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Dedicated to Full Member of the Russian Academy of Sciences
I.P. Beletskaya on occasion of her jubilee

Features of Reactions of Polyfluorinated Ethyl 4-Oxo-2-pnenyl-4*H*-chromene-3-carboxylates with *N*-Nucleophiles

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Abstract—Ethyl 5,6,7,8-tetrafluoro-4-oxo-2-phenyl-4H-chromene-3-carboxylate in reactions with primary amines is characterized by a chromone-coumarin rearrangement affording 3-[amino(phenyl)methylene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-diones, and ethyl 4-oxo-2-phenyl-5,6,7,8-tetrafluoro-4*H*-chromene-3-carboxylate characteristically adds the amine at the C^2 site of the flavone furnishing 3-amino-3-phenyl-2-(2,3,4,5-tetrafluoro-6-hydroxybenzoyl)acrylates which depending on the substituent at the amino group are capable of intramolecular cyclization into 3-[(alkylamino)(phenyl)methylene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione or in the case of benzylamine substituent, into ethyl 1-benzyl-5-hydroxy-4-oxo-2-phenyl-6,7,8-trifluoro-1,4-dihydroquinoline-3-carboxylate. The main process in the reaction of tri- and tetrafluoroflavones with secondary amine (1-methylpiperazine) is the nucleophilic substitution at the C^7 of flavone. In the reaction with 1,2-phenylenediamine 3-[(2-aminophenyl)amino]-3-phenyl-2-(2,3,4,5-tetrafluoro-6-hydroxybenzoyl)acrylate was obtained from tetrafluoroflavone and 1*H*-benzimidazol-2-yl(3,4,5-trifluoro-2-hydroxyphenyl)methanone, from trifluoroflavone.

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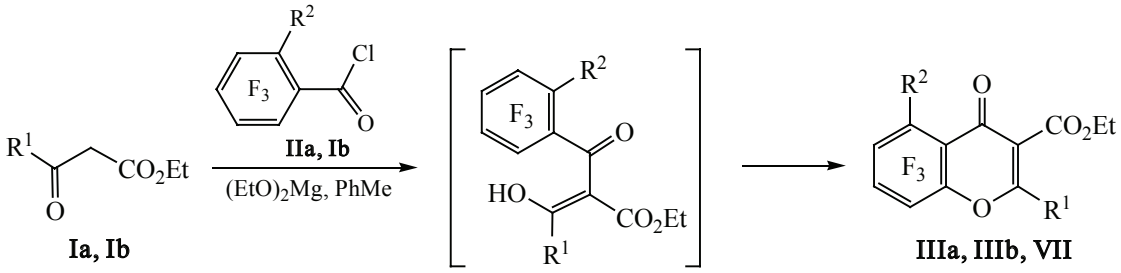
Flavones belong to an important class of heterocycles of the chromen-4-ones series that besides the versatile biological activity are attractive as objects for chemical modification [1, 2]. Both to flavones and 2-unsubstituted chromones and their methyl analogs are characteristic the reactions of pyrone ring opening under the action of amines leading to 1,3-aminoenones. The presence of an alkoxycarbonyl substituent in the position *3* of chromen-4-one provides a possibility of subsequent cyclization of 1,3-aminoenones into 3-substituted 4-hydroxycoumarins [3, 4]. The most versatile reactivity in reactions with nucleophiles was exhibited by ethyl 2-methyl-4-oxo-5,6,7,8-tetrafluoro-4*H*-chromene-3-carboxylate. It reacted with primary amines with the opening of the heterocycle giving ethyl 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)but-2-enoates and (or) their cyclic derivatives, *N*-substituted 4-hydroxy-5,6,7,8-tetrafluoro-3-ethanimidoylcoumarins [4, 5]. Its reactions with secondary amines occur with the retention of the pyrone ring and the formation of 7-substituted chromones [4], at the use of S-nucleophiles three fluorine atoms at C^5, C^7, and C^8 are substituted [6]. At the action of the α-dinucleophiles the pyrone ring undergoes the opening leading to the formation of substituted azoles which may suffer cyclization into azolocoumarins [4].

The goal of this work was the study of the features of the conversions of polyfluorinated ethyl 4-oxo-2-phenyl-4*H*-chromene-3-carboxylates under the action of *N*-mononucleophiles.

Ethyl 6,7,8-tri- and 6,7,8-tetrafluoroflavone-3-carboxylates **IIIa, IIIb** were obtained by one-pot synthesis via the acylation of benzoylacetic ester (**Ia**) with tetra- and pentafluorobenzoyl chlorides **IIa, IIb** in the presence of magnesium ethylate (Scheme 1) along procedure [7, 8]. The formation of flavones **IIIa, IIIb**

Scheme 1.



R^1 = Ph (**Ia**); R^2 = H (**IIa, IIIa**), F (**IIb, IIIb**); R^1 = Me (**Ib**), R^2 = H (**VII**).

is due to the ease and irreversibility of the cyclization of the formed *in situ* and nonisolable 3-hydroxy-3-phenyl-2-(polyfluorobenzoyl)acrylates resulting from the intramolecular nucleophilic substitution reaction of the ortho-fluorine atom in the polyfluorophenyl ring for a hydroxy group [7–10].

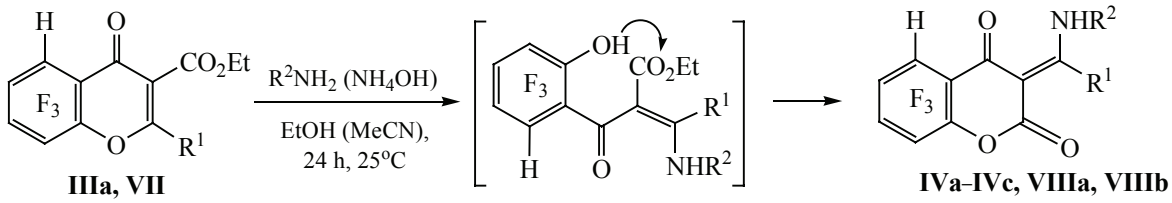
The ethyl 2-methyl-4-oxo-5,6,7,8-tetrafluoro-4*H*-chromene-3-carboxylate in reactions with primary amines (methylamine, benzylamine) and ammonium hydroxide in mild conditions characteristically suffered an opening of the pyrone ring to give a mixture of 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)but-2-enoates and the products of their intramolecular condensation, 3-(1-aminoethylidene)-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-diones [4, 5].

We found that the reactions of trifluoro-substituted flavone **IIIa** with the same amines at room temperature did not stop at the stage of the pyrone ring opening and the corresponding enamioesters formation, but results in the cyclization products of the latter, 3-[amino(phenyl) methylene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-diones **IVa–IVc** due to the chromone-coumarin rearrangement (Scheme 2).

Unlike trifluoro-containing analog **IIIa** the tetrafluoroflavone **IIIb** under similar conditions reacted with ammonium hydroxide, benzyl-, hexyl, and cyclohexylamines with the formation exclusively of the products of the opening of the pyrone ring, 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylates **Va**, **Vc–Ve** (Scheme 3). However from the reaction products of flavone **IIIb** with hexyl- and cyclohexylamines alongside esters **Vd, Ve** after stirring for 24 h in ethanol we isolated coumarins **VId, VIe** as minor components (10–15%). A selective synthesis of these coumarins was performed by heating. The one-pot preparation of coumarin **VIa** from tetrafluoroflavone **IIIb** is only possible at carrying out the reaction with ammonium chloride in anhydrous ethanol in the presence of sodium hydrogen carbonate at heating. We failed to obtain [(benzylamino)(phenyl) methylidene]-substituted coumarin **VIc** from flavone **IIIb** and benzylamine.

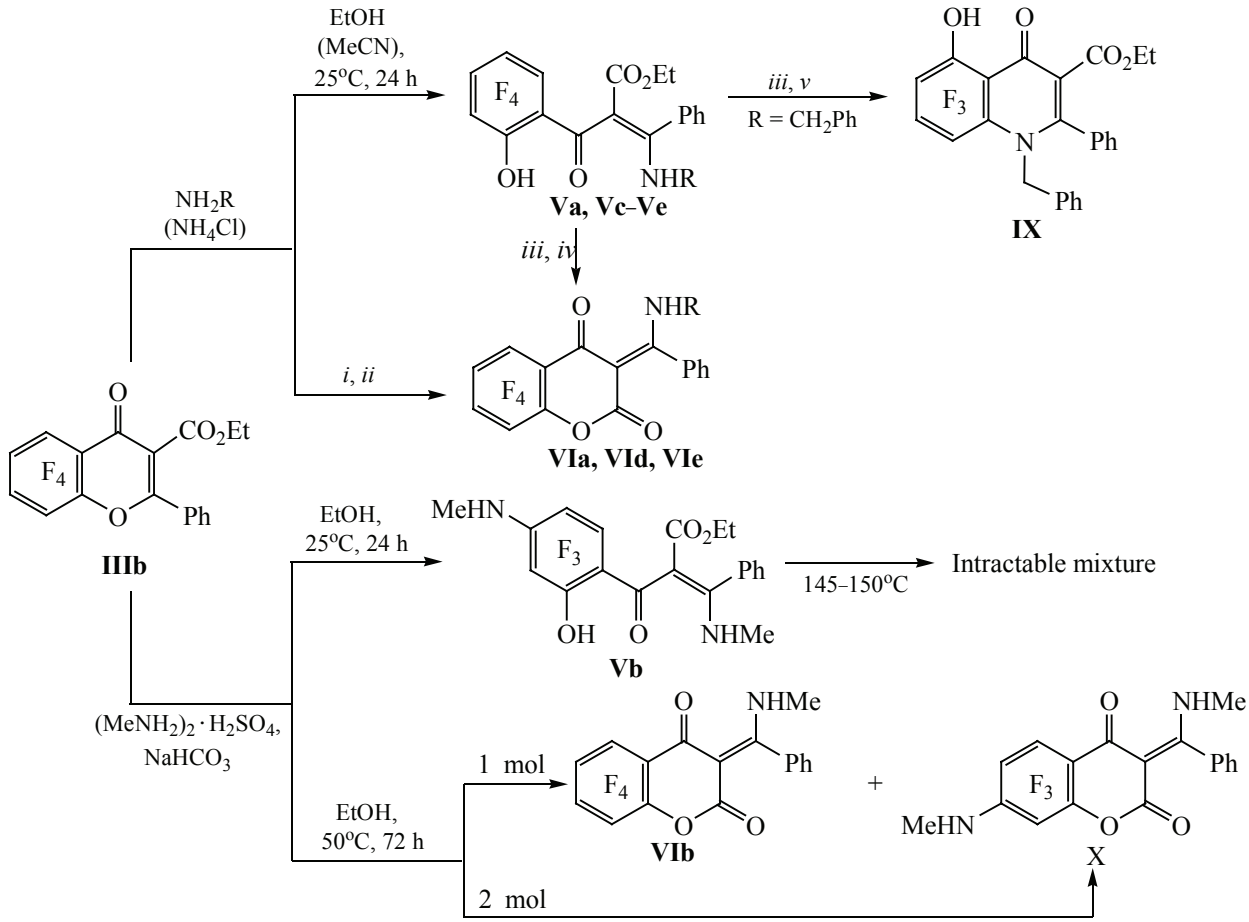
At vigorous stirring at room temperature of a mixture of flavone **IIIb** even with equimolar amount of methylamine sulfate in ethanol in the course of 24 h we obtained ethyl 2-[2-hydroxy-4-(methylamino)-3,5,6-trifluorobenzoyl]-3-(methylamino)-3-phenylacrylate (**Vb**), formed as a result of two parallel reactions: the nucleophilic addition of the amine to the atom C^2 and the nucleophilic substitution of a fluorine atom at the atom C^7 of flavone (Scheme 3). The reaction in ethanol at heating carried out for 72 h led to the formation of a

Scheme 2.



R^1 = Ph (**IIIa**, **IVa–IVc**); R^2 = H (**IVa**), Me (**IVb**), $PhCH_2$ (**IVc**); R^1 = Me (**VII, VIIIa, VIIIb**), R^2 = H (**VIIIa**), Me (**VIIIb**).

Scheme 3.



R = H (**Va, VIa**), $PhCH_2$ (**Vc**), C_6H_{13} (**Vd, VId**), cyclo-C_6H_{11} (**Ve, VIe**); *i*: NH_4Cl–anhydr. EtOH, $NaHCO_3$, 50°C, 24 h; *ii*: NH_2R–EtOH, 50°C, 24 h; *iii*: $(AcO)_2Ni$, EtOH, 25°C, 24 h; *iv*: 120–125°C, 1 h; *v*: 175–180°C, 1 h.

mixture of coumarins **VIb, X** in approximately equal amounts. The use under these conditions of excess of the methylamine salt made it possible to obtain as a single reaction product 7-(methylamino)-3-[(methylamino)(phenyl)methylidene]-5,6,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (**X**).

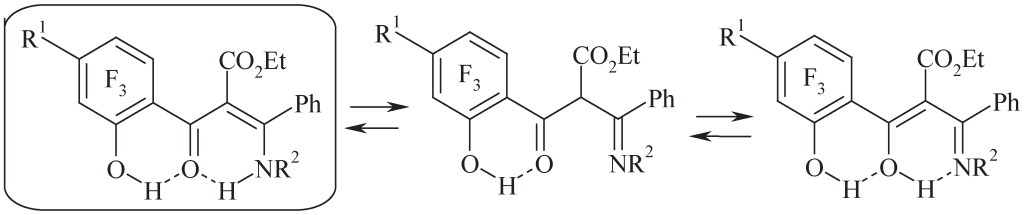
The attempts to bring into the reaction with flavones **IIIa, IIIb** the aromatic amines (aniline and *p*-anisidine) were unsuccessful, even after long boiling in ethanol or acetonitrile only the initial heterocycles were isolated. The capability of aliphatic amines in contrast to aromatic amines to react with flavones **IIIa, IIIb** is due to the higher nucleophilicity of the former which correlates with the basicity.

3-Amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylates **Va–Ve** may be liable to keto-enol and imino-enamine tautomerism, therefore they may exist in three tautomeric forms (Scheme 4).

However in the ^1H and ^{19}F NMR spectra of compounds **Va–Ve** in $(CD_3)_2SO$ a set of signals of a single tautomeric form is observed. The presence in the downfield part of ^1H NMR spectra of two or three proton signals from the protons of hydroxy and amino groups alongside the absence of the methine proton signal allows the exclusion of the keto-imine form. It is not possible to choose between the remaining tautomeric forms due to the scanty information contained in the spectral data. However the literature data suggest the preferred existence of the enamino-ketone form in similar systems [4, 5].

The preferred formation of 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylates **Va–Ve** in the reactions of tetrafluoroflavone **IIIb** with primary amine as compared with the transformations of trifluoroflavone **IIIa** leading under similar conditions to

Scheme 4.



R^1 = F, R^2 = H (**Va**), CH_2Ph (**Vc**), Hex (**Vd**), *cyclo*-Hex (**Ve**); $R^1 = R^2$ = NHMe (**Vb**).

the products of further cyclization, coumarins **IVa**–**IVc**, is apparently caused by the higher acidity of the hydroxy group in the intermediate enaminoesters **Va–Ve** due to the combined effect of the four fluorine atoms. Owing to the increased acidity of the hydroxy group in the tetrafluorophenyl substituent the esters **Va–Ve** may exist in the form of internal salts whose cyclization requires more severe conditions.

Evidently the fluorine substitution observed in the reaction with the highly nucleophilic methylamine is also due to the higher electrophilicity of the tetrafluorinated benzene ring of flavone **IIIb**.

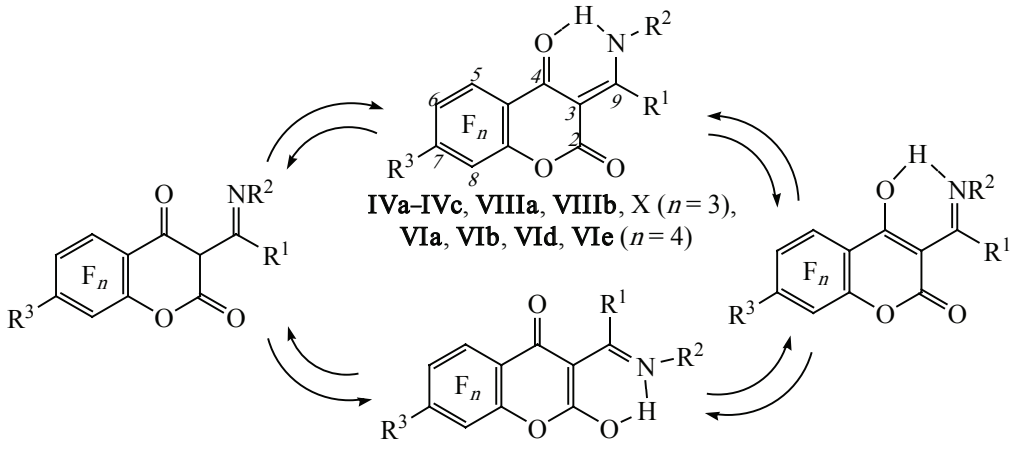
We studied for comparison the reactions of 2-methyl-4-oxo-6,7,8-trifluoro-4*H*-chromene-3-carboxylate (**VII**) (Scheme 1) with ammonium hydroxide and methylamine. It turned out that in these reaction the only separable products were 3-(1-aminoethylidene)-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-diones **VIIIa, VIIIb** (Scheme 2). This fact proves the effect of the fluorine atoms in the benzene ring on the recyclization process: tetrafluoro-substituted analog of chromone **VII** afforded under these conditions a mixture of the products of ring opening and recyclization [4, 5].

The heterocyclic compounds **IVa–IVc, VIa, VIb, VId, VIe, VIIIa, VIIIb, X** are prototropic systems having three functional groups in their composition (at atoms C^2, C^4, and C^9) capable of participation in keto-enol and imino-enamine transformations, therefore four tautomeric forms are expectable (Scheme 5).

According to XRD data compound **VIa** exists in the crystal as a crystal solvate of 3-[amino-(phenyl) methylidene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione with an ethanol molecule (Fig. 1). The carbonyl atom O^3 and the atom H^{1A} of the amino group are linked by an intramolecular hydrogen bond [$O^3\cdots H^{1A}$ 1.83(2), $O^3\cdots N^1$ 2.596(3) Å; $N^1H^{1A}O^3$ 139(2), $H^{1A}O^3C^4$ 101.2(7)°]. The chromene fragment of molecule **VIa** is practically flat. The greatest deflection from the plane going through the carbon atoms of the fluoroaromatic ring is the position of the lactone atom C^2 (0.115 Å).

The unit cell of coumarin **VIa** crystal is formed of two molecules placed antiparallel one over another. In the molecular packing layers form by the *ABAB* type owing to shortened intermolecular contacts between atoms $C^{8a}\cdots O^2$

Scheme 5.



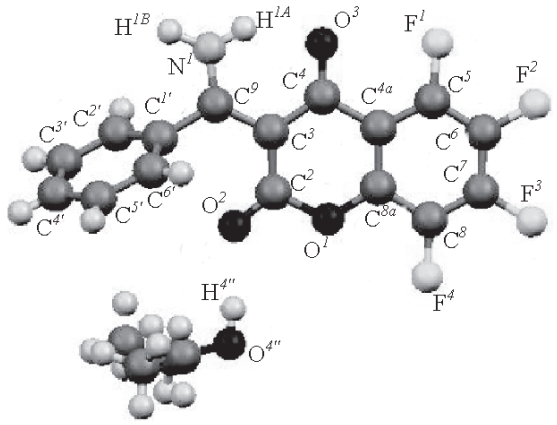


Fig. 1. Structure of 3-[amino(phenyl)methylidene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione (**VIa**) crystal solvate according to XRD data.

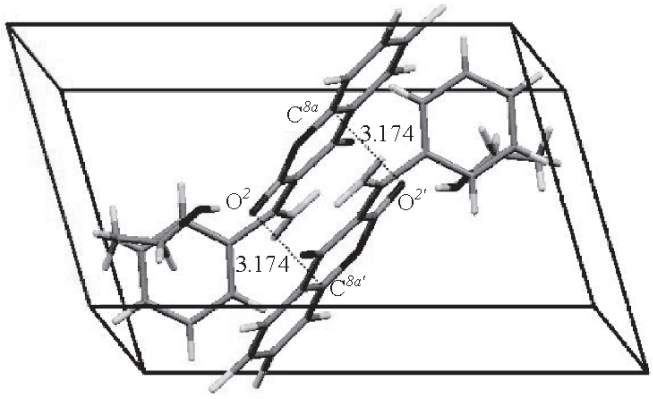


Fig. 2. Unit cell of the crystal of coumarin **VIa** according to XRD data.

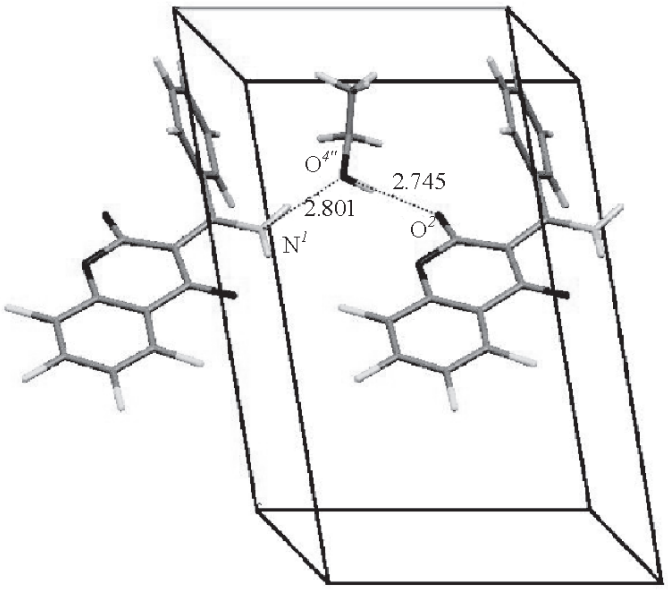


Fig. 3. Stabilization of coumarin **VIa** molecules in a layer.

of two contiguous molecules [3.174(3) Å] (Fig. 2).

Within the layer the molecules of coumarin **VIa** are stabilized by ethanol molecules due to the formation of the intermolecular hydrogen bonds. The distances $O^{2}\cdots O^{4''}$ and $N^{1}\cdots O^{4''}$ are 2.745(2) and 2.801(3) Å (Fig. 3). The hydrogen atoms involved in the formation of the hydrogen bonds are present materially on the line connecting the atoms of the corresponding intermolecular contacts, angles $N^{1a}HO^{4''}$ and $O^{2}HO^{4''}$ equal respectively 168(2) and 174.9(1) deg.

The comparative analysis of IR spectra of compounds **IVa–IVc, VIa, VIb, VId, VIe, VIIIa, VIIIb, X** did not reveal essential difference in their structure. The characteristic absorption bands for these heterocycles are those of the lactone carbonyl group (1736–1705 cm^{-1}), of γ-carbonyl group involved in the intramolecular hydrogen bond (1648–1604 cm^{-1}), and of the stretching vibrations of the amino group (3418–3029 cm^{-1}).

The ^{1}H, ^{19}F NMR spectra of compounds **IVa–IVc, VIa, VIb, VId, VIe, VIIIa, VIIIb, X** in $(CD_3)_2SO$ are characterized by a single set of signals indicating the presence of one tautomer. The lack of the signals of methine proton attached to the atom C^{3} allows the exclusion from the consideration of the diketoimine form. The downfield shifts of the protons of hydroxy and amino groups of the alternative tautomers confirm their involvement into the intramolecular hydrogen bond.

The ^{13}C NMR spectrum of compound **IVa** in $(CD_3)_2SO$ proved to be more informative. It indicated the presence of lactone C^{2} (δ 159.87 ppm), ketone C^{4} (δ 176.75 ppm), and enamine C^{9} (δ 175.89 ppm) carbon atoms. The chemical shifts of the atoms C^{2}, C^{4}, and C^{9} decisive for the structure of coumarin **IVa** coincide completely with the shifts of these atoms in the previously obtained and extensively characterized methyl analogs, 3-(1-aminoethylidene)- and 3-[1-(methylamino) ethylidene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-diones [12, 13].

The combined spectral data make it possible to conclude on the common property of the 4-hydroxypolyfluorocoumarins containing in the position C^{3} alkylamino(phenyl)methylidene substituent consisting in the capability to exist in the diketoenamine tautomeric form 2*H*-chromene-2,4(3*H*)-diones independent of the number

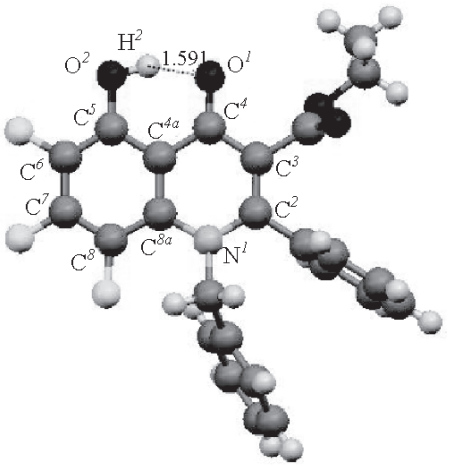
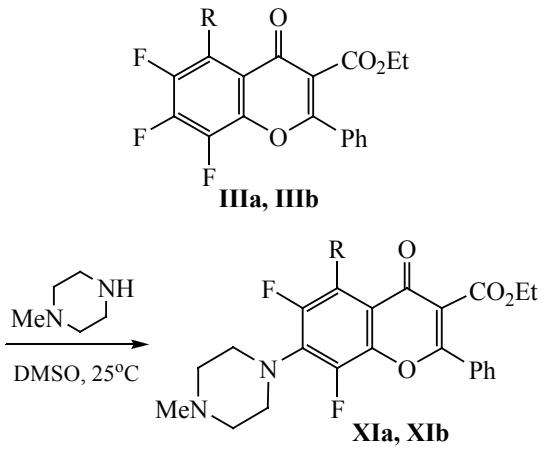


Fig. 4. Structure of ethyl 1-benzyl-5-hydroxy-4-oxo-2-phenyl-6,7,8-trifluoro-1,4-dihydroquinoline-3-carboxylate (**IX**) according to XRD data.

Scheme 6.



R = H (**a**), F (**b**).

of the fluorine atoms in the aromatic ring.

We attempted to bring 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylates **Va–Vc** into the cyclization. In the enaminoesters obtained from 2-methyl-4-oxo-5,6,7,8-tetrafluoro-4*H*-chromene-3-carboxylate and primary amines are characteristic of the thermal cyclization into 3-(1-aminoethylidene)-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-diones occurred at their melting point [4]. The cyclization of esters **Va–Vc** was carried out at temperatures close to their melting points: 120–125 (**Va**), 145–150 (**Vb**), 175–180°C (**Vc**).

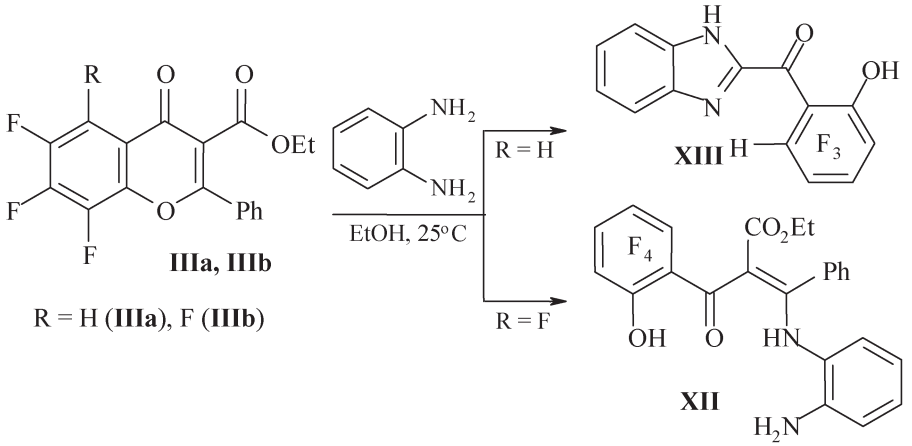
Enaminoester **Va** under the conditions of the thermal cyclization afforded coumarin **VIa** (Scheme 3) due to the intramolecular condensation involving hydroxy groups of the benzoyl fragment and ethoxycarbonyl substituent with ethanol elimination. Enaminoester **Vb** at 145–150°C furnished an intractable mixture of substances. Enaminoester **Vc** instead of giving the expected 3-[(benzylamino)(phenyl)methylidene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione suddenly suffered the cyclization at 175–180°C into quinolone **IX** (Scheme 3) resulting from the nucleophilic substitution of the *ortho*-fluorine atom for an amino group with hydrogen fluoride liberation. However the thermal cyclization of ester **Vc** into quinolone **IX** is not selective and is accompanied with the formation of intractable side products. The cyclization can be performed better at milder conditions: in ethanol, at room temperature, in the presence of nickel(II) acetate tetrahydrate. Apparently ester **Vc** forms with the nickel cation an intermediate complex compound where the hydroxy group involved in the condensation with the ethoxycarbonyl substituent in the course of coumarin formation is blocked due to the covalent bonding to the metal, and the cyclization occurs by the alternative route through the fluorine substitution.

We tried to extend the discovered effect of the metal complex catalysis to the cyclization of enaminesters **Va, Vb, Vd, Ve**. However in the presence of nickel(II) acetate tetrahydrate we obtained only the corresponding coumarins **VIa, VIb, VId, VIe** formed by intramolecular condensation.

The structure of quinolone **IX** was proved by XRD analysis (Fig. 4), according to which the compound in the crystal existed as ethyl 1-benzyl-5-hydroxy-4-oxo-2-phenyl-6,7,8-trifluoro-1,4-dihydroquinoline-3-carboxylate. In the molecule of compound **IX** an intramolecular hydrogen bond is present between atoms O^1 of the carbonyl group and H^2 of the hydroxy group of quinoline [$O^1\cdots H^2$ 1.59(2), $O^1\cdots O^2$ 2.500(1) Å; $O^2H^2O^1$ 155(1), $H^2O^1C^4$ 99.7(6)°]. The quinoline fragment of the molecule **IX** is virtually planar, the strongest deflection from the plane going through the carbon atoms of the fluoroaromatic ring is observed for the atoms C^2 and C^3 (0.190 and 0.243 Å). Practically normal to this plane are located the benzene rings at the atoms N^1 and C^2 of the quinolone moiety.

The conversion of enaminoester **Vc** (and only this one) into quinolone **IX** is found for the first time. The possibility of cyclization through intramolecular nucleophilic substitution exists only for tetrafluoro-substituted esters possessing an *ortho*-fluorine. This cyclization

Scheme 7.



occurs only in ester **Vc** containing two closely situated bulky phenyl substituents. These groups probably due to the steric hindrances take a position which favors an increased nucleophilicity of the amino group involved into the cyclization.

With the secondary amine (*1*-methylpiperazine) flavones **IIIa, IIIb** react analogously to ethyl 2-methyl-4-oxo-5,6,7,8-tetrafluorochromene-3-carboxylate forming in DMSO at room temperature the polyfluorinated 7-(4-methylpiperazin-1-yl)-4-oxo-2-phenyl-4*H*-chromene-3-carboxylates **XIa, XIb** through a nucleophilic aromatic substitution of the fluorine atom in the position C^7 of the flavone (Scheme 6).

However in the reaction with 1,2-phenylenediamine flavones **IIIa, IIIb** exhibit different reactivities. The tetrafluoroflavone **IIIb** yielded ethyl 3-[(2-aminophenyl) amino]-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylate (**XII**) (Scheme 7) resulting from the opening of the pyrone ring at the addition of the amine to the atom C^2 of the flavone. Just in this way flavone **IIIb** reacted with primary monoamines (Scheme 3). The attempts to force ester **XII** into cyclization under heating or acid catalysis provided intractable mixture of substances.

The reaction of flavone **IIIa** with 1,2-phenylenediamine under the same conditions led to the formation of a mixture of compounds from which we succeeded to isolate only 1*H*-benzimidazol-2-yl(2-hydroxy-3,4,5-trifluorophenyl)methanone (**XIII**) (Scheme 7). Obviously compound **XIII** results from the decomposition of the intermediately formed enaminoester. The structure of compound **XIII** is confirmed by the mass spectrum where the maximum registered peak corresponded to the dideprotonated molecular ion $[M - 2H]^+$, *m/z* 290.

Thus we discovered the characteristic features of the reactions of polyfluorinated flavones **IIIa, IIIb** with amines. The reaction with primary amines of both trifluoroflavone **IIIa** and trifluorochromone **VII** is characterized by the chromone–coumarin rearrangement to form in mild conditions coumarins **IVa–IVc**. Tetrafluoroflavone **IIIb** in similar conditions only adds amine to the atom C^2 resulting in the opening of the pyrone ring and in the formation of enaminoesters **Va–Ve**. The reduced ability of tetrafluoroflavone **IIIb** to reciclization in coumarins **VI** is apparently due to the higher acidity of the hydroxy group of the tetrafluorophenyl substituent in the intermediate enaminoesters **V**. It was found for the first time that enaminoesters **V** depending on the substituent at the amino group are capable of intramolecular cyclization forming not only coumarins **VI**, but in the case of a benzyl substituent, quinolone **IX**. However in the reaction with the secondary amine (1-methylpiperazine) tri- and tetrafluoroflavones **IIIa, IIIb** demonstrated the same reactivity as previously studied tetrafluorochromones [4, 5]. This is evidently due to the steric factors impeding the attack of the secondary amino group on the atom C^2. Methylamine, combining the high basicity with a small size of the molecule is able to react simultaneously in both directions.

EXPERIMENTAL

Melting points have been measured on an instrument Stuart SMP3 in open capillaries and are reported without correction. IR spectra were recorded on a spectrometer Perkin Elmer Spectrum One using Diffuse Reflection Accessory (DRA) in the range 4000–400 cm^{-1}. NMR spectra

were registered on a spectrometer Bruker DRX-400 (^{1}H: 400 MHz with respect to $SiMe_4$; ^{19}F: 376.4 MHz relative to C_6F_6) $(CD_3)_2SO$. Mass spectrum of compound **XIII** was taken on an instrument Agilent GC 7890A MS 5975C (EI). Single crystals of compounds **VIa, IX** were obtained by crystallization from ethanol. XRD experiment was performed on a diffractometer Xcalibur 3 equipped with a CCD-detector [graphite monochromator, $\lambda(MoK_\alpha)$ 0.71073 E, 293(2) (**VIa**), 150(2) K (**IX**), ω-scanning] (see the table). The extinction was accounted for analytically along the model of multifacet crystal using the program CrysAlis RED v.1.171.29.9. The structure was solved by the direct method from the difference Fourier syntheses. The positions and the thermal parameters of the nonhydrogen atoms were refined by least-squares method in the full-matrix anisotropic approximation. Elemental analysis was carried out on an analyzer Perkin Elmer PE 2400 series II CHNS-O EA 1108. For TLC were used ALUGRAM® SIL G/ UV_{254} plates.

Flavones (IIIa, IIIb, VII). To 1.2 g (50 mmol) of magnesium turnings several iodine crystals were added. The flask was heated till vigorous iodine sublimation, then 3 ml of anhydrous ethanol was added dropwise and several drops of tetrachloromethane. At the beginning of the intensive self-heating of the reaction mixture 20 ml of anhydrous toluene and 3 ml of anhydrous ethanol was added. Then 50 mmol of ester **Ia, Ib** in 20 ml of anhydrous toluene was added dropwise. The reaction mixture was maintained till complete dissolution of the magnesium turnings and cooled to room temperature. At stirring the equimolar amount of polyfluorobenzoyl chloride **IIa, IIb** in 20 ml of anhydrous toluene was added dropwise. The reaction mixture was stirred for 6 h. On the completion of the reaction the reaction mixture was poured into ice-cold H_2SO_4 solution (50 ml, 10 wt%), toluene layer was separated and dried with Na_2SO_4. Toluene was distilled off in a vacuum, the residue was crystallized from ethanol.

Ethyl 4-oxo-2-phenyl-6,7,8-trifluoro-4*H*-chromene-3-carboxylate (IIIa). Yield 11.493 g (66%), colorless powder, mp 114°C. IR spectrum, ν, cm^{-1}: 1732 (CO_2Et), 1653, 1638 (C=O), 1589, 1568, 1521, 1484, 1447 (C=C), 1109, 1083 (CF). ^{1}H NMR spectrum, δ, ppm: 1.10 t (3H, $\underline{CH_3}CH_2$, ^3J 7.1 Hz), 4.20 q (2H, $CH_3\underline{CH_2}$, ^3J 7.1 Hz), 7.59–7.75 m (5H, C_6H_5), 7.90 m (1H, H^5). ^{19}F NMR spectrum, δ, ppm: 11.44 m, 12.84 m, 26.60 m (1F each). Found, %: C 61.83; H 2.92; F 16.86. $C_{18}H_{11}F_3O_4$. Calculated, %: C 62.08; H 3.18; F 16.36.

Ethyl 4-oxo-2-phenyl-5,6,7,8-tetrafluoro-4*H*-chromene-3-carboxylate (IIIb). Yield 12.819 g (70%), colorless powder, mp 111°C. IR spectrum, ν, cm^{-1}: 1735 (CO_2Et), 1650 (C=O), 1594, 1573, 1522, 1498, 1447 (C=C), 1122, 1112 (CF). ^{1}H NMR spectrum, δ, ppm: 1.11 t (3H, $\underline{CH_3}CH_2$, ^3J 7.1 Hz), 4.21 q (2H, $CH_3\underline{CH_2}$, ^3J 7.1 Hz), 7.60–7.73 m (5H, C_6H_5). ^{19}F NMR spectrum, δ, ppm: 1.41 m, 4.39 m, 14.69 m, 18.43 m (1F each). Found, %: C 58.88; H 2.76; F 20.69. $C_{18}H_{10}F_4O_4$. Calculated, %: C 59.03; H 2.75; F 20.75.

Ethyl 2-methyl-4-oxo-6,7,8-trifluoro-4*H*-chromene-3-carboxylate (VII). Yield 9.731 g (68%), colorless powder, mp 100°C. IR spectrum, ν, cm^{-1}: 1723 (CO_2Et), 1634 (C=O), 1592, 1522, 1481 (C=C), 1121, 1087 (CF). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, $\underline{CH_3}CH_2$, ^3J 7.1 Hz), 2.51 s (3H, CH_3), 4.33 q (2H, $CH_3\underline{CH_2}$, ^3J 7.1 Hz), 7.83 m (1H, H^5). ^{19}F NMR spectrum, δ, ppm: 11.11 m, 12.45 m, 26.23 m (1F each). Found, %: C 54.19; H 2.79; F 20.37. $C_{13}H_9F_3O_4$. Calculated, %: C 54.56; H 3.17; F 19.91.

Reaction of flavones IIIa, IIIb and chromone VII with amines. To a solution of 1 mmol of compound **IIIa, IIIb, VII** in 15 ml of an appropriate solvent was added 1 mmol of amine (or 1 mmol of methylamine sulfate at the preparation of ester **Vb**, coumarins mixture **VIb, VII**, 2 mmol for the synthesis of coumarin **X**). Ethanol or acetonitrile were used in the syntheses of compounds **Va–Ve, XII, VIa, VIb, VId, VIe, X, XIII**, DMSO, for preparation of chromones **XIa, XIb**. The reaction mixture was vigorously stirred for 24 h at 25°C (at the synthesis of compounds **Va–Ve, XII, IVa–IVc, VIIIa, VIIIb, XIa, Xb, XIII**) or at 50°C (at the synthesis of coumarins **VIa, VIb, VId, VIe, X**). The reaction progress was monitored by TLC. The solvent was distilled off, the solid residue was crystallized from an appropriate solvent.

The mixtures of esters **Vd, Ve** or coumarins **VId, VIe**, and also the mixture of coumarins **VIb, X** were separated by column chromatography, eluent chloroform.

3-[Amino(phenyl)methylidene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (IVa). Yield 0.185 g (58%), colorless powder, mp 214–217°C (from ethanol). IR spectrum, ν, cm^{-1}: 3292 (NH_2), 1712 (O–C=O), 1630 (C=O), 1599, 1520, 1482, 1450, 1435 (C=C, NH_2), 1017, 1000, 989 (CF). ^{1}H NMR spectrum, δ, ppm: 7.42–7.57 m (5H, C_6H_5), 7.92 d.d.d (1H, H^5, J_{HF} 10.0, 8.1, 2.2 Hz), 11.06 s (2H, NH_2). ^{19}F NMR spectrum, δ, ppm: 9.09 m, 10.46 m, 21.92 m (1F each). ^{13}C NMR spectrum, δ, ppm: 176.75 s (C^9), 175.89 s (C^4), 159.87 s (C^2), 146.21 d.m

(C^7, *J* 258 Hz), 142.47 d.m (C^6, *J* 236 Hz), 139.70 m (C^{8a}), 138.54 d.m (C^8, *J* 254 Hz), 136.09 s (C^u), 130.35 s (C^p), 127.81 s (Cm), 127.33 s (C^o), 116.97 s (C^5), 107.24 s (C^{4a}), 94.91 s (C^9). Found, %: C 60.27; H 2.48; F 17.66; N 4.08. $C_{16}H_8F_3NO_3$. Calculated, %: C 60.20; H 2.53; F 17.85; N 4.39.

3-[(Methylamino)(phenyl)methylidene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (IVb). Yield 0.317 g (95%), colorless powder, mp 240°C (from ethanol). IR spectrum, ν, cm^{-1}: 3418 (NH), 1723 (O–C=O), 1646 (C=O), 1595, 1569, 1522, 1489, 1461, 1415 (C=C, NH), 1063, 1039, 1007 (CF). ^1H NMR spectrum, δ, ppm: 2.89 s (3H, CH_3), 7.32–7.53 m (5H, C_6H_5), 7.71d.d.d (1H, H^5, J_{HF} 10.4, 8.3, 2.3 Hz), 13.06 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 9.13 m, 10.54 m, 21.98 m (1F each). Found, %: C 61.54; H 2.98; F 17.40; N 3.93. $C_{17}H_{10}F_3NO_3$. Calculated, %: C 61.27; H 3.02; F 17.10; N 4.20.

3-[(Benzylamino)(phenyl)methylidene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (IVc). Yield 0.397 g (97%), colorless powder, mp 176°C (from ethanol). IR spectrum, ν, cm^{-1}: 3068, 3029 (NH), 1723 (O–C=O), 1646 (C=O), 1595, 1569, 1504, 1489, 1461 (C=C, NH), 1063, 1039, 1007 (CF). ^1H NMR spectrum, δ, ppm: 4.46 s (2H, CH_2), 7.21–7.53 m (10H, $2C_6H_5$), 7.73 d.d.d (1H, H^5, J_{HF} 10.3, 8.3, 2.1 Hz), 13.58 c (1H, NH). ^{19}F NMR spectrum, δ, ppm: 9.15 m, 10.94 m, 22.13 m (1F each). Found, %: C 67.31; H 3.12; F 14.09; N 3.19. $C_{23}H_{14}F_3NO_3$. Calculated, %: C 67.48; H 3.45; F 13.92; N 3.42.

Ethyl 3-amino-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylate (Va). Yield 0.284 g (74%), yellow powder, mp 117°C (from ethanola). IR spectrum, ν, cm^{-1}: 3381 (NH_2), 1735 (CO_2Et), 1648 (C=O), 1594, 1523, 1492, 1447 (C=C, NH_2), 1036, 1030 (CF). ^1H NMR spectrum, δ, ppm: 0.54 t (3H, $\underline{CH_3}CH_2$, ^3J 7.1 Hz), 3.53 q (2H, $CH_3\underline{CH_2}$, ^3J 7.1 Hz), 7.37–7.53 m (5H, C_6H_5), 9.13 br.s, 10.65 br.s, 10.84 br.s (1H each, NH_2, OH). ^{19}F NMR spectrum, δ, ppm: –9.17 m, 0.98 m, 2.85 m, 16.06 m (1F each). Found, %: C 56.24; H 3.52; F 19.99; N 3.46. $C_{18}H_{13}F_4NO_4$. Calculated, %: C 56.40; H 3.42; F 19.83; N 3.65.

Ethyl 2-[2-hydroxy-4-(methylamino)-3,5,6-trifluorobenzoyl]-3-(methylamino)-3-phenylacrylate (Vb). Yield 0.233 g (57%), colorless powder, mp 151°C (from ethanol). IR spectrum, ν, cm^{-1}: 3352, 3248 (NH), 1704 (CO_2Et), 1632 (C=O), 1585, 1557, 1499, 1470, 1443 (C=C, NH), 1032, 984 (CF). ^1H NMR spectrum, δ, ppm: 0.51 t (3H, $\underline{CH_3}CH_2$, ^3J 7.1 Hz), 2.31 s, 2.76 s (po 3H, $2NH\underline{CH_3}$), 3.41 q (2H, $CH_3\underline{CH_2}$, ^3J 7.0 Hz), 7.27–7.48 m (5H, C_6H_5), 8.60 br.s, 12.05 br.s (1H each, 2NH). ^{19}F NMR spectrum, δ, ppm: –3.21 m, –0.34 m, 14.16 m (1F each). Found, %: C 58.66; H 4.40; F 13.81; N 6.62. $C_{20}H_{19}F_3N_2O_4$. Calculated, %: C 58.82; H 4.69; F 13.96; N 6.86.

Ethyl 3-(benzylamino)-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylate (Vc). Yield 0.322 g (68%), colorless powder, mp 175°C (from ethanola). IR spectrum, ν, cm^{-1}: 3232 (NH), 1711 (CO_2Et), 1670 (C=O), 1590, 1521, 1491, 1442, 1423 (C=C, NH), 1000, 981 (CF). ^1H NMR spectrum, δ, ppm: 0.51 t (3H, $\underline{CH_3}CH_2$, ^3J 7.0 Hz), 3.44 q (2H, $CH_3\underline{CH_2}$, ^3J 7.0 Hz), 4.37 d (2H, $\underline{CH_2}C_6H_5$, *J* 6.1 Hz), 7.19–7.49 m (10H, $2C_6H_5$), 10.69 br.s (1H, NH), 12.40 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –9.10 m, 1.10 m, 3.19 m, 16.23 m (1F each). Found, %: C 63.39; H 3.74; F 16.22; N 3.08. $C_{25}H_{19}F_4NO_4$. Calculated, %: C 63.43; H 4.05; F 16.05; N 2.96.

Ethyl 3-(hexylamino)-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylate (Vd). Yield 0.257 g (55%), yellow powder, mp 173°C (from ethanol). IR spectrum, ν, cm^{-1}: 3275 (NH), 1708 (CO_2Et), 1645 (C=O), 1553, 1483, 1445 (C=C, NH), 1030, 992 (CF). ^1H NMR spectrum, δ, ppm: 1.06 t (3H, $\underline{CH_3}CH_2$, ^3J 7.0 Hz), 1.15–1.95 m (11H, $NHC_6\underline{H}_{13}$), 3.44 m (2H, $NHC_6\underline{H}_{13}$), 4.17 q (2H, $CH_3\underline{CH_2}$, ^3J 7.0 Hz), 7.29–7.46 m (5H, C_6H_5), 12.38 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: 4.16 m, 5.02 m, 14.60 m, 15.09 m (1F each). Found, %: C 61.24; H 5.43; F 16.13; N 3.07. $C_{24}H_{25}F_4NO_4$. Calculated, %: C 61.67; H 5.39; F 16.26; N 3.00.

Ethyl 2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenyl-3-(cyclohexylamino)acrylate (Ve). Yield 0.223 g (48%), yellow powder, mp 178°C (from ethanol). IR spectrum, ν, cm^{-1}: 3303 (NH), 1700 (CO_2Et), 1651 (C=O), 1552, 1475, 1440 (C=C, NH), 1014, 981 (CF). ^1H NMR spectrum, δ, ppm: 1.06 t (3H, $\underline{CH_3}CH_2$, ^3J 7.0 Hz), 1.20–1.96 m (10H, $NHC_6\underline{H}_{11}$), 3.46 m (1H, $NHC_6\underline{H}_{11}$), 4.17 q (2H, $CH_3\underline{CH_2}$, ^3J 7.0 Hz), 7.36–7.52 m (5H, C_6H_5), 12.42 br.s (1H, OH). ^{19}F, δ, ppm: 4.10 m, 4.99 m, 14.09 m, 15.09 m (1F each). Found, %: C 61.71; H 5.13; F 16.18; N 3.07. $C_{24}H_{23}F_4NO_4$. Calculated, %: C 61.93; H 4.98; F 16.33; N 3.01.

3-[Amino(phenyl)methylene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione (VIa). Yield 0.263 g (78%), colorless powder, mp 240°C (from ethanol). IR spectrum, ν, cm^{-1}: 3301, 3133 (NH_2), 1711 (O–C=O),

1648 (C=O), 1610, 1524, 1490, 1451, 1435 (C=C, NH_2), 1032, 986 (CF). ^{1}H NMR spectrum, δ, ppm: 7.43–7.56 m (5H, C_6H_5), 10.38 br.s, 11.64 br.s (1H each, NH_2). ^{19}F NMR spectrum, δ, ppm: –2.74 m, 2.17 m, 11.82 m, 1672 m (1F each). Found, %: C 56.65; H 2.00; F 22.56; N 3.94. $C_{16}H_7F_4NO_3$. Calculated, %: C 56.99; H 2.09; F 22.53; N 4.15.

3-[(Methylamino)(phenyl)methylene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione (VIв). Yield 0.155 g (44%), yellow powder, mp 201°C (from ethanol). IR spectrum, ν, cm^{-1}: 3011 (NH), 1715 (O–C=O), 1648 (C=O), 1499, 1452, 1414 (C=C, NH), 1027, 1001 (CF). ^{1}H NMR spectrum, δ, ppm: 2.80 d (3H, NH$\underline{CH_3}$, ^3J 4.8 Hz), 7.28–7.35 m (5H, C_6H_5), 12.99 br.s (1H, $\underline{NH}CH_3$). ^{19}F NMR spectrum, δ, ppm: –2.77 m, 2.15 m, 11.84 m, 16.78 m (1F each). Found, %: C 58.63; H 2.39; F 22.02; N 3.95. $C_{17}H_9F_4NO_3$. Calculated, %: C 58.13; H 2.58; F 21.64; N 3.99.

3-[(Hexylamino)(phenyl)methylidene]-5,6,7,8-tetrafluoro-2*H*-chromene-2,4(3*H*)-dione (VId). Yield 0.270 g (64%), colorless powder, mp 206°C (from ethanol). IR spectrum, ν, cm^{-1}: 3060 (NH), 1744 (O–C=O), 1650 (C=O), 1574, 1489, 1455, 1408 (C=C, NH), 1030, 1011 (CF). ^{1}H NMR spectrum, δ, ppm: 1.09–1.73 m (12H, $NHC_6\underline{H}_{13}$), 3.20 m (1H, $NHC_6\underline{H}_{13}$), 7.36–7.52 m (5H, C_6H_5), 12.60 br.s (1H, $\underline{NH}C_6H_{13}$). ^{19}F NMR spectrum, δ, ppm: –2.61 m, 2.21 m, 12.23 m, 17.20 m (1F each). Found, %: C 62.63; H 4.64; F 17.76; N 3.53. $C_{22}H_{19}F_4NO_3$. Calculated, %: C 62.71; H 4.54; F 18.03; N 3.32.

5,6,7,8-Tetrafluoro-3-[(cyclohexylamino)-(phenyl) methylene]-2*H*-chromene-2,4(3*H*)-dione (VIe). Yield 0.298 g (71%), yellow powder, mp 210°C (from ethanol). IR spectrum, ν, cm^{-1}: 3063 (NH), 1742 (O–C=O), 1646 (C=O), 1583, 1489, 1455, 1408 (C=C, NH), 1011, 989 (CF). ^{1}H NMR spectrum, δ, ppm: 1.09–1.78 m (10H, $NHC_6\underline{H}_{11}$), 3.20 m (1H, $NHC_6\underline{H}_{11}$), 7.36–7.53 m (5H, C_6H_5), 13.50 br.s (1H, $\underline{NH}C_6H_{11}$). ^{19}F NMR spectrum, δ, ppm: –2.60 m, 2.22 m, 12.26 m, 17.24 m (1F each). Found, %: C 63.23; H 4.28; F 17.81; N 3.77. $C_{22}H_{17}F_4NO_3$. Calculated, %: C 63.01; H 4.09; F 18.12; N 3.34.

3-(1-Aminoethylidene)-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (VIIIa). Yield 0.190 g (74%), colorless powder, mp 291°C (from ethanol). IR spectrum, ν, cm^{-1}: 3238, 3071 (NH_2), 1705 (O–C=O), 1631 (C=O), 1604, 1523, 1488, 1462 (C=C, NH_2), 1061, 1008 (CF). ^{1}H NMR spectrum, δ, ppm: 2.58 s (3H, CH_3), 7.66 d.d.d (1H, H^5, J_{HF} 10.4, 8.3, 2.3 Hz), 10.23 br.s, 11.80 br.s (1H each, NH_2). ^{19}F NMR spectrum, δ, ppm: 9.03 m, 10.33 m, 21.91 m (1F each). Found, %: C 51.20; H 2.21; F 22.41; N 5.21. $C_{11}H_6F_3NO_3$. Calculated, %: C 51.37; H 2.35; F 22.16; N 5.45.

3-[1-(Methylamino)ethylidene]-6,7,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (VIIIb). Yield 0.258 g (95%), colorless powder, mp 236°C (from ethanol). IR spectrum, ν, cm^{-1}: 3074 (NH), 1736 (O–C=O), 1622 (C=O), 1520, 1493 (C=C, NH), 1068, 1048 (CF). ^{1}H NMR spectrum, δ, ppm: 2.64 c, 3.24 c (po 3H, $2CH_3$), 7.69 d.d.d (1H, H^5, J_{HF} 10.4, 8.3, 2.3 Hz), 13.09 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 8.90 m, 10.21 m, 21.93 m (1F each). Found, %: C 52.99; H 2.87; F 20.82; N 5.13. $C_{12}H_8F_3NO_3$. Calculated, %: C 53.15; H 2.97; F 21.02; N 5.16.

Ethyl 1-benzyl-5-hydroxy-4-oxo-2-phenyl-6,7,8-trifluoro-1,4-dihydroquinoline-3-carboxylate (IX). *a*. To a solution of 0.47 g (1 mmol) of ester **Vb** in 10 ml of ethanol was added 0.30 g (1.2 mmol) of nickel(II) tetrahydrate. The reaction mixture was vigorously stirred for 24 h at 25°C. Then ethanol was distilled off in a vacuum, the solid residue was crystallized from a mixture acetone–hexane, 1:5. Yield 0.339 g (75%).

b. 0.47 g (1 mmol) of ester **Vb** was heated without solvent at 180°C for 2 h. Yield 0.226 g (50%), yellow powder, mp >300°C. IR spectrum, ν, cm^{-1}: 1729 (CO_2Et), 1566 (C=O), 1453, 1421 (C=C, C–N), 1071, 1027 (CF). ^{1}H NMR spectrum, δ, ppm: 0.80 t (3H, $CH_2\underline{CH_3}$, ^3J 7.1 Hz), 3.86 q (2H, $\underline{CH_2}CH_3$, ^3J 7.1 Hz), 5.34 s (2H, $\underline{CH_2}C_6H_5$), 6.98–7.54 m (10H, $2C_6H_5$), 14.90 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –1.53 m, 8.31 m, 14.02 m (1F each). Found, %: C 66.49; H 3.54; F 12.71; N 3.01. $C_{25}H_{18}F_3NO_4$. Calculated, %: C 66.22; H 4.00; F 12.57; N 3.09.

7-(Methylamino)-3-[(methylamino)(phenyl) methylidene]-5,6,8-trifluoro-2*H*-chromene-2,4(3*H*)-dione (X). Yield 0.341 g (94%), yellow powder, mp 221°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 2.80 s (3H, C^{7}NH$\underline{CH_3}$), 3.33 s (3H, C^{9}NH$\underline{CH_3}$), 6.62 br.s (C$^7\underline{NH}CH_3$), 7.28–7.51 m (5H, C_6H_5), 12.19 br.s (1H, C$^9\underline{NH}CH_3$). ^{19}F NMR spectrum, δ, ppm: –1.37 m, 1.59 m, 14.09 m (1F each). Found, %: C 63.18; H 4.59; F 15.61; N 8.05. $C_{19}H_{15}F_3N_2O_2$. Calculated, %: C 63.33; H 4.20; F 15.82; N 7.77.

Ethyl 7-(4-methylpiperazin-1-yl)-4-oxo-2-phenyl-6,8-difluoro-4*H*-chromene-3-carboxylate (XIa). Yield 0.266 g (62%), colorless powder, mp 236°C (from ethanol). IR spectrum, ν, cm^{-1}: 2974, 2942, 2845,

2799 (N–CH_3, CH), 1727 (CO_2Et), 1644 (C=O), 1630, 1566, 1504, 1465 (C=C), 1395, 1372 (C–N), 1029, 1005 (CF). ^{1}H NMR spectrum, δ, ppm: 1.09 t (3H, $CH_2\underline{CH_3}$, ^3J 7.1 Hz), 2.23 s (3H, CH_3), 2.45–2.53 m [4H, $(CH_2)_2$], 3.32–3.34 m [4H, $(CH_2)_2$], 4.18 q (2H, $\underline{CH_2}CH_3$, ^3J 7.1 Hz), 7.58–7.72 m (5H, C_6H_5), 7.53 d.d (1H, H^5, J_{HF} 11.9, 1.8 Hz). ^{19}F NMR spectrum, δ, ppm: 20.63 m, 41.52 m (1F each). Found, %: C 64.46; H 4.98; F 9.15; N 6.36. $C_{23}H_{22}F_2N_2O_4$. Calculated, %: C 64.48; H 5.18; F 8.87; N 6.54.

Ethyl 7-(4-methylpiperazin-1-yl)-4-oxo-2-phenyl-5,6,8-trifluoro-4*H*-chromene-3-carboxylate (XIb). Yield 0.344 g (77%), colorless powder, mp 163°C (from ethanol). IR spectrum, ν, cm^{-1}: 2979, 2947, 2848, 2799 (C–H, N–CH_3), 1727 (CO_2Et), 1645 (C=O), 1615, 1567, 1507, 1478, 1448 (C=C), 1372, 1341 (C–N), 1020, 1004 (CF). ^{1}H NMR spectrum, δ, ppm: 1.10 t (3H, $CH_2\underline{CH_3}$, ^3J 7.1 Hz), 2.25 s (3H, CH_3), 2.48–2.51 m [4H, $(CH_2)_2$], 3.34–3.40 m [4H, $(CH_2)_2$], 4.19 q (2H, $\underline{CH_2}CH_3$, ^3J 7.1 Hz), 7.58–7.70 m (5H, C_6H_5). ^{19}F NMR spectrum, δ, ppm: 12.51 m, 14.11 m, 16.09 m (1F each). Found, %: C 61.61; H 4.62; F 12.71; N 6.34. $C_{23}H_{21}F_3N_2O_4$. Calculated, %: C 61.88; H 4.74; F 12.77; N 6.28.

Ethyl 3-[(2-aminophenyl)amino]-2-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)-3-phenylacrylate (XII). Yield 0.289 g (61%), colorless powder, mp 133°C (from a mixture ethanol–water). IR spectrum, ν, cm^{-1}: 3406, 3190 (NH, NH_2), 1745 (CO_2Et), 1670, 1655 (C=O), 1639, 1541, 1523, 1494, 1459 (C=C, NH), 1036, 1001 (CF). ^{1}H NMR spectrum, δ, ppm: 1.23 t (3H, $CH_2\underline{CH_3}$, ