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Condensation of Fluorine-Substituted Benzaldehydes with Amines and Cyclic Ketones

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Abstract—Condensation of fluorine-containing benzaldehydes with naphthalen-2-amine or quinolin-6-amine and cyclic ketones (cyclopentanone, cyclohexanone, and 4-methylcyclohexanone) gave new fluorine-containing derivatives of cyclopenta[*c*]benzo[*f*]quinoline, benzo[*a*]phenanthridine, and cyclopenta[*a*]- and benzo[*a*]-[4,7]phenanthroline. Intermediate products, 2-[(fluorophenyl)(2-naphthylamino or quinolin-6-ylamino)methylidene]cyclohexanones, dihydrobenzo[*f*]quinolines, and dihydro-4,7-phenanthrolines, were isolated.

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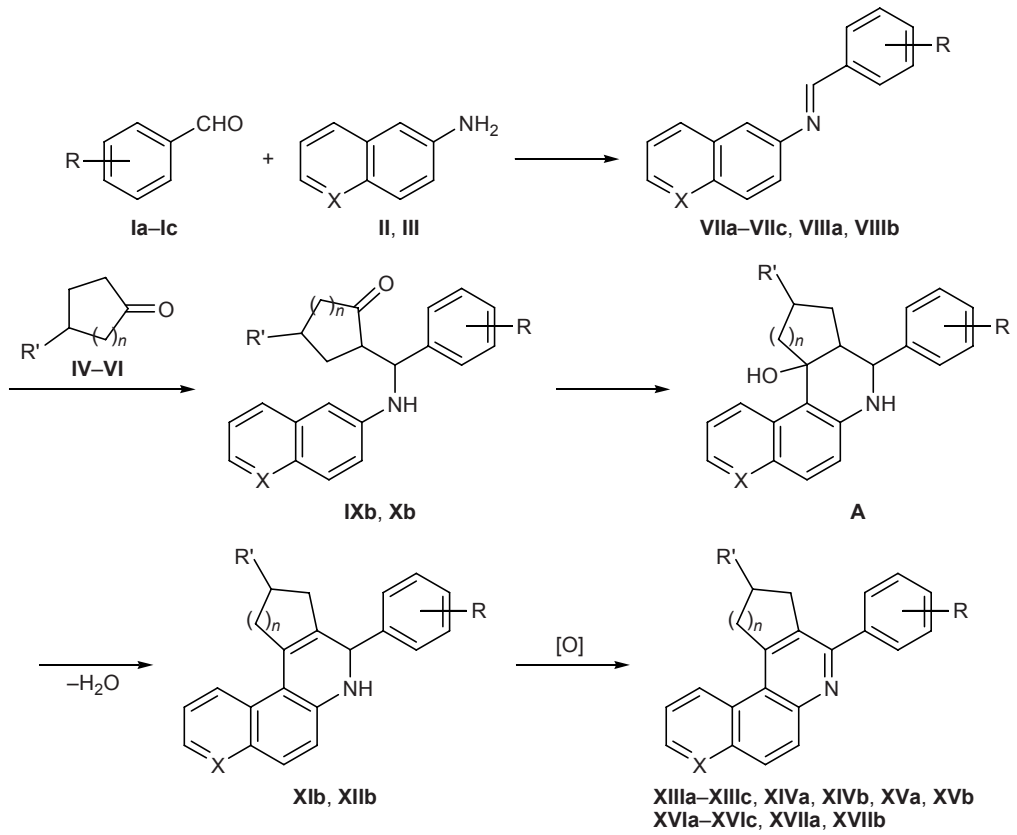
Three-component condensations of aldehydes with aromatic (heteroaromatic) amines and various CH acids are widely used for the synthesis of fused nitrogen-containing heterocycles [1–4]. Reactions of fluorine-containing benzaldehydes with aromatic amines and cyclic ketones attract specific interest, for they provide a synthetic route to aza heterocycles containing a quinoline ring and fluorine atoms. Such compounds are structurally related to antibiotics of the fluoroquinolinone series, pesticides, antitumor agents, bactericides, and enzyme inhibitors [5–9].

