

Crotonization in the Benzo[*a*]acridine Series. Synthesis of Naphtho[2,1-*j*][1,7]phenanthroline Derivatives

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Abstract—8,9,10,11-Tetrahydrobenzo[*a*]acridin-11-one reacted with aromatic aldehydes to give the corresponding 10-arylmethylidene-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-ones. Reactions of the latter with malononitrile in the presence of a base catalyst led to the formation of polynuclear partially hydrogenated systems, 2-alkoxy-4-aryl-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitriles, whose absorption and luminescence spectra in solution and polycrystalline state were studied.

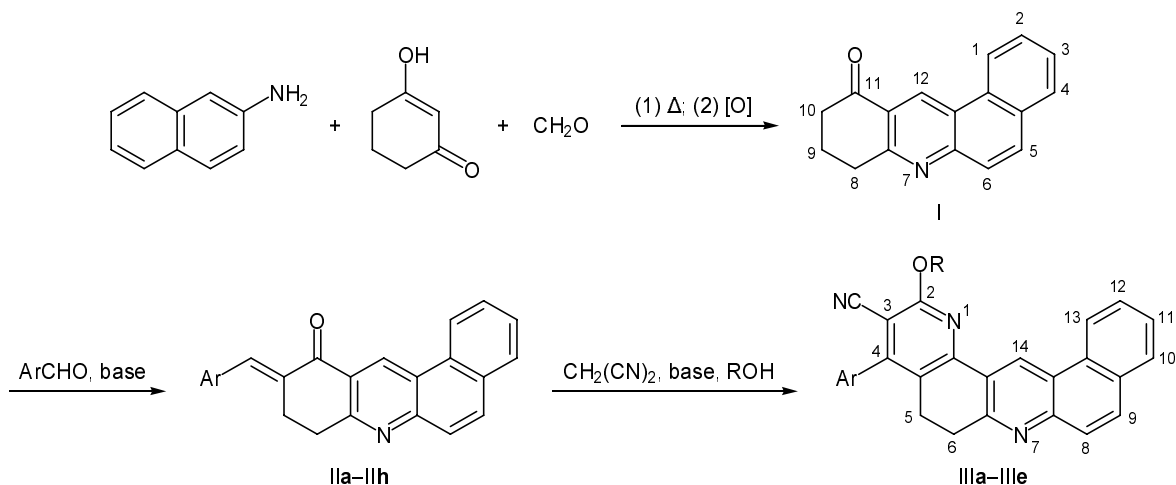
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Benzoacridine derivatives exhibit a broad spectrum of biological activity, which stimulates synthesis and further studies of new compounds of this series. Many benzoacridine compounds possess antitumor properties due to intercalation of the plane aromatic ring with DNA; they are also active against DNA topoisomerases [1, 2]. There are published data on anti-metabolic [3] and carcinogenic effects [4] of benzo[*a*]acridine derivatives. Martinez et al. [5] recently revealed an ap-

preciable cytostatic activity of partially hydrogenated benzoacridine compounds.

