

β -Oxoacids Esters in the Synthesis of Benzo[f]quinoline Derivatives

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Abstract—Condensation of ethyl acetoacetate and ethyl 3-oxo-3-(2-furyl-, 2-quinolyl-, 3-pyridyl)propanoates with azomethines of 2-naphthylamine series led to the formation of ethyl (3-arylbenzo[f]quinol-1-yl)acetates and of esters of the corresponding 3-aryl-1-heteryl-2-benzo[f]quinolylcarboxylic acids. The intermediate reaction products were isolated: ethyl 5-(2-naphthylamino)-3-oxo-5-phenylpentanoate, 2-[(aryl)(2-naphthylamino)methyl]-3-heteryl-3-oxopropanoates, dihydro and tetrahydro derivatives of benzoquinolylacetic and benzoquinolinecarboxylic acids.

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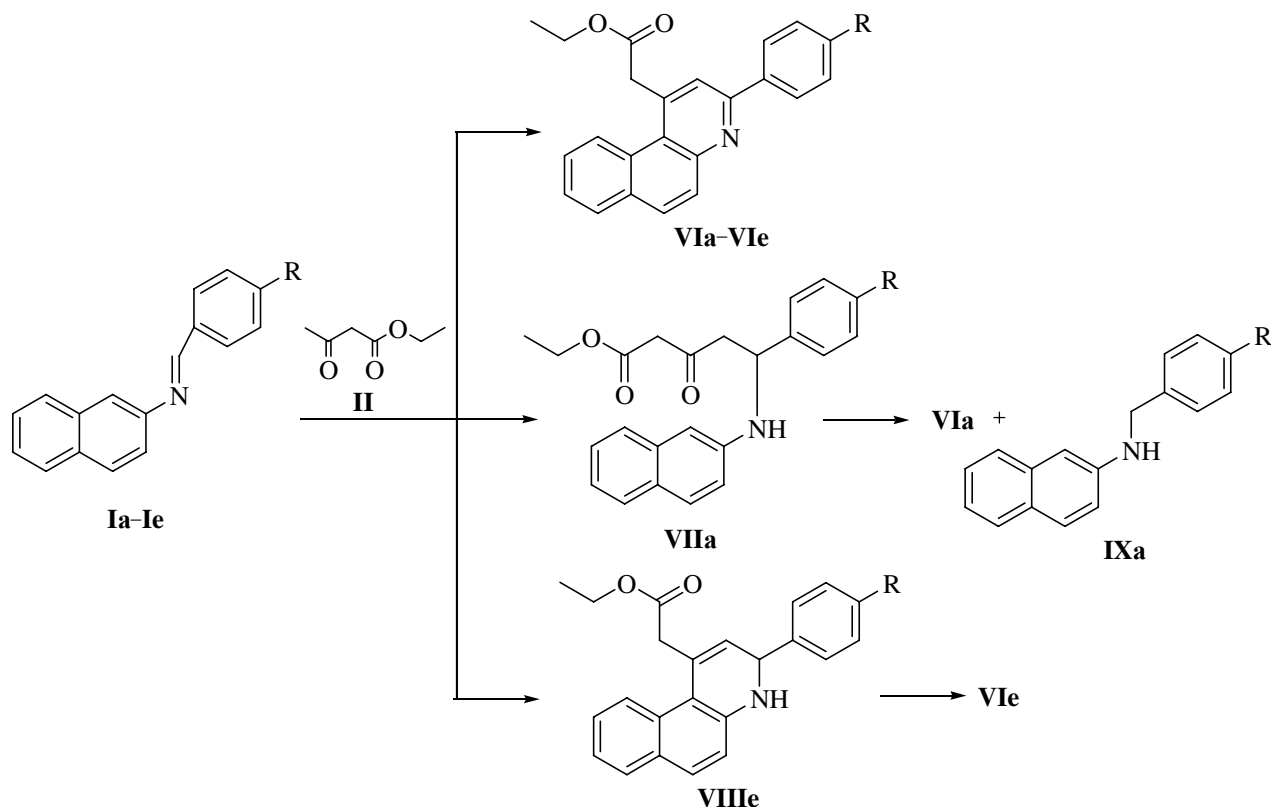
Reactions of ethyl acetoacetate and of other β -oxoacids and β -dicarboxylic acids esters with primary aromatic amines known under the names of Conrad–Limpach and Knorr reactions are extensively applied to the synthesis of fused nitrogen-containing heterocycles with oxygen-including moieties [1–4].

Aiming at the synthesis of previously unknown heterocyclic compounds belonging to azaphenanthrene series we investigated a condensation of 2-naphthylamine with ethyl β -oxocarboxylates adding the third component, aromatic aldehyde. The opportunity of substituents variation in the benzene ring of the aldehyde molecule as well as the use of β -ketoesters of various structures is promising for the synthesis of substituted carboxy derivatives of benzo[f]quinoline possessing high potential of biological action [5–7]. Note that introduction of aldehyde into the condensation with amine and oxoester reduced the selectivity and hampered the isolation of individual target products. Alongside the amine reaction with β -ketoester involving the carbonyl or alkoxy carbonyl groups of the ketoester occurs the amine reaction with aldehyde and the aldehyde condensation with the oxoester with participation of the CH-acidic function of the latter. As a result various side, intermediate, and final reaction products form simultaneously. The selectivity of the process was improved by preliminary condensation of 2-naphthylamine with arylaldehydes followed by reaction of

azomethines obtained **Ia–Ie** with ethyl acetoacetate (**II**) and ethyl 3-oxo-3-(2-furyl-, 2-quinolyl-, 3-pyridyl)propanoates (**III–V**).

The condensation of azomethines **Ia–Ie** with ethyl acetoacetate (**II**) was carried out by boiling the reagents mixture in aliphatic alcohol (EtOH, *i*-PrOH) in the presence of catalytic quantities of concn. HCl that activated both the molecules of azomethine and the β -dicarbonyl compound [1]. The process resulted in a selective formation in 30–56% yield of ethyl (3-arylbenzo[f]quinol-1-yl)acetates **Vla–Vle**.

Ester **II** in reactions with Schiff's bases with a polarized C=N bond like in reaction with benzaldehyde behaves as a CH-acid; therewith both methyl and methylene groups of ketoester **II** possess CH-acid qualities. Although the methylene group protons are more labile, the first reaction stage, the addition of ester **II** to the C=N bond in azomethine, involves the sterically less hindered methyl resulting in formation of intermediate products, aminoketoesters of 5-arylpentanoic acids. Subsequently an intramolecular cyclocondensation of aminoketoesters occurs at the α -position of the naphthalene ring leading to 3,4-dihydrobenzo[f]quinolylacetic acid esters that undergo dehydrogenation or aromatization into benzo[f]quinolylacetic acid esters **Vla–Vle**. The first stage of this process pathway was confirmed by formation of ethyl 5-(2-naphthylamino)-3-oxo-5-phenylpentanoate (**VIIa**) at boiling benzyldiene-2-



naphthylamine (**Ia**) with ester **II** in ethanol without catalyst (concn. HCl). The second intermediate, ethyl [3-(*p*-methoxyphenyl)-3,4-dihydrobenzo[*f*]quinol-1-yl]-acetate (**VIIIe**) we succeeded to obtain from *p*-methoxyphenylmethylene-2-naphthylamine (**Ie**) by adding HCl to ethanol solution of azomethine **Ie** and ester **II** heated to 70°C.

Aminoester **VIIa** and dihydro derivative **VIIIe** at boiling in ethanol in the presence of concn. HCl were converted into the corresponding ethyl benzo[*f*]quinolylacetates **VIa** and **VIe**.

The cyclization of aminoketoester **VIIa** alongside the cyclic compound **VIa** led to the formation of benzyl-2-naphthylamine (**IXa**) whose appearance was caused likely by partial decomposition of compound **VIIa** to initial ketoester **II** and azomethine, and the latter was reduced by hydrogen liberated in dehydrocyclization of amine **VIIa**. The cyclization of ester **VIIa** in the presence of an oxidant (nitrobenzene) prevented the formation of amine **IXa**, but the yield of benzo[*f*]quinoline **VIa** did not considerably grow.

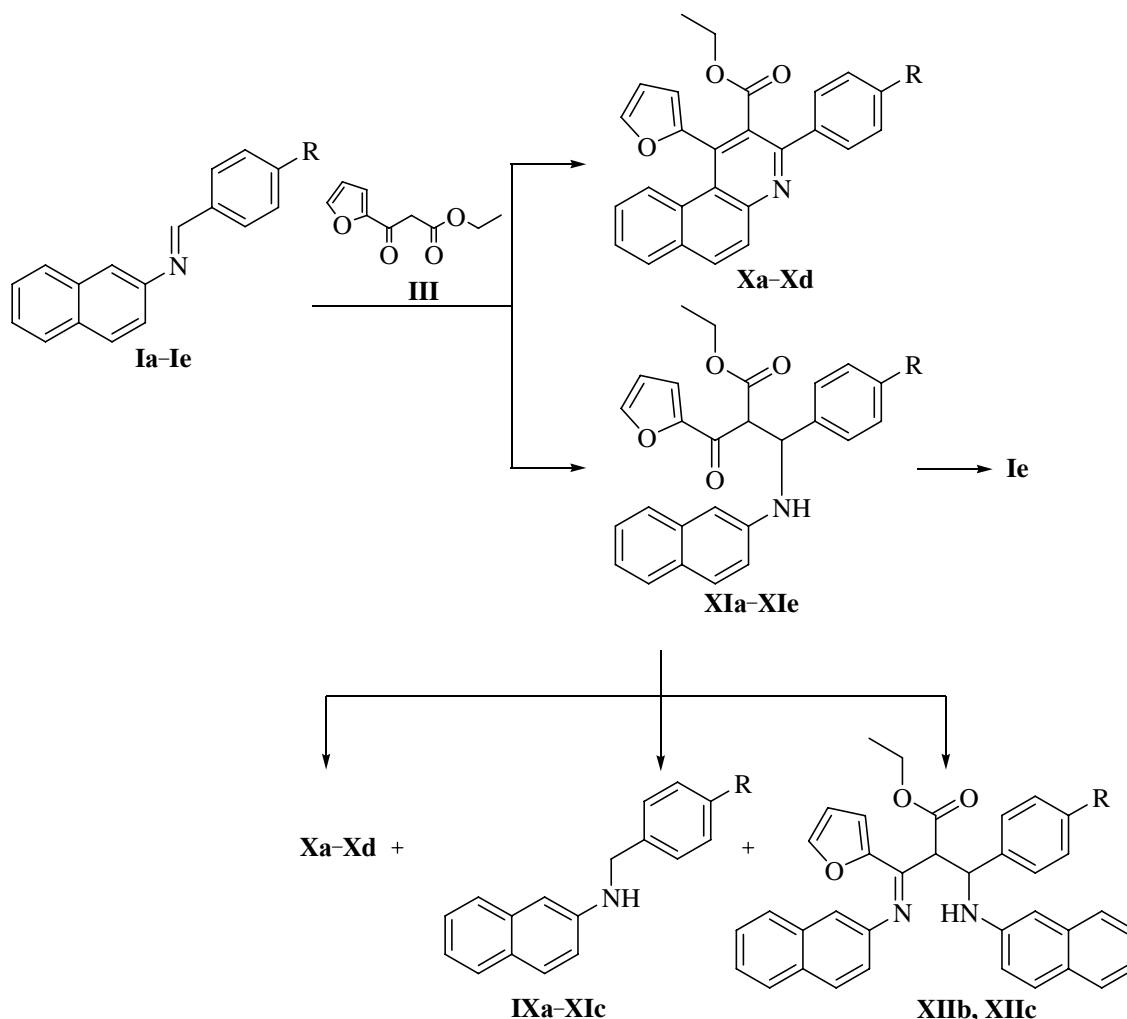
The substituents in the aldehyde part of the azomethine molecule somewhat affect the yield of target

benzo[*f*]quinolylacetates **VIa–VIe**. Schiff's bases **Ib–Id** with electron-withdrawing substituents (Hlg, NO₂) that increase the polarization of the azomethine bond provide higher yields of the reaction products **VIIb–VIIe** compared with those obtained from benzylidene- and *p*-methoxyphenylmethylene-2-naphthylamines **Ia** and **Id**.

In reactions of azomethines with heteryl-substituted ketoesters the reaction direction and products yield depend both on the substituent in the benzene ring of the azomethine and on the heteryl moiety at the carbonyl group of the ketoester.

The boiling of azomethines **Ia–Id** with furoylacetate **III** in the presence of HCl and nitrobenzene gave rise to ethyl 3-aryl-1-(2-furyl)-benzo[*f*]quinoline-2-carboxylates **Xa–Xd**. Like in the case of ethyl acetoacetate (**II**) the yield of benzo[*f*]quinolines **Xb–Xd** (38–57%) obtained from halo- and nitro-substituted azomethines **Ib–Id** was higher than that (29%) of the product prepared from ester **III** and benzylidene-2-naphthylamine (**Ia**). No benzo[*f*]quinolinecarboxylate formed from azomethine **Ie**.

In the molecules of heteryl-substituted oxoesters **III–V** a single center with labile hydrogen atom is present: the methylene group. The addition of furoylacetate **III**



to the C=N bond of azomethine **Ia-Ie** involving the methylene group at boiling the alcoholic solution of reagents without catalyst and oxidant occurred with formation in high yields (78–94%) of ethyl 3-aryl-3-(2-naphthylamino)-2-(2-furoyl)propanoates **XIa-XIe**. At boiling in ethanol in the presence of HCl and nitrobenzene aminoesters **XIa-XId** underwent cyclization into the corresponding benzoquinolinecarboxylates **Xa-Xd**. Methoxy-substituted aminoester **XIe** suffered a cleavage of a C–C bond to give the initial ketoester **III** and azomethine **Ie** easily isolable from the reaction mixture.

Compared to compound **VIIa** aminoesters **XIa-XIe** are more prone to cleavage under the cyclization conditions. In contrast to the cyclization of compound **VIIa** secondary amines **IXa-IXc** formed during cyclization of aminoesters **XIa-XIc** alongside benzoquinolinecarboxylates **Xa-Xc** also in the presence of nitrobenzene apparently because of the higher concentration of

azomethines **Ia-Ic** in the reaction mixture due to the higher decomposition rate of aminoketoesters **XIa-XIc**. This assumption is supported by the considerably higher yield of amines **IXa-IXc** (15–20%) in the cyclization of esters **XIa-XIc** compared to the yield of compound **IXa** (5%) isolated in the cyclization of ester **VIIa**.

The cyclization products of aminoesters **XIb** and **XIc** besides benzo[f]quinolines **Xb** and **Xc** and amines **IXb** and **IXc** contained ketoesters naphthylimino derivatives **XIIb** and **XIIc**. Azomethines **Ib** and **Ic** formed at the cleavage of aminoesters **XIb** and **XIc** under the conditions of the cyclization alongside the reduction are likely to suffer hydrolysis into the corresponding aldehydes and 2-naphthylamine; the latter reacts with the carbonyl of esters **XIb** and **XIc** giving compounds **XIIb** and **XIIc**.

Ethyl 3-(2-quinolyl)-3-oxopropanoate (**IV**) did not react with azomethines **Ia-Ie** without catalyst. In all likelihood the most important here is the steric factor of the bulky quinolyl substituent. Beside the $-I$ -effect of

the nitrogen in the quinoline ring of the oxoester **IV** molecule is less than the *I*-effect of the oxygen in the molecule of furyl-substituted ester **III**, and therefore in molecule **IV** the lability of the hydrogen of methylene group decreases, therefore its activation for addition to the C=N bond of azomethine requires the protonation of carbonyl groups in the molecule of ketoester **IV**.

In the presence of HCl ester **IV** reacted with azomethines **Ia–Ic** and **Ie** under mild conditions (reagents were maintained at room temperature in ethanol solution for 10–20 min) and led to the formation of ethyl 3-aryl-3-(2-naphthylamino)-2-(quinoline-2-carbonyl)propanoates **XIIIa–XIIIc** and **XIIIe**.

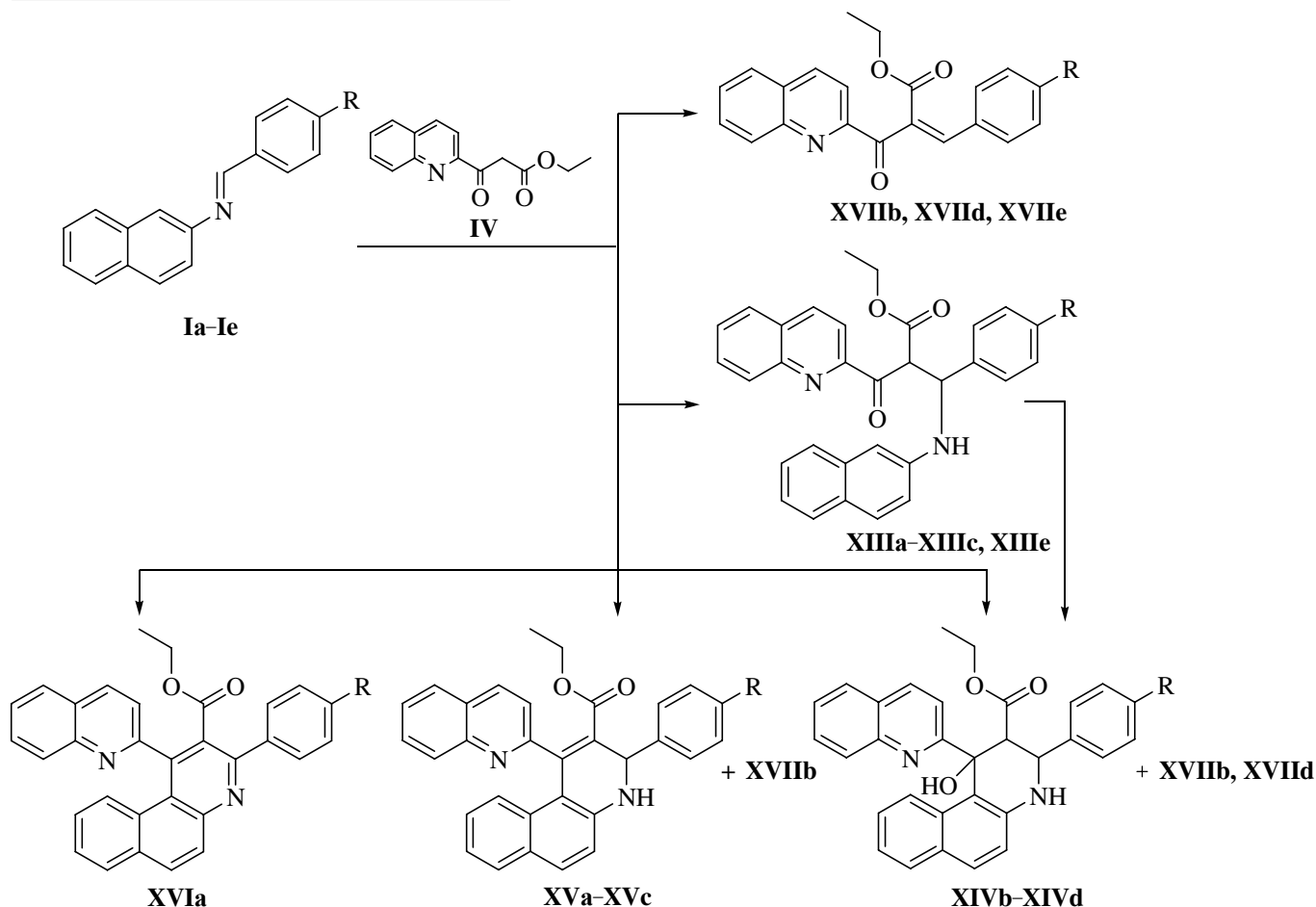
The heating of mixtures of azomethines **Ib–Id** with ester **IV** or of aminoketoesters **XIIIb**, **XIIIc**, and **XIIIe** at 80°C or at their prolonged storage (for several days) at room temperature in ethanol or benzene solution in the presence of a catalyst (HCl, BF₃ etherate) resulted in the formation of ethyl 3-aryl-1-hydroxy-1-(2-quinoly)-

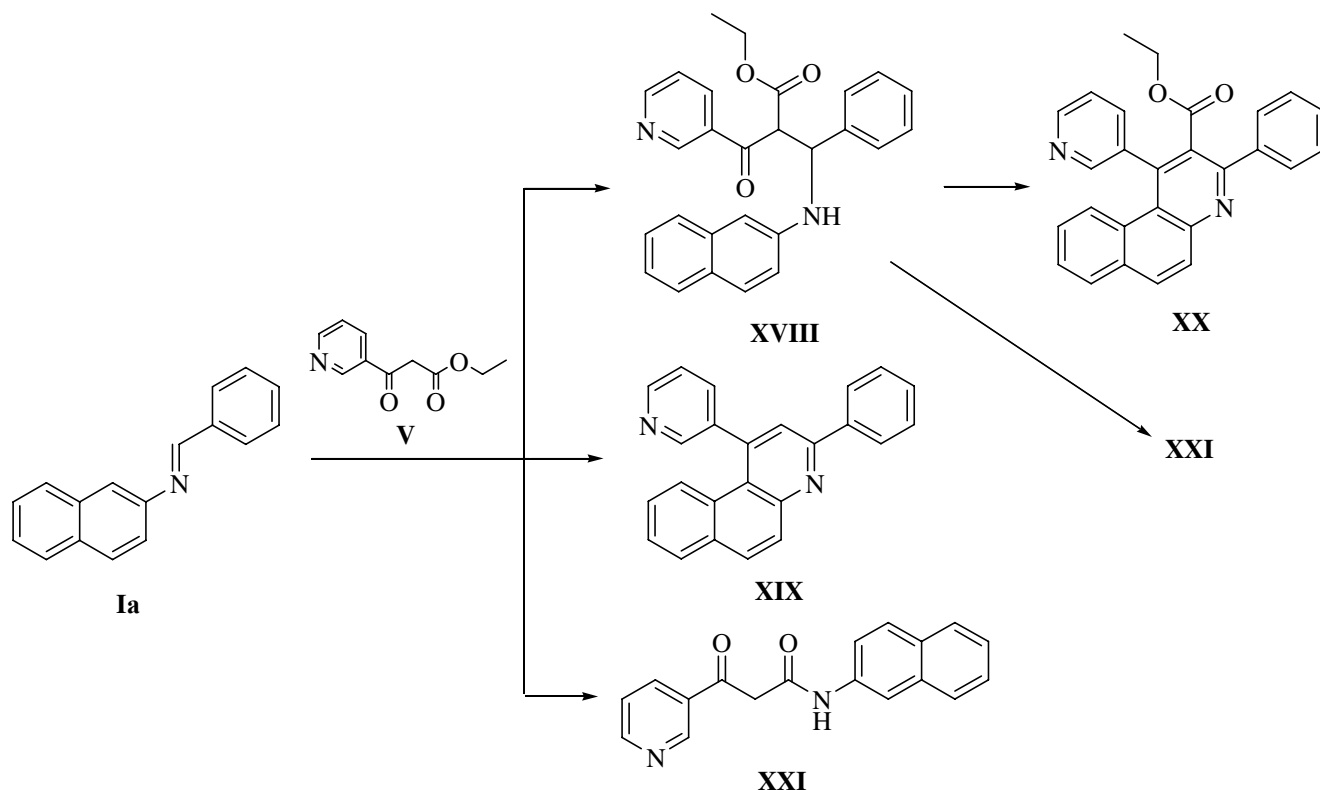
1,2,3,4-tetrahydrobenzo[*f*]quinoline-2-carboxylates **XIVb–XIVd**. By now a similar compound has been isolated only in the condensation of azomethine **Ia** with cyclohexanone [8].

At prolonged heating of a solution of **Ia–Ic** and **IV** in ethanol or dimethylformamide in the presence of HCl we obtained ethyl 3-aryl-1-(2-quinoly)-3,4-dihydrobenzo[*f*]quinoline-2-carboxylates **XVa–XVc** resulting from dehydration of intermediate hydroxyesters **XIVb** and **XIVc** and their hypothetical analog **XIVa**.

In reaction carried out in rigid conditions (heating at 100°C in a sealed ampule reagents **Ia** and **IV** in DMF solution in the presence of HCl) a dihydration product of dihydro derivative **XVa** was obtained: ethyl 1-(2-quinoly)-3-phenylbenzo[*f*]quinoline-2-carboxylate (**XVIa**).

Under the conditions of the synthesis of tetrahydro- and dihydrobenzoquinoline derivatives **XIVb–XIVd** and **XVa–XVc** alongside the target products **XIVb–XIVd** and **XVa–XVc** side products were formed [ethyl 3-aryl-





2-(2-quinoline-2-carbonyl)acrylates **XVIIb**, **XVIIc**, and **XVIIe**], and methoxy-substituted azomethine **Ie** yielded under these conditions a single reaction product ester **XVIIe**. Taking into consideration the results of previous studies [9, 10] we believe that the formation of unsaturated ketoesters **XVIIa–XVIIe** can occur on the one hand by aldol condensation of ketoester **IV** with the aldehyde liberated by the hydrolysis of the initial azomethine and on the other hand by hydramine cleavage of intermediate aminoketoesters **XIIIa–XIIIc** and **XIIIe**. Evidently the cleavage and cyclization of intermediates **XIII** are governed by the nature of substituent R. At R = H, NO₂, Br, and F the cyclization dominates over the cleavage of esters **XIII**, and prevailing reaction products are benzoquinolinecarboxylic acids derivatives. On the contrary, the electron-donor methoxy group shifts the reaction towards the cleavage of aminoketoester **XIIIe**, and the corresponding cyclization products do not form.

Comparing the behavior of arylmethylene-2-naphthylamines **Ia–Ie** in reactions with compound **IV** and acetoacetate **II** or furoylacetate **III** we showed that the presence of a bulky quinoline substituent in the molecule of oxoester **IV** led to the deceleration of cyclization, dehydration, and dehydrogenation of the intermediate compounds. It is therefore possible to stop the process

at any stage and to obtain all theoretically presumable reaction products.

Ethyl 3-(3-pyridyl)-3-oxopropanoate (**V**) unlike quinolyl-substituted ester **IV** added to the C=N bond of azomethine **Ia** without catalyst. At heating reagents **Ia** and **V** in ethanol to 40–50°C ethyl 3-(2-naphthylamino)-2-nicotinoyl-3-phenylpropanoate (**XVIII**) was obtained in quantitative yield.

At heating the same reagents in ethanol in the presence of concn. HCl in a sealed ampule at 100°C the only product obtained was 1-(3-pyridyl)-3-phenylbenzo[f]quinoline (**XIX**). We presume that under given conditions hydrolysis and decarboxylation of ester group occurs in ethyl 3-(3-pyridyl)-3-β-oxopropanoate (**V**) giving 3-acetylpyridine that further undergoes condensation with azomethine **Ia** yielding benzo[f]quinoline **XIX**.

Aminoketoester **XVIII** is less prone to decarboxylation than ester **V**. The heating of compound **XVIII** in the presence of HCl under severe conditions brings about its cyclization into ethyl 1-(3-pyridyl)-3-phenylbenzo[f]quinolinecarboxylate (**XX**).

From the reaction mixture obtained from azomethine **Ia** and ester **V** in toluene solution in the presence of a basic catalyst (piperidine) an individual product was isolated, 3-(3-pyridyl)-3-oxopropanoic acid N-(2-

naphthyl)amide (**XXI**). Amide **XXI** might form by reaction of ester **V** with 2-naphthylamine liberated by hydrolysis of azomethine **Ia** catalysed by the base. We also obtained amide **XXI** attempting to perform the cyclization of aminoketoester **XVIII** in the presence of piperidine. In all likelihood in the same way as with amino derivatives of furoylacetates **XIa–XIe** a C–C bond in the molecule of aminoketoester **XVIII** suffered cleavage generating benzylidene-2-naphthylamine (**Ia**) and pyridyloxopropanoate **V**. The hydrolysis of azomethine **Ia** and the reaction of the liberated 2-naphthylamine with ketoester **V** along the above described pathway led to the formation of amide **XXI**.

The composition and structure of compounds synthesized were confirmed by elemental analysis, IR, UV, NMR and mass spectra.

In IR spectra of aminoketoesters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** the characteristic absorption band of the stretching vibrations of NH group appeared at 3400–3375 cm^{-1} and the absorption band ν_{CO} of ester group vibrations was observed at 1740–1730 cm^{-1} . Carbonyl group in the spectrum of ester **VIIa** gave rise to a band at 1715 cm^{-1} , in the spectra of compounds **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** this band is displaced to the region 1680–1660 cm^{-1} apparently due to the conjugation with the adjacent heterocyclic ring. In the IR spectra of cyclic hydroxyesters **XIVb–XIVd** a strong broad absorption band was observed in the region 3600–3380 cm^{-1} . In the spectrum of the same compounds taken in CCl_4 solution this absorption appeared as two bands at 3410 (ν_{NH}) and 3605 (ν_{OH}) cm^{-1} . The stretching vibrations ν_{CO} of the ester group were present at 1720 cm^{-1} . In the spectra of compounds **XIVb–XIVd** lacks the absorption band of the keto group stretching vibrations characteristic of aminoketoesters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** indicating the fulfilled cyclization.