In the present work we were the first to study three-component condensations of 2-fluoro-, 4-fluoro-, and 4-(2-fluorobenzyloxy)benzaldehydes **Ia**–**Ic** with naphthalen-2-amine (**II**) or quinolin-6-amine (**III**) and cyclic ketones, cyclopentanone (**IV**), cyclohexanone (**V**), and 4-methylcyclohexanone (**VI**). The reactions were carried out in aliphatic alcohol (ethanol or butan-1-ol) as solvent in the presence of an acid catalyst. Taking into account the results of our previous studies [2, 10], we presume that aldehyde **I** initially reacts with aromatic amine **II** or **III** to give the corresponding Schiff base **VII** or **VIII**, and reaction of the latter with cyclic ketone **IV**–**VI** follows the known mechanism [11] involving addition of the activated methylene carbon atom of ketone **IV**–**VI** at the C=N bond of Schiff base **VII** or **VIII**, intramolecular attack by the carbonyl group in adduct **IX** or **X** at position *1* of the naphthalene ring or position *5* of the quinoline ring, dehydration of cyclic alcohol **A**, and dehydrogenation of the dihydropyridine ring in fused heterocyclic system **XI** or **XII** (Scheme 1). As a result, compounds **XIII**–**XVII** containing a benzo[*f*]quinoline or 4,7-phenanthroline fragment are formed as final products. Kozlov et al. [12] studied the reaction of *N*-benzylidenenaphthalen-2-amine with cyclohexanone and isolated all possible intermediate products, the corresponding β-amino ketone **IX** (R = H), hydroxy derivative of fused tetrahydrobenzo[*f*]quinoline **A** (R = R′ = H, X = CH, *n* = 2), and dihydrobenzo[*f*]quinoline **XI** (R = H); the final product was 5-phenyl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (**XIII**, R = H) having fused cyclohexene and benzo[*f*]quinoline fragments.

We performed three-component condensations of fluorine-containing benzaldehydes **Ia**–**Ic** with equimolar amounts of amines **II** and **III** and ketones **IV**–**VI** under different conditions: the temperature, reaction time, and the amount of catalyst (concentrated hydrochloric acid) were varied. In order to preliminarily obtain the corresponding Schiff base, aldehyde **I** was added to a solution of amine **II** or **III** in alcohol, the mixture was kept for 5–10 min, and cyclic ketone **IV**–**VI** was then added. 4-Fluorobenzaldehyde (**Ib**) reacted with amines **II** and **III** and cyclohexanone **V** under mild conditions (without heating) in the presence of 1–2 drops of concentrated hydrochloric acid per 10 mmol of the reagent to give amino ketones **IXb** and **Xb**. Under analogous conditions, the reactions with benzaldehydes **Ia** and **Ic** having a fluorine atom in the *ortho* position of the benzene ring or benzyl

Scheme 1.



R = 2-F (**a**), 4-F (**b**), 4-(2-$FC_6H_4CH_2O$) (**c**); **IV**, **V**, **IX**-**XIV**, **XVI**, **XVII**, R′ = H; **VI**, **XV**, R′ = Me; **II**, **VII**, **IX**, **XI**, **XIII**, **XV**, **XVI**, X = CH; **III**, **VIII**, **X**, **XII**, **XIV**, **XVII**, X = N; **IV**, **XI**, **XII**, **XVI**, **XVII**, *n* = 1; **V**, **VI**, **IX**, **X**, **XIII**–**XV**, *n* = 2.

substituent stopped at the stage of formation of the corresponding Schiff base which failed to take up cyclic ketone at the C=N bond. In the attempted condensation of 2-fluorobenzaldehyde (**Ia**) with naphthalen-2-amine (**II**) and cyclohexanone (**V**) we isolated *N*-(2-fluorobenzylidene)quinolin-6-amine (**VIIIb**). Presumably, the presence of a fluorine atom in the *ortho* position of the benzene ring or bulky 2-fluorobenzyloxy group hampers approach of cyclohexanone molecule to intermediate Schiff base for steric reasons, and the three-component condensation of aldehydes **Ia** and **Ic** with amines **II** and **III** and ketone **V** requires more severe conditions. The corresponding cyclization products, 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines **XIIIa**–**XIIIc** and 8-aryl-9,10,11,12-tetrahydrobenzo[*a*][4,7]phenanthrolines **XIVa** and **XIVb** were obtained by heating the reactants for 5–6 h in boiling ethanol or butan-1-ol in the presence of concentrated hydrochloric acid (1 ml per 10 mmol of **I**). Under these conditions we were unable to isolate intermediate products. Preliminarily isolated amino ketones **IXb** and **Xb** were converted into the corresponding phenanthridine and phenanthroline derivatives **XVb** and **XVIb** by heating in boiling butan-1-ol in the presence of concentrated hydrochloric acid.