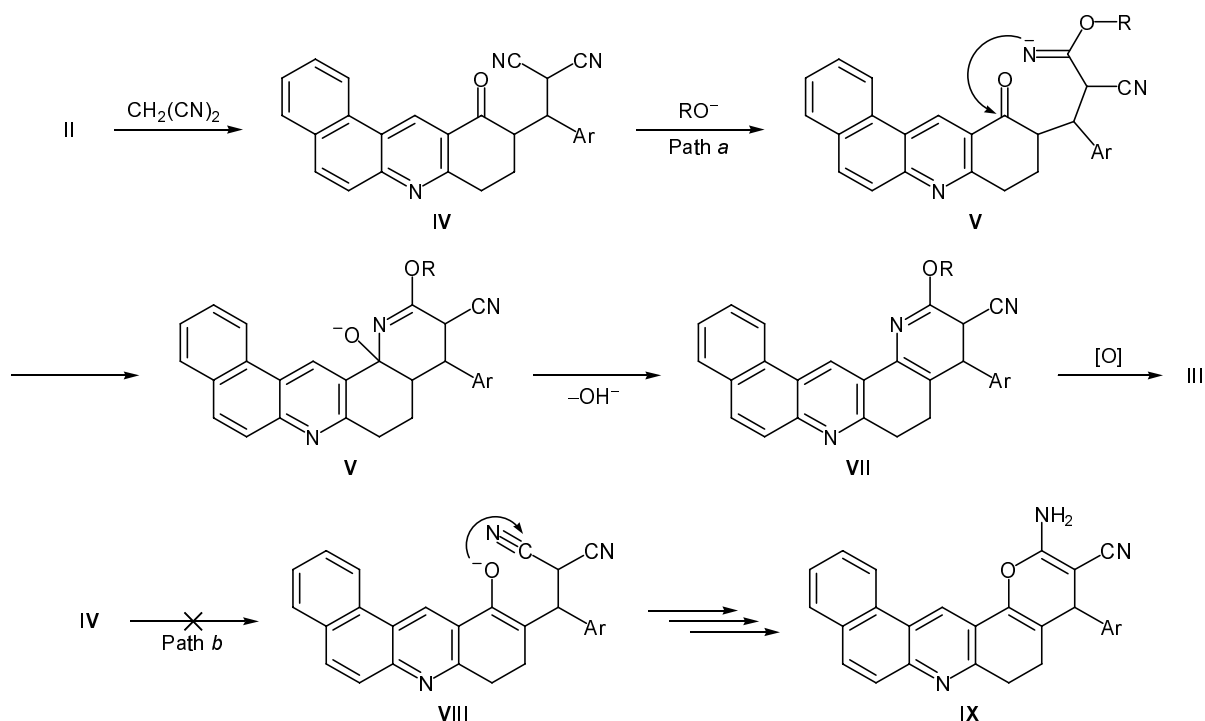
With a view to obtain new compounds containing a partially hydrogenated benzo[*a*]acridine fragment we synthesized 8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (**I**) and examined its reactions with various aromatic aldehydes. Ketone **I** was prepared by triple condensation of β-naphthylamine with formaldehyde and cyclohexane-1,3-dione, followed by oxidation of the

Scheme 1.



II, Ar = 4-FC₆H₄ (**a**), 4-ClC₆H₄ (**b**), 4-BrC₆H₄ (**c**), 4-MeC₆H₄ (**d**), 3,4-CH₂O₂C₆H₃ (**e**), 2-furyl (**f**), 5-methyl-2-thienyl (**g**), 3-(*o*-fluorophenyl)-1*H*-pyrazol-4-yl (**h**); **III**, Ar = 4-ClC₆H₄, R = Me (**a**), Et (**b**); Ar = 2-furyl, R = Me (**c**), Et (**d**); Ar = 3,4-CH₂O₂C₆H₃, R = Me (**e**).

Scheme 2.



dihydro derivative thus formed according to the procedure used previously to synthesize 12-arylbenzo[*a*]-acridin-11-ones [6]. The reactions of **I** with aromatic aldehydes were carried out by heating equimolar amounts of the reactants in ethanol in the presence of aqueous potassium hydroxide. As expected, we isolated the corresponding classical crotonization products, 10-arylmethylidene-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-ones **IIa–IIh** (Scheme 1).

Compounds **II** are α,β -unsaturated ketones which should react with CH acids according to Michael. In fact, arylmethylidene derivatives **II** reacted with malononitrile in boiling methanol or ethanol in the presence of 50% aqueous potassium hydroxide. The final products were partially hydrogenated 2-alkoxy-4-aryl-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitriles **IIIa–IIIe**. The alkoxy group in **III** corresponded to the alcohol in which the condensation occurred.