The IR spectra of dihydro derivatives **VIIIe** and **XVa–XVc** contain a medium band at 3400–3365 (ν_{NH}) and a strong band of ester group (ν_{CO}) at 1700–1690 cm^{-1} . In the IR spectra of final cyclization products **VIa–VIe**, **Xa–Xd**, **XVIa**, and **XX** the characteristic band of NH group stretching vibrations is absent but the band ν_{CO} of the ester group is retained. In the IR spectrum of all mentioned esters **VIa–VIe**, **VIIa**, **VIIIe**, **Xa–Xd**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, **XIVb–XIVd**, **XVa–XVc**, **XVIa**, **XVIII**, and **XX** a strong band is observed in the region 1230–1180 cm^{-1} belonging to the fragment C–O–C of the ester group, and for compounds **VIe**, **VIIIe**,

XIe, and **XIIIe**, also to the methoxyphenyl substituent; also the bands are present of the stretching vibrations of aliphatic C–H bonds in the region 2920–2890 cm^{-1} and of C–H bonds in aromatic and heteroaromatic rings at 3060–3030 cm^{-1} . The vibrations of the fragment C–O–C in the furan ring in the spectra of compounds **Xa–Xd** and **XIa–XIe** appear as a strong band at 1255–1230 cm^{-1} . In the spectra of nitro derivatives **VId**, **Xd**, **XId**, and **XIVd** characteristic absorption bands of the NO_2 group are observed at 1530 and 1355 cm^{-1} .

In the mass spectra of aminoketoesters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** the molecular ion peak is of low intensity (12–25%). The most abundant (100%) are fragment ions corresponding to the initial compounds **Ia–Ie** and **II–V** and those arising from to the rupture of C–C bond and recombination of fragment ions with simultaneous disproportionation of hydrogen ions. In the spectra of esters **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** intensive peaks are present (I_{rel} 65–75%) of ions $[M - \text{C}_{10}\text{H}_7\text{NH}_2]^+$.

In the mass spectra of hydroxyesters **XIVb–XIVd** the molecular ion peaks are the most abundant, and the other rather strong peaks (45–60%) are those of $[M - 18]^+$ corresponding to water molecule elimination from the molecular ion thus confirming the presence of a hydroxy group in compounds **XIVb–XIVd**.

The mass spectra of dihydro derivatives **VIIIe** and **XVa–XVc** alongside the most abundant molecular ion peaks contain also fragment ions peaks: $[M - \text{COOEt}]^+$ (I_{rel} 35–40%), $[M - \text{C}_6\text{H}_4\text{R}]^+$ (I_{rel} 48–55%), and the spectra of quinolyl-substituted compounds **XIVb–XIVd** contain also peaks of ions $[M - \text{C}_9\text{H}_6\text{N}-\text{CH}=\text{CH}-\text{COOEt}]^+$ (I_{rel} 42–47%).

Mass spectra of final aromatic products **VIa–VIe**, **Xa–Xd**, **XVIa**, and **XX** reveal the stability of these compounds against the electron impact: The spectra contain the strongest peak of molecular ion and peaks of low intensity (8–12%) corresponding to $[M - \text{COOEt}]^+$ and $[M - \text{C}_6\text{H}_4\text{R}]^+$.

UV spectra of aminoketoesters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** containing the naphthalene skeleton as the main chromophore fragment resemble the spectrum of 2-naphthylamine [UV spectrum, λ_{max} , nm ($\log \epsilon$): 246 (4.38), 280 (3.66), 338 (3.25)]. As compared to the latter spectrum, in the spectra of esters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** the intensity of all bands was greater evidently because of the presence in the molecule of additional benzyl chromophore, and in propanoates **XIa–XIe**, **XIIIa–**

XIIIc, **XIIIe**, and **XVIII** the spectrum is also affected by the introduction of the heterocyclic ring..

In the UV spectra of hydroxyesters **XIVb–XIVd** the increased intensity of the short-wave absorption band was observed as compared with the spectra of the noncyclic precursors **XIIIa–XIIIc** and **XIIIe**. Besides due to the transformation of the carbonyl into a hydroxy group the former does not affect the quinoline framework, and in the spectra of hydroxyesters **XIVb–XIVd** the absorption band characteristic of quinoline structure is easily isolated (316–317 nm) since it plays the role of an independent chromophore [11]. The long-wave band in the spectra of compounds **XIVb–XIVd** is less strong and suffers a red shift with respect to its position in the spectra of aminoketoesters **XIII**.

The long-wave band in the UV spectra of dihydro derivatives **VIIIe** and **XVa–XVc** suffered a considerable red shift evidently because of the formation of a new double bond in the closed cyclic system. This bond in the molecule of dihydroquinolylacetate **VIIIe** is in conjugation only with the naphthalene core and therefore produces in the spectra a large red shift of the long-wave band (λ 412 nm) compared with the spectra of dihydrobenzoquinolinecarboxylates **XVa–XVc** (λ 368–384 nm) where the conjugation system involves also the quinoline moiety and the ester group.

The aromatization of the benzoquinoline framework results in the appearance in the UV spectra of the final cyclization products **VIa–VIe**, **Xa–Xd**, **XVIa**, and **XX** of a strong band at 278–290 nm and less strong bands at 230–241, 250–269, and 341–353, 361–374 nm whose presence makes the spectra of compounds **VIa–VIe**, **Xa–Xd**, **XVIa**, and **XX** to resemble the spectra of 1,3-diarylbenzo[*f*]quinolines [1] and permits interpretation of the existing bands as Clar *p*-, β -, and α -bands. The heteryl moiety and the substituent in the phenyl ring of the benzo[*f*]quinoline molecule virtually do not affect the position and intensity of the spectral bands.

In the ^1H NMR spectra of aminoketoesters **VIIa**, **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** proton signals are observed from ethyl group at 1.08–1.20 and 4.00–4.14 ppm, multiplets from aromatic protons in the region 6.61–8.24 ppm, signal of the methine proton attached to the aryl-substituted carbon in the region 4.14–4.90 ppm, broadened singlet of the amino group proton at 8.60 ppm for pentanoate **VIIa** and 5.42–5.60 ppm for propanoates **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII**. Methylene protons at the C^2 atom in the spectrum of ester **VIIa** appear as a multiplet in the region 5.20–5.45 ppm, those

at the C^4 atom, as a multiplet at 4.58 ppm. Methine proton at the C^2 atom in the spectra of propanoates **XIa–XIe**, **XIIIa–XIIIc**, **XIIIe**, and **XVIII** gives rise to a signal in the region 5.28–5.49 ppm. In the NMR spectra of hydroxyesters **XIVb–XIVd** proton signal from the OH group is observed at 8.40–8.48 ppm. In the spectra of dihydro derivatives **VIIIe** and **XVa–XVc** this signal disappears as well as the signal of the methine proton H^2 indicating the dehydration of the hydroxyesters. The signal of methine proton H^3 in the spectra of esters **VIIIe** and **XVa–XVc** is shifted downfield compared to its position in the spectra of compounds **XIVb–XIVd** (δ 4.65–4.70 ppm) and appears at 5.98–6.18 ppm like in the spectra of fused azaphenanthrenes with the partially hydrogenated pyridine ring [12]. The amino group proton in the spectra of dihydro derivatives **VIIIe** and **XVa–XVc** is observed at 4.72–4.98 ppm. In the spectra of oxidized benzo[*f*]quinolines **VIa–VIe**, **Xa–Xd**, **XVIa**, and **XX** the proton signals of NH and H^3 disappear, and remain proton signals from the CO_2Et group at 1.06–1.22 and 4.05–4.22 ppm and from the aromatic protons in the region 6.71–8.60 ppm. In the spectra of esters **VIa–VIe** a singlet of methylene protons of the fragment CH_2CO is also observed at 4.44–4.66 ppm proving the fact that the condensation of azomethines **Ia–Ie** with ethyl acetoacetate (**II**) occurs at the methyl group of the latter. Methoxy-substituted aminoketoesters **XIe** and **XIIIe** and benzo[*f*]quinolines **VIIIe** and **VIe** contain in the spectra a singlet from the methoxy group protons at 3.70–3.80 ppm.

Hence every oxoester imparts specific features to the reaction with azomethines remaining an efficient synthon for preparation of functionally substituted benzo[*f*]quinolines and of semiproducts of their synthesis which having in the structure pharmacophore groups and heterocyclic fragments are promising as bioactive substances of a wide range of activity.

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, ionizing electrons energy 70 eV, and on GC-MS Hewlett-Packard HP 5890/5972 device in the electron impact mode at the energy 70 eV; column HP-5MS [30 m $\times$ 0.25 mm, stationary phase film (5% PLMe Silicone) 0.25 μm thick], vaporizer temperature 250°C. UV spectra of compounds solutions in ethanol (C 10^{-4} mol/l) 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) from solutions in DMSO-*d*₆ and chloroform-*d*; internal reference TMS.

The melting points were measured on a K ffler heating block.

Arylmethylene-2-naphthylamines **Ia–Ie** were prepared by procedure [13].

Ethyl 3-oxo-3-(2-furyl)propanoate (**III**) was obtained by acylating ethyl acetoacetate with 2-furancarboxyl chloride [14].

Ethyl 3-oxo-3-(2-quinolyl-, 3-pyridyl)propanoates **IV** and **V** were prepared by ester condensation of ethyl acetates and ethyl esters of quinaldic and nicotinic acids respectively [15, 16].

1-(3-Pyridyl)-3-phenylbenzo[*f*]quinoline (**XIX**) was identified by the melting point, IR, UV, and mass spectra [1].