The condensation of benzaldehydes **Ib** and **Ic** with amine **II** and 4-methylcyclohexanone (**VI**) to give 5-aryl-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines **XVb** and **XVc** required exceptionally drastic conditions. By contrast, cyclopentanone **IV** reacted with aldehydes **Ia**–**Ic** and amines **II** and **III** under mild conditions with direct formation of dihydro derivatives **XI** and **XII** containing a small amount of cyclic products **XVI** and **XVII**. Compounds **XIb** and **XIIb** were isolated as individual substances. If difficultly separable mixtures were formed, the reactions were carried out under more severe conditions (boiling ethanol or butan-1-ol, concentrated hydrochloric acid) to ensure complete conversion of intermediate products into cyclopenta[*c*]benzo[*f*]quinolines **XVIa**–**XVIc** and cyclopenta[*a*][4,7]phenanthrolines **XVIIa** and **XVIIb**. The same conditions promoted dehydrogenation of the isolated compounds **XIb** and **XIIb** to benzo[*f*]quinoline **XVIb** and 4,7-phenanthroline **XVIIb**, respec-

tively. Shorter reaction time (3 h) and higher yields (66–72%) of cyclopentane derivatives **XVIa**–**XVIc**, **XVIIa**, and **XVIIb** as compared to benzophenanthridines **XIIIa**–**XIIIc**, **XVb**, and **XVc** and benzophenanthrolines **XIVa** and **XIVb** (yield 48–62%) indicate higher reactivity of cyclopentanone (**IV**) as compared to ketones of the cyclohexane series **V** and **VI**.

The amine nature also affects the yield of the products: the yields of 4,7-phenanthroline derivatives **XIVa**, **XIVb**, **XVIIa**, and **XVIIb** were lower (48–55%) than those of phenanthridine derivatives **XIIIa**–**XIIIc** and **XVIa**–**XVIc** (56–72%). Obviously, nucleophilicity of the amino group in **III** is reduced due to the presence of electron-withdrawing nitrogen atom in the *para* position; therefore, the reactivity of **III** in the condensation with aldehydes is lower than that of amine **II** and polarization of the C=N bond in the intermediate Schiff base is weaker.

The condensations of cyclic ketones with preliminarily prepared and purified (by recrystallization from aliphatic alcohol) Schiff bases **VIIa**–**VIIc** and **VIIIa**–**VIIIc** gave the same products as those obtained from mixtures of their precursors, aldehydes **Ia**–**Ic** and amines **II** and **III**.

Amino ketones **IXb** and **Xb** characteristically showed in the IR spectra absorption bands due to stretching vibrations of the carbonyl and amino groups at 1700–1690 and 3400–3380 cm^{-1}, respectively. The IR spectra of compounds **XIb** and **XIIb** lacked carbonyl absorption band but retained the NH stretching vibration band at 3400–3385 cm^{-1}. Neither carbonyl nor NH absorption was observed in the spectra of cyclization products **XIII**–**XVII**. Both compounds **XIII**–**XVII** and their precursors **IX**–**XII** displayed absorption bands belonging to stretching vibrations of aliphatic and aromatic C–H bonds in the regions 2920–2890 and 3060–3030 cm^{-1}, respectively. A strong absorption band in the region 1235–1230 cm^{-1}, corresponding to stretching vibrations of the C–O–C fragment (benzyloxyphenyl group), was present in the IR spectra of **XIIIc**, **XVc**, and **XVIc**.