Scheme 2 illustrates the mechanism of formation of 5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline derivatives **III**. In the first step, malononitrile adds at the exocyclic double bond of α,β -unsaturated ketone **II** to give the corresponding oxo dinitrile **IV**. Attack by alkoxide ion on one cyano group in **IV** (path *a*) leads to the formation of alkyl imidoate anion **V** in which the negative charge is localized on the nitrogen atom. Analogous anions are typical intermediates in many

electrophilic reactions of nitriles under conditions of base catalysis [7, 8]. Intramolecular cyclization of intermediate **V** with participation of the anionic nitrogen atom and carbonyl carbon atom yields pentacyclic anion **VI** which loses hydroxide ion to produce intermediate **VII**. The 3,4-dihydropyridine ring in **VII** is unstable, and it is oxidized during the process to afford nitrile **III** as final product.

In some cases, arylmethylidenecycloalkanones react with malononitrile according to a different scheme, leading to compounds having a pyran ring [9] (path *b* in Scheme 2). However, we observed no formation of benzopyranoacridine derivatives **IX** in the reaction under study; presumably, the carbonyl group in intermediate oxo nitrile **IV** is difficult to access for steric reasons, and its enolization is unfavorable from the energy considerations.

2-Alkoxy-4-aryl-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitriles **IIIa–IIIe** are crystalline substances which are poorly soluble in most organic solvents. Their electronic absorption spectra (in ethanol) contain a series of bands (see table). All compounds **IIIa–IIIe** exhibit a strong fluorescence both in ethanolic solution and in the polycrystalline state. The positions of the main fluorescence maxima of compounds **IIIa–IIIe** in ethanol and in the polycrystalline state at room temperature are given in table.

The structure of compounds **I–III** was confirmed by the IR and NMR spectra. Ketone **I** showed in the IR spectrum an absorption band at 1680 cm⁻¹ due to stretching vibrations of the carbonyl group, stretching vibrations of aromatic C–H bonds appeared in the region 3065–3050 cm⁻¹, and CH₂ groups gave rise to absorption at 2950–2830 cm⁻¹. The IR spectra of arylmethylidene derivatives **IIa–IIh** contained a set of strong absorption bands in the region 1400–1680 cm⁻¹ (C=O, C=C_{arom}); it was difficult to assign these bands more rigorously. The IR spectra of 5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline derivatives **IIIa–IIIe** lacked absorption in the region 1680–1600 cm⁻¹, typical of the initial arylmethylidenetetrahydrobenzoacridinones, but a strong band belonging to the cyano group was present at 2220 cm⁻¹. Stretching vibrations of aromatic C–H bonds appeared in the region 3000–3100 cm⁻¹, and those of aliphatic C–H bonds (CH₂ and CH₃ groups), at 2830–2970 cm⁻¹.

In the ¹H NMR spectrum of ketone **I** we observed signals from three methylene groups at 2.20, 2.77, and 3.25 ppm (C⁹H₂, C⁸H₂, and C¹⁰H₂, respectively), and signals from aromatic protons occupied the δ region 7.5–8.2 ppm. Signals from protons on C¹ and C¹² are characteristic: the first of these is a one-proton doublet at δ 8.78 ppm (*J* = 8.0 Hz), and the second, a singlet at δ 9.42 ppm (1H). No 10-H signal was present in the ¹H NMR spectra of arylmethylidene derivatives **IIa–IIh**, and methylene protons on C⁹ and C⁸ resonated at about δ 3.3 ppm. The signal from the ArCH= proton appeared as a singlet in the aromatic region (δ 7.6–7.9 ppm, depending on the substituent). The positions of the 1-H and 12-H signals were almost the same as in the spectrum of ketone **I**. The ¹H NMR spectra of 5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline derivatives **IIIa–IIIe** contained no vinyl proton signal typical of compounds **IIa–IIh**, but signals from the corresponding alkoxy group were present (a three-proton singlet at δ 4.27 ppm for methoxy derivatives or a 3H-triplet at δ 1.6 ppm and a 2-H quartet at δ 4.7 ppm for ethoxy analogs).

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protege-460 Fourier-transform spectrometer. The ¹H NMR spectra were measured on Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) spectrometers using DMSO-*d*₆ as solvent and TMS (unless otherwise stated) as internal reference. The electronic absorption spectra were obtained on a Varian Cary-500

Absorption and fluorescence maxima of 2-alkoxy-4-aryl-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitriles **IIIa–IIIe** in ethanol and in the polycrystalline state at room temperature

Comp. no.	UV spectrum (EtOH), λ _{max} , nm (log ε)	Fluorescence maximum, nm (λ _{excit} 360 nm)	
		EtOH	polycrystalline state
IIIa	230 (4.38), 260 (4.37), 384 (4.36)	400	500
IIIb	228 (4.42), 263 (4.33), 384 (4.38)	403	438
IIIc	228 (4.55), 263 (4.59), 388 (4.58)	410	452
IIId	230 (4.60), 263 (4.63), 389 (4.64)	410	448

spectrophotometer (USA) at room temperature. The fluorescence spectra were measured on an SFL-1211A spectrofluorimeter (SOLAR, Belarus). The melting points were determined on a Kofler melting point apparatus.

8,9,10,11-Tetrahydrobenzo[*a*]acridin-11-one (I). Sodium hydroxide, ~20 mg, was added to a mixture of 0.3 g (0.01 mol) of paraformaldehyde and 1.43 g (0.01 mol) of 2-naphthylamine in 20 ml of ethanol, and the mixture was heated on a water bath until paraformaldehyde dissolved completely (3–7 min). To the resulting transparent solution we added under stirring a solution of 1.12 g (0.01 mol) of cyclohexane-1,3-dione in 10 ml of ethanol, and the mixture was quickly heated until a solid began to separate. The mixture was cooled, and the precipitate (dihydro derivative) was filtered off, washed with ethanol, and dried. The product, 1.7 g (yield 70%) was dissolved in 10 ml of concentrated sulfuric acid, the solution was cooled to 0°C, and 0.7 g (0.007 mol) of chromium(VI) oxide was added. The mixture was heated for 25–30 min on a boiling water bath, cooled, and poured onto ice. The precipitate was filtered off, washed with water and aqueous ammonia, and dried. Recrystallization from DMF gave 1.5 g (~88%) of compound **I** with mp 187°C. IR spectrum, ν, cm⁻¹: 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ, ppm (relative to DMSO-*d*₅, δ 2.50 ppm): 2.20 m (2H, C⁹H₂), 2.77 d.d (2H, C⁸H₂, *J* = 7.5, 5.8 Hz), 3.25 d.d (2H, C¹⁰H₂, *J* = 6.5, 5.8 Hz), 7.70 d.d.d (1H, 3-H, *J* = 7.9, 7.1, 1.3 Hz), 7.76 d.d.d (1H, 2-H, *J* = 8.0, 7.1, 2.5 Hz), 7.85 d.d (1H, 5-H, *J* = 9.1, 0.8 Hz), 8.03 d.d (1H, 4-H, *J* = 7.9, 1.2 Hz), 8.16 d (1H, 6-H, *J* = 9.1 Hz), 8.78 d (1H, 1-H, *J* = 8.0 Hz), 9.42 s (1H, 12-H). Found, %: C 82.63;

H 5.14; N 5.80. $C_{17}H_{13}NO$. Calculated, %: C 82.57; H 5.30; N 5.66.

10-Arylmethylidene-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-ones IIa–IIh (general procedure). A solution of 500 mg of potassium hydroxide in 1 ml of water was added to a mixture of 1.25 g (0.005 mol) of ketone **I** and 0.005 mol of the corresponding aromatic aldehyde in 30 ml of ethanol, and the mixture was heated for 15–20 min on a water bath. The mixture was cooled, and the precipitate was filtered off, washed in succession with ethanol, water, and acetone, dried, and recrystallized from DMF.

