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Condensation of Fluorosubstituted Benzaldehydes with Amines and Cyclic 1,3-Diketones

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Abstract—Condensation of fluorosubstituted benzaldehydes with 2-naphthyl or 6-quinolylamine and cyclic β-diketones (,3-cyclohexanedione, dimedone, and 1,3-indandione) provided new fluoroderivatives of benzo[*a*]-acridine, 4,7-phenanthroline, and benzo[*f*]indeno[1,2-*b*]quinoline. Forming in the course of the reaction fluorophenylmethylene-2-naphthyl-(or 6-quinolyl)amines, arylbis(cyclohexane-1,3-dion-2-yl)methanes, and 2-(fluorophenylmethylene)-1,3-indandiones were isolated.

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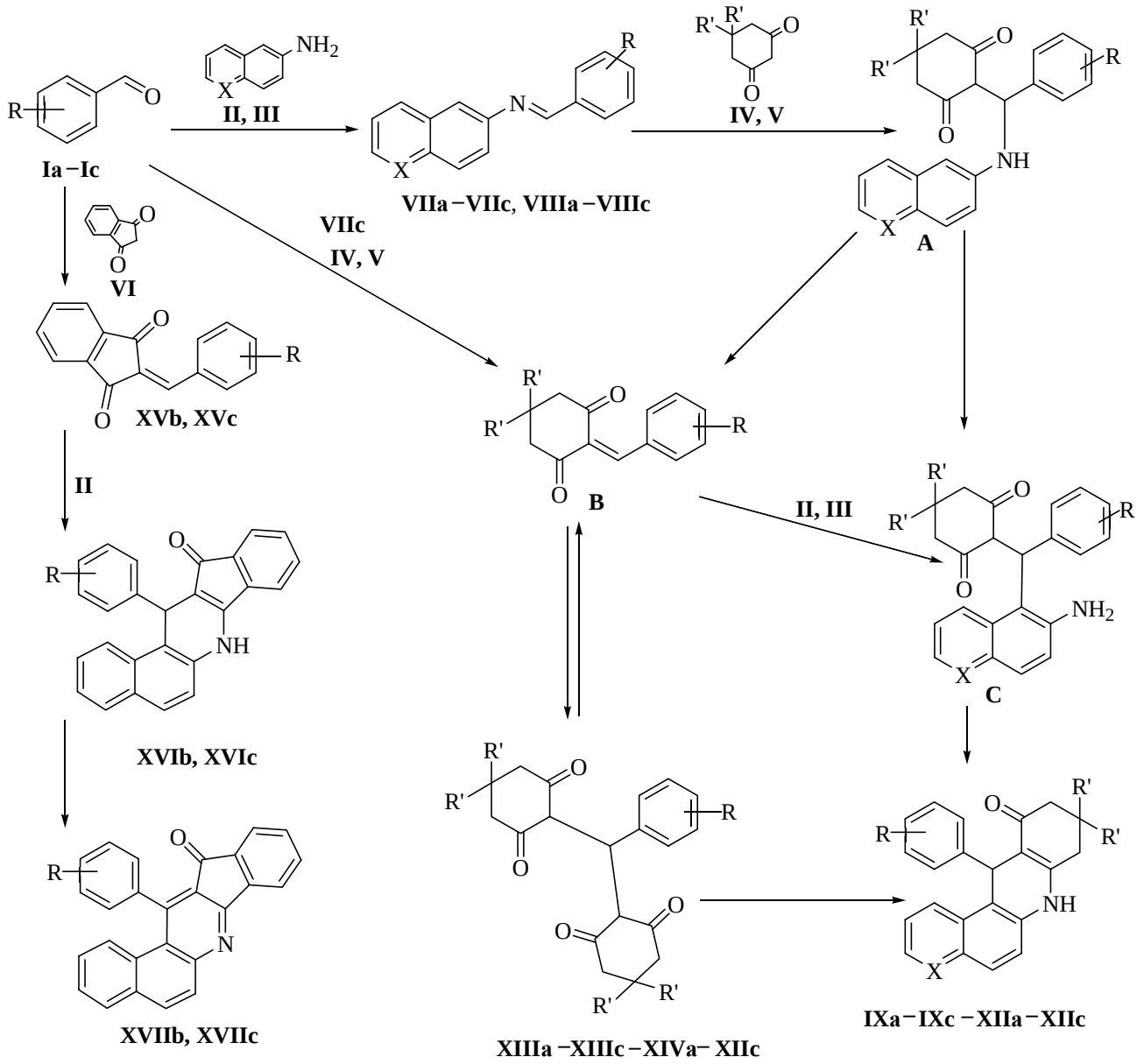
Three-component condensation of aldehydes with aromatic (heteroaromatic) amines and CH-acids of various classes got recently impact as an efficient synthetic procedure for fused nitrogen-containing heterocycles [1–4]. Especially worthy of attention are reactions of fluorosubstituted benzaldehydes with arylamines and cyclic β-diketones as a pathway to preparation of aza-heterocycles containing in the molecule a partially hydrogenated quinoline fragment, oxo group, and a fluorine atom thus belonging to analogs of antibiotics from the fluoroquinolone series, pesticides, compounds with antitumor, bactericidal, and antienzyme action [5–9].