The molecular ion peaks in the mass spectra of amino ketones **IXb** and **Xb** had a moderate intensity (I_{rel} = 25–30%), while the base peak (I_{rel} = 100%) was that of the $[M - C_6H_{10}O]^+$ ion. Also, weak (I_{rel} = 6–7%) $[M - F]^+$ and $[M - F - C_6H_{10}O]^+$ ion peaks were observed. In the mass spectra of compounds **XIb** and **XIIb** and final cyclization products **XIII**–**XVII**, the molecular ion was the most abundant, the $[M - H]^+$ ion peak had a fairly strong intensity (I_{rel} = 60–65%), and medium-intensity $[M - H - F]^+$ ion peak was present (I_{rel} = 21–24%).

The electronic absorption spectra of amino ketones **IXb** and **Xb** in the UV region were analogous to those of naphthalen-2-amine and quinolin-6-amine [UV spectrum, λ_{max}, nm (logε): 246–247 (4.35–4.37), 279–280 (3.64–3.65), 337–338 (3.25–3.27)]; they consisted of three bands in the regions λ 253–256, 292–299, and 360–363 nm, corresponding to π–π* transitions in the aromatic system. Bathochromic shift of all absorption maxima and simultaneous increase in their intensity in the spectra of amino ketones **IXb** and **Xb** are likely to be related to the presence of a fluorophenyl chromophore and cycloalkanone fragment. Dihydro derivatives **XIb** and **XIIb** showed in the UV spectra [λ_{max}, nm (logε): 258–260 (4.46–4.49), 284–285 (3.99–4.00), 381–384 (3.8–43.87)] a considerable red shift of the long-wave absorption band, obviously as a result of formation of a new double bond in the closed cyclic system. Aromatization of the azaphenanthrene nucleus leads to appearance in the UV spectra of cyclization products **XIII**–**XVII** of a very strong absorption band at λ 278–293 nm and less intense bands at λ 230–241, 250–269 and 341–353, 361–374 nm; as a result, the UV spectra of **XIII**–**XVII** resemble those of 1,3-diarylbenzo[*f*]quinolines and 4,7-phenanthrolines [11, 13]. Therefore, the observed absorption bands may be interpreted as *p*-, β-, and α-bands according to Clar. The R and R′ substituents almost do not affect the spectral pattern.

In the ^{1}H NMR spectra of amino ketones **IXb** and **Xb**, methylene protons in the cyclohexane ring resonated as multiplets in the region δ 1.73–2.40 ppm, and the 2-H signal appeared as a multiplet at δ 2.80 ppm. The proton on the carbon atom linked to the amino group and phenyl and cyclohexane rings gave a broadened singlet at δ 4.67–4.70 ppm. A broadened singlet at δ 5.12–5.15 ppm was assigned to the NH proton. Signals from aromatic protons in the fluorophenyl substituent and naphthalene or quinoline ring were located in the region δ 6.50–8.56 ppm. The spectra of compounds **XIb** and **XIIb** lacked signals assignable to 2-H in the cycloalkane fragment and proton in position *1* of the naphthalene ring or position *5* of the quinoline ring, indicating that the cyclization involved the corresponding carbon atoms. The signal from the CH group neighboring to the fluorophenyl substituent was displaced downfield relative to its position in the spectra of **IXb** and **Xb**; it was located at δ 5.90–6.08 ppm, as in the spectra of fused azaphenanthrenes with partially hydrogenated pyridine ring [1]. The NH proton in the

^{1}H NMR spectra of **XIb** and **XIIb** resonated at δ 4.76–4.91 ppm. The spectra of benzophenanthridines benzo[*f*]quinoline, and 4,7-phenanthroline derivatives **XIII**–**XVII** contained no NH and ArC**H** signals; signals in the regions δ 1.29–3.70 and 7.10–9.00 ppm were assigned to protons in the cycloaliphatic and aromatic fragments, respectively. Protons of the methyl group in methyl-substituted benzophenanthridines **XVb** and **XVc** gave a singlet at δ 1.02–1.08 ppm; and methylene protons in the 2-fluorobenzyloxy substituent in compounds **XIIIc**, **XVc**, and **XVIc** resonated as a singlet at δ 5.23–5.29 ppm.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protégé-460 spectrometer with Fourier transform. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT Incos-50 instrument and on a Hewlett–Packard HP 5972 mass-selective detector coupled with an HP 5890 gas chromatograph (HP-5MS capillary column, 30 m × 0.25 mm; stationary phase 5% PhMe Silicone, film thickness 0.25 μm; injector temperature 250°C). The UV spectra were measured from solutions in ethanol ($c = 10^{-4}$ M) on a Specord UV-Vis spectrophotometer. The NMR spectra were recorded on Bruker AC-500 (500 MHz) and Tesla BS-567 spectrometers (100 MHz) using DMSO-d_6 or chloroform-*d* as solvent and tetramethylsilane as internal reference. The melting points were determined using a Kofler microscope.

N-Benzylidenenaphthalen-2-amines **VIIa**–**VIIc** and *N*-Benzylidenequinolin-6-amines **VIIIa** and **VIIIb** were synthesized according to the procedure described in [14].

2-[(2-Fluorophenyl)(2-naphthylamino)methyl]-cyclohexan-1-one (IXb) and 2-[(2-fluorophenyl)-(quinolin-6-ylamino)methyl]cyclohexan-1-one (Xb) (*general procedure*). *a*. A solution of 5 mmol of aldehyde **Ib** and 5 mmol of amine **II** or **III** in 20 ml of ethanol was heated for 10 min at 40–50°C. The mixture was cooled to 20°C, 5 mmol of cyclohexanone **V** and one drop of concentrated hydrochloric acid were added, and the mixture was left to stand for 24 h at room temperature. The solvent was removed, the residue was treated with aqueous ammonia, and the precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

b. A solution of 5 mmol of ketone **V** and 5 mmol of Schiff base **VIIb** or **VIIIb** in 20 ml of ethanol containing one drop of concentrated hydrochloric acid was kept for 24 h at room temperature. The product was isolated as described above in *a*.

Compound **IXb**. Yield 76% (*a*), 74% (*b*); mp 145–146°C. ^{1}H NMR spectrum, δ, ppm: 1.77 m, 1.95 m, and 2.40 m (8H, CH_2); 2.80 m (1H, CH); 4.67 br.s (1H, CH); 5.12 br.s (1H, NH); 6.6–7.93 m (11H, H_{arom}). Found, %: N 3.74. $C_{23}H_{22}FNO$. Calculated, %: N 4.03.

Compound **Xb**. Yield 57% (*a*), 59% (*b*); mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 1.73 m, 1.96 m, and 2.39 m (8H, CH_2); 2.80 m (1H, CH); 4.70 br.s (1H, CH); 5.15 br.s (1H, NH); 6.50 d (5′-H, ^4J = 2.6 Hz); 7.00 t and 7.39 d (4H, H_{arom}, ^3J = 8.4 Hz); 7.10 d.d (1H, 4′-H, ^3J = 8.6, ^4J = 2.2 Hz); 7.18 d.d (1H, 3′-H, ^3J = 8.6, ^4J = 4.2 Hz); 7.74 d and 7.82 d (1H each, 7′-H, 8′-H, ^3J = 9.1 Hz); 8.56 d.d (1H, 2′-H, ^3J = 4.2, ^4J = 2.2 Hz). Found, %: N 7.92. $C_{22}H_{21}FN_2O$. Calculated, %: N 8.04.

4-(2-Fluorophenyl)-2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]benzo[*f*]quinoline (XIb) and 8-(2-fluorophenyl)-8,9,10,11-tetrahydro-7*H*-cyclopenta[*a*][4,7]-phenanthroline (XIIb) (*general procedure*). Cyclopentanone (**IV**), 5 mmol, and concentrated hydrochloric acid, 2 drops, were added to a solution of 5 mmol of aldehyde **Ib** and 5 mmol of amine **II** or **III** (method *a*) or of 5 mmol of Schiff base **VIIb** or **VIIIb** (method *b*) in 20 ml of ethanol. The mixture was left to stand for 6 h at room temperature, and the precipitate was filtered off, treated with aqueous ammonia, washed with water, dried, and recrystallized from ethanol.

Compound **XIb**. Yield 63% (*a*), 68% (*b*); mp 161–162°C. ^{1}H NMR spectrum, δ, ppm: 2.22 m, 3.29 m, and 3.67 m (6H, CH_2); 4.76 br.s (1H, NH); 5.90 s (1H, CH); 7.28–8.59 m (10H, H_{arom}). Found, %: N 4.41. $C_{22}H_{18}FN$. Calculated, %: N 4.44.

Compound **XIIb**. Yield 58% (*a*), 53% (*b*); mp 153–154°C. ^{1}H NMR spectrum, δ, ppm: 2.24 m, 3.31 m, and 3.70 m (6H, CH_2); 4.91 br.s (1H, NH); 6.08 s (1H, CH); 7.31 t and 7.78 d (4H, H_{arom}, ^3J = 8.5 Hz); 7.49 d.d (1H, 2-H, ^3J = 7.9, ^4J = 4.2 Hz); 8.16 d (2H, 5-H, 6-H, ^3J = 8.9 Hz); 8.86 d (1H, 3-H, ^3J = 4.2 Hz); 8.91 d (1H, 1-H, ^3J = 7.9 Hz). Found, %: N 8.62. $C_{21}H_{17}FN_2$. Calculated, %: N 8.86.

5-Aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines XIIIa–XIIIc (*general procedure*). A solution of 5 mmol of aldehyde **Ia**–**Ic**, 5 mmol of naphthalen-2-amine (**II**), and 5 mmol of cyclohexanone (**V**) (method *a*) or a solution of 5 mmol of ketone **V** and 5 mmol of

Schiff base **VIIa–VIIc** (method *b*) in 20 ml of ethanol containing 0.5 ml of concentrated hydrochloric acid was heated for 6 h under reflux. The products were isolated as described above for **XIb** and **XIIb**.

5-(2-Fluorophenyl)-1,2,3,4-tetrahydrobenzo[*a*]-phenanthridine (XIIIa). Yield 56% (*a*), 60% (*b*); mp 236–237°C. ^{1}H NMR spectrum, δ, ppm: 1.89 m, 2.88 m, and 3.60 m (8H, CH_2); 7.38 m, 7.69 m, 8.10 m, and 8.81 m (10H, H_{arom}). Found, %: N 4.07. $C_{23}H_{18}FN$. Calculated, %: N 4.28.

5-(4-Fluorophenyl)-1,2,3,4-tetrahydrobenzo[*a*]-phenanthridine (XIIIb). Yield 62% (*a*), 65% (*b*); mp 258–259°C. ^{1}H NMR spectrum, δ, ppm: 1.85 m, 2.90 m, and 3.65 m (8H, CH_2); 7.44 m, 7.87 s, 8.11 m, and 8.84 m (10H, H_{arom}). Found, %: N 4.12. $C_{23}H_{18}FN$. Calculated, %: N 4.28.

5-[4-(2-Fluorobenzyloxy)phenyl]-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (XIIIc). Yield 61% (*a*), 60% (*b*); mp 213–214°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m, 2.90 m, and 3.70 m (8H, CH_2); 5.29 s (2H, OCH_2); 7.27 m and 8.95 m (14H, H_{arom}). Found, %: N 3.08. $C_{30}H_{24}FNO$. Calculated, %: N 3.23.

8-Aryl-9,10,11,12-tetrahydrobenzo[*a*][4,7]phenanthrolines XIVa and XIVb were synthesized as described above for compounds **XIIIa–XIIIc** from the corresponding aldehyde **Ia** or **Ib**, quinolin-6-amine (**III**), and cyclohexanone (**V**) (method *a*) or from ketone **V** and Schiff base **VIIIa** or **VIIIb** (method *b*) using butan-1-ol as solvent. The solvent was evaporated, and the solid residue was treated with aqueous ammonia. Compound **XIVa** was recrystallized from ethanol–benzene (3:1), and compound **XIVb**, from ethanol.

8-(2-Fluorophenyl)-9,10,11,12-tetrahydrobenzo-[*a*][4,7]phenanthroline (XIVa). Yield 48% (*a*), 51% (*b*); mp 171–172°C. ^{1}H NMR spectrum, δ, ppm: 1.88 m, 2.91 m, and 3.62 m (8H, CH_2); 7.31 m and 7.59 m (4H, H_{arom}); 7.52 d.d (1H, 2-H, ^3J = 7.9, ^4J = 4.1 Hz); 8.23 d (2H, 5-H, 6-H, ^3J = 9.0 Hz); 8.89 d (1H, 3-H, ^3J = 4.1 Hz); 9.02 d (1H, 1-H, ^3J = 7.9 Hz). Found, %: N 8.41. $C_{22}H_{17}FN_2$. Calculated, %: N 8.54.

8-(4-Fluorophenyl)-9,10,11,12-tetrahydrobenzo-[*a*][4,7]phenanthroline (XIVb). Yield 51% (*a*), 57% (*b*); mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m, 2.87 m, and 3.58 m (8H, CH_2); 7.30 m and 7.54 m (5H, 2-H, C_6H_4F); 8.20 d (2H, 5-H, 6-H, ^3J = 9.2 Hz); 8.97 d (1H, 3-H, ^3J = 4.5 Hz); 9.13 d (1H, 1-H, ^3J = 8.7 Hz). Found, %: N 8.29. $C_{22}H_{17}FN_2$. Calculated, %: N 8.54.

5-Aryl-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines XVb and XVc were synthesized from the corresponding aldehyde **Ib** or **Ic**, naphthalen-2-amine (**II**), and 4-methylcyclohexan-1-one (**VI**) (method *a*) or from ketone **VI** and Schiff base **VIIb** or **VIIc** (method *b*), following the procedure described above for the synthesis of compounds **XIIIa–XIIIc** but using 10 mmol of ketone **VI** and double volume of ethanol (60 ml). After removal of 3/4 of the solvent, the tarry material was treated with diethyl ether. The precipitate of **XVb** or **XVc** hydrochloride was treated with aqueous ammonia, washed with water, and recrystallized from ethanol–benzene (2:1).

5-(2-Fluorophenyl)-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (XVb). Yield 52% (*a*), 56% (*b*); mp 205–206°C. ^{1}H NMR spectrum, δ, ppm: 1.08 s (3H, Me); 1.30 m, 1.88 m, 2.52 m, 2.93 m, 3.61 m, and 3.70 m (7H, CH_2, CH); 7.47 m, 7.71 m, and 7.98–8.86 m (10H, H_{arom}). Found, %: N 3.95. $C_{24}H_{20}FN$. Calculated, %: N 4.11.

5-[4-(2-Fluorobenzyloxy)phenyl]-3-methyl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (XVc). Yield 57% (*a*), 55% (*b*); mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 1.02 s (3H, Me); 1,29 m, 1.91 m, 2.42 m, 2.97 m, 3.57 m, and 3.67 m (7H, CH_2, CH); 5.23 s (2H, OCH_2); 7.28–7.61 m (8H, H_{arom}); 7.69 d (2H, 10-H, 11-H, ^3J = 8.0 Hz); 7.82 d and 8.01 m (2H, 7-H, 8-H, ^3J = 9.0 Hz); 8.06 d (1H, 9-H, ^3J = 8.0 Hz); 8.83 s (1H, 12-H). Found, %: N 3.04. $C_{31}H_{26}FNO$. Calculated, %: N 3.13.

4-Aryl-2,3-dihydro-1*H*-cyclopenta[*c*]benzo[*f*]-quinolines XVIa–XVIc and 8-aryl-10,11-tetrahydro-9*H*-cyclopenta[*a*][4,7]phenanthrolines XVIIa and XVIIb (*general procedure*). Cyclopentanone (**IV**), 5 mmol, and concentrated hydrochloric acid, 0.5 ml, were added to a solution of 5 mmol of aldehyde **Ia–Ic** and 5 mmol of amine **II** or **III** (method *a*) or to a solution of 5 mmol of Schiff base **VIIa–VIIc**, **VIIIa**, or **VIIIb** (method *b*) in 20 ml of butan-1-ol, and the mixture was heated for 3 h under reflux. After cooling, the precipitate was filtered off, treated with aqueous ammonia, washed with water, dried, and recrystallized from ethanol.

Benzo[*f*]quinoline **XVIb** and 4,7-phenanthroline **XVIIb** were also synthesized by heating for 3 h under reflux 2.5 mmol of compound **XIb** or **XIIb**, respectively, in 20 ml of butan-1-ol containing 10 drops of concentrated hydrochloric acid. The products were isolated as described above; yield 74% (**XVIb**), 69% (**XVIIb**).

4-(2-Fluorophenyl)-2,3-dihydro-1*H*-cyclopenta-[*c*]benzo[*f*]quinoline (XIVa). Yield 70% (*a*), 71% (*b*); mp 240–241°C. ^{1}H NMR spectrum, δ, ppm: 2.24 m, 3.26 m, and 3.69 m (6H, CH_2); 7.21–8.09 and 8.73 m (10H, H_{arom}). Found, %: N 4.23. $C_{22}H_{16}FN$. Calculated, %: N 4.47.

4-(4-Fluorophenyl)-2,3-dihydro-1*H*-cyclopenta-[*c*]benzo[*f*]quinoline (XIVb). Yield 72% (*a*), 74% (*b*); mp 240–241°C. ^{1}H NMR spectrum, δ, ppm: 2.21 m, 3.19 m, and 3.59 m (6H, CH_2); 7.14–8.10 m and 8.62 m (10H, H_{arom}). Found, %: N 4.19. $C_{22}H_{16}FN$. Calculated, %: N 4.47.

4-[4-(2-Fluorobenzyloxy)phenyl]-2,3-dihydro-1*H*-cyclopenta[*c*]benzo[*f*]quinoline (XIVc). Yield 66% (*a*), 69% (*b*); mp 265–266°C. ^{1}H NMR spectrum, δ, ppm: 2.18 m, 3.20 m, and 3.63 m (6H, CH_2); 5.23 s (2H, OCH_2); 7.10–8.08 m and 8.55 m (14H, H_{arom}). Found, %: N 3.26. $C_{29}H_{22}FNO$. Calculated, %: N 3.34.

8-(2-Fluorophenyl)-10,11-dihydro-9*H*-cyclopenta[*a*][4,7]phenanthroline (XVIIa). Yield 52% (*a*), 59% (*b*); mp 163–164°C. ^{1}H NMR spectrum, δ, ppm: 2.29 m, 3.30 t, and 3.70 t (6H, CH_2, ^3J = 8.0 Hz); 7.46 t and 7.82 d (4H, H_{arom}); 7.58 d.d (1H, 2-H, ^3J = 8.4, ^4J = 4.2 Hz); 8.25 d (2H, 5-H, 6-H, ^3J = 9.1 Hz); 8.88 d (1H, 3-H, ^3J = 8.4 Hz); 9.00 d (1H, 1-H, ^3J = 4.2 Hz). Found, %: N 8.69. $C_{21}H_{15}FN_2$. Calculated, %: N 8.92.

8-(4-Fluorophenyl)-10,11-dihydro-9*H*-cyclopenta[*a*][4,7]phenanthroline (XVIIb). Yield 55% (*a*), 58% (*b*); mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 2.25 m, 3.36 t, and 3.65 t (6H, CH_2, ^3J = 8.0 Hz); 7.28 t and 7.79 d (4H, H_{arom}, ^3J = 7.9 Hz); 7.50 d.d (1H, 2-H, ^3J = 8.2, ^4J = 4.1 Hz); 8.19 d (2H, 5-H, 6-H, ^3J = 9.0 Hz); 8.89 d (1H, 3-H, ^3J = 8.2 Hz); 8.99 d (1H, 1-H, ^3J = 4.1 Hz). Found, %: N 8.74. $C_{21}H_{15}FN_2$. Calculated, %: N 8.92.

Cyclization of amino ketones IXb and Xb (*general procedure*). A mixture of 2.5 mmol of compound **IXb** or **Xb**, 10 drops of concentrated hydrochloric acid, and 20 ml of butan-1-ol was heated for 4 h under reflux. The precipitate was treated as described above for the synthesis of **XIIIb** and **XIVb**. Yield 68% (**XIIIb**), 61% (**XIVb**).

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