CH_3)_2$], 2.47 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.65 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.12 s (1H, H^{10}), 3.52 s (3H, OCH_3), 5.67 s (1H, H^{12}), 6.61 d (^3J 7.3 Hz), 6.91 d (^3J 7.3 Hz), 7.30–7.48 m (5H, H^2, C_6H_4); 7.60 d (1H, H^5, $J_{5,6}$ 7.8 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 9.1 Hz), 8.34 d (1H, H^6, $J_{6,5}$ 7.8 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 9.12 s (1H, OH), 9.99 s (NH).

Methyl 12-(3-hydroxyphenyl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VId). ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.68 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.43 s (1H, H^8), 3.52 s (3H, OCH_3), 5.67 s (1H, H^{12}), 6.60 d (^3J 7.8 Hz), 6.92 d (^3J 7.8 Hz), 7.30–7.50 m (5H, H^2, C_6H_4), 7.59 d (1H, H^5, $J_{5,6}$ 7.8 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 9.1 Hz), 8.34 d (1H, H^6, $J_{6,5}$ 7.8 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 9.12 s (1H, OH), 10.04 s (NH).

10,12-*cis*-Isomer (VIId). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.68 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.10 s (1H, H^8), 3.52 s (3H, OCH_3), 5.67 s (1H, H^{12}), 6.60 d (^3J 7.3 Hz), 6.92 d (^3J 7.3 Hz), 7.30–7.50 m (5H, H^2, C_6H_4); 7.59 d (1H, H^5, $J_{5,6}$ 7.8 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 9.1 Hz), 8.34 d (1H, H^6, $J_{6,5}$ 7.8 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 9.12 s (1H, OH), 9.99 s (NH).

Compounds (IVe–VIIe) were obtained in an overall yield 77%.

Methyl 9,9-dimethyl-11-oxo-12-(3,4,5-trimethoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVe). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.46 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.73 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.48 s (1H, H^{10}), 3.54 s (6H, 2OMe), 3.58 s (3H, $COOCH_3$), 3.65 s (3H, OMe), 5.72 s (1H, H^{12}), 6.92 d (^3J 8.9 Hz), 6.41 s, 7.25–7.50 m (3H, H^2, C_6H_2), 7.57 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.35 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.96 s (NH).

10,12-*cis*-Isomer (Ve). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 2.46 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.73 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.09 s (1H, H^{10}), 3.54 s (2OMe), 3.58 s (3H, $COOCH_3$), 3.65 s (OMe), 5.72 s (1H, H^{12}), 6.92 d (^3J 8.9 Hz), 6.41 s, 7.25–7.50 m (3H, H^2, C_6H_2), 7.57 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.35 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.90 C (NH).

Methyl 10,12-*trans*-9,9-dimethyl-11-oxo-12-(3,4,5-trimethoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8- carboxylate. 10,12-*trans*-Isomer (VIe). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.46 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.73 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.48 s (1H, H^8), 3.54 s (2OMe), 3.58 s (3H, OCH_3), 3.65 s (OMe), 5.72 s (1H, H^{12}); 6.41 s, 7.25–7.50 m (3H, H^2, C_6H_2); 7.57 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.35 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.96 s (NH).

10,12-*cis*-Isomer (VIIe). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 2.46 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.73 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.09 s (1H, H^8), 3.54 s (2OMe), 3.58 s (3H, OCH_3), 3.65s (OMe), 5.72 s (1H, H^{12}); 6.41 s, 7.25–7.50 m (3H, H^2, C_6H_2); 7.57 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.35 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.67 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.94 s (NH).

Compounds (IVf–VIIf) were obtained in an overall yield 57%.

Methyl 9,9-dimethyl-12-(3,4-methylenedioxyphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVf). ^{1}H NMR spectrum, δ, ppm: 0.99 s (3H), 1.06 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.68 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.44 C (1H, H^{10}), 3.59 s (3H, OCH_3), 5.85 m (2H, OCH_2O), 5.94 s (1H, H^{12}); 6.64 s, 6.80 s, 7.30–7.45 m (4H, H^2, C_6H_3); 7.48 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 8.7 Hz), 8.40 d (1H,

H^1, $J_{1,2}$ 7.6 Hz), 8.69 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 s (NH).

