The reaction of acid fluoride **2** and urea occurs only in the presence of concentrated sulfuric acid.

The transformation of urea **3** into uracil **1** depends on the temperature, pressure, duration of the reaction, compositions of the condensed and gas phases, and the material and design of the reactor. The main side processes (saponification with decarboxylation of trifluoromethyl groups before and after the cyclization of compound **3**) could be prevented by performing the reaction under pressure in a polytetrafluoroethylene vessel in an atmosphere of CO_2.

Reaction of compound 2 with urea and H_2SO_4. Acid fluoride **2** (2.6 g, 0.011 mol) and urea (0.67 g, 0.011 mol) were placed in a quartz flask. 96% H_2SO_4 (1.13 g, 0.011 mol) was added dropwise with ice-water cooling and stirring. Thirty min later, cold water (20 mL) and a solution of $NaHCO_3$ were added to pH 5. The target product was extracted with ether (10×10 mL), and the extract was dried with Na_2SO_4. After evaporation of the ether, compound **1** (1.20 g, 60%) was obtained.

Cyclization of compound 3. A polytetrafluoroethylene tube containing a solution of urea **3** (2.22 g, 0.01 mol) and H_2O (0.18 g, 0.01 mol) in 1,4-dioxane (8 mL) was placed in a steel autoclave with $NaHCO_3$ (5 g). The autoclave was heated at 130 °C for 30 min. The solution was cooled to −20 °C, placed in a quartz flask, and concentrated to half its volume at 13 Torr. Hexane (4 mL) was added. The residue was filtered off and dried to obtain uracil **1** (0.83 g, 46%).

In both cases, the product **1** obtained had m.p. 240–243 °C (decomp.) (*cf.* Ref. 2: 245–246 °C (decomp.)). ^1H NMR (acetone-d_6), δ: 8.10 (m, 1 H, HC); 10.55 (br.s, 1 H, NH); 10.71 (br.s, 1 H, NH). ^{19}F NMR (acetone-d_6, CF_3COOH as the external standard), δ: 14.93 (d, 3 F, CF_3, $^4J_{F,H}$ = 1.08 Hz). The ^{13}C NMR spectrum (DMSO-d_6) corresponds completely to the published data.[10] MS (EI, 70 eV), *m/z* (I_{rel} (%)): 181 $[M+1]^+$ (8), 180 $[M]^+$ (100), 165 $[M-HN]^+$ (3), 161 $[M-F]^+$ (3), 137 $[M-HNCO]^+$ (62), 118 $[M-HNCO-F]^+$ (10), 110 $[M-CF_3-H]^+$ (36), 109 $[M-HNCO-CO]^+$ (15).

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Cross-coupling of 4-chloro- and 4-bromocinnolines with alk-1-ynes

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The behavior 4-chloro- and 4-bromocinnoline derivatives, prepared recently by cyclization of *ortho*-ethynylphenyldiazonium salts,[1,2] in the acetylenic condensation has not been studied.

We found that condensation of phenylacetylene with 4-chloro- (**1a**) and 4-bromo-3-phenylcinnoline (**2a**) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N is accompanied by the addition of phenylacetylene to the N=N bond and results in the formation of a compound of a new type, 3-phenyl-1,4-di(phenylethynyl)-1,2-dihydrocinnoline (**3**) instead of the expected 3-phenyl-4-phenylethynylcinnoline (**4a**). In the case of 4-chloro-

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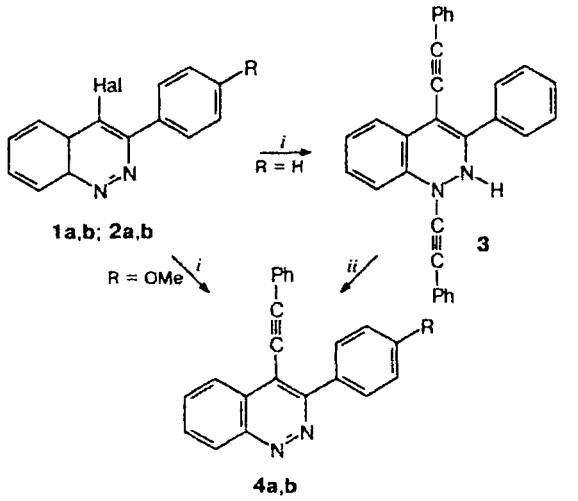
(**2a**) and 4-bromo-3-(4-methoxyphenyl)cinnoline (**2b**), only phenylethynylcinnoline (**4b**) is produced.



Reagents and conditions: *i.* HC≡CPh, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 90 °C, 3—6 h; *ii.* NaOH, MeOH, 20 °C, 1.5 h.

The resulting adduct **3** is converted into phenylethynylcinnoline **4a** on treatment with a methanolic solution of NaOH. Cinnoline **4a** does not react with phenylacetylene under the conditions of the Pd/Cu-catalyzed cross-coupling reaction.

The structure of **3** can be derived from the data of elemental analysis, and the IR, ^1H NMR, and mass spectra. The signal for the proton in position 8 of the ring in the spectra of 1,2-dihydrocinnolines occurs in the 7.07—7.29 ppm region.[3] In this particular case, the signal corresponding to this proton is shifted downfield due to the electron-withdrawing and anisotropic influence of the C≡C bond in position 1 of the ring.

