Studies on cyclization of *o*-(alka-1,3-diynyl)arenediazonium salts

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The Richter reaction of *o*-(alka-1,3-diynyl)arenediazonium salts, obtained by diazotization of diacetylenic derivatives of anilines, leads to 3-alkynyl-4-chloro- or 3-alkynyl-4-bromocinnolines and/or 3-alkynyl-4-hydroxycinnolines (the latter cyclize into furo[3,2-*c*]-cinnolines under the reaction conditions). 3-Alkynyl-4-chlorocinnolines undergo solvolysis in methanol giving rise to 3-alkynyl-4-methoxycinnolines, the subsequent hydrolysis of which also gives furo[3,2-*c*]cinnolines. Effects of the nature of substituents in the aromatic ring and of the reaction conditions on the product composition and yields have been established. The reaction course has been studied by spectrophotometry.

Key words: diacetylenes, anilines, diazotization, diazonium salts, the Richter cyclization, cinnolines, furo[3,2-*c*]cinnolines, spectrophotometry.

Chemistry of cinnolins is an intensively developing field of organic chemistry since these compounds display a wide range of biological activity and can be used as anticancer,[1] antifungal,[2] and antithrombocentic[3] drugs. Cinnoline derivatives also possess fluorescence[4] and are potential objects for the use in nonlinear optics.[5]

The synthesis of cinnoline core was accomplished for the first time by Richter by diazotization of *o*-aminophenylpropyolic acid and cyclization of the arenediazonium salt thus obtained with the formation of 4-hydroxycinnoline-3-carboxylic acid.[6] Afterwards, it was shown that the cyclization of *o*-ethynyl-substituted arenediazonium salts (the Richter reaction), along with 4-hydroxycinnolines, leads to the formation of 4-halocinnolines.[7,8]. The latter are of special interest for the combinatorial chemistry since they can be derivatized by substitution of the halogen atom for various nucleophiles.[9]

When *o*-(buta-1,3-diynyl)aniline was diazotized, 4-chloro-3-ethynylcinnoline[7] was isolated, however, for a long time this example remained the only one in the series of diacetylenic derivatives of arenediazonium salts due to the poor availability of such starting compounds.

A suggested by us earlier method for the synthesis of functional derivatives of 1-arylalka-1,3-diynes by the sequence of the "diacetylenic zipper" reaction and the Sonogashira reaction allow one to obtain alka-1,3-diynyl-substituted aryl- or hetarylamines in good yields.[10] Since the cyclization of diacetylenic derivatives of arenediazonium salts can serve as a one-step pathway to 4-halo-3-ethynylcinnolines, the promising building blocks, in particular, for the synthesis of polyfused heterocycles,[11] we continued our efforts in this field. Earlier, we briefly reported that the result of diazotization of *o*-(alka-1,3-diynyl)anilines greatly depends on the reaction conditions and the nature of substituents in the aromatic ring.[12] In the present work, detailed results on the study of factors influencing a cyclization course of *o*-(alka-1,3-diynyl)arenediazonium salts are presented.

Results and Discussion

The synthesis of starting diacetylenic arylamines **1a—i** was accomplished in accordance with the procedure suggested in Ref. 10. A diazotization of *o*-(alka-1,3-diynyl)-arylamines **1a—i** was carried out with the use of procedures ***A—F*** (Scheme 1), the experimental data are given in Table 1. By diazotization of amines **1b** and **1d** with sodium nitrite in concentrated hydrochloric acid (procedure ***A***) under conditions used earlier for acetylenic amines of benzene and pyrazole series,[7] the corresponding 3-(alk-1-ynyl)-4-chlorocinnolines **2b,d** were obtained in 23% and 10% yield, respectively (Table 1, entries *1* and *2*). In addition, the products of reductive deamination, *viz.*, (alka-1,3-diynyl)benzenes **3b,d**, were formed in the reaction. The starting compounds are poorly soluble in aqueous medium, that leads to an increase in the reaction time and resinification. Therefore, the subsequent reactions with compounds **1a—d** were carried out with addition of organic solvents or with the use of organic diazotizing agent, butyl nitrite (Table 1, entries *3—6*).

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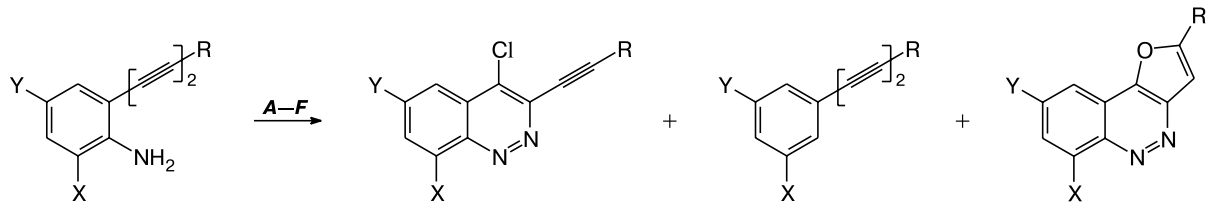
Scheme 1



1a—i **2a—i** **3b,d,f,h,i** **4c,h,i**

A: $NaNO_2$, HCl (36%); ***B***: BuONO, HCl (36%); ***C***: $NaNO_2$, HCl (36%), THF; ***D***: $NaNO_2$, HCl (36%), Et_2O—hexane; ***E***: BuONO, H_2SO_4 (conc.), Et_2O; ***F***: $NaNO_2$ (solid), MeOH saturated with HCl.

The use of BuONO in water (procedure ***B***) or in THF (procedure ***C***) did not lead to considerable increase in the yield of 4-chlorocinnolines, whereas the formation of deamination product **3b** also occurred. Conducting the reaction in Et_2O—hexane (procedure ***D***) was found to be the optimum. For diacetylenic derivatives of arenediazonium-salts containing donating (Me) or weakly withdrawing (Br) substituents in *ortho*- or *para*-positions, the target 3-alkynyl-4-chlorocinnolines **2** were the only reaction products in this case (entries *5—10*).

When strong withdrawing groups, COOMe (**1h**) or NO_2 (**1i**), are present in the molecule of the starting amines, furo[3,2-*c*]cinnolines **4h,i** were isolated as the major reaction products in addition to 3-alkynyl-4-chlorocinnolines **2h,i** (entries *11*, *12*), the formation of which results from the intramolecular cyclization of corresponding 3-alkynyl-4-hydroxycinnolines. These results are in agreement with a suggestion that the latter can be obtained by hydrolysis of 4-halocinnolines in the reaction course.[7] It is known that hydrolysis in the series of cinnolines proceeds by the S_{NAr} mechanism of "addition—elimination" and should be promoted by electron-withdrawing substituents.[13] In the case of 2-(deca-1,3-diynyl)-4-nitroaniline (**1i**) (entry *12*), strong resinification of the reaction mixture was observed, therefore, the cyclization time was decreased to 2 h. This allowed us to increase the total yield of the products (entry *13*), however, in contrast to experiment *12*, a significant amount of the reductive deamination product **3i** was isolated resulted from decomposition of unreacted diazonium salt.

During the diazotization of amine hydrochloride **1h** with butyl nitrite in the presence of catalytic amount of conc. sulfuric acid and at lower temperature as –20 °C

Table 1. Results of the Richter reaction of *o*-(alka-1,3-diynyl)arylamines

Entry	Starting compound	R	X	Y	Procedure[a]	Product yields (%)		
						2	**3**	**4**
1	**1b**	C_8H_{17}	H	H	***A***	**2b** (23)	**3b** (7)	—
2	**1d**	C_6H_{13}	H	Br	***A***	**2d** (10)	**3d** (5)	—
3	**1b**	C_8H_{17}	H	H	***B***	**2b** (24)	**3b** (5)	—
4	**1d**	C_6H_{13}	H	Br	***C***	**2d** (12)	**3d** (12)	—
5	**1a**	C_6H_{13}	H	H	***D***	**2a** (36)	—	—
6	**1b**	C_8H_{17}	H	H	***D***	**2b** (54)	—	—
7	**1c**	$C_{10}H_{21}$	H	H	***D***	**2c** (34)	—	—
8	**1e**[b]	C_8H_{17}	H	Br	***D***	**2e** (27)	—	—
9	**1f**[b]	C_8H_{17}	H	Me	***D***	**2f** (28)	—	—
10	**1g**[b]	C_8H_{17}	Br	Me	***D***	**2g** (33)	—	—
11	**1h**	C_8H_{17}	H	COOMe	***D***	**2h** (15)	—	**4h** (27)
12	**1i**	C_6H_{13}	H	NO_2	***D***	**2i** (3.5)	—	**4i** (12)
13	**1i**[c]	C_6H_{13}	H	NO_2	***D***	**2i** (4.7)	**3i** (20)	**4i** (47)
14	**1h**[b]	C_8H_{17}	H	COOMe	***E*** (–20 °C)	**2h** (5)	**3h** (25)	—
15	**1h**[b]	C_8H_{17}	H	COOMe	***D*** (–20 °C)	**2h** (14)	**3h** (13)	**4h** (15)
16	**1f**[b]	C_8H_{17}	H	Me	***D*** (–20 °C)	**2f** (6)	**3f** (34)	—
17	**1c**	$C_{10}H_{21}$	H	H	***F***	—	—	**4c** (39)
18	**1h**[c]	C_8H_{17}	H	COOMe	***F***	—	**3h** (11)	**4h** (54)

[a] Conditions are given in Scheme 1. Diazotization was carried out at –5 °C, cyclization at room temperature for 8—16 h.
[b] Hydrochlorides of starting amines were used.
[c] The reaction time was 2 h.

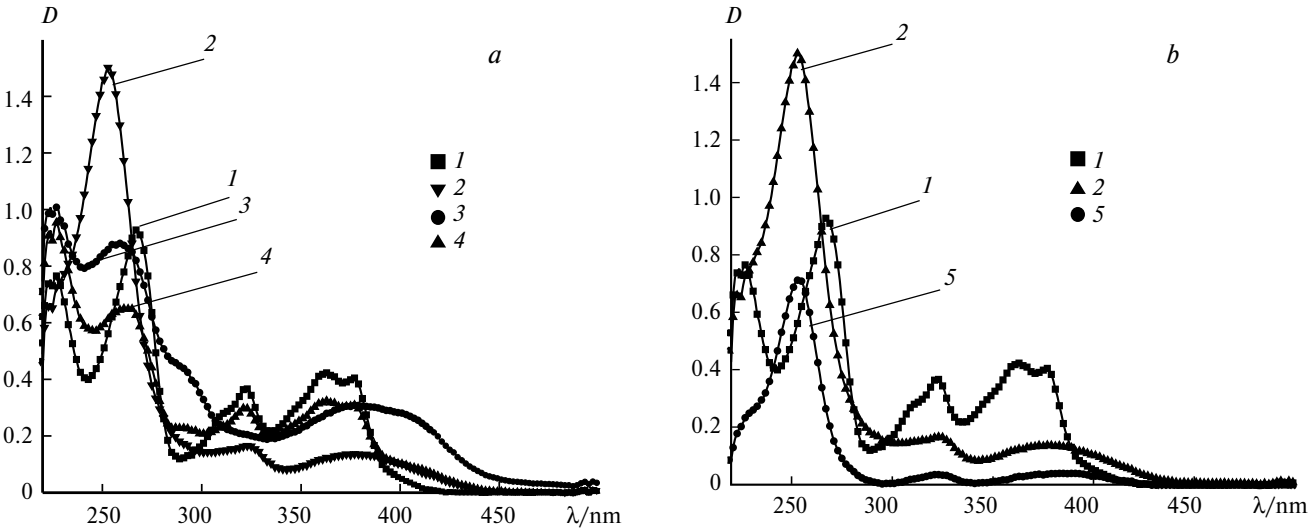


Fig. 1. Spectrophotometric monitoring of the cyclization of diazonium salt **1h** at the beginning of the process (*a*) and at the end (*b*): *1*, the spectrum of 4-chlorocinnoline; *2*, the spectrum of furo[3,2-*c*]cinnoline; *3*—*5*, the spectra of the reaction mixture after 5 min (*3*), 3 h 30 min (*4*), 24 h (*5*).

(procedure ***E***, entry *14*), the formation of furo[3,2-*c*]-cinnoline was not observed. However, chlorocinnoline **2h** was isolated in 5% yield only with deaminated compound **3h** being the major product. Apparently, lowering temperature leads to a decrease in the cyclization rate and the process of deamination becomes a competing one to the process of the cinnoline formation. This suggestion was confirmed by subsequent experiments, in which the Richter reaction for compounds **1f,h** was carried out with the use of procedure ***C*** at −20 °C, and in which an increase in the yield of products **3f,h** was also observed (*cf.* entries *9*, *16* and *11*, *15*).

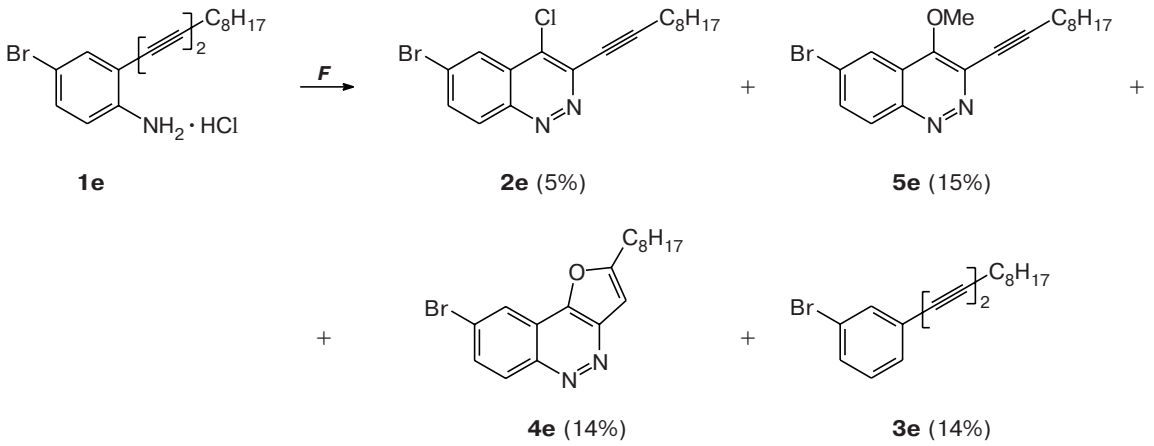
An interesting result was obtained when the Richter reaction was carried out in MeOH. The reaction for compounds **1c,h** was accomplished under anhydrous conditions, when dry MeOH saturated with HCl was used. In this case, the formation of 4-chlorocinnolines was not observed even during diazotization of *o*-(tetradeca-1,3-diynyl)aniline **1c** containing no electron-withdrawing substituents, rather furo[3,2-*c*]cinnolines were the major reaction products (entries *17* and *18*). TLC monitoring of the reaction course in experiment *18* showed formation of the products having much lower R_f in comparison with the used authentic samples of 4-chlorocinnoline **2h** and furo[3,2-*c*]cinnoline **4h**. However, treatment of the reaction mixture with alkaline solution already after 2 h from the beginning of the reaction led to furo[3,2-*c*]cinnoline **4h** as the major product in 54% yield.