In this study we investigated for the first time a three-component condensation of 2- and 4-fluorobenzaldehydes (**Ia** and **Ib**), 4-(2-fluorobenzyloxy)benzaldehyde (**Ic**) with 2-naphthyl- and 6-quinolylamine (**II** and **III**), and β-diketones [1,3-cyclohexanedione (**IV**), dimedone (**V**), and 1,3-indandione (**VI**)].

The condensation of aldehydes **Ia–Ic**, amines **II** and **III**, and diketones **IV** and **V** was performed by heating an equimolar mixture of reagents in butanol without catalyst. The process of building up a structure of a fused heterocycle involved a cascade of transformations and could take several routes. Firstly, aldehyde **Ia–Ic** can initially condense with arylamine **II** or **III** giving azomethine **VIIa–VIIc** or **VIIIa–VIIIc** that further takes up dione **IV** or **V** yielding aminodiketone **A**. The latter in the alcoholic medium suffers a hydramine cleavage into amine and 2-(arylmethylene)cyclohexane-1,3-dione **B** which having a double bond activated by conjugation with two neighboring carbonyl groups reacts with the aromatic ring of the amine **II** or **III** at the carbon atom possessing the largest electron density and located in the α-position to the amino group to give aminodiketone **C**. The dehydrocyclization of intermediate **C** results in a selective formation of 12-[2-(4-)fluorophenyl- or 4-(2-fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*a*]-acridin-11-one **IXa–IXc**, 12-[2-(4-)fluorophenyl- or 4-(2-fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo-[*b*][4,7]phenanthrolin-11-one **Xa–Xc**, and their 9-dimethyl derivatives **XIa–XIc** and **XIIa–XIIc** in 68–84% yield.

The conversion of aminodiketone **A** into aminodione **C** analogously to the data of [10] can be interpreted as a rearrangement of intermediate **A** by the type of Hofmann–Martius rearrangement (migration of N-alkyl substituents in alkylanilines into the aromatic ring [11]).

We synthesized azomethines **VIIa–VIIc** and **VIIIa–VIIIc**, where compounds **VIIc** and **VIIIc** had not been described before, by condensation of aldehydes **Ia–Ic** with amines **II** and **III** at boiling in ethanol without catalyst. On reacting azomethines **VIIa–VIIc** and **VIIIa–VIIIc** with diketones **IV** and **V** under the above described conditions of three-component condensation cleanly formed benzoacridones and 4,7-phenanthrolinones **IXa–IXc– XIIa–XIIc**.



I, VII–XVII: R = 2-F (**a**), 4-F (**b**), 4-$OCH_2(2\text{-}FC_6H_4)$ (**c**); R' = H (**IV, IXa–IXc, Xa–Xc, XIIIa–XIIIc**), Me (**V, XIa–XIc, XIIa–XIIc, XIVa–XIVc**); X = CH (**II, VIIa–VIIc, IXa–IXc, XIa–XIc**), N (**III, VIIIa–VIIIc, Xa–Xc, XIIa–XIIc**).

In a three-component reagents mixture (aldehyde + amine + diketone) 2-(arylmethylene)cyclohexane-1,3-dione **B** could form directly from aldehyde **Ia–Ic** and dione **IV** or **V** and react further with amine **II** or **III** along the above described mechanism. At attempt to obtain enediones **B** by heating an equimolar mixture of aldehyde **Ia–Ic** with diketones **IV** or **V** aiming at involving them further into reaction with amines **II** or **III** we isolated bisdicarbonyl derivatives **XIIIa–XIIIc** and **XIVa–XIVc** whose formation was consistent with the data of [1]. At boiling with amines **II** or **III** in butanol solution bisdiketones **XIIIa–XIIIc** and **XIVa–XIVc** were converted into aza- and diazaphenanthrenes **IXa–IXc–XIIa–XIIc**. Apparently the bisadduct eliminated a molecule of dione **IV** or **V** separating 2-arylidenedione **B** that further reacted with amine **II** or **III** through a stage of formation of aminodiketone **C** to give finally fused reaction product **IXa–IXc–XIIa–XIIc**. Thus the second probable route of the three-component condensation may be initial reaction between aldehyde **Ia–Ic** with diketone **IV** or **V** and involvement of arylmethylenedione **B** in the next stage of amine **II** or **III** addition in situ.

In the course of the condensation of aldehydes **Ia** and **Ib** with amine **II** and indane-1,3-dione (**VI**) in butanol without catalyst we established that before the target products of the benzoindenoquinoline series started to form in the reaction mixture analogs of hypothetical intermediate **B** were present, 2-[4-fluoro-phenyl- or 4-(2-fluorobenzyloxy)phenyl]methyleneindane-1,3-diones **XVb** and **XVc**. These compounds were obtained in individual state by boiling equimolar amounts of aldehyde **Ia** and **Ib** and dione **VI** in ethanol, and in reaction with amine **II** under the conditions of the three-component condensation they led to the formation of 13-[4-fluorophenyl- or 4-(2-fluorobenzyloxy)phenyl]-7,13-dihydro-12*H*-benzo[*f*]-indeno[1,2-*b*]quinoline-12-ones (**XVIb** and **XVIc**). The synthesis of indenoquinolines **XVIb** and **XVIc** evidently involves the stages of arylmethylenedione **XVb** and **XVc** addition to amine **II** at the electron-rich α-position of the naphthalene skeleton and of cyclization of the intermediate aminodiketone analogous to intermediate **C**. Dihydro compounds **XVIb** and **XVIc** on boiling in nitrobenzene undergo dehydrogenation into 13-[4-fluorophenyl- or 4-(2-fluoro-benzyloxy)phenyl]-12*H*-benzo[*f*]indeno[1,2-*b*]-quinoline-12-ones (**XVIIb** and **XVIIc**).

In the IR spectra of compounds **IXa–IXc–XIIa–XIIc, XVIb** and **XVIc** characteristic absorption bands are present of stretching and bending vibrations of the NH group from the dihydropyridine ring at 3330–3260 and 1635–1630 cm^{-1}. The stretching vibrations of the carbonyl conjugated with the eneamine fragment are observed at 1655–1605 cm^{-1}. The bands of the stretching vibrations of the cycloaliphatic CH bonds appear at 2955–2870 cm^{-1}, of CH bonds in the aromatic rings, at 3060–3030 cm^{-1}. In the spectra of the oxidation products **XVIIb** and **XVIIc** the band of stretching vibrations of the carbonyl group is present at 1665 cm^{-1}, and the bands of NH group vibrations are lacking. The spectra of compounds **IXc–XIIc**, **XVIc**, and **XVIIc** contain an absorption band in the region 1240–1230 cm^{-1} corresponding to the stretching vibrations of C–O–C bonds in the benzoxyphenyl substituent.

In mass spectra of azaphenanthrenes the peaks of molecular ions $[M]^+$ appear, I_{rel} 29–44% for compounds **IXa–IXc–XIIa–XIIc, XVIb** and **XVIc**, and 100% for indenoquinolines **XVIIb** and **XVIIc**, ion peaks $[M - C_6H_4R]^+$, I_{rel} 100% for hydrogenated derivatives **IXa–IXc–XIIa–XIIc, XVIb** and **XVIc** and 38% for oxidation products **XVIIb** and **XVIIc** (*m/z* 248 for compounds **IXa–IXc**, 249 for phenanthrolines **Xa–Xc**, 276 and 277 for dimethyl derivatives **XIa–XIc** and **XIIa–XIIc**, 282 and 280 for indenoquinolines **XVIb** and **XVIc**, **XVIIb** and **XVIIc**). In the spectra of compounds **IXa–IXc–XIIa–XIIc** a relatively strong peak (21–28%) is also present of ion with *m/z* 192 for acridones **IXa–IXc** and **XIa–XIc**, and 193 for phenanthrolinones **Xa–Xc** and **XIIa–XIIc** corresponding to elimination from ion $[M - R]^+$ of a fragment CH_2CH_2CO for compounds **IXa–IXc** and **Xa–Xc**, and Me_2CCH_2CO for dimedone derivatives **XIa–XIc** and **XIIa–XIIc**.

The UV absorption spectra of compounds **IXa–IXc–XIIa–XIIc, XVIb** and **XVIc** possess pronounced vibronic structure. The molecules of partially hydrogenated benzoacridones **IXa–IXc** and **XIa–XIc** and benzophenanthrolinones **Xa–Xc** and **XIIa–XIIc** contain three independent chromophore fragments: fluorophenyl substituent, carbonyl group, and naphthalene or quinoline fragment. The latter contribute the most into the system of π,π^*-electronic transitions. Therefore the bands in the range 214–290 nm in the spectra of acridones **IXa–IXc** and **XIa–XIc** may be assigned to the system of 2-naphthylamine (**II**) [UV spectrum, λ_{max}, nm (log ε): 204 (4.06), 246 (4.35), 280 (3.63)], and in the spectra of phenanthrolinones **Xa–Xc** and **XIIa–XIIc**, to the system of 6-quinolylamine (**III**) [UV spectrum, λ_{max}, nm (log ε): 206 (4.08), 247 (4.35), 279 (3.59)]. The considerable red shift, increased intensity of the bands, and stronger vibronic structure observed for acridones in the mentioned spectral range were apparently due to the superposition of the absorption bands of the fluorophenyl substituent. The absorption bands in the longwave spectral region (330–340, 371–382 nm) are due according to [1] to the presence of carbonyl group. In the spectra of compounds **XVIb** and **XVIc** a significant shift is observed of the longwave absorption maximum (476–480 nm) into the visible spectral range caused evidently by the presence of a fused indenone ring in the structure of azaphenanthrene. In the UV spectra of dehydration products **XVIIb** and **XVIIc** appeared a very strong band at 295–314 nm and a less strong band with a vibronic structure at 223–255 nm. The presence of these bands (β- and *p*-bands according to Clar) makes the spectrum of compounds **XVIIb** and **XVIIc** resembling the spectra of 1,3-diarylbenzo[*f*]quinolines [12]. The increase in the intensity of the mentioned band observed in the spectra of compounds **XVIIb** and **XVIIc** is apparently caused by the conjugation of the benzo[*f*]quinoline core with the indenone system. The longwave band in the spectra of indenoquinolines **XVIIb** and **XVIIc** at 384–386 nm corresponds to the α-band in the spectra of benzoquinolines [12], but suffered a red shift as compared to the latter.

^{1}H NMR spectra of compounds **IXa–IXc–XIIa–XIIc** with respect to the position and multiplicity of signals from aromatic and cycloaliphatic protons, and protons of NH group are identical to the previously published spectra of acridones and 4,7-phenanthrolinones [1, 2, 4]. In the ^{1}H NMR spectra of of indeno derivatives **XVIb** and **XVIc, XVIIb** and **XVIIc** the signals of aromatic protons appear in the region 6.81–8.22 ppm. The signals in the spectra of dihydro compounds **XVIb** and **XVIc** at 9.70–9.84 and 5.72–5.84 ppm corresponding respectively to the protons of NH group and H*13* of dihydropyridine ring are absent in the spectra of oxidation products **XVIIb** and **XVIIc** evidencing the aromatization of the azaphenanthrene ring.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrometer Nicolet Protege-460 from KBr pellets. Mass spectra were measured on FINNIGAN MAT INCOS 50 instrument at the ionizing electrons energy 70 eV and on a chromato-mass spectrometer Hewlett-Packard HP 5890/5972 in an electron impact ionization mode with an energy 70 eV; column HP-5MS [30 m × 0.25 mm, stationary phase film 0.25μm thick (5% PLMe Silicone)]; vaporizer temperature 250°C. UV spectra of compounds in ethanol (*c* 10^{-4} mol l^{-1}) were taken on a spectrophotometer Specord UV-Vis. NMR spectra were registered on spectrometers Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) in DMSO-d_6 and $CDCl_3$, internal reference TMS. Melting points were measured on a Koeffler heating block.

2- or 4-Fluorophenylmethylene-2-naphthyl(6-quinolyl)amines VIIa, VIIb and VIIIa, VIIIb were prepared by method [13], **2-(4-fluorophenylmethylene)indane-1,3-dione (XVb)** was obtained and identified by procedure [14].

4-(2-Fluorobenzyloxy)phenylmethylene-2-naphthyl-(6-quinolyl)amine (VIIc and VIIIc). A solution of 5 mmol of aldehyde **Ic**, 5 mmol of 2-naphthylamine (**II**) for azomethine **VIIc** or 6-quinolylamine (**III**) for compound **VIIIc** in 20 ml of ethanol was boiled for 15 min. The precipitate separated on cooling was filtered off and recrystallized from ethanol.

4-(2-Fluorobenzyloxy)phenylmethylene-2-naphthylamine (VIIc). Yield 82%, mp 100–101°C. UV spectrum, λ_{max}, nm (log ε): 205 (4.43), 236 (4.42), 265 (4.39), 330 (4.06). ^{1}H NMR spectrum, δ, ppm: 5.07 s (2H, OCH_2), 7.02–8.03 m ($15H_{arom}$), 8.54 s (1H, CH=N). Found, %: N 3.76. $C_{24}H_{18}FNO$. Caculated, %: N 3.94.

4-(2-Fluorobenzyloxy)phenylmethylene-6-quinolylamine (VIIIc). Yield 79%, mp 97–98°C. UV spectrum, λ_{max}, nm (log ε): 207 (4.49), 235 (4.43), 266 (4.40), 328 (4.10). ^{1}H NMR spectrum, δ, ppm: 5.10 s (2H, OCH_2), 7.04 d, 7.66 d, 7.38 m ($8H_{arom}$), 7.30 d.d (1H, H*3*), 7.46 s (1H, H*5*), 7.68 d.d (1H, H*4*), 8.12 d (2H, H*7,8*), 8.56 s (1H, CH=N), 8.83 d.d (1H, H*2*). Found, %: N 7.59. $C_{23}H_{17}FN_2O$. Caculated, %: N 7.87.

12-Aryl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]-acridin-11-ones IXa–IXc and 12-aryl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones Xa–Xc. *a*. A mixture of 5 mmol of aldehyde **Ia–Ic**, 5 mmol of 2-naphthylamine (**II**) for compounds **IXa–IXc** or 6-quinolylamine for phenanthrolines **Xa–Xc**, 5 mmol of cyclohexane-1,3-dione (**IV**), and 20 ml of butanol was boiled for 3–4 h. The separated precipitate was filtered off and recrystallized from a mixture ethanol–benzene, 2:1.

b. A solution of 5 mmol of azomethine **VIIa–VIIc** or **VIIIa–VIIIc**, 5 mmol of diketone **IV** in 20 ml of butanol was boiled for 3 h. Reaction products **IXa–IXc** and **Xa–Xc** were isolated as described above.