Ethyl (3-arylbenzo[*f*]quinol-1-yl)-acetates VIa–VIe. A mixture of 10 mmol of azomethine **Ia–Ie**, 40 mmol of ethyl acetoacetate (**II**), 20 ml of 2-propanol (azomethines **Ia–Id**) or ethanol (azomethine **Ie**), and 10 drops of concn. HCl was boiled for 1 h. The reaction mixture was neutralized with 25% water solution of ammonia at room temperature, the separated precipitate of the product was filtered off and recrystallized from a mixture 2-propanol–tolylene, 2:1.

Ethyl (3-phenylbenzo[*f*]quinol-1-yl)-acetate (VIa). Yield 30%, mp 133–134°C. UV spectrum, λ_{max} , nm (log ϵ): 231 (4.42), 278 (4.61), 344 (3.68), 362 (3.72). ¹H NMR spectrum, δ , ppm: 1.21 t, 4.22 q (5H, OEt, ²*J* 14.2, ³*J* 6.1 Hz), 4.66 s (2H, CH₂), 7.55 d, 8.22 m (5H, Ph, ³*J* 8.2 Hz), 7.62 d.d (2H, H^{8,9}, ³*J* 7.2, ⁴*J* 2.8 Hz), 7.88 s (1H, H²), 7.92–8.06 m (3H, H^{5–7}), 8.58 d.d (1H, H¹⁰, ³*J* 7.2, ⁴*J* 2.8 Hz). Found, %: C 80.69; H 5.35; N 3.97. C₂₃H₁₉NO₂. Calculated, %: C 80.94; H 5.57; N 4.11.

Ethyl {3-(*p*-bromophenyl)benzo[*f*]quinol-1-yl}-acetate (VIb). Yield 56%, mp 143–144°C. UV spectrum, λ_{max} , nm (log ϵ): 230 (4.48), 268 (4.58), 282 (4.72), 349 (3.86), 366 (3.91). ¹H NMR spectrum, δ , ppm: 1.22 t, 4.12 q (5H, OEt, ²*J* 14.2, ³*J* 6.0 Hz), 4.44 s (2H, CH₂), 7.62 d.d (2H, H^{8,9}, ³*J* 7.3, ⁴*J* 2.9 Hz), 7.64 d, 8.12 m (4H_{arom}, ³*J* 8.0 Hz), 7.83 s (1H, H²), 7.93–8.08 m (3H, H^{5–7}), 8.59 d.d (1H, H¹⁰, ³*J* 7.3, ⁴*J* 2.9 Hz). Found, %: C 65.53; H 4.19; Br 18.81; N 3.34. C₂₃H₁₈BrNO₂. Calculated, %: C 65.72; H 4.28; Br 19.05; N 3.33.

Ethyl {3-(*p*-fluorophenyl)benzo[*f*]quinol-1-yl}acetate (VIc). Yield 40%, mp 109–110°C. UV

spectrum, λ_{max} , nm (log ϵ): 236 (4.41), 267 (4.59), 279 (4.68), 346 (3.83), 363 (3.85). ¹H NMR spectrum, δ , ppm: 1.22 t, 4.14 q (5H, OEt, ²*J* 14.0, ³*J* 6.0 Hz), 4.46 s (2H, CH₂), 7.20 m, 8.22 d (4H_{arom}, ³*J* 8.2 Hz), 7.64 d.d (2H, H^{8,9}, ³*J* 7.5, ⁴*J* 2.7 Hz), 7.82 s (1H, H²), 7.95–8.10 m (3H, H^{5–7}), 8.53 d.d (1H, H¹⁰, ³*J* 7.5, ⁴*J* 2.7 Hz). Found, % N 3.75. C₂₃H₁₈FNO₂. Calculated, %: N 3.90.

Ethyl {3-(*p*-nitrophenyl)benzo[*f*]quinol-1-yl}acetate (VIId). Yield 43%, mp 196–197°C. UV spectrum, λ_{max} , nm (log ϵ): 230 (4.21), 269 (4.40), 282 (4.48), 341 (4.00), 362 (3.98). ¹H NMR spectrum, δ , ppm: 1.22 t, 4.20 q (5H, OEt, ²*J* 14.1, ³*J* 6.1 Hz), 4.60 s (2H, CH₂), 7.65 d.d (2H, H^{8,9}, ³*J* 7.9, ⁴*J* 2.6 Hz), 7.94–8.08 m (3H, H^{5–7}), 8.25 s (1H, H²), 8.36 d, 8.54 d (4H_{arom}, ³*J* 8.1 Hz), 8.58 d.d (1H, H¹⁰, ³*J* 7.9, ⁴*J* 2.6 Hz). Found, %: C 71.41; H 4.46; N 7.17. C₂₃H₁₈N₂O₄. Calculated, %: C 71.50; H 4.66; N 7.25.

Ethyl {3-(*p*-methoxyphenyl)benzo[*f*]quinol-1-yl}acetate (VIe). Yield 31%, mp 133–134°C. UV spectrum, λ_{max} , nm (log ϵ): 234 (4.43), 269 (4.57), 285 (4.69), 354 (4.08), 366 (4.08). ¹H NMR spectrum, δ , ppm: 1.20 t, 4.21 q (5H, OEt, ²*J* 14.0, ³*J* 6.1 Hz), 3.85 s (3H, OMe), 4.45 s (2H, CH₂), 7.12 d, 8.28 d (4H_{arom}, ³*J* 7.7 Hz), 7.62 d.d (2H, H^{8,9}, ³*J* 7.8, ⁴*J* 2.7 Hz), 7.80 s (1H, H²), 7.94–8.08 m (3H, H^{5–7}), 8.56 d.d (1H, H¹⁰, ³*J* 7.8, ⁴*J* 2.7 Hz). Found, %: C 77.61; H 5.72; N 3.52. C₂₄H₂₁NO₃. Calculated, %: C 77.63; H 5.66; N 3.77.

Ethyl 5-(2-naphthylamino)-3-oxo-5-phenylpentanoate (VIIa). A solution of 10 mmol of azomethine **Ia** and 40 mmol of ethyl acetoacetate (**II**) in 30 ml of ethanol was boiled for 1 h. The precipitate separated on cooling the reaction mixture was recrystallized from 2-propanol. Yield 65%, mp 90–91°C. UV spectrum, λ_{max} , nm (log ϵ): 220 (4.60), 272 (4.42), 338 (4.00), 362 (3.72). ¹H NMR spectrum, δ , ppm: 1.20 t, 3.90–4.14 m (6H, OEt, H⁵, ²*J* 14.2, ³*J* 6.1 Hz), 4.58 m (2H, H²), 5.20–5.45 m (2H, H⁴), 7.48–8.56 m (13H_{arom}), 8.60 br.s (1H, NH). Found, %: C 76.17; H 6.30; N 3.70. C₂₃H₂₃NO₃. Calculated, %: C 76.45; H 6.37; N 3.88.

Ethyl {3-(*p*-methoxyphenyl)-3,4-dihydrobenzo[*f*]quinol-1-yl}acetate (VIIe). To a solution of 10 mmol of azomethine **Ie** and 40 mmol of ethyl acetoacetate (**II**) in 25 ml of ethanol heated to 70°C was added 5 drops of concn. HCl. The solution was cooled, neutralized with NH₄OH, the precipitate was filtered off and recrystallized from ethanol. Yield 37%, mp 155–156°C. UV spectrum, λ_{max} , nm (log ϵ): 245 (4.50), 276 (4.39), 412 (3.71). ¹H NMR spectrum, δ , ppm: 1.18 t, 4.08 q (5H, OEt, ²*J* 14.0, ³*J* 6.1 Hz), 3.48 s (2H, CH₂),

3.72 s (3H, OMe), 4.72 m (1H, NH), 6.18 s (1H, H³), 6.88 d, 7.26 d (4H_{arom}, ³J 7.9 Hz), 7.00–7.75 m (6H, H^{2,5-9}), .90 d (1H, H¹⁰, ³J 7.8, ⁴J 2.7 Hz). Found, %: C 76.99; H 6.13; N 3.58. C₂₄H₂₃NO₃. Calculated, %: C 77.21; H 6.17; N 3.75.

Cyclization of ethyl 5-(2-naphthylamino)-3-oxo-5-phenylpentanoate (VIIa). A solution of 10 mmol of compound VIIa and 7 drops of concn. HCl in 40 ml of ethanol was boiled for 0.5 h. The tarry precipitate of benzyl-2-naphthylamine hydrochloride (IXa) was filtered off, boiled with a water solution of NH₄OH, ground with water, and recrystallized from 2-propanol.

Benzyl-2-naphthylamine (IXa). Yield 5%, mp 65–66°C. UV spectrum, λ_{max}, nm (log ε): 214 (4.62), 253 (4.70), 292 (4.06), 370 (3.82). ¹H NMR spectrum, δ, ppm: 4.30 d (2H, CH₂, ²J 14.0 Hz), 6.30 br.s (1H, NH), 6.70–7.72 m (12H_{arom}). Found, %: C 87.24; H 6.40; N 5.73. C₁₇H₁₅NO. Calculated, %: C 87.55; H 6.44; N 6.01.

The mother liquor after separating the amine hydrochloride was neutralized with NH₄OH and evaporated by 1/4 of its volume. The separated precipitate was treated with ethyl ether to obtain benzo[f]-quinolylacetate VIa. Yield 25%.

Dehydrogenation of ethyl {3-(*p*-methoxyphenyl)-3,4-dihydrobenzo[f]quinol-1-yl}-acetate (VIIIe). A solution of 5 mmol of dihydro derivative VIIIe and 10 drops of concn. HCl in 20 ml of ethanol was boiled for 1 h. The separated precipitate was filtered off, treated with a water solution of NH₄OH, and recrystallized from a mixture 2-propanol–toluene, 2:1. Yield of ester VIe 56%.