10,12-*cis*-Isomer (Vf). ^{1}H NMR spectrum, δ, ppm: 0.98 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.68 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.12 s (1H, H^{10}), 3.58 s (3H, OCH_3), 5.84 m (2H, OCH_2O), 5.94 s (1H, H^{12}); 6.64 s, 6.80 s, 7.30–7.45 m (4H, H^2, C_6H_3); 7.48 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 8.7 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.69 d (1H, H^3, $J_{3,2}$ 4.9 Hz), 9.96 s (NH).

Methyl 9,9-dimethyl-12-(3,4-methylenedioxyphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIf). ^{1}H NMR spectrum, δ, ppm: 0.99 s (3H), 1.05 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.68 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.45 s (1H, H^8), 3.59 s (3H, OCH_3), 5.85 m (OCH_2O), 5.94 s (H^{12}); 6.64 s, 6.80 s, 7.30–7.45 m (4H, H^2, C_6H_3); 7.48 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 8.7 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.69 d (1H, H^3, $J_{3,2}$ 4.9 Hz), 9.98 s (NH).

10,12-*cis*-Isomer (VIIf). ^{1}H NMR spectrum, δ, ppm: 0.98 s (3H), 1.04 s (3H) [$C^9(CH_3)_2$], 2.45 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.68 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.11 s (1H, H^8), 3.58 s (3H, OCH_3), 5.84 m (OCH_2O), 5.94 s (H^{12}); 6.64 s, 6.80 s, 7.30–7.45 m (4H, H^2, C_6H_3); 7.48 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 8.7 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 7.6 Hz), 8.69 d (1H, H^3, $J_{3,2}$ 4.9 Hz), 9.97 s (NH).

Compounds (IVg–VIIg) were obtained in an overall yield 73%.

Methyl 9,9-dimethyl-11-oxo-12-(4-ethoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVg). ^{1}H NMR spectrum, δ, ppm: 1.20 t, 4.11 q (OEt), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.54 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.82 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.42 s (1H, H^{10}), 3.60 s (3H, OCH_3), 5.75 s (1H, H^{12}); 6.70 d, 7.08 d, 7.12–7.28 m (5H, H^2, C_6H_4, ^3J 7.2 Hz); 7.48 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.79 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.27 d (1H, H^1, $J_{1,2}$ 7.7 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.92 s (NH).

10,12-*cis*-Isomer (Vg). ^{1}H NMR spectrum, δ, ppm: 1.18 t, 4.10 q (OEt), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.54 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.82 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.13 s (1H, H^{10}), 3.61 s (3H, OCH_3), 5.75 s (1H, H^{12}); 6.71 d, 7.09 d, 7.12–7.28 m (5H, H^2, C_6H_4, ^3J 7.2 Hz); 7.49 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.80 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.27 d (1H, H^1, $J_{1,2}$ 7.7 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.86 s (NH).

Methyl 9,9-dimethyl-11-oxo-12-(4-ethoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIg). ^{1}H NMR spectrum, δ, ppm: 1.20 t, 4.12 q (OEt), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.54 d (1H, H^{10a}, $^2J_{10a,10\varepsilon}$ 19.0 Hz), 2.82 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.42 s (1H, H^8), 3.60 s (3H, OCH_3), 5.75 s (1H, H^{12}); 6.70 d, 7.08 d, 7.12–7.28 m (5H, H^2, C_6H_4, ^3J 7.2 Hz); 7.48 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.79 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.27 d (1H, H^1, $J_{1,2}$ 7.7 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.93 s (NH).

10,12-*cis*-Isomer (VIIg). ^{1}H NMR spectrum, δ, ppm: 1.19 t, 4.11 q (OEt), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.54 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.82 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.13 s (1H, H^8), 3.61 s (3H, OCH_3), 5.75 s (1H, H^{12}); 6.70 d, 7.08 d, 7.12–7.28 m (5H, H^2, C_6H_4, ^3J 7.2 Hz); 7.48 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.79 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.27 d (1H, H^1, $J_{1,2}$ 7.7 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.8 Hz), 9.85 s (NH).

Compounds (IVh–VIIh) were obtained in an overall yield 70%.

Methyl 9,9-dimethyl-11-oxo-12-(4-propoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVh). ^{1}H NMR spectrum, δ, ppm: 0.95 t, 1.63 q, 3.78 t (OPr), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.52 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.76 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.42 s (1H, H^{10}), 3.60 s (3H, OCH_3), 5.68 s (1H, H^{12}); 6.70 d (2H, *J* 7.0 Hz), 7.13 d (2H, *J* 7.0 Hz) (C_6H_4); 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.89 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.39 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.70 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 (NH).