12-(2-Fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (IXa). Yield 72% (*a*), 75% (α), mp 306–307°C. UV spectrum, λ_{max}, nm (log ε): 215 (4.50), 232 (4.61), 277 (4.20), 290 (4.28), 337 (3.98), 372 (3.96). ^{1}H NMR spectrum, δ, ppm: 1.89 m (2H, CH_2), 2.20 m (2H, CH_2), 2.63 m (2H, CH_2), 5.82 s (1H, H*12*), 6.81–8.00 m ($10H_{arom}$), 9.75 s (1H, NH). Found, %: N 3.79. $C_{23}H_{18}FNO$. Caculated, %: N 4.08.

12-(4-Fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (IXb). Yield 70% (*a*), 76% (α), mp 301–302°C. UV spectrum, λ_{max}, nm (log ε): 216 (4.52), 231 (4.63), 279 (4.21), 291 (4.30), 338 (3.96), 373 (3.95). ^{1}H NMR spectrum, δ, ppm: 1.86 m (2H, CH_2), 2.22 m (2H, CH_2), 2.64 m (2H, CH_2), 5.85 s (1H, H*12*), 6.83–7.98 m ($10H_{arom}$), 9.76 s (1H, NH). Found, %: N 3.84. $C_{23}H_{18}FNO$. Caculated, %: N 4.08.

2-[4-(2-Fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (IXc). Yield 68% (*a*), 66% (α), mp 268–269°C. UV spectrum, λ_{max}, nm (log ε): 216 (4.50), 230 (4.61), 280 (4.18), 292 (4.29), 337 (3.98), 375 (3.96). ^{1}H NMR spectrum, δ, ppm: 1.93 m (2H, CH_2), 2.27 m (2H, CH_2), 2.63 m (2H, CH_2), 4.98 s (2H, OCH_2), 5.80 s (1H, H*12*), 6.76–7.52 m, 7.70–8.00 m ($14H_{arom}$), 9.63 C (1H, NH). Found, %: N 2.96. $C_{30}H_{24}FNO_2$. Caculated, %: N 3.12.

12-(2-Fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (Xa). Yield 82%

(*a*), 80% (*α*), mp 301–302°C. UV spectrum, λ_{max}, nm (log ε): 216 (4.60), 241 (4.26), 293 (4.04), 332 (4.01), 378 (3.90). ^{1}H NMR spectrum, δ, ppm: 1.88 m (2H, CH_2), 2.20 m (2H, CH_2), 2.62 m (2H, CH_2), 5.80 s (1H, H*12*), 7.28 m (4H$_{arom}$), 7.38 d.d (1H, H*2*), 7.50 d, 7.85 d (2H, H*5,6*), 8.38 d (1H, H*1*), 8.66 d (1H, H*3*), 9.85 s (1H, NH). Found, %: N 7.95. $C_{22}H_{17}FN_2O$. Calculated, %: N 8.14.

12-(4-Fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (Xb). Yield 79% (*a*), 76% (*α*), mp 312–313°C. UV spectrum, λ_{max}, nm (log ε): 215 (4.62), 242 (4.33), 297 (4.17), 335 (4.05), 378 (3.92). ^{1}H NMR spectrum, δ, ppm: 1.87 m (2H, CH_2), 2.21 m (2H, CH_2), 2.59 m (2H, CH_2), 5.82 s (1H, H*12*), 6.90 t, 7.18 d.d (4H$_{arom}$), 7.35 d.d (1H, H*2*), 7.52 d, 7.86 d (2H, H*5,6*), 8.30 d (1H, H*1*), 8.60 d (1H, H*3*), 9.82 s (1H, NH). Found, %: N 8.01. $C_{22}H_{17}FN_2O$. Caculated, %: N 8.14.

12-[(4-(2-Fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (Xc). Yield 69% (*a*), 72% (*α*), mp 293–294°C. UV spectrum, λ_{max}, nm (log ε): 218 (4.61), 249 (4.33), 296 (4.21), 330 (4.09), 382 (4.00). ^{1}H NMR spectrum, δ, ppm: 1.89 m (2H, CH_2), 2.24 m (2H, CH_2), 2.60 m (2H, CH_2), 5.00 s (2H, OCH_2), 5.90 s (1H, H*12*), 6.79 m, 7.10 d, 7.48 m (8H$_{arom}$), 7.31 d.d (1H, H*2*), 7.51 d, 7.89 d (2H, H*5,6*), 8.31 d (1H, H*1*), 8.60 d (1H, H*3*), 9.80 C (1H, NH). Found, %: N 6.13. $C_{29}H_{23}FN_2O_2$. Caculated, %: N 6.22.