Spectrophotometric study of the cyclization of the diazonium salt, obtained from amine **1h** in Et_2O—HCl, confirmed that 4-chloro-3-ethynylcinnoline was the only product of the Richter reaction, whereas 4-hydroxy-3-ethynylcinnoline and the product of its cyclization, furo[3,2-*c*]cinnoline, result from the hydrolysis of 4-chlorocinnoline during the reaction course.[14] The diazonium salt cyclization rate is significantly higher than the rate of subsequent hydrolysis of chlorocinnoline.

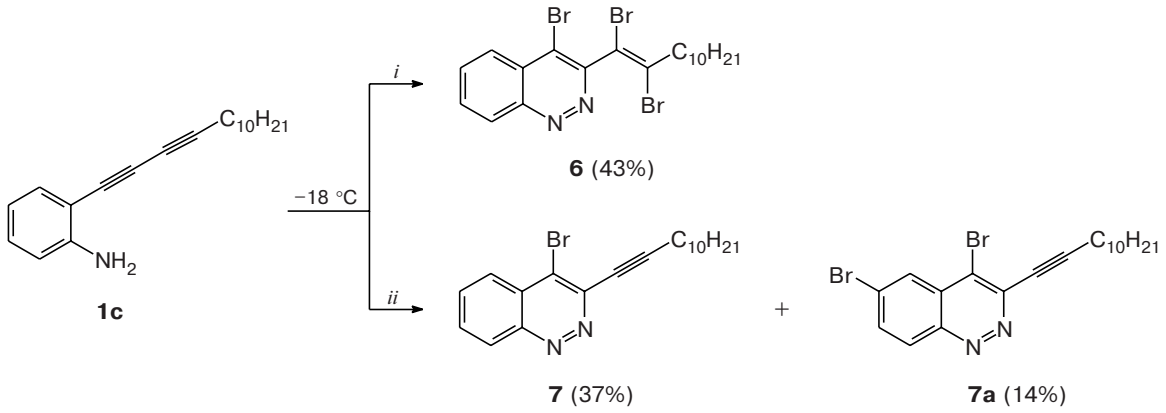
To clarify processes taking place in MeOH saturated with HCl, we carried out spectrophotometric study of the cyclization process of the diazonium salt obtained from compound **1h** (Fig. 1). The UV spectra of 4-chlorocinnoline **2h** and furo[3,2-*c*]cinnoline **4h** were obtained preliminary under the same conditions. During the first three hours, in the spectrum of the reaction mixture (see Fig. 1, *a*), no appearance of absorption bands of furo[3,2-*c*]cinnoline **4h** was observed, while the product formed had absorption band characteristic of the spectrum of 4-chlorocinnoline (λ = 268, 322, 363, and 385 nm, *cf.* spectra *1* and *3*). However, after 1 day the spectrum of the reaction mixture completely corresponded to the spectrum of furo[3,2-*c*]cinnoline **4h** (see Fig. 1, *b*, *cf.* spectra *2* and *3*).

These data confirmed that in MeOH the reaction first leads to the formation of 4-chlorocinnoline, too, but its hydrolysis and subsequent cyclization of 4-hydroxycinnoline proceed significantly faster in comparison with the reaction in diethyl ether.[14] The TLC monitoring of the cyclization also revealed that, in comparison with the reactions carried out under other conditions, in anhydrous methanol saturated with HCl the products formed have considerably lower R_f values. Detection of more polar products in the reaction mixture allowed us to suggest that under these conditions the cinnoline system of the products is protonated, while the electron-withdrawing substituent facilitate hydrolysis of 4-chlorocinnoline both in the course of the reaction and during the isolation step.

Scheme 2



Scheme 3



i. $NaNO_2$ (2 equiv.), Et_2O/hexane/HBr; *ii*. $NaNO_2$ (1.1 equiv.), Et_2O/hexane/HBr.

An additional experiment on cyclization of the diazonium salt obtained by diazotization of compound **1e** in MeOH (procedure ***F***) has been conducted, in which quenching of the reaction mixture was carried out with anhydrous Et_3N (Scheme 2).

In this case, we succeeded in the isolation of 4-chlorocinnoline **2e**, in addition, 4-methoxycinnoline **5e** was obtained as one of the major products. It was also found that in methanol saturated with HCl, 4-chlorocinnoline **2e** is completely converted into 4-methoxycinnoline **5e** for 30 min. Interestingly that in the UV spectra of 4-chlorocinnoline **2e** and 4-methoxycinnoline **5e**, the absorption band maxima positions coincide, however, the bands of 4-chlorocinnoline have higher extinction. When 4-chlorocinnoline **2h** was dissolved in MeOH saturated with HCl, the process of its fast transformation was demonstrated spectrophotometrically: in 15 min, a sharp decrease in intensity of the absorption band maximum at 268 nm was observed, however, there was no shift of the maximum (Fig. 2). The changes

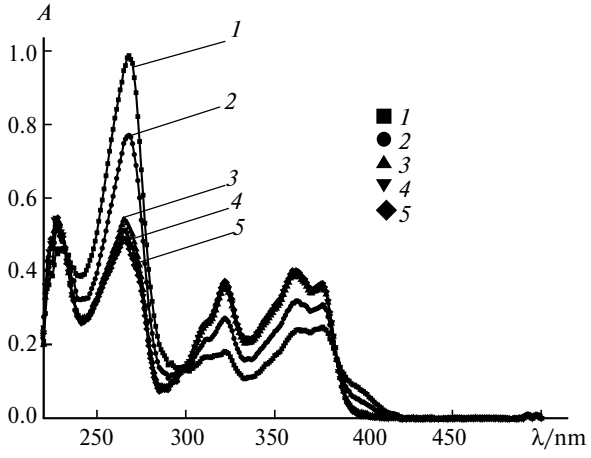
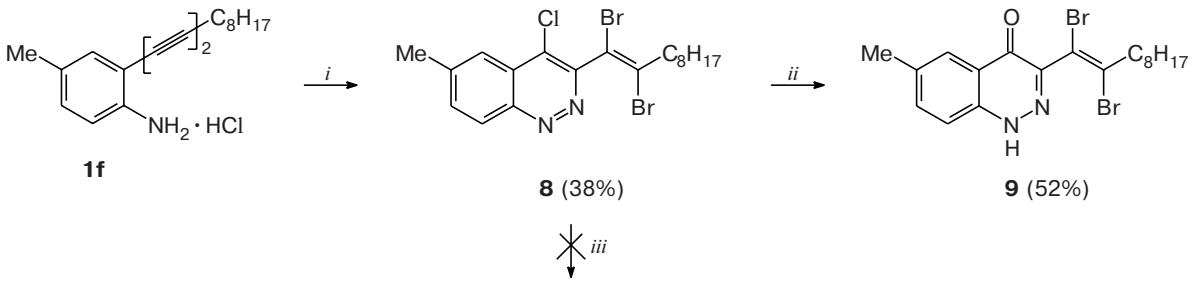


Fig. 2. Spectrophotometric monitoring of the solvolysis of 4-chlorocinnoline **2h** in MeOH, τ/min: 2 (*1*), 4 (*2*), 8 (*3*), 10 (*4*), 15 (*5*).

Scheme 4



i. 1) $NaNO_2$ (solid), HBr; 2) Hexane. *ii*. MeOH, HCl (36%), 50 °C, 24 h. *iii*. MeOH, KOH, H_2O, 50 °C, 24 h.

observed correspond to the formation of 4-methoxycinnoline by solvolysis of 4-chlorocinnoline.