10,12-*cis*-Isomer (Vh). ^{1}H NMR spectrum, δ, ppm: 0.84 t, 1.63 q, 3.78 t (OPr), 0.93 s (3H), 0.98 s (3H) [$C^9(CH_3)_2$], 2.52 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.76 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.08 s (1H, H^{10}), 3.60 s (3H, OCH_3), 5.70 s (1H, H^{12}); 6.69 d (2H, *J* 7.0 Hz), 7.14 d (2H, *J* 7.0 Hz) (C_6H_4); 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.88 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.38 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.69 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.03 (NH).

Methyl 9,9-dimethyl-11-oxo-12-(4-propoxyphenyl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIh). ^{1}H NMR spectrum, δ, ppm: 0.93 t, 1.64 q, 3.79 t (OPr), 0.92 s (3H), 1.10 s (3H) [$C^9(CH_3)_2$], 2.04 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.41 d (1H, H^{10e},

$^2J_{10e,10a}$ 18.0 Hz), 3.37 s (1H, H^8), 3.70 s (3H, OCH_3), 5.75 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.18 d (2H, *J* 7.0 Hz) (C_6H_4); 7.43 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.84 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.93 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.65 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.92 (NH).

10,12-*cis*-Isomer (VIIh). ^{1}H NMR spectrum, δ, ppm: 0.93 t, 1.64 q, 3.79 t (OPr), 0.92 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 1.96 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.43 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.06 s (1H, H^8), 3.69 s (3H, OCH_3), 5.81 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.17 d (2H, *J* 7.0 Hz) (C_6H_4); 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.55 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.85 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 7.93 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.66 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 (NH).

Compounds (IVi–VIIi) were obtained in an overall yield 78%.

Methyl 12-(4-benzyloxyphenyl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVi). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 1.00 s (3H) [$C^9(CH_3)_2$], 2.41 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.70 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.42 s (1H, H^{10}), 3.58 s (3H, OCH_3), 4.94 s (2H, OCH_2Ph), 5.69 s (1H, H^{12}); 6.89 d (2H, *J* 7.0 Hz), 7.16 d (2H, *J* 7.0 Hz) (C_6H_4); 7.28–7.40 m (5H Ph), 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.38 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 s (NH).

10,12-*cis*-Isomer (Vi). ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H), 1.01 s (3H) [$C^9(CH_3)_2$], 2.41 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.70 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.09 s (1H, H^{10}), 3.58 s (3H, OCH_3), 4.94 s (2H, OCH_2Ph), 5.72 s (1H, H^{12}); 6.89 d (2H, *J* 7.0 Hz), 7.16 d (2H, *J* 7.0 Hz) (C_6H_4); 7.28–7.40 m (5H, Ph), 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.38 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.03 s (NH).

Methyl 12-(4-benzyloxyphenyl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIi). ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H), 1.06 s (3H) [$C^9(CH_3)_2$], 2.41 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.70 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.38 s (1H, H^8), 3.58 C (3H, OCH_3), 4.94 s (2H, OCH_2Ph), 5.75 s (1H, H^{12}); 6.89 d (2H, *J* 7.0 Hz), 7.17 d (2H, *J* 7.0 Hz) (C_6H_4); 7.28–7.40 m (5H, Ph), 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.38 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.90 s (NH).

10,12-*cis*-12-Isomer (VIIi). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H), 1.10 s (3H) [$C^9(CH_3)_2$], 2.41 d (1H, H^{10a}, $^2J_{10a,10e}$ 16.0 Hz), 2.70 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.08 s (1H, H^8), 3.58 s (3H, OCH_3), 4.94 s (2H, OCH_2Ph), 5.82 s (1H, H^{12}); 6.89 d (2H, *J* 7.0 Hz), 7.18 d (2H, *J* 7.0 Hz) (C_6H_4); 7.28–7.40 m (5H Ph), 7.42 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.88 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.38 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.68 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.96 s (NH).

Compounds (IVj–VIIj) were obtained in an overall yield 68%.

Methyl 9,9-dimethyl-12-(4-methylsulfanylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVj). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.36 s (3H, SCH_3), 2.43 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.70 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.50 s (1H, H^{10}), 3.56 s (3H, OCH_3), 5.71 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.18 d (2H, *J* 7.0 Hz) (C_6H_4); 7.41 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.54 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.80 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 9.0 Hz), 8.63 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.99 s (NH).