12-Aryl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones XIa–XIc and 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-ones XIIa–XIc were obtained from aldehydes **Ia–Ic**, amines **II** or **III**, and dimedone (**V**) (method *a*) or from ketone **V** and azomethine **VIIa–VIIc** or **VIIIa-VIIIc** (method *b*) in the same way as compounds **IXa–IXc** and **Xa–Xc**. Reaction products were recrystallized from a mixture ethanol–benzene, 4:1.

9,9-Dimethyl-(2-fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-oneOν (XIa). Yield 71% (*a*), 67% (*b*), mp 288–289°C. UV spectrum, λ_{max}, nm (log ε): 217 (4.49), 233 (4.60), 278 (4.19), 291 (4.29), 338 (3.90), 371 (3.93). ^{1}H NMR spectrum, δ, ppm: 0.90 C (3H, Me), 1.11 s (3H, Mε), 2.19 m (2H, CH_2), 2.57 m (2H, CH_2), 5.83 s (1H, H*12*), 6.85 m, 7.12–7.96 m, 8.02 m (10H$_{arom}$), 9.71 s (1H, NH). Found, %: N 3.49. $C_{25}H_{22}FNO$. Caculated, %: N 3.77.

9,9-Dimethyl-(4-fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIb). Yield 78 % (*a*), 80% (*b*), mp 313–314°C. UV spectrum, λ_{max}, nm (lgε): 216 (4.52), 231 (4.58), 277 (4.20), 293 (4.32), 339 (3.89), 373 (3.85). ^{1}H NMR spectrum, δ, ppm: 0.90 s (3H, Me), 1.10 s (3H, Me), 2.21 m (2H, CH_2), 2.54 m (2H, CH_2), 5.85s (1H, H*12*), 6.83–7.96 m (10H$_{arom}$), 9.79 s (1H, NH). Found, %: N 3.58. $C_{25}H_{22}FNO$. Caculated, %: N 3.77.

9,9-Dimethyl-12-[4-(2-fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIc). Yield 74% (*a*), 69% (*b*), mp 271–272°C. UV spectrum, λ_{max}, nm (log ε): 215 (4.50), 234 (4.60), 275 (4.19), 291 (4.41), 340 (3.90), 375 (3.94). ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, Me), 1.10 s (3H, Me), 2.13 d (2H, CH_2), 2.52 d (2H, CH_2), 4.99 s (2H, OCH_2), 5.76 s (1H, H*12*), 6.78 d, 7.07–7.56 m, 7.70-8.03 m (14H$_{arom}$), 9.68 s (1H, NH). Found, %: N 2.81. $C_{32}H_{28}FNO_2$. Caculated, %: N 2.94.

9,9-Dimethyl-12-(2-fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (XIIa). Yield 71% (a), 66% (*b*), mp 299–300°C. UV spectrum, λ_{max}, nm (log ε): 215 (4.49), 239 (4.26), 290 (4.31), 337 (4.00), 380 (3.89). ^{1}H NMR spectrum, δ, ppm: 0.89 s (3H, Me), 1.10 s (3H, Me), 2.08 d.d (2H, CH_2), 2.48 m (2H, CH_2), 5.77 s (1H, H*12*), 6.99 m, 7.19–7.28 m (4H$_{arom}$), 7.30 d.d (1H, H*2*), 7.49 d, 7.80 d (2H, H*5,6*), 8.29 d (1H, H*1*), 8.62 d (1H, H*3*), 9.51 s (1H, NH). Found, %: N 7.43. $C_{24}H_{21}FN_2O$. Caculated, %: N 7.53.

9,9-Dimethyl-12-(4-fluorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (XIIb). Yield 78% (a), 75% (*b*), mp 308–309°C. UV spectrum, λ_{max}, nm (log ε): 214 (4.50), 242 (4.61), 254 (4.22), 289 (4.30), 338(3.97), 376 (3.84). ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, Me), 1.03 s (3H, Me), 2.10 d.d (2H, CH_2), 2.43 m (2H, CH_2), 5.80 s (1H, H*12*), 6.91 t, 7.18 m (4H$_{arom}$), 7.34 d.d (1H, H*2*), 7.51 d, 7.88 d (2H, H*5,6*), 8.32 d (1H, H^1), 8.64 d (1H, H^3), 9.80 s (1H, NH). Found, %: N 7.38. $C_{24}H_{20}FN_2O$. Caculated, %: N 7.53.

9,9-Dimethyl-12-[4-(2-fluorobenzyloxy)phenyl]-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (XIIc). Yield 72% (a), 65% (*b*), mp 269–270°C. UV spectrum, λ_{max}, nm (log ε): 215 (4.51), 241 (4.60), 252 (4.19), 288 (4.29), 339 (3.99), 373 (3.97). ^{1}H NMR spectrum, δ, ppm: 0.89 s (3H, Me), 1.06 s (3H, Me), 2.12 d.d (2H, CH_2), 2.50 m (2H, CH_2), 5.02 s (2H, OCH_2), 5.87 s (1H, H*12*), 6.80 d, 7.14 d, 7.47 m (8H$_{arom}$), 7.32 d.d (1H, H^2), 7.52 d, 7.84 d (2H, H^{5,6}), 8.32 d (1H, H*1*), 8.59 d (1H, H*3*), 9.79 s (1H, NH). Found, %: N 5.61. $C_{31}H_{27}FN_2O_2$. Caculated, %: N 5.86.