On the basis of data obtained, a conclusion has been drawn that 4-chlorocinnoline is too the product of the cyclization in MeOH saturated with HCl, which undergoes fast solvolysis to 4-methoxycinnoline. Since water is present in the reaction mixture, formed in the course of diazotization, 4-methoxycinnoline hydrolyzes already in the course of the reaction. This hydrolysis is irreversible because of the cyclization of 4-hydroxy-3-alkynylcinnoline into furo[3,2-*c*]cinnoline.

Earlier, it was shown that diazotization of monoacetylenic amines in HBr allows one to considerably increase the yield of 4-bromocinnolines in the Richter reaction in comparison with 4-chloro derivatives.[7] We also carried out a research on the diazotization of *o*-(alka-1,3-diynyl)anilines in the presence of hydrobromic acid.

A mixed solvent Et_2O—hexane—HBr_{conc} in the ratio of 1 : 1 : 6 (Scheme 3) has been used for conducting the reaction. The diazotization reaction of **1c** and subsequent cyclization were carried out at −18 °C and no deamination occurred, but other side processes took place.

A two-fold excess of solid $NaNO_2$ was added in the first diazotization experiment. It was found that in the reaction course, the triple bond of the alkynyl substituent of forming 4-bromocinnoline underwent bromination and 4-bromo-3-(1,2-dibromododec-1-enyl)cinnoline (**6**) was obtained in 43% yield. In the second experiment, the diazotization was carried out with aq. $NaNO_2$ taken in 10% excess. The target 4-bromo-3-(dodec-1-ynyl)cinnoline (**7**) was the major product in this case, the yield was 37%. However, a side bromination of the benzene ring occurred in this experiment and 4,6-dibromo-3-(dodec-1-ynyl)cinnoline (**7a**) was isolated along with bromocinnoline **7**.

Another experiment was also conducted, in which amine hydrochloride **1f** was taken as the starting compound for the diazotization in HBr (Scheme 4). Despite of the excess of bromine anions and their high nucleophilicity, the ring closure took place with participation of chlorine anion present as the intimate ion pair with diazonium cation. 4-Chlorocinnoline **8** was obtained as the only reaction product, in which the triple bond turned out to be brominated.

To confirm a position of the Cl atom in the cinnoline ring, the acid- and base-catalyzed hydrolyses of compound **8** have been undertaken. It turned out that the presence of an acid facilitates the hydrolysis, which results in 4-cinnolinone **9**.

These data make the possibility of participation of external nucleophile in the cyclization step questionable, as well as confirm the possibility of hydrolysis of 4-chlorocinnoline under the reaction conditions.

In conclusion, the Richter reaction of *ortho*-(alka-1,3-diynyl)arenediazonium salts, obtained by diazotization of arylamines, leads to 4-chloro- or bromo-3-ethynylcinnolines. In the absence of strong electron-withdrawing substituents in the benzene ring, 4-chloro-3-ethynylcinnolines can be obtained in moderate yields. The presence of electron-withdrawing substituents in the benzene ring, as well as conducting the reaction in MeOH saturated with HCl facilitate hydrolysis of 3-(alk-1-ynyl)-4-chlorocinnolines in the course of the reaction. The formed 3-(alk-1-ynyl)-4-hydroxycinnolines undergo a spontaneous cyclization giving rise to 2-alkylfuro-[3,2-*c*]cinnolines. In MeOH saturated with HCl, the hydrolysis is preceded by the reaction with the solvent resulting in the formation of 4-methoxycinnolines. The diazotization in hydrobromic acid is accompanied by the side bromination of the triple bond and benzene ring of 3-alkynyl-4-bromocinnolines.

Experimental

Elemental analysis data were obtained on a Hewlett-Packard 185B instrument. IR spectra were recorded on a Specord-IR 75 instrument in the range of 4000—400 cm^{-1} and on a UR-20 instrument for 2% solutions in CCl_4 and for samples in KBr pellets. ^1H NMR (300.13 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Bruker AM-300 spectrometer for solutions in $CDCl_3$, DMSO-d_6, and DMSO-d_6 : CCl_4 in ratios 1 : 4 and 1 : 10. Assignment of signals was made relatively to the residual signals of the solvents: (for the $^1H/^{13}C$ spectra in $CDCl_3$

δ 7.280/77.16, in DMSO-d_6 δ = 2.50/39.52). Mass spectra were recorded on a Agilent 68-90 instrument with ionization energy of 70 eV, electron impact, and an Agilent 5973 detector. UV spectra were recorded on a CC 103 spectrophotometer in the range of 180—500 nm in an 1-cm pathlength cuvette; the range of concentrations 3.6—38 • 10^{-5} mol L^{-1}.

The Richter reaction in the series of alkadiynylamines (general procedure). The diazotization and cyclization were carried out in a flask equipped with magnetic stirrer, thermometer, dropping funnel, and a cooling bath under conditions ***A—E***. When a diazotizing agent was being added, the temperature of the reaction was kept in the range of −5—0 °C. After the diazotization was complete (TLC monitoring), the reaction mixture was stirred under cooling for 20—30 min; then the stirring was continued at room temperature for 8—16 h. After the time was up, the reaction mixture was poured in aqueous soda and extracted with ethyl acetate (3×15 mL). Combined organic layers were washed with water until neutral pH of the reaction medium and died with $MgSO_4$. After the solvent was removed, the products were isolated by column chromatography on silica gel 40—60 μm.

1. Procedures *A* (see Ref. 7) and ***B***. Hydrochloric acid (36% aq., 3 mL) was added to aromatic amine **1** or its hydrochloride (2 mmol) at room temperature. When a free amine was used, the reaction mixture was preliminary stirred at room temperature for 1 h for the complete formation of the salt. Then, $NaNO_2$ (152 mg, 2.2 mmol) in water (1 mL) (procedure ***A***) or freshly distilled BuONO (350 mg, 2.2 mmol) (procedure ***B***) was added dropwise with stirring to the mixture cooled to −10 °C.

2. Procedures *C* and ***D***. Aromatic amine **1** or its hydrochloride (2 mmol) was added to a mixture of 36% aq. HCl (3 mL) with THF (3 mL, procedure ***C***) or diethyl ether (3 mL, procedure ***D***) at room temperature. After the diazotization was complete in the case of procedure ***C***, hexane (3 mL) was added to the reaction mixture.

Procedure *E*. A mixture of amine hydrochloride (2 mmol) and diethyl ether (7 mL) was cooled to −5 °C followed by addition of catalytic amount of H_2SO_4 and dropwise addition of freshly distilled BuONO (227 mg, 2.2 mmol).

Procedure *F*. Methanol (15 mL) was saturated with dry HCl for 1 h. A starting amine hydrochloride **1** (2 mmol) and $NaNO_2$ (152 mg, 2.2 mmol) were added to the solution obtained keeping the temperature in the range of −5—0 °C. After the diazotization was complete, the reaction mixture was stirred at room temperature, then poured in 10% aq. NaOH, extracted with EtOAc (3×15 mL), and dried with $CaCl_2$. Alternatively, a mixture of MeOH with Et_3N (1 : 2) was added dropwise to the reaction mixture cooled on an ice bath until the solution became basic (pH ~8); the solution obtained was concentrated on rotary evaporator *in vacuo* of water-jet aspirator pump, the precipitate of triethylamine hydrochloride was filtered off. The products were isolated by chromatography on silica gel 40—60 μm.

The structures of products of reductive deamination **3** were established by analysis of the NMR spectra, and by TLC analysis with the use of the corresponding 1-arylalka-1,3-diynes, obtained earlier by the reaction of Pd/Cu-catalyzed cross-coupling, as the authentic samples.[10,15]

4-Chloro-3-(oct-1-ynyl)cinnoline (2a). IR (CCl_4), ν/cm^{-1}: 2965, 2925, 2860 (C_{sp^3}—H); 2230 (C≡C). ^{1}H NMR ($CDCl_3$), δ: 0.91 (t, 3 H, Me, *J* = 7.5 Hz); 1.32—1.79 (m, 8 H, 4 CH_2); 2.63 (t, 3 H, C≡CCH_2, *J* = 7.5 Hz); 7.85—7.91 (m, 2 H, C(6)H, C(7)H); 8.16—8.20 (m, 1 H, C(5)H); 8.52—8.57 (m, 1 H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.4 (CH_3); 20.3 (C≡C$\underline{C}H_2$); 22.9, 28.6, 29.0, 31.7 (4 CH_2); 76.5, 101.2 (C≡C); 123.5, 124.6, 130.6, 131.5, 132.8, 136.4, 141.2, 149.2 (C_{Ar}). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 272 $[M]^+$ (2), 257 $[M - CH_3]^+$ (4); 244 $[M - C_2H_4]^+$ (100); 237 $[M - Cl]^+$ (54); 215 $[M - C_4H_9]^+$ (19). Found (%): C, 70.44; H, 6.33; N, 12.86. $C_{16}H_{17}ClN_2$. Calculated (%): C, 70.45; H, 6.28; N, 13.00.

4-Chloro-3-(dec-1-ynyl)cinnoline (2b). IR (CCl_4), ν/cm^{-1}: 2960, 2925, 2850 (C_{sp^3}—H); 2225 (C≡C). ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, 3 H, Me, *J* = 7.5 Hz); 1.32—1.79 (m, 12 H, 6 CH_2); 2.62 (t, 3 H, C≡CCH_2, *J* = 7.5 Hz); 7.86—7.90 (m, 2 H, C(6)H, C(7)H); 8.18—8.22 (m, 1 H, C(5)H); 8.5—8.59 (m, 1 H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 20.3, 23.1, 28.6, 29.4, 29.5, 29.6, 32.2 (7 CH_2); 76.5, 101.2 (C≡C); 123.5, 124.7, 130.7, 131.4, 132.8, 136.4, 141.2, 149.2 (C_{Ar}). Found (%): C, 71.75; H 7.11; N 8.98. $C_{18}H_{21}ClN_2$. Calculated (%): C, 71.73; H, 7.02; N, 9.29.

4-Chloro-3-(dodec-1-ynyl)cinnoline (2c). ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, Me, *J* = 7.5 Hz); 1.19—1.39 (m, 12 H, 6 CH_2); 1.50—1.62 (m, 2 H, C≡C$CH_2CH_2C\underline{H}_2$); 1.68—1.84 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.63 (t, 2 H, C≡C$\underline{C}H_2$, *J* = 7.5 Hz); 7.82—7.91 (m, 2 H, C(6)H, C(7)H); 8.12—8.21 (m, 1 H, C(5)H); 8.51—8.61 (m, 1 H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 20.3 (C≡C$\underline{C}H_2$); 23.1, 28.6, 29.3, 29.5, 29.7, 29.9, 30.0, 32.3 (8 CH_2); 76.5, 101.2 (C≡C); 123.5, 124.6, 130.7, 131.4, 132.9, 136.4, 141.2, 149.2 (C_{Ar}).

6-Bromo-4-chloro-3-(oct-1-ynyl)cinnoline (2d). IR (CCl_4), ν/cm^{-1}: 2950, 2932, 2860 (C_{sp^3}—H); 2240 (C≡C); 1548; 1456; 1416. ^{1}H NMR ($CDCl_3$), δ: 0.93 (t, 3 H, Me, *J* = 7.5 Hz); 1.26—1.58 (m, 8 H, 4 CH_2); 2.64 (t, 2 H, C≡CCH_2, *J* = 7.5 Hz); 7.91 (dd, 1 H, C(7)H, *J* = 7.8 Hz, *J* = 2.4 Hz); 8.35 (d, 1 H, C(5)H, *J* = 2.4 Hz); 8.42 (d, 1 H, C(8)H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 20.3, 22.9, 28.5, 29.0, 31.7 (5 CH_2); 76.4, 102.2 (C≡C); 125.7, 125.8 128.4, 132.3, 134.9, 135.2, 141.7, 147.6 (C_{Ar}). Found (%): C, 54.86; H, 4.83; N, 7.84. $C_{16}H_{16}BrClN_2$. Calculated (%): C, 54.64; H, 4.59; N, 7.97.

6-Bromo-4-chloro-3-(dec-1-ynyl)cinnoline (2e). M.p. 41—43 °C (hexane—diethyl ether, 1 : 2). UV (MeOH saturated with HCl), λ_{max}/nm (ε): 267 (5.9 • 10^4). ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me, *J* = 7.5 Hz); 1.30—1.54 (m, 10 H, 5 CH_2); 1.72—1.77 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.63 (t, 2 H, C≡CCH_2, *J* = 7.5 Hz); 7.91 (d, 1 H, C(7)H, *J* = 7.8 Hz); 8.34 (s, 1 H, C(5)H); 8.41 (d, 1 H, C(8)H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 20.3, 23.1, 28.6, 29.3, 29.5, 29.6, 32.2 (7 CH_2); 76.4, 102.2 (C≡C); 125.7, 125.8 128.4, 132.3, 134.9, 135.2, 141.7, 147.6 (C_{Ar}). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 381 $[M + 2]^+$ (8), 379 $[M]^+$ (17); 344 $[M - Cl]^+$ (98), 342 $[M - Cl]^+$ (100). Found (%): C, 57.04; H, 5.39; N, 7.27. $C_{18}H_{20}BrClN_2$. Calculated (%): C, 56.94; H, 5.31; N, 7.38.

4-Chloro-3-(dec-1-ynyl)-6-methylcinnoline (2f). IR (CCl_4), ν/cm^{-1}: 2970, 2940, 2870 (C_{sp^3}—H); 2250 (C≡C); 1720; 1610; 1480. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me, *J* = 7.5 Hz); 1.30—1.33 (m, 8 H, 4 (CH_2)); 1.54—1.57 (m, 2 H, C≡C$CH_2CH_2C\underline{H}_2$); 1.74 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.62 (t, 2 H, C≡CCH_2, *J* = 7.5 Hz); 2.62 (s, 3 H, C(6)Me); 7.66 (d, 1 H, C(7)H, *J* = 9.2 Hz); 7.89 (s, 1 H, C(5)H); 8.41 (d, 1 H, C(8)H, *J* = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.5 (CH_3); 20.3 (C≡C$\underline{C}H_2$); 22.8 (C(6)$\underline{C}H_3$); 23.1, 28.6, 29.4, 29.5, 29.6, 32.2 (6 CH_2); 76.6, 100.9 (C≡C); 121.9, 124.8, 130.3, 134.0, 135.7, 141.1, 144.1, 148.28 (C_{Ar}). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 316 $[M + 2]^+$ (8), 314 $[M]^+$ (23); 287 $[M + 2 - C_2H_5]^+$ (10), 285 $[M - C_2H_5]^+$ (13); 279 $[M - Cl]^+$ (100).

8-Bromo-4-chloro-3-(dec-1-ynyl)-6-methylcinnoline (2g). M.p. 52—54 °C (hexane—diethyl ether, 1 : 2). IR (CCl_4), ν/cm^{-1}: 2980, 2950, 2875 (C_{sp^3}—H); 2250 (C≡C); 1625; 1485; 1450. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 7.5 Hz); 1.31—1.77 (m, 12 H, 6 CH_2); 2.61 (s, 3 H, C(6)Me); 2.64 (t, 2 H, C≡CCH_2, J = 7.5 Hz); 7.87 (s, 1 H, C(7)H); 7.99 (s, 1 H, C(5)H). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 20.3 (C≡C$\underline{C}H_2$); 20.5 (C(6)$\underline{C}H_3$); 23.1, 28.6, 29.3, 29.5, 29.6, 32.2 (6 CH_2); 76.5, 101.9 (C≡C); 122.0, 126.1, 126.1, 135.3, 137.5, 141.9, 144.4, 144.9 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 396 $[M + 4]^+$ (5), 394 $[M + 2]^+$ (22), 392 $[M]^+$ (17); 359 $[M - Cl]^+$ (100), 357 $[M - Cl]^+$ (100); 317 $[M - Cl - C_3H_6]^+$ (78), 315 $[M - Cl - C_3H_6]^+$ (78). Found (%): C, 58.09; H, 5.73; N, 7.15. $C_{19}H_{22}BrClN_2$. Calculated (%): C, 57.96; H, 5.63; N, 7.11.

Methyl 4-chloro-3-(dec-1-ynyl)cinnoline-6-carboxylate (2h). UV (Et_2O : HCl (36%) 1 : 1), λ_{max}/nm (ε): 271 ($4.2 \cdot 10^4$), 382 ($5.7 \cdot 10^3$), 411 ($2.5 \cdot 10^3$). IR (CCl_4), ν/cm^{-1}: 2970, 2940, 2860 (C_{sp^3}—H); 2250 (C≡C); 1730 (C=O); 1460; 1440; 1430. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 7.5 Hz); 1.34—1.48 (m, 8 H, 4 CH_2); 1.54—1.58 (m, 2 H, C≡C$CH_2CH_2C\underline{H}_2$); 1.74—1.79 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.66 (t, 2 H, C≡CCH_2, J = 7.5 Hz); 4.06 (s, 3 H, OMe); 8.43 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.63 (d, 1 H, C(8)H, J = 9.2 Hz); 8.91 (d, 1 H, C(5)H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.2 (CH_3); 20.0, 22.9, 28.3, 29.1, 29.2, 29.3, 32.0 (7 CH_2); 53.1 (OMe); 76.0, 101.9 (C≡C); 123.9, 126.4, 130.5, 130.9, 133.4, 137.1, 141.8, 149.3, (C_{Ar}); 165.5 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 360 $[M + 2]^+$ (5), 358 $[M]^+$ (16); 323 $[M - Cl]^+$ (100); 295 $[M - Cl - CH_3 + H]^+$ (20); 281 $[M - Cl - C_2H_4]^+$ (88); 267 $[M - Cl - C_3H_6]^+$ (59). Found (%): C, 66.97; H, 6.41; N, 7.60. $C_{20}H_{23}ClN_2O_2$. Calculated (%): C, 66.93; H, 6.46; N, 7.81.

4-Chloro-6-nitro-3-(oct-1-ynyl)cinnoline (2i). IR (CCl_4), ν/cm^{-1}: 2975, 2948, 2870 (C_{sp^3}—H); 2250 (C≡C); 1740; 1630; 1570; 1530; 1460; 1440. ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, 3 H, Me, J = 7.5 Hz); 1.27—1.78 (m, 8 H, 4 CH_2); 2.68 (t, 2 H, C≡CCH_2, J = 7.5 Hz); 8.60 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.79 (d, 1 H, C(8)H, J = 9.2 Hz); 9.12 (d, 1 H, C(5)H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.5 (CH_3); 20.4, 23.1, 28.5, 29.0, 31.7 (5 CH_2); 76.0, 103.8 (C≡C); 120.4, 123.8, 124.1, 132.8, 137.0, 142.22, 148.4, 148.9 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 319 $[M + 2]^+$ (1), 317 $[M]^+$ (8), 282 $[M - Cl]^+$ (100), 254 $[M - Cl - C_2H_4]^+$ (62), 236 $[M - Cl - NO_2]^+$ (23), 165 $[M - Cl - NO_2 - C_5H_{11}]^+$ (21), 137 $[M - Cl - NO_2 - C_7H_{13}]^+$ (39).

2-Decylfuro[3,2-*c*]cinnoline (4c). M.p. 27—29 °C (CH_2Cl_2). IR (CCl_4), ν/cm^{-1}: 2970, 2940, 2880 (C_{sp^3}—H); 1750; 1620; 1600; 1525; 1490. ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, Me, J = 7.5 Hz); 1.21—1.99 (m, 14 H, 7 CH_2); 1.84 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.93 (t, 2 H, C≡C$C\underline{H}_2$, J = 7.5 Hz); 7.08 (s, 1 H, C(3)H); 7.76—7.81 (m, 2 H, C(7)H, C(8)H); 8.19—8.24 (m, 1 H, C(9)H); 8.60—8.63 (m, 1 H, C(6)H). ^{13}C NMR ($CDCl_3$), δ: 14.50 (Me); 23.07, 27.93, 29.07, 29.53, 29.69, 29.90, 29.95, 30.05, 32.28 (9 CH_2); 103.08, 114.42, 119.48, 128.81, 130.57, 131.38, 143.38, 147.25, 150.74, 163.38 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 310 $[M]^+$ (68); 239 $[M - C_5H_{11}]^+$ (38); 197 $[M - C_8H_{17}]^+$ (100); 183 $[M - C_9H_{21}]^+$ (54). Found (%): C, 77.41; H, 8.35; N, 8.79. $C_{20}H_{26}N_2O$. Calculated (%): C, 77.38; H, 8.44; N, 9.02.

8-Bromo-2-octylfuro[3,2-*c*]cinnoline (4e). UV (MeOH saturated with HCl), λ_{max}/nm (ε): 259 ($4.0 \cdot 10^4$). IR (CCl_4), ν/cm^{-1}: 2990, 2940, 2860 (C_{sp^3}—H); 1710; 1625; 1600; 1580. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me, J = 7.5 Hz); 1.30—1.46 (m, 10 H, 5 CH_2); 1.80—1.90 (m, 2 H, C(Ar)$CH_2C\underline{H}_2$); 2.95 (t, 2 H, C(Ar)CH_2, J = 7.5 Hz); 7.10 (s, 1 H, C(3)H); 7.84 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.40 (d, 1 H, C(9)H, J = 2.4 Hz); 8.49 (d, 1 H, C(6)H, J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.5 (Me); 23.0, 27.9, 29.1, 29.5, 29.6, 29.6, 32.2 (7 CH_2); 103.2, 115.3, 121.9, 126.3, 132.4, 132.6, 141.9, 146.6, 147.7, 164.1 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 362 $[M + 2]^+$ (55), 360 $[M]^+$ (56); 333 $[M + 2 - C_2H_5]^+$ (13), 331 $[M - C_2H_5]^+$ (13); 305 $[M + 2 - C_4H_9]^+$ (13), 303 $[M - C_4H_9]^+$ (13), 291 $[M + 2 - C_5H_{11}]^+$ (11), 289 $[M - C_5H_{11}]^+$ (11); 277 $[M + 2\text{-}C_6H_{13}]^+$ (70), 275 $[M - C_6H_{13}]^+$ (72); 263 $[M + 2 - C_7H_{15}]^+$ (98), 261 $[M - C_7H_{15}]^+$ (100). Found (%): C, 59.81; H, 5.71; N, 7.60. $C_{18}H_{21}BrN_2O$. Calculated (%): C, 59.84; H, 5.86; N, 7.75.

Methyl 2-octylfuro[3,2-*c*]cinnoline-8-carboxylate (4h). UV (Et_2O : HCl (36%) 1 : 1), λ_{max}/nm (ε): 256 ($3.6 \cdot 10^4$), 325 ($3.5 \cdot 10^3$), 389 ($3.5 \cdot 10^3$). IR (CCl_4), ν/cm^{-1}: 2970, 2940, 2860 (C_{sp^3}—H); 1730 (C=O); 1600; 1450; 1410. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 7.5 Hz); 1.31—1.48 (m, 10 H, 5 CH_2); 1.86—1.91 (m, 2 H, C(Ar)$CH_2C\underline{H}_2$); 2.98 (t, 2 H, C(Ar)CH_2, J = 7.5 Hz); 4.07 (s, 3 H, OMe); 7.15 (s, 1 H, C(3)H); 8.36 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.70 (d, 1 H, C(6)H, J = 9.2 Hz); 9.01 (d, 1 H, C(9)H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.2 (CH_3); 22.7, 27.6, 28.1, 29.2, 2·29.3, 31.9 (7 CH_2); 52.9 (OMe); 102.9, 113.3, 122.8, 127.9, 130.7, 131.9, 143.4, 147.8, 148.2, 163.9 (C_{Ar}); 165.9 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 340 $[M]^+$ (22); 269 $[M - C_5H_{11}]^+$ (15); 241 $[M - C_7H_{15}]^+$ (100). Found (%): C, 70.35; H, 7.09; N, 7.94. $C_{20}H_{24}N_2O_3$. Calculated (%): C, 70.56; H, 7.11; N, 8.23.

2-Hexyl-8-nitrofuro[3,2-*c*]cinnoline (4i). IR (CCl_4), ν/cm^{-1}: 2970, 2940, 2880 (C_{sp^3}—H); 1750; 1620; 1600; 1525. ^{1}H NMR ($CDCl_3$), δ: 0,93 (t, 3 H, CH_3, J = 7.5 Hz); 1.36—1.52 (m, 6 H, 3 CH_2); 1.85—2.06 (m, 2 H, C(Ar)$CH_2C\underline{H}_2$); 3.02 (t, 2 H, C(Ar)CH_2, J =7.5 Hz); 7.22 (s, 1 H, C(3)H); 8.53 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.84 (d, 1 H, C(6)H, J = 9.2 Hz); 9.21 (d, 1 H, C(9)H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.4 (Me); 22.9, 27.8, 29.2, 29.2, 31.8 (5 CH_2); 103.4, 113.8, 117.5, 122.2, 133.1, 143.8, 147.8, 148.4, 148.6, 165.4 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 299 $[M]^+$ (100); 270 $[M - C_2H_5]^+$ (25); 228 $[M - C_5H_{11}]^+$ (91); 182 $[M - C_5H_{11} - NO_2]^+$ (84). Found (%): C, 64.08; H, 5.78; N, 14.10. $C_{16}H_{17}N_3O_3$. Calculated (%): C, 64.20; H, 5.72; N, 14.04.

6-Bromo-3-(dec-1-ynyl)-4-methoxycinnoline (5e). UV (MeOH saturated with HCl), λ_{max}/nm (ε): 265 ($4.5 \cdot 10^4$). IR (CCl_4), ν/cm^{-1}: 2950, 2900, 2820 (C_{sp^3}—H); 2200 (C≡C); 1725; 1650; 1600; 1550. ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 7.5 Hz); 1.30—1.33 (m, 8 H, 4 CH_2); 1.49—1.54 (m, 2 H, C≡C$CH_2CH_2C\underline{H}_2$); 1.69—1.75 (m, 2 H, C≡C$CH_2C\underline{H}_2$); 2.61 (t, 2 H, C≡CCH_2, J = 7.5 Hz); 4.46 (s, 3 H, OMe); 7.85 (dd, 1 H, C(7)H, J = 9.2 Hz, J = 2.4 Hz); 8.32—8.35 (m, 2 H, C(3)H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.2 (Me); 20.1, 22.8, 28.3, 29.2, 29.26, 29.32, 32.0 (7 CH_2); 61.0 (OMe); 76.3, 100.2 (C≡C); 121.4, 123.6, 125.6, 131.1, 134.4, 137.7, 148.2, 153.5 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 376 $[M + 2]^+$ (8), 374 $[M]^+$ (9); 345 $[M + 2 - C_2H_5]^+$ (52), 343 $[M - C_2H_5]^+$ (46); 319 $[M + 2 - C_4H_9]^+$ (36), 317 $[M - C_4H_9]^+$ (36); 291 $[M + 2 - C_6H_{13}]^+$ (98), 289 $[M - C_6H_{13}]^+$ (100); 277 $[M + 2 - C_7H_{15}]^+$ (54), 275 $[M - C_7H_{15}]^+$ (55), 165 $[M - Br - OMe - C_7H_{15}]^+$ (23). Found (%): C, 60.85; H, 6.11; N, 7.36. $C_{19}H_{23}BrN_2O$. Calculated (%): C, 60.81; H, 6.18; N, 7.46.

4-Bromo-3-(1,2-dibromododec-1-enyl)cinnoline (6) was obtained from **1c** (1.4 g, 5 mmol) under conditions of procedure

D (−15÷−18 °C) in conc. HBr with the use of crystalline $NaNO_2$ (690 mg, 10 mmol). The yield of the product was 43% (1.15 g, 2.2 mmol). M.p. 65—67 °C (from EtOAc). ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, Me, J = 7.5 Hz); 1.26—1.45 (m, 14 H, 7 CH_2); 1.80 (m, 2 H, C≡CCH$_2$C$\underline{H}_2$); 2.98 (dt, 2 H, C≡C$\underline{C}$H$_2$, J = 7.5 Hz, J = 7.5 Hz); 7.86—8.02 (m, 2 H, C(6)H, C(7)H); 8.22—8.24 (m, 1 H, C(5)H); 8.59—8.62 (m, 1 H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.54 (Me); 23.11; 27.75, 29.01, 29.75, 29.82, 29.97, 30.02, 32.33 (8 CH_2); 40.26 (C≡C$\underline{C}$H$_2$); 112.23, 126.69, 126.99, 127.36, 130.29, 130.72, 132.18, 133.14, 150.20, 155.39. MS (EI, 70 eV), m/z (I_{rel} (%)): 536 $[M + 6]^+$ (3); 534 $[M + 4]^+$ (7); 532 $[M+2]^+$ (7); 530 $[M]^+$ (3); $[M - Br]^+$ 455 (49), 453 (100), 451 (49); 261 $[M + 2 - C_8H_{17}]^+$ (15); 259 $[M - C_8H_{17}]^+$ (15). Found (%): C, 45.05; H, 4.62; N, 4.95. $C_{20}H_{25}Br_3N_2$. Calculated (%): C, 45.06; H, 4.73; N, 5.25.

4-Bromo-3-(dodec-1-ynyl)cinnoline (7) was obtained from **1c** under conditions of procedure ***D*** (15 h, −18 °C) in conc. HBr in 37% yield (690 mg, 1.85 mmol), 4,6-dibromo-3-(dodec-1-ynyl)cinnoline was isolated along with the major product in 14% yield (316 mg, 0.7 mmol). M.p. 74—76 °C (from EtOAc). ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me, J = 7.5 Hz); 1.21—1.42 (m, 12 H, 6 CH_2); 1.49—1.66 (m, 2 H, C≡CCH$_2$CH$_2$C$\underline{H}_2$); 1.76 (m, 2 H, C≡CCH$_2$C$\underline{H}_2$); 2.63 (t, 2 H, C≡C$\underline{C}$H$_2$, J = 7.5 Hz); 7.79—7.95 (m, 2 H, C(6)H, C(7)H); 8.09—8.19 (m, 1 H, C(5)H); 8.51—8.60 (m, 1 H, C(8)H). ^{13}C NMR ($CDCl_3$), δ: 14.50 (Me); 20.25 (C≡C$\underline{C}$H$_2$); 23.08, 28.59, 29.36, 29.53, 29.71, 29.94, 29.99, 32.30 (8 CH_2); 78.41, 100.43 (C≡C); 126.41, 127.59, 130.72, 131.43, 133.07, 134.38, 143.47, 148.93 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 374 $[M + 2]^+$ (16); 372 $[M]^+$ (16); 293 $[M - Br]^+$ (100); 261 $[M + 2 - C_8H_{17}]^+$ (25); 259 $[M - C_8H_{17}]^+$ (25); 152 $[M - Br - C_{10}H_{21}]^+$ (23). Found (%): C, 64.56; H, 6.81; N, 6.80. $C_{20}H_{25}BrN_2$. Calculated (%): C, 64.34; H, 6.75; N, 7.50.

4,6-Dibromo-3-(dodec-1-ynyl)cinnoline (7a). ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, Me, J = 7.5 Hz); 1.21—1.43 (m, 12 H, 6 CH_2); 1.48—1.63 (m, 2 H, C≡CCH$_2$CH$_2$C$\underline{H}_2$); 1.74 (m, 2 H, C≡CCH$_2$C$\underline{H}_2$); 2.63 (t, 2 H, C≡C$\underline{C}$H$_2$, J = 7.5 Hz); 7.90 (d, 1 H, C(7)H, J = 9.2 Hz); 8.29 (s, 1 H, C(5)H); 8.41 (d, 1 H, C(8)H, J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.50 (Me); 20.27 (C≡C$\underline{C}$H$_2$); 23.07, 28.54, 29.36, 29.52, 29.71, 29.93, 29.98, 32.29 (8 CH_2); 78.25, 101.41 (C≡C); 125.77, 127.44, 127.76, 128.59, 132.26, 135.16, 144.00, 147.29 (C_{Ar}). MS (EI, 70 eV), m/z (I_{rel} (%)): 454 $[M + 4]^+$ (7); 452 $[M + 2]^+$ (15); 450 $[M]^+$ (7); 373 $[M + 2 - Br]^+$ (64); 371 $[M - Br]^+$ (64); 317 $[M + 2 - Br - C_4H_8]^+$ (18); 315 $[M - Br - C_4H_8]^+$ (18); 303 $[M + 2 - Br - C_5H_{10}]^+$ (46); 301 $[M - Br - C_5H_{10}]^+$ (46); 289 $[M + 2 - Br - C_6H_{12}]^+$ (25); 287 $[M - Br - C_6H_{12}]^+$ (29). Found (%): C, 53.31; H, 5.48; N, 5.94. $C_{20}H_{24}Br_2N_2$. Calculated (%): C, 53.12; H, 5.35; N, 6.19.

3-(1,2-Dibromodec-1-enyl)-4-chloro-6-methylcinnoline (8). Hydrochloride **1f** (560 mg, 1.8 mmol) was diazotized with a solution of $NaNO_2$ (137 mg, 2 mmol) in H_2O (1 mL) and conc. HBr (10 mL) at −5 – 0 °C. After the diazotization was complete (TLC monitoring), hexane (5 mL) was added to the reaction mixture and the stirring was continued at room temperature for 16 h. The reaction mixture was then treated in accordance with the general procedure. The yield was 38% (333 mg, 0.7 mmol). Yellow oil. IR (CCl_4), ν/cm^{-1}: 2960, 2940, 2870 (C_{sp^3}—H); 1640; 1550; 1480. ^{1}H NMR ($CDCl_3$), δ: 0.91 (t, 3 H, Me, J =7 Hz); 1.32—1.51 (m, 10 H, 5 CH_2); 1.74—1.84 (m, 2 H, BrC=CBr—CH$_2$C$\underline{H}_2$); 2.65 (s, 1 H, C(Ar)Me); 2.83—2.92 (m, 1 H, =CBr—CH$_2$); 3.02—3.11 (m, 1 H, =CBr—CH$_2$); 7.74 (d, 1 H, C(7)H, J = 9.2 Hz); 8.01 (s, 1 H, C(5)H); 8.49 (d, 1 H, C(8)H, J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.6 (CH_3); 22.8 (C(Ar)Me); 23.1, 27.3, 29.0, 29.6, 29.8, 32.3, 40.3 (7 CH_2); 110.7, 122.4, 125.3, 130.3, 130.4, 133.1, 134.6, 144.2, 149.6, 153.3. MS (EI, 70 eV), m/z (I_{rel} (%)): 476 $[M + 4]^+$ (3), 474 $[M + 2]^+$ (5), 472 $[M]^+$ (2); $[M - Cl]^+$ 441 (4.5), 439 (9), 437 (4.5); $[M - Cl - Et - Me]^+$ 397 (28), 395 (100), 393 (74); 165 $[M - Cl - 2\,Br - C_7H_{15} - Me]^+$ (11). Found (%): C, 47.62; H, 4.91; N, 5.74. $C_{19}H_{23}Br_2ClN_2$. Calculated (%): C, 48.08; H, 4.88; N, 5.90.

3-(1,2-Dibromodec-1-enyl)-6-methyl-(1*H*)-cinnolin-4-one (9) was obtained by heating of a solution of 4-chlorocinnoline (**18**) (230 mg, 0.48 mmol) in a mixture of MeOH (5 mL) and conc. HCl (3 mL). The reaction was carried out for 1 day at 50 °C. After the reaction was complete (TLC monitoring), the solvent was partially removed *in vacuo* of water-jet aspirator pump, the precipitate of the product was filtered off and purified by recrystallization from MeOH. The yield of the product was 52% (114 mg, 0.25 mmol). IR (CCl_4), ν/cm^{-1}: 3178 (NH); 2980, 2922, 2850 (C_{sp^3}—H); 1568 (C=O); 1488; 1338. ^{1}H NMR (DMSO-d_6), δ: 0.87 (t, 3 H, Me, J = 7.5 Hz); 1.14—1.62 (m, 12 H, 6 CH_2); 2.44 (s, 3 H, C(Ar)Me); 2.80 (t, 2 H, C=C$\underline{C}$H$_2$, J = 7.5 Hz); 7.59 (d, 1 H, C(8)H, J = 8.3 Hz); 7.68 (d, 1 H, C(7)H, J = 8.3 Hz); 7.88 (s, 1 H, C(5)H); 13.74 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 14.0 (Me); 20.9 (C(Ar)Me); 22.1, 26.9, 27.7, 28.6, 28.7, 29.0, 31.2 (7 CH_2); 110.8, 116.9, 123.1, 123.8, 127.1, 135.5, 135.7, 139.2, 147.1; 166.2 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 377 $[M - {}^{79}Br]^+$ (100), 375 $[M - {}^{81}Br]^+$ (98); 211 $[M - 2Br - C_6H_{13}]^+$ (17); 197 $[M - 2Br - C_7H_{15}]^+$ (19). Found (%): C, 49.84; H, 5.86; N, 5.72. $C_{19}H_{24}Br_2N_2O$. Calculated (%): C, 50.02; H, 5.30; N, 6.14.

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