10,12-*cis*-Isomer (Vj). ^{1}H NMR spectrum, δ, ppm: 0.91 s (3H), 1.02 s (3H) [$C^9(CH_3)_2$], 2.36 s (3H, SCH_3), 2.41 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.80 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.04 s (1H, H^{10}), 3.58 s (3H, OCH_3), 5.70 s (1H, H^{12}); 6.99 d (2H, *J* 7.0 Hz), 7.15 d (2H, *J* 7.0 Hz) (C_6H_4), 7.40 d.d (1H, H^2, $J_{2,1}$ 8.0 Hz, $J_{2,3}$ 4.0 Hz), 7.56 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.82 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.39 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.63 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.08 C (NH).

Methyl 9,9-dimethyl-12-(4-methylsulfanylphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIj). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.03 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.36 s (3H, SCH_3) 2.41 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.45 s (1H, H^8), 3.56 s (3H, OCH_3), 5.70 s (1H, H^{12}); 7.00 d (2H, *J* 7.0 Hz), 7.17 d (2H, *J* 7.0 Hz) (C_6H_4); 7.41 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.54 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.80 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.64 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.98 s (NH).

10,12-*cis*-Isomer (VIIj). ^{1}H NMR spectrum, δ, ppm: 0.91 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 1.97 d (1H, H^{10a},

$^2J_{10a,10e}$ 18.0 Hz), 2.34 s (3H, SCH_3), 2.42 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.02 s (1H, H^8), 3.56 s (3H, OCH_3), 5.71 s (1H, H^{12}); 7.01 d (2H, *J* 7.0 Hz), 7.16 d (2H, *J* 7.0 Hz) (C_6H_4); 7.40 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.53 d (1H, H^5, $J_{5,6}$ 10.0 Hz), 7.81 d (1H, H^6, $J_{6,5}$ 10.0 Hz), 8.40 d (1H, H^1, $J_{1,2}$ 8.0 Hz), 8.64 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 10.02 s (NH).

Compounds (IVk–VIIk) were obtained in an overall yield 63%.

Methyl 12-(3-methylthien-2-yl)-9,9-di-methyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVk). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.43 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.50 C (3H, Me), 2.72 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.46 C (1H, H^{10}), 3.56 C (3H, OCH_3), 6.03 C (1H, H^{12}), 6.64 m, 7.02 m, 7.36–7.50 m (3H, H^2, $2H_{heteroarom}$), 7.54 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.90 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.23 d (1H, H^1, $J_{1,2}$ 7.3 Hz), 8.72 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 10.09 s (NH).

10,12-*cis*-Isomer (Vk). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 c (3H) [$C^9(CH_3)_2$], 2.43 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.50 C (3H, Me), 2.72 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.13 C (1H, H^{10}), 3.56 C (3H, OCH_3), 6.03 C (1H, H^{12}), 6.64 m, 7.02 m, 7.36–7.50 m (3H, H^2, $2H_{heteroarom}$), 7.54 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.90 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.23 d (1H, H^1, $J_{1,2}$ 7.3 Hz), 8.72 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 10.02 c (NH).

Methyl 12-(3-methylthien-2-yl)-9,9-dimethyl-11-oxo-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIk). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.43 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.50 s (3H, Me), 2.72 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.46 s (1H, H^8), 3.56 s (3H, OCH_3), 6.03 s 1H, H^{12}), 6.64 m, 7.02 m, 7.36–7.50 m (3H, H^2, $2H_{heteroarom}$), 7.54 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.90 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.23 d (1H, H^1, $J_{1,2}$ 7.3 Hz), 8.72 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 10.08 s (NH).

10,12-*cis*-Isomer (VIIk). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 2.43 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.50 s (3H, Me), 2.72 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.13 s (1H, H^8), 3.56 s (3H, OCH_3), 6.03 s (1H, H^{12}), 6.64 m, 7.02 m, 7.36–7.50 m (3H, H^2, $2H_{heteroarom}$), 7.54 d (1H, H^5, $J_{5,6}$ 8.9 Hz), 7.90 d (1H, H^6, $J_{6,5}$ 8.9 Hz), 8.23 d (1H, H^1, $J_{1,2}$ 7.3 Hz), 8.72 d (1H, H^3, $J_{3,2}$ 4.7 Hz), 10.03 s (NH).

Compounds (IVl–VIIl) were obtained in an overall yield 49%.

Methyl 9,9-dimethyl-11-oxo-12-(cyclohexen-4-yl)-7,8,9,10,11,12-hexahydrobenzo[*b*]-4,7-phenanthroline-10-carboxylate. 10,12-*trans*-Isomer (IVl). ^{1}H NMR spectrum, δ, ppm 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 0.94–1.90 m $7H_{cycloaliph}$), 2.53 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.63 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.46 s (1H, H^{10}), 3.57 s (3H, OCH_3), 4.80 d, 5.42 d (CH=CH), 5.53 s (1H, H^{12}), 7.47 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.52 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H^1, $J_{1,2}$ 9.0 Hz), 8.48 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.75 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.92 s (NH).

10,12-*cis*-Isomer (Vl). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 0.94–1.90 m $7H_{cycloaliph}$), 2.53 d (1H, H^{8a}, $^2J_{8a,8e}$ 16.0 Hz), 2.63 d (1H, H^{8e}, $^2J_{8e,8a}$ 16.0 Hz), 3.46 s (1H, H^{10}), 3.57 s (3H, OCH_3), 4.80 d, 5.42 d (CH=CH), 5.53 C (1H, H^{12}), 7.47 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.52 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H^1, $J_{1,2}$ 9.0 Hz), 8.48 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.75 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.88 s (NH).

Methyl 9,9-dimethyl-11-oxo-12-(cyclohexen-4-yl)-7,8,9,10,11,12-hexahydrobenzo-[*b*]-4,7-phenanthroline-8-carboxylate. 10,12-*trans*-Isomer (VIl). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 0.94–1.90 m ($7H_{cycloaliph}$), 2.53 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.63 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.46 s (1H, H^8), 3.57 s (3H, OCH_3), 4.80 d, 5.42 d (CH=CH), 5.53 s (1H, H^{12}), 7.47 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.52 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H^1, $J_{1,2}$ 9.0 Hz), 8.48 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.75 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.91 s (NH).

10,12-*cis*-Isomer (VIIl). ^{1}H NMR spectrum, δ, ppm: 0.92 s (3H), 1.03 s (3H) [$C^9(CH_3)_2$], 0.94–1.90 m ($7H_{cycloaliph}$), 2.53 d (1H, H^{10a}, $^2J_{10a,10e}$ 18.0 Hz), 2.63 d (1H, H^{10e}, $^2J_{10e,10a}$ 18.0 Hz), 3.07 s (1H, H^8), 3.56 s (3H, OCH_3), 4.80 d, 5.42 d (CH=CH), 5.53 s (1H, H^{12}), 7.47 d.d (1H, H^2, $J_{2,1}$ 8.0, $J_{2,3}$ 4.0 Hz), 7.52 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H^1, $J_{1,2}$ 9.0 Hz), 8.48 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.75 d (1H, H^3, $J_{3,2}$ 4.0 Hz), 9.87 s (NH).

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REFERENCES

1. Kozlov, N.S. and Gusak, K.N., *Dokl. Akad. Nauk SSSR*, 1990, vol. 314, p. 1419.
2. Kozlov, N.G. and Gusak, K.N., *Zh. Org. Khim.,* 2006, vol. 42, p. 1680.
3. Kozlov, N.G., Tereshko, A.B., and Gusak, K.N., *Zh. Org. Khim.,* 2006, vol. 42, p. 281.
4. Kozlov, N.G. and Gusak, K.N., *Zh. Obshch. Khim.,* 2006, vol. 76, p. 294.
5. Gusak, K.N., Tereshko, A.B., and Kozlov, N.G., *Zh. Obshch. Khim.,* 2000, vol. 70, p. 320.
6. Gusak, K.N., Tereshko, A., and Kozlov, N.G., *Zh. Org. Khim.,* 2001, vol. 37, p. 1564.
7. Martinez, R., Cortes, E., and Toscano, R.A. *J. Heterocycl. Chem*., 1990, vol. 27, p. 363.
8. Vorlander, D., *Ann.,* 1897, vol. 294, p. 254.
9. Gusak, K.N., Tereshko, A.B., and Kozlov, N.G., *Zh. Obshch. Khim.,* 2000, vol. 70, p. 323.
10. Gusak, K.N., Tereshko, A.B., and Kozlov, N.G., *Zh. Org. Khim.,* 2004, vol. 40, p. 1709.