Arylbis(cyclohexane-1,3-dion-2-yl)methanes XIIIa–XIIIc and XIVa–XIVc. A solution of 5 mmol of

an appropriate aldehyde **Ia–Ic**, 10 mmol of cyclohexane-1,3-dione (**IV**) for compounds **XIIIa–XIIIc** or dimedone (**V**) for dimethyl derivatives **XIVa–XIVc** in 20 ml of ethanol was boiled for 20–30 min. Reaction products **XIIIa, XIIIb** and **XIVa, XIVb** were recrystal-lized from ethanol, compounds **XIIIc** and **XIVc**, from methanol.

2-[(2,6-Dioxocyclohexyl)(2-fluorophenyl)-methyl]cyclohexane-1,3-dione (XIIIa). Yield 76%, mp 200–201°C. UV spectrum, λ_{max}, nm (log ε): 204 (4.63), 251 (4.64), 276 (4.29), 329 (3.85). ^{1}H NMR spectrum, δ, ppm: 1.99 m, 2.28 m, 2.59 m (12H, CH_2), 4.98 s (1H, CH), 6.82–7.10 m ($4H_{arom}$), 11.98 br.s (2H, OH). Found, %: F 5.38. $C_{19}H_{19}FO_4$. Caculated, %: F 5.76.

2-[(2,6-Dioxocyclohexyl)(4-fluorophenyl)-methyl]-1,3-cyclohexanedione (XIIIb). Yield 70%, mp 186–187°C. UV spectrum, λ_{max}, nm (log ε): 205 (4.66), 260 (4.67), 279 (4.30), 330 (3.87). ^{1}H NMR spectrum, δ, ppm: 1.92 m, 2.29 m, 2.60 m (12H, CH_2), 5.10 s (1H, CH), 6.90 t, 7.12 d ($4H_{arom}$), 11.93 br.s (2H, OH). Found, %: F 5.49. $C_{19}H_{19}FO_4$. Caculated, %: F 5.76.

2-{(2,6-Dioxocyclohexyl)[4-(2-fluorobenzyloxy)-phenyl]methyl}cyclohexane-1,3-dione (XIIIc). Yield 71%, mp 197–198°C. UV spectrum, λ_{max}, nm (log ε): 206 (4.61), 260 (4.64), 280 (4.28), 329 (3.90). ^{1}H NMR spectrum, δ, ppm: 2.00 m, 2.30 m, 2.58 m (12H, CH_2), 4.73 s (1H, CH), 5.04 s (2H, OCH_2), 6.78–7.11 m ($8H_{arom}$), 11.96 br.s (2H, OH). Found, %: F 4.11. $C_{26}H_{25}FO_5$. Caculated, %: F 4.36.

2-[(4,4-Dimethyl-2,6-dioxocyclohexyl)(2-fluorophenyl)methyl]-5,5-dimethylcyclohexane-1,3-dione (XIVa). Yield 68%, mp 153–154°C. UV spectrum, λ_{max}, nm (log ε): 207 (4.61), 258 (4.63), 272 (4.20), 331 (3.83). ^{1}H NMR spectrum, δ, ppm: 1.12 s (12H, Me), 2.30–2.51 m (8H, CH_2), 5.60 s (1H, CH), 6.90–7.30 m ($4H_{arom}$), 11.94 br.s (2H, OH). Found, %: F 4.67. $C_{23}H_{27}FO_4$. Caculated, %: F 4.92.

2-[(4,4-Dimethyl-2,6-dioxocyclohexyl)(4-fluorophenyl)methyl]-5,5-dimethylcyclohexane-1,3-dione (XIVb). Yield 76%, mp 167–168°C. UV spectrum, λ_{max}, nm (log ε): 206 (4.58), 257 (4.67), 273 (4.19), 329 (3.92). ^{1}H NMR spectrum, δ, ppm: 1.11 s, 1.18 s (12H, Me), 2.34–2.45 m, (8H, CH_2), 5.53 s (1H, CH), 6.89 t, 7.28 d ($4H_{arom}$), 11.97 br.s (2H, OH). Found, %: F 4.74. $C_{23}H_{27}FO_4$. Caculated, %: F 4.92.

2-{(4,4-Dimethyl-2,6-dioxocyclohexyl)[4-(2-fluorobenzyloxy)phenyl]methyl}cyclohexane-1,3-dione (XIVc). Yield 67%, mp 177–178°C. UV spectrum, λ_{max}, nm (log ε): 207 (4.60), 259 (4.69), 271 (4.23), 330 (3.90). ^{1}H NMR spectrum, δ, ppm: 1.10 s, 1.22 s (12H, Mε), 2.36–2.48 m, (8H, CH_2), 5.10 s (2H, OCH_2), 5.50 s (1H, CH), 6.85–7.60 m ($8H_{arom}$), 11.90 br.s (2H, OH). Found, %: F 3.59. $C_{30}H_{33}FO_5$. Caculated, %: F 3.86.

Condensation of arylbis(cyclohexane-1,3-dion-2-yl)methanes XIIIa–XIIIc and XIVa–XIVc with 2-naphthyl- and 6-quinolylamines (II and III). A solution of 5 mmol of tetraketone **XIIIa–XIIIc and XIVa–XIVc**, 5 mmol of amine **II** or **III** in 20 ml of ethanol was boiled for 3 h The separated precipitate was filtered off, compounds **IXa–IXc** and **Xa–Xc** were recrystallized from a mixture ethanol–benzene, 2:1, compounds **XIa–XIc** and **XIIa–XIIc**, from a mixture ethanol–benzene, 4:1. Yield of azaphenanthrenes **IXa–IXc** – **XIIa–XIIc** was 62–76%.

2-[4-(2-Fluorobenzyloxy)phenyl]methylene-indane-1,3-dione (XVc). A solution of 5 mmol of aldehyde **Ic** and 5 mmol of diketone **VI** in 20 ml of butanol was boiled for 2 h, the precipitate separated on cooling was filtered off, washed with ether, and recrystallized from dioxane. Yield 78%, mp 170–171°C. UV spectrum, λ_{max}, nm (log ε): 204 (4.23), 248 (4.19), 260 (4.10), 300 (3.53), 370 (4.23). ^{1}H NMR spectrum, δ, ppm: 5.21 s (2H, OCH_2), 7.00–7.52 m, 7.70–8.02 m, 8.52 m ($13H_{arom}$, C=CH). Found, %: F 5.18. $C_{23}H_{15}FO_3$. Caculated, %: F 5.31.

13-Aryl-7,13-dihydro-12*H*-benzo[*f*]indeno[1,2-*b*]quinoline-12-ones XVIb and XVIc. A solution of 5 mmol of an appropriate aldehyde **Ib** or **Ic**, 5 mmol of 2-naphthylamine (**II**), 5 mmol of indane-1,3-dione (**VI**) (*a*) or 5 mmol of amine **II** and 5 mmol of dione **XVb** or **XVc** (*b*) in 20 ml of butanol was boiled for 6 h. The precipitate of reaction product was boiled with benzene and washed with ether.

13-(4-Fluorophenyl)-7,13-dihydro-12*H*-benzo-[*f*]indeno[1,2-*b*]quinolin-12-one (XVIb). Yield 84% (*a*), 78% (*b*), mp 313–314°C. UV spectrum, λ_{max}, nm (log ε): 219 (4.79), 238 (4.76), 274 (4.78), 350 (3.98), 500 (3.57). ^{1}H NMR spectrum, δ, ppm: 5.94 s (1H, H^{13}), 7.20–7.92 m ($14H_{arom}$), 9.82 s (1H, NH). Found, %: N 3.56. $C_{26}H_{16}FNO$. Caculated, %: N 3.71.

13-[4-(2-Fluorobenzyloxy)phenyl]-7,13-dihydro-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-one (XVIc). Yield 64% (*a*), 60% (*b*), mp 321–322°C. UV spectrum, λ_{max}, nm (log ε): 220 (4.69), 235 (4.68), 275 (4.76), 354 (3.92), 496 (3.61). ^{1}H NMR spectrum, δ, ppm: 5.00 s (2H, OCH_2), 5.72 s (1H, H^{13}), 6.81 d, 7.08–7.67 m, 7.80–7.97 m ($18H_{arom}$), 9.70 s (1H, NH). Found, %: N 2.69. $C_{33}H_{22}FNO_2$. Caculated, %: N 2.90.

13-Aryl-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-ones XVIIb and XVIIc. A solution of 1 mmol of an appropriate dihydro derivative **XVIb** or **XVIc** in 10 ml of nitrobenzene was boiled for 8 h. The reaction products were recrystallized from a mixture toluene–nitrobenzene, 2:1.

13-(4-Fluorophenyl)-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-one (XVIIb). Yield 62%, mp 301–302°C. UV spectrum, λ_{max}, nm (log ε): 224 (4.65), 255 (4.59), 295 (4.66), 314 (4.62), 386 (3.81). ^{1}H NMR spectrum, δ, ppm: 7.18–7.98 m ($14H_{arom}$). Found, %: N 3.49. $C_{26}H_{14}FNO$. Caculated, %: N 3.73.

13-[4-(2-Fluorobenzyloxy)phenyl]-12*H*-benzo-[*f*]indeno[1,2-*b*]quinolin-12-one (XVIIc). Yield 79%, mp 229–230°C. UV spectrum, λ_{max}, nm (lgε): 223 (4.63), 252 (4.60), 297 (4.64), 313 (4.61), 384 (3.89). ^{1}H NMR spectrum, δ, ppm: 5.34 s (2H, OCH_2), 7.10–8.22 m ($18H_{arom}$). Found, %: N 2.74. $C_{33}H_{20}FNO_2$. Caculated, %: N 2.91.

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