Ethyl 3-aryl-1-(2-furyl)benzo[f]quinoline-2-carboxylate (Xa–Xd). A mixture of 10 mmol of azomethine Ia–Id, 20 mmol of furoylacetate III, 20 ml of ethanol, 10 drops of concn. HCl, and 12 drops of nitrobenzene was boiled for 2 h, cooled, neutralized with a water solution of NH₄OH, and the precipitate was filtered off. Compounds Xa–Xc were recrystallized from 2-propanol, carboxylate Xd, from nitromethane.

Ethyl 3-phenyl-1-(2-furyl)benzo[f]-quinoline-2-carboxylate (Xa). Yield 29%, mp 111–112°C. UV spectrum, λ_{max}, nm (log ε): 239 (4.40), 267 (4.50), 284 (4.74), 348 (3.82), 365 (3.80). ¹H NMR spectrum, δ, ppm: 1.07 t, 4.08 q (5H, OEt, ²J 14.0, ³J 6.1 Hz), 6.71–8.18 m (14H_{arom}). Found, %: C 79.15; H 4.62; N 3.44. C₂₆H₁₉NO₃. Calculated, %: C 79.39; H 4.85; N 3.56.

Ethyl 3-(*p*-bromophenyl)-1-(2-furyl)-benzo[f]-quinoline-2-carboxylate (Xb). Yield 57%, mp 144–

145°C. UV spectrum, λ_{max}, nm (log ε): 241 (4.36), 260 (4.49), 284 (4.69), 348 (3.76), 367 (3.72). ¹H NMR spectrum, δ, ppm: 1.08 t, 4.15 q (5H, OEt, ²J 14.2, ³J 6.0 Hz), 6.80–8.20 m (13H_{arom}). Found, %: C 65.91; H 3.58; Br 16.74; N 3.01. C₂₆H₁₈BrNO₃. Calculated, %: C 66.10; H 3.81; Br 16.95; N 2.97.

Ethyl 3-(*p*-fluorophenyl)-1-(2-furyl)-benzo[f]-quinoline-2-carboxylate (Xc). Yield 39%, mp 97–98°C. UV spectrum, λ_{max}, nm (log ε): 240 (4.39), 265 (4.51), 286 (4.72), 349 (3.90), 367 (3.78). ¹H NMR spectrum, δ, ppm: 1.10 t, 4.13 q (5H, OEt, ²J 14.1, ³J 6.1 Hz), 6.73–8.11 m (13H_{arom}). Found, %: N 3.26. C₂₆H₁₈FNO₃. Calculated, %: N 3.41.

Ethyl 3-(*p*-nitrophenyl)-1-(2-furyl)-benzo[f]quinoline-2-carboxylate (Xd). Yield 40%, mp 188–189°C. UV spectrum, λ_{max}, nm (log ε): 247 (4.40), 261 (4.43), 290 (4.69), 348 (3.73), 366 (3.69). ¹H NMR spectrum, δ, ppm: 1.06 t, 4.16 q (5H, OEt, ²J 14.0, ³J 6.0 Hz), 7.02–8.74 m (13H_{arom}). Found, %: C 71.12; H 3.95; N 6.27. C₂₆H₁₈N₂O₅. Calculated, %: C 71.23; H 4.11; N 6.39.

Ethyl 3-aryl-3-(2-naphthylamino)-2-(2-furoyl)propanoate XIa–XIe. A solution of 10 mmol of azomethine Ia–Ie and 20 mmol of ester III in 30 ml of ethanol was boiled for 1 h, cooled, and the precipitate was filtered off. Compound XIa was recrystallized from ethanol.

Ethyl 3-(2-naphthylamino)-3-phenyl-2-(2-furoyl)propanoate (XIa). Yield 78%, mp 107–108°C. UV spectrum, λ_{max}, nm (log ε): 231 (4.60), 247 (4.69), 272 (4.43), 320 (4.11). ¹H NMR spectrum, δ, ppm: 1.08 t, 4.00 q (5H, OEt, ²J 14.1, ³J 6.1 Hz), 4.81 d (1H, H³, ³J 9.2 Hz), 5.43 br.s (1H, NH), 5.47 d (1H, H², ³J 9.2 Hz), 6.85–7.82 m (15H_{arom}). Found, %: C 75.35; H 5.48; N 3.17. C₂₆H₂₃NO₄. Calculated, %: C 75.54; H 5.57; N 3.39.

Ethyl 3-(*p*-bromophenyl)-3-(2-naphthylamino)-2-(2-furoyl)propanoate (XIb). Yield 87%, mp 103–104°C. UV spectrum, λ_{max}, nm (log ε): 230 (4.58), 249 (4.66), 270 (4.41), 319 (4.13). ¹H NMR spectrum, δ, ppm: 1.10 t, 4.12 q (5H, OEt, ²J 14.2, ³J 6.2 Hz), 4.89 d (1H, H³, ³J 9.0 Hz), 5.40 br.s (1H, NH), 5.45 d (1H, H², ³J 9.0 Hz), 6.90–8.01 m (14H_{arom}). Found, %: C 63.33; H 4.41; Br 15.96; N 2.77. C₂₆H₂₂BrNO₄. Calculated, %: C 63.41; H 4.47; Br 16.26; N 2.85.

Ethyl 3-(2-naphthylamino)-3-(*p*-fluorophenyl)-2-(2-furoyl)propanoate (XIc). Yield 84%, mp 93–94°C. UV spectrum, λ_{max}, nm (log ε): 234 (4.56), 248 (4.70), 273 (4.45), 322 (4.19). ¹H NMR spectrum, δ, ppm: 1.11 t, 4.03 q (5H, OEt, ²J 14.0, ³J 6.0 Hz), 4.90 d (1H, H³,

3J 9.1 Hz), 5.40 d (1H, H^2 , 3J 9.1 Hz), 5.44 br.s (1H, NH), 6.84–8.00 m ($14H_{\text{arom}}$). Found, %: N 3.09. $C_{26}H_{22}FNO_4$. Calculated, %: N 3.25.

Ethyl 3-(2-naphthylamino)-3-(*p*-nitrophenyl)-2-(2-furoyl)propanoate (XIId). Yield 93%, mp 92–93°C. UV spectrum, λ_{max} , nm (log ϵ): 230 (4.59), 246 (4.63), 269 (4.40), 320 (4.09). 1H NMR spectrum, δ , ppm: 1.10 t, 4.04 q (5H, OEt, 2J 14.1, 3J 6.0 Hz), 4.90 d (1H, H^3 , 3J 8.9 Hz), 5.42 d (1H, H^2 , 3J 8.9 Hz), 5.46 br.s (1H, NH), 7.13–8.24 m ($14H_{\text{arom}}$). Found, %: C 67.89; H 4.67; N 5.92. $C_{26}H_{22}N_2O_6$. Calculated, %: C 68.12; H 4.80; N 6.11.

Ethyl 3-(*p*-methoxyphenyl)-3-(2-naphthylamino)-2-(2-furoyl)propanoate (XIe). Yield 78%, mp 94–95°C. UV spectrum, λ_{max} , nm (log ϵ): 233 (4.61), 247 (4.68), 273 (4.48), 314 (4.06). 1H NMR spectrum, δ , ppm: 1.09 t, 4.03 q (5H, OEt, 2J 14.2, 3J 6.1 Hz), 3.70 s (3H, OMe), 4.88 d (1H, H^3 , 3J 8.8 Hz), 5.43 br.s (1H, NH), 5.49 d (1H, H^2 , 3J 8.8 Hz), 6.63–7.94 m ($14H_{\text{arom}}$). Found, %: C 72.92; H 5.41; N 3.04. $C_{27}H_{25}NO_5$. Calculated, %: C 73.14; H 5.64; N 3.16.

Cyclization of ethyl 3-aryl-3-(2-naphthylamino)-2-(2-furoyl)propanoates XIa–XIe. A solution of 10 mmol of aminoester XIa–XIe, 10 drops of concn. HCl, and 12 drops of nitrobenzene in 30 ml of ethanol was boiled for 2 h. The tarry precipitate formed from compound XIa–XIc was filtered off, boiled with a water solution of NH_4OH , then ground with water. We obtained compounds IXa–IXc. Yield of benzylnaphthylamine IXa 18%, its characteristics are given above.

***p*-Bromobenzyl-2-naphthylamine (IXb).** Yield 15%, mp 110–111°C. UV spectrum, λ_{max} , nm (log ϵ): 215 (4.65), 257 (4.72), 291 (4.03), 372 (3.90). 1H NMR spectrum, δ , ppm: 4.28 d (2H, CH_2 , 2J 14.1 Hz), 6.31 br.s (1H, NH), 7.00–7.82 m ($11H_{\text{arom}}$). Found, %: C 65.23; H 4.31; Br 25.28; N 4.11. $C_{17}H_{14}BrN$. Calculated, %: C 65.38; H 4.49; Br 25.64; N 4.49.

***p*-Fluorobenzyl-2-naphthylamine (IXc).** Yield 20%, mp 86–87°C. UV spectrum, λ_{max} , nm (log ϵ): 214 (4.60), 251 (4.69), 290 (4.00), 368 (3.80). 1H NMR spectrum, δ , ppm: 4.32 d (2H, CH_2 , 2J 14.0 Hz), 6.25 br.s (1H, NH), 6.92–7.74 m ($11H_{\text{arom}}$). Found, %: N 5.36. $C_{17}H_{14}FN$. Calculated, %: N 5.58.

The mother liquor obtained after separating amines IXa–IXc was evaporated to dryness, the solid residue was treated with a water solution of NH_4OH , with water, and then was dissolved in 2-propanol. The insoluble residue of compounds XIId and XIIf was filtered off and recrystallized from nitromethane.

Ethyl 2-[(*p*-bromophenyl)(2-naphthylamino)-methyl]-3-(2-naphthylimino)-3-(2-furyl)propanoate (XIIf). Yield 6%, mp 227–228°C. UV spectrum, λ_{max} , nm (log ϵ): 227 (4.60), 249 (4.70), 278 (4.49), 316 (4.18). 1H NMR spectrum, δ , ppm: 1.14 t, 4.10 q (5H, OEt, 2J 14.0, 3J 6.0 Hz), 4.83 d (1H, H^3 , 3J 8.9 Hz), 5.23 d (1H, H^2 , 3J 8.9 Hz), 5.60 br.s (1H, NH), 6.81–8.02 m ($21H_{\text{arom}}$). Found, %: C 69.91; H 4.58; Br 12.66; N 4.37. $C_{36}H_{29}BrN_2O_3$. Calculated, %: C 70.02; H 4.70; Br 12.97; N 4.54.

Ethyl 2-[(*p*-fluorophenyl)(2-naphthylamino)-methyl]-3-(2-naphthylimino)-3-(2-furyl)propanoate (XIIf). Yield 7%, mp 270–271°C. UV spectrum, λ_{max} , nm (log ϵ): 226 (4.62), 246 (4.71), 275 (4.45), 318 (4.22). 1H NMR spectrum, δ , ppm: 1.11 t, 4.02 q (5H, OEt, 2J 14.1, 3J 6.2 Hz), 4.81 d (1H, H^3 , 3J 9.1 Hz), 5.29 d (1H, H^2 , 3J 9.1 Hz), 5.60 br.s (1H, NH), 6.78–8.00 m ($21H_{\text{arom}}$). Found, %: N 4.92. $C_{36}H_{29}FN_2O_3$. Calculated, %: N 5.04.

From the cooled mother liquors in 2-propanol benzo[f]carboxylates Xa–Xc were isolated in respective yields 28, 30, and 25%. Benzo[f]quinolinecarboxylate Xd was isolated by neutralization of the reaction mixture with a water solution of NH_4OH and recrystallization of the separated precipitate from nitromethane. Yield 26%. In the case of aminoketoester Ie the treatment of the reaction mixture with NH_4OH and evaporation of the mixture by 1/3 of volume a precipitate was obtained of azomethine Ie.

Ethyl 3-aryl-3-(2-naphthylamino)-2-(quinoline-2-carbonyl)propanoates XIIIa–XIIIc and XIIIe. A solution of 10 mmol of azomethine Ia–Ic and Ie, 10 mmol of ester IV, 3 drops of concn. HCl in 20 ml of ethanol was stirred for 10–20 min at 20°C. The precipitate formed was treated with aqueous NH_4OH and recrystallized from ethanol.

Ethyl 3-(2-naphthylamino)-3-phenyl-2-(quinoline-2-carbonyl)propanoate (XIIIa). Yield 79%, mp 115–116°C. UV spectrum, λ_{max} , nm (log ϵ): 213 (4.63), 224 (4.65), 248 (4.69), 270 (4.48), 320 (4.30). 1H NMR spectrum, δ , ppm: 1.20 t, 4.00 q (5H, OEt, 2J 14.0, 3J 6.1 Hz), 4.88 d (1H, H^3 , 3J 9.0 Hz), 5.46 br.s (1H, NH), 5.49 d (1H, H^2 , 3J 9.0 Hz), 6.69–8.20 m ($18H_{\text{arom}}$). Found, %: C 78.21; H 5.19; N 5.83. $C_{31}H_{26}N_2O_3$. Calculated, %: C 78.48; H 5.49; N 5.91.

Ethyl 3-(*p*-bromophenyl)-3-(2-naphthylamino)-2-(quinoline-2-carbonyl)propanoate (XIIIb). Yield 64%, mp 121–122°C. UV spectrum, λ_{max} , nm (log ϵ): 215 (4.62), 226 (4.64), 249 (4.66), 273 (4.46), 280 m (4.28),

330 (4.21). ^1H NMR spectrum, δ , ppm: 1.18 t, 4.01 q (5H, OEt, 2J 14.2, 3J 6.1 Hz), 4.73 d (1H, H^3 , 3J 9.3 Hz), 5.32 d (1H, H^2 , 3J 9.3 Hz), 5.48 br.s (1H, NH), 6.82–8.19 m (17H_{arom}). Found, %: C 67.20; H 4.35; Br 14.10; N 4.83. $\text{C}_{31}\text{H}_{25}\text{BrN}_2\text{O}_3$. Calculated, %: C 67.27; H 4.52; Br 14.47; N 5.06.

Ethyl 3-(2-naphthylamino)-3-(*p*-fluorophenyl)-2-(quinoline-2-carbonyl)propanoate (XIIIc). Yield 58%, mp 117–118°C. UV spectrum, λ_{max} , nm (log ϵ): 214 (4.61), 228 (4.63), 256 (4.68), 286 (4.48), 326 (4.00). ^1H NMR spectrum, δ , ppm: 1.15 t, 4.00 q (5H, OEt, 2J 14.1, 3J 6.01 Hz), 4.63 d (1H, H^3 , 3J 9.1 Hz), 5.28 d (1H, H^2 , 3J 9.1 Hz), 5.51 br.s (1H, NH), 6.73–8.16 m (17H_{arom}). Found, %: N 5.51. $\text{C}_{31}\text{H}_{25}\text{FN}_2\text{O}_3$. Calculated, %: N 5.69.

Ethyl 3-(*p*-methoxyphenyl)-3-(2-naphthylamino)-2-(quinoline-2-carbonyl)propanoate (XIIIe). Yield 68%, mp 103–104°C. UV spectrum, λ_{max} , nm (log ϵ): 214 (4.65), 229 (4.69), 238 (4.65), 286 (4.50), 326 (4.32). ^1H NMR spectrum, δ , ppm: 1.11 t, 4.08 q (5H, OEt, 2J 14.2, 3J 6.0 Hz), 3.70 s (3H, OMe), 4.65 d (1H, H^3 , 3J 8.9 Hz), 5.28 d (1H, H^2 , 3J 8.9 Hz), 5.60 br.s (1H, NH), 6.61–8.12 m (17H_{arom}). Found, %: C 75.93; H 5.37; N 5.44. $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_4$. Calculated, %: C 76.19; H 5.56; N 5.56.

Ethyl 3-aryl-1-hydroxy-1-(2-quinolyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline-2-carboxylates XIVb–XIVd. An equimolar mixture (5 mmol each) of Schiff's base **Ib–Id** and ester **IV** or 2.5 mmol of aminoketoester **XIIb–XIIId** in 20 ml of benzene containing 5 drops of BF_3 etherate for azomethines **Ib** and **Ic** or in 20 ml of ethanol containing 3 drops of concn. HCl for compound **Id** was heated at 80°C for 20 min or maintained for 72 h at 20°C. Reaction products **XIVb–XIVd** were isolated as described for compounds **XIIb–XIIId**.

Ethyl 3-(*p*-bromophenyl)-1-hydroxy-1-(2-quinolyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline-2-carboxylate (XIVb). Yield 29%, mp 218–219°C. UV spectrum, λ_{max} , nm (log ϵ): 208 (4.76), 236 (4.80), 249 (4.63), 288 (4.24), 316 (3.84), 342 (4.63). ^1H NMR spectrum, δ , ppm: 1.07 t, 4.12 q (5H, OEt, 2J 14.0, 3J 6.0 Hz), 4.70 d (1H, H^3 , 3J 9.5 Hz), 5.22 br.s (1H, NH), 5.68 d (1H, H^2 , 3J 9.5 Hz), 6.98–8.20 m (16H_{arom}), 8.44 C (1H, OH). Found, %: C 67.01; H 4.43; Br 14.24; N 4.91. $\text{C}_{31}\text{H}_{25}\text{BrN}_2\text{O}_3$. Calculated, %: C 67.27; H 4.52; Br 14.47; N 5.06.

Ethyl 1-hydroxy-3-(*p*-fluorophenyl)-1-(2-quinolyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline-2-carboxylate (XIVc). Yield 38%, mp 140–141°C. UV spectrum,

λ_{max} , nm (log ϵ): 208(4.75), 235 (4.83), 256 (4.68), 246 (4.67), 284 (4.10), 317 (3.80), 349 (3.60). ^1H NMR spectrum, δ , ppm: 1.08 t, 4.07 q (5H, OEt, 2J 14.1, 3J 6.00 Hz), 4.65 d (1H, H^3 , 3J 9.2 Hz), 5.27 d (1H, H^2 , 3J 9.2 Hz), 5.66 br.s (1H, NH), 6.78–8.14 m (16H_{arom}), 8.40 C (1H, OH). Found, %: N 5.46. $\text{C}_{31}\text{H}_{25}\text{FN}_2\text{O}_3$. Calculated, %: N 5.69.

Ethyl 1-hydroxy-3-(*p*-nitrophenyl)-1-(2-quinolyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline-2-carboxylate (XIVd). Yield 36%, mp 249–250°C. UV spectrum, λ_{max} , nm (log ϵ): 207(4.77), 235 (4.81), 246 (4.70), 281 (4.30), 317 (3.91), 347 (3.60). ^1H NMR spectrum, δ , ppm: 1.09 t, 4.03 q (5H, OEt, 2J 14.2, 3J 6.2 Hz), 4.69 d (1H, H^3 , 3J 8.9 Hz), 5.14 d (1H, H^2 , 3J 8.9 Hz), 5.62 br.s (1H, NH), 7.12–8.44 m (16H_{arom}), 8.48 C (1H, OH). Found, %: C 71.49; H 4.76; N 7.88. $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_5$. Calculated, %: C 71.68; H 4.82; N 8.09.

Ethyl 3-aryl-1-(2-quinolyl)-3,4-dihydrobenzo[*f*]quinoline-2-carboxylates XVa–XVc. A solution of equimolar mixture (5 mmol each) of azomethine **Ia–Ic** and ester **IV** containing 5 drops of concn. HCl in 5 ml of DMF for benzylidene-2-naphthylamine (**Ia**) or in 20 ml of ethanol for compounds **Ib** and **Ic** was heated for 2.5 h at 80–100°C. The solution was evaporated to 1/2 of volume. The tarry precipitate was treated with NH_4OH , hexane, and recrystallized from 2-propanol (ester **XVa**) or ethanol (esters **XVb** and **XVc**).

Ethyl 3-phenyl-1-(2-quinolyl)-3,4-dihydrobenzo[*f*]quinoline-2-carboxylate (XVa). Yield 63%, mp 119–120°C. UV spectrum, λ_{max} , nm (log ϵ): 206 (4.64), 239 (4.59), 265 (4.41), 317(3.92), 368 (3.15). ^1H NMR spectrum, δ , ppm: 1.14 t, 4.09 q (5H, OEt, 2J 14.1, 3J 6.1 Hz), 4.98 br.s (1H, NH), 5.98 s (1H, H^3), 6.74–8.09 m (17H_{arom}). Found, %: C 81.36; H 5.19; N 5.94. $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_2$. Calculated, %: C 81.58; H 5.26; N 6.14.

Ethyl 3-(*p*-bromophenyl)-1-(2-quinolyl)-3,4-dihydrobenzo[*f*]quinoline-2-carboxylate (XVb). Yield 52%, mp 207–208°C. UV spectrum, λ_{max} , nm (log ϵ): 207 (4.63), 238 (4.58), 270 (4.43), 316 (3.90), 384 (3.60). ^1H NMR spectrum, δ , ppm: 1.10 t, 4.03 q (5H, OEt, 2J 14.2, 3J 6.1 Hz), 4.43 br.s (1H, NH), 6.00 s (1H, H^3), 6.96–8.12 m (16H_{arom}). Found, %: C 69.21; H 4.11; Br 14.59; N 5.08. $\text{C}_{31}\text{H}_{23}\text{BrN}_2\text{O}_2$. Calculated, %: C 69.53; H 4.30; Br 14.95; N 5.23.

Ethyl 3-(*p*-fluorophenyl)-1-(2-quinolyl)-3,4-dihydrobenzo[*f*]quinoline-2-carboxylate (XVc). Yield 34%, mp 131–132°C. UV spectrum, λ_{max} , nm (log ϵ): 208 (4.62), 235 (4.56), 266 (4.40), 315 (3.88), 373 (3.15). ^1H NMR spectrum, δ , ppm: 1.07 t, 4.01 q (5H, OEt,

2J 14.0, 3J 6.02 Hz), 4.90 br.s (1H, NH), 5.95 C (1H, H^3), 6.82–8.05 m ($16H_{\text{arom}}$). Found, %: N 5.73. $C_{31}H_{23}FN_2O_2$. Calculated, %: N 5.91.

Ethyl 3-phenyl-1-(2-quinolyl)benzo-[f]quinoline-2-carboxylate (XVIa). An equimolar mixture (5 mmol each) of azomethine **Ia** and ester **IV** in 5 ml of DMF and 1 ml of concn. HCl was heated in a sealed ampule for 3 h at 100°C. The tarry mass obtained was kept in air for 48 h, treated with aqueous NH_4OH , ground with 2-propanol, and recrystallized from ethanol. Yield 26%, mp 187–188°C. UV spectrum, λ_{max} , nm (log ϵ): 209 (4.70), 217 (4.69), 234 (4.69), 279 (4.78), 318 (4.10), 347 (3.66), 361 (3.61). 1H NMR spectrum, δ , ppm: 1.12 t, 4.05 q (5H, OEt, 2J 14.0, 3J 6.1 Hz), 6.77–8.11 m ($17H_{\text{arom}}$). Found, %: C 81.75; H 4.58; N 6.02. $C_{31}H_{22}N_2O_2$. Calculated, %: C 81.94; H 4.85; N 6.17.

Ethyl 3-aryl-2-(quinoline-2-carbonyl)acrylates XVIb, XVIId, and XVIIe were obtained by procedures described for compounds **XIVb–XIVd** and **XVa–XVc** by evaporating the mother liquors after isolating precipitates of benzo[f]quinolines **XIVb**, **XIVd**, and **XVb** for esters **XVIb** and **XVIId** and by evaporating the reaction mixture by 1/3 of volume for compound **XVIIe**. The tarry residues of esters **XVIb** and **XVIId** and the precipitate of the methoxy derivative **XVIIe** were treated with aqueous NH_4OH , 2-propanol, and recrystallized from ethanol (compounds **XVIb** and **XVIIe**) or nitromethane (nitroester **XVIId**).

Ethyl 3-(p-bromophenyl)-2-(quinoline-2-carbonyl)-acrylate (XVIIb). Yield 11%, mp 149–150°C. UV spectrum, λ_{max} , nm (log ϵ): 210 (4.43), 253 (4.51), 273 (4.46), 270 (4.39), 329 (4.20). 1H NMR spectrum, δ , ppm: 1.15 t, 4.08 q (5H, OEt, 2J 14.1, 3J 6.0 Hz), 6.83–8.22 m (12H, $10H_{\text{arom}}$, CH=CH). Found, %: C 61.29; H 3.63; Br 19.11; N 3.26. $C_{21}H_{16}BrNO_3$. Calculated, %: C 61.46; H 3.90; Br 19.51; N 3.41.

Ethyl 3-(p-nitrophenyl)-2-(quinoline-2-carbonyl)-acrylate (XVIIId). Yield 14%, mp 179–180°C. UV spectrum, λ_{max} , nm (log ϵ): 213 (4.41), 255 (4.49), 272 (4.23), 326 (4.16). 1H NMR spectrum, δ , ppm: 1.19 t, 4.10 q (5H, OEt, 2J 14.2, 3J 6.1 Hz), 7.22–8.44 m (12H, $10H_{\text{arom}}$, CH=CH). Found, %: C 66.84; H 4.20; N 7.33. $C_{21}H_{16}N_2O_5$. Calculated, %: C 67.02; H 4.26; N 7.45.

Ethyl 3-(p-methoxyphenyl)-2-(quinoline-2-carbonyl)acrylate (XVIIe). Yield 54%, mp 101–102°C. UV spectrum, λ_{max} , nm (log ϵ): 211 (4.40), 254 (4.50), 238 (4.65), 274 (4.43), 336 (4.21). 1H NMR spectrum, δ , ppm: 1.16 t, 4.04 q (5H, OEt, 2J 14.1, 3J 6.0 Hz), 3.70 s (3H, OMe), 6.60–7.98 m (12H, $10H_{\text{arom}}$, CH=CH).

Found, %: C 73.01; H 5.08; N 3.63. $C_{22}H_{19}NO_4$. Calculated, %: C 73.13; H 5.26; N 3.88.

Ethyl 3-(2-naphthylamino)-2-nicotinoyl-3-phenylpropanoate (XVIII). A mixture of 10 mmol of azomethine **Ia**, 12.5 mmol of ester **V**, and 30 ml of ethanol was heated on a water bath at 40–60°C for 30 min. The precipitate separated on cooling was filtered off and recrystallized from 2-propanol. Yield 97%, mp 101–102°C. UV spectrum, λ_{max} , nm (log ϵ): 232 (4.62), 248 (4.70), 271 (4.46), 318 (4.20). 1H NMR spectrum, δ , ppm: 1.12 t, 4.00 q (5H, OEt, 2J 14.0, 3J 6.0 Hz), 4.70 d (1H, H^3 , 3J 9.3 Hz), 5.42 d (1H, H^2 , 3J 9.3 Hz), 5.60 br.s (1H, NH), 6.73–8.58 m ($16H_{\text{arom}}$). Found, %: C 76.41; H 5.66; N 6.60. $C_{27}H_{24}N_2O_3$. Calculated, %: C 76.19; H 5.52; N 6.36.

Ethyl 3-phenyl-1-(3-pyridyl)benzo[f]quinoline-2-carboxylate (XX). A mixture of 5 mmol of aminoester **XVIII**, 30 ml of ethanol, 0.5 ml of concn. HCl, and 0.5 ml of nitrobenzene was heated in a sealed ampule for 12 h at 100°C. The reaction mixture was evaporated to 1/4 of volume, the tarry residue was treated with alcoholic NH_4OH , with water, dried, and ground with 2-propanol. The precipitate of reaction product was filtered off and recrystallized from ethanol. Yield 30%, mp 151–152°C. UV spectrum, λ_{max} , nm (log ϵ): 234 (4.42), 250 (4.40), 282 (4.67), 353 (3.77), 374 (3.72). 1H NMR spectrum, δ , ppm: 1.19 t, 4.10 q (5H, OEt, 2J 14.1, 3J 6.1 Hz), 6.79–8.60 m ($15H_{\text{arom}}$). Found, %: C 80.43; H 5.11; N 6.31. $C_{27}H_{20}N_2O_2$. Calculated, %: C 80.57; H 5.26; N 6.48.

3-Oxo-3-(3-pyridyl)propanoic acid N-(2-naphthyl)amide (XXI). In 20 ml of toluene containing 5 drops of piperidine was boiled for 3 h 5 mmol of amine ketoester **XVIII** or a mixture of 10 mmol of azomethine **Ia** and 12.5 mmol of ester **V**. The precipitate separated on cooling was filtered off and recrystallized from 2-propanol. Yield 18% from ester **XVIII** and 36% from reagents mixture **Ia** and **V**, mp 170–171°C. UV spectrum, λ_{max} , nm (log ϵ): 216 (4.76), 245 (4.82), 278 (4.46), 330 (4.50). 1H NMR spectrum, δ , ppm: 5.22 s (2H, CH_2), 6.38 br.s. (1H, NH), 7.41–8.51 m ($11H_{\text{arom}}$). Found, %: C 74.25; H 4.81; N 9.53. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.46; H 4.87; N 9.65.

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