3-Phenyl-1,4-di(phenylethynyl)-1,2-dihydrocinnoline (3). A mixture of **2a** (2.85 g, 0.01 mol), phenylacetylene (2.05 g, 0.02 mol), $Pd(PPh_3)_2Cl_2$ (40 mg), and CuI (20 mg) were heated for 3 h in 25 mL of Et_3N at 80—90 °C in a flow of Ar. After cooling, the reaction mixture was diluted with 30 mL of $CHCl_3$ and filtered through a layer of Al_2O_3 (20×50 mm), and the filtrate was concentrated to dryness *in vacuo*. The residue was triturated in hexane, filtered off, washed on a filter with a concentrated aqueous solution of Na_2CO_3 and water, and dried. Chromatography on silica gel in $CHCl_3$ afforded 2.95 g (72.3%) of compound **3**, m.p. 182—183 °C (hexane—benzene). Found (%): C, 88.20; H, 5.05; N, 6.75. $C_{30}H_{20}N_2$. Calculated (%): C, 88.21; H, 4.93; N, 6.86. IR, $CHCl_3$, ν/cm^{-1}: 2200 (C≡C); 2220 (C≡C); 3400 (N—H). ^1H NMR ($CDCl_3$), δ: 6.92 (dd, 2 H, H(2′), H(6′), J = 8 and 2 Hz); 7.18—7.28 (m, 3 H, H arom.); 7.42—7.51 (m, 6 H, H arom.); 7.78 (br.s, 1 H, NH); 7.82—8.00 (m, 6 H, H arom.); 8.28 (dd, 1 H, H(5), J = 9 and 2 Hz); 8.58 (dd, 1 H, H(8), J = 9 and 2). MS (EI, 70 eV), m/z (I_{rel}(%)): 408 $[M]^+$ (100), 409 $[M+1]^+$ (33), 410 $[M+2]^+$ (8.3).

A similar procedure starting from 4-chlorocinnoline **1a** gave **3** in 65.2% yield.

3-Phenyl-4-phenylethynylcinnoline (4a). A mixture of **3** (4.08 g, 0.01 mol) and 1.0 g of NaOH in 20 mL of MeOH was stirred at 20 °C for 1.5 h, diluted with 50 mL of water, and extracted with $CHCl_3$. The extract was dried with $MgSO_4$ and filtered through a thin layer of Al_2O_3; the product was eluted with $CHCl_3$, and the solvent was evaporated *in vacuo*. Preparative TLC (Al_2O_3; $CHCl_3$ as the eluent) and subsequent recrystallization from a benzene—hexane (1 : 5) mixture gave 2.64 g (86.3%) of compound **4a**, m.p. 121—122 °C. Found (%): C, 86.47; H, 4.89; N, 8.64. $C_{22}H_{14}N_2$. Calculated (%): C, 86.25; H, 4.61; N, 9.14. IR ($CHCl_3$), ν/cm^{-1}: 2200 (C≡C). ^1H NMR ($CDCl_3$), δ: 7.42 (t, 2 H, H(3′), H(5′), J = 8 Hz); 7.52—7.64 (m, 5 H, H arom.); 7.81—7.90 (m, 3 H, H arom.); 8.26 (d, 2 H, H(2″), H(6″), J = 9); 8.43 (dd, 1 H, H(5), J = 9 and 2); 8.61 (dd, 1 H, H(8), J = 9 and 2). MS (EI, 70 eV), m/z (I_{rel}(%)): 306 $[M]^+$ (100), 307 $[M+1]^+$ (25), 308 $[M+2]^+$ (3.0).

3-(4-Methoxyphenyl)-4-phenylethynylcinnoline (4b). Compound **2b** (3.15 g, 0.01 mol) was condensed with phenylacetylene (2.05 g, 0.02 mol) under similar conditions to give 1.73 g (51.4%) of **4b**. At a 1 : 1 ratio of the reagents, the yield of **4b** amounted to 72.9%, m.p. 134—135 °C (from benzene). Found (%): C, 82.61; H, 4.86; N, 8.12. $C_{23}H_{16}N_2O$. Calculated (%): C, 82.12; H, 4.79; N, 8.33. IR, ($CHCl_3$), ν/cm^{-1}: 2225 (C≡C). ^1H NMR ($CDCl_3$), δ*: 2.52 (s, 3 H, OCH_3); 7.32 (d, 2 H, H(3′), H(5′), J = 8 Hz); 7.62—7.90 (m, 7 H, H arom.); 8.26 (d, 2 H, H(2″), H(6″), J = 9 Hz); 8.38 (dd, 1 H, H(5), J = 9 Hz and 2); 8.60 (dd, 1 H, H(8), J = 9 and 2 Hz).

A similar procedure starting from 4-chlorocinnoline **1b** gave **4b** in 41.0% yield. At a 1 : 1 ratio of the reagents, the yield of **4b** was 55.8%.

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* The prime refers to a phenyl group, and the double primes refers to a phenylethynyl group.

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