10-(4-Fluorobenzylidene)-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (IIa). Yield 65%, mp 204°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.3 m (4H, C⁸H₂, C⁹H₂), 7.32 m (2H, H_{arom}), 7.65 m (2H, H_{arom}), 7.74 m (1H, 3-H), 7.82 m (1H, 2-H), 7.84 s (1H, C=CH), 7.92 d (1H, 5-H, $J = 9$ Hz), 8.07 d (1H, 4-H, $J = 8$ Hz), 8.22 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H, $J = 8$ Hz), 9.62 s (1H, 12-H). Found, %: C 82.63; H 5.14; N 5.80. $C_{24}H_{16}FNO$. Calculated, %: C 81.57; H 4.56; N 3.96.

10-(4-Chlorobenzylidene)-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (IIb). Yield 82%, mp 229°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.3 m (4H, C⁸H₂, C⁹H₂), 7.32 m (2H, H_{arom}), 7.65 m (2H, H_{arom}), 7.74 m (1H, 3-H), 7.82 m (1H, 2-H), 7.84 s (1H, C=CH), 7.92 d (1H, 5-H, $J = 9$ Hz), 8.07 d (1H, 4-H, $J = 8$ Hz), 8.22 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H, $J = 8$ Hz), 9.62 s (1H, 12-H). Found, %: C 80.03; H 4.24; N 3.80. $C_{24}H_{16}ClNO$. Calculated, %: C 77.94; H 4.36; N 3.79.

10-(4-Bromobenzylidene)-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (IIc). Yield 77%, mp 241°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.28 m (4H, C⁸H₂, C⁹H₂), 7.54 m (2H, H_{arom}), 7.67 m (2H, H_{arom}), 7.75 m (1H, 3-H), 7.80 s (1H, C=CH), 7.82 m (1H, 2-H), 7.92 d (1H, 5-H, $J = 9$ Hz), 8.07 d (1H, 4-H, $J = 8$ Hz), 8.22 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H, $J = 8$ Hz), 9.62 s (1H, 12-H). Found, %: C 70.00; H 3.84; N 3.36. $C_{24}H_{16}BrNO$. Calculated, %: C 69.58; H 3.89; N 3.38.

10-(4-Methylbenzylidene)-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (II d). Yield 53%, mp 163°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 2.5 s (3H, CH₃), 3.13 m (2H, C⁹H₂), 3.28 m (2H, C⁸H₂), 7.32 m (4H, H_{arom}), 7.75 m (1H, 3-H), 7.85 m (1H, 2-H), 7.92 s (1H, C=CH), 7.93 d (1H, 5-H, $J = 9$ Hz), 8.09 d (1H, 4-H, $J = 8$ Hz), 8.23 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H,

$J = 8$ Hz), 9.62 s (1H, 12-H). Found, %: C 85.99; H 5.52; N 4.09. $C_{25}H_{19}NO$. Calculated, %: C 85.93; H 5.48; N 4.01.

10-(1,3-Benzodioxol-5-ylmethylidene)-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (IIe). Yield 70%, mp 199°C. IR spectrum, ν , cm^{-1} : 1040 (C–O–C), 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.30 s (4H, C⁸H₂, C⁹H₂), 6.10 s (2H, OCH₂O), 7.00 d (1H, H_{arom}, $J = 1.7$ Hz), 7.15 m (2H, H_{arom}), 7.74 m (1H, 3-H), 7.79 s (1H, C=CH), 7.81 m (1H, 2-H), 7.92 d (1H, 5-H, $J = 9$ Hz), 8.08 d (1H, 4-H, $J = 8$ Hz), 8.22 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H, $J = 8$ Hz), 9.60 s (1H, 12-H). Found, %: C 78.99; H 4.54; N 3.81. $C_{25}H_{17}NO_3$. Calculated, %: C 79.14; H 4.52; N 3.69.

10-Furfurylidene-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (II f). Yield 76%, mp 188°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.35 m (2H, C⁹H₂), 3.45 m (2H, C⁸H₂), 6.70 m (1H, H_{arom}), 7.03 m (1H, H_{arom}), 7.65 s (1H, C=CH), 7.75 m (1H, 3-H), 7.85 m (1H, 2-H), 7.92 m (1H, 5-H), 8.02 d (1H, 4-H, $J = 8$ Hz), 8.23 d (1H, 6-H, $J = 9$ Hz), 8.90 d (1H, 1-H, $J = 8$ Hz), 9.60 s (1H, 12-H). Found, %: C 81.43; H 4.64; N 4.27. $C_{22}H_{15}NO_2$. Calculated, %: C 81.21; H 4.65; N 4.30.

10-(5-Methylthiophen-2-ylmethylidene)-8,9,10,11-tetrahydro-8*H*-benzo[*a*]acridin-11-one (II g). Yield 72%, mp 250°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 2.5 s (3H, CH₃), 3.36 m (4H, C⁸H₂, C⁹H₂), 7.11 d (1H, H_{arom}), 7.74 m (2H, 3-H, H_{arom}), 7.81 m (1H, 2-H), 7.93 d (1H, 5-H, $J = 9$ Hz), 8.07 d (1H, 4-H, $J = 8$ Hz), 8.11 s (1H, C=CH), 8.21 d (1H, 6-H, $J = 9$ Hz), 8.87 d (1H, 1-H, $J = 8$ Hz), 9.58 s (1H, 12-H). Found, %: C 77.73; H 4.85; N 3.88. $C_{23}H_{17}NOS$. Calculated, %: C 77.72; H 4.82; N 3.94.

10-[3-(*o*-Fluorophenyl)-1*H*-pyrazol-4-ylmethylidene]-8,9,10,11-tetrahydrobenzo[*a*]acridin-11-one (II h). Yield 67%, mp 279–284°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 3065 (C–H_{arom}), 3250 (NH). ¹H NMR spectrum, δ , ppm: 3.33 m (4H, C⁸H₂, C⁹H₂), 7.30–8.15 m (11H, H_{arom}, C=CH), 8.80 d (1H, 1-H, $J = 8$ Hz), 9.52 s (1H, 12-H), 13.3 br.s (1H, NH). Found, %: C 77.33; H 4.54; N 10.51. $C_{27}H_{18}FN_3O$. Calculated, %: C 77.31; H 4.33; N 10.02.

2-Alkoxy-4-aryl-5,6-dihydronaphtho[2,1-*j*][1,7]-phenanthroline-3-carbonitriles IIIa–IIIe (general procedure). A solution of 1 g of potassium hydroxide in 1 ml of water was added to a mixture of 0.005 mol of the corresponding α,β -unsaturated ketone **II** and 0.4 g (0.006 mol) of malononitrile in 30 ml of methanol or ethanol, and the mixture was heated for

15–20 min on a water bath. The mixture was cooled, and the precipitate was filtered off, washed in succession with ethanol, water, and acetone, dried, and recrystallized from DMF.

4-(4-Chlorophenyl)-2-methoxy-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitrile (IIIa). Yield 56%, mp >300°C. IR spectrum, ν , cm^{-1} : 2220 (CN), 3000–3100 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 2.85 m (2H, C⁵H₂), 3.23 m (2H, C⁶H₂), 4.18 s (3H, OCH₃), 7.20–8.30 m (9H, H_{arom}), 8.80 d (1H, 13-H, $J = 8$ Hz), 9.55 s (1H, 14-H). Found, %: C 75.20; H 4.00; N 9.40. C₂₈H₁₈ClN₃O. Calculated, %: C 75.08; H 4.05; N 9.38.

4-(4-Chlorophenyl)-2-ethoxy-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitrile (IIIb). Yield 61%, mp 246°C. IR spectrum, ν , cm^{-1} : 2220 (CN), 3000–3100 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 1.60 t (3H, OCH₂CH₃), 2.85 m (2H, C⁵H₂), 3.20 m (2H, C⁶H₂), 4.78 q (2H, OCH₂CH₃), 7.35–8.18 m (9H, H_{arom}), 8.80 d (1H, 13-H, $J = 8$ Hz), 9.70 s (1H, 14-H). Found, %: C 75.60; H 4.32; N 9.12. C₂₉H₂₀ClN₃O. Calculated, %: C 75.40; H 4.36; N 9.10.

4-(2-Furyl)-2-methoxy-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitrile (IIIc). Yield 60%, mp 273°C. IR spectrum, ν , cm^{-1} : 2220 (CN), 3000–3100 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 3.16 t (2H, C⁵H₂, $J = 7.7$ Hz), 3.29 t (2H, C⁶H₂, $J = 7.7$ Hz), 4.29 s (3H, OCH₃), 6.75 d.d (1H, 4'-H, $J = 3.4, 1.8$ Hz), 7.12 d.d (1H, 3'-H, $J = 3.4, 0.7$ Hz), 7.73 d.d.d (1H, 12-H, $J = 8.0, 7.0, 1.4$ Hz), 7.80 d.d.d (1H, 11-H, $J = 8.0, 7.0, 1.1$ Hz), 7.95 d.d (1H, 5'-H, $J = 1.8, 0.7$ Hz), 8.03 d.d (1H, 10-H, $J = 8.0, 1.0$ Hz), 8.04 d (1H, 9-H, $J = 9.0$ Hz), 8.12 d (1H, 8-H, $J = 9.0$ Hz), 8.92 d (1H, 13-H, $J = 8.0$ Hz), 9.83 s (1H, 14-H). Found, %: C 77.43; H 4.24; N 10.38. C₂₆H₁₇N₃O₂. Calculated, %: C 77.41; H 4.25; N 10.42.

2-Ethoxy-4-(2-furyl)-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitrile (III d). Yield 59%, mp 260°C. IR spectrum, ν , cm^{-1} : 2220 (CN), 3000–3100 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 1.50 t (3H, OCH₂CH₃), 2.85 t (2H, C⁵H₂), 3.20 t (2H, C⁶H₂), 4.72 q (2H, OCH₂CH₃), 6.77 d.d (1H, 4'-H, $J = 3.4, 1.8$ Hz), 7.12 d.d (1H, 3'-H, $J = 3.4, 0.7$ Hz), 7.65–8.22 m (6H, H_{arom}), 8.80 d (1H, 13-H, $J = 8$ Hz), 9.72 s (1H, 14-H). Found, %: C 77.69; H 4.61; N 10.11. C₂₇H₁₉N₃O₂. Calculated, %: C 77.68; H 4.59; N 10.07.

4-(1,3-Benzodioxol-5-yl)-2-methoxy-5,6-dihydronaphtho[2,1-*j*][1,7]phenanthroline-3-carbonitrile (IIIe). Yield 75%, mp 267°C. IR spectrum, ν , cm^{-1} : 2220 (CN), 3000–3100 (C–H_{arom}). ¹H NMR spectrum, δ , ppm: 2.84 t (2H, C⁵H₂, $J = 7.7$ Hz), 3.20 t (2H, C⁶H₂, $J = 7.7$ Hz), 4.27 s (3H, OCH₃), 6.13 s (2H, OCH₂O), 6.94 d.d (1H, H_{arom}, $J = 8.0, 1.7$ Hz), 7.03 d (1H, H_{arom}, $J = 1.7$ Hz), 7.09 d (1H, H_{arom}, $J = 8.0$ Hz), 7.70 d.d.d (1H, 11-H, $J = 8.0, 7.0, 1.1$ Hz), 7.80 d.d.d (1H, 12-H, $J = 8.0, 7.0, 1.4$ Hz), 7.98 d.d (1H, 9-H, $J = 9.0, 0.8$ Hz), 8.02 d.d (1H, 10-H, $J = 8.0, 1.3$ Hz), 8.10 d (1H, 8-H, $J = 9.0$ Hz), 8.89 d (1H, 13-H, $J = 8.0$ Hz), 9.77 s (1H, 14-H). Found, %: C 76.44; H 4.50; N 8.89. C₃₀H₂₁N₃O₃. Calculated, %: C 76.42; H 4.49; N 8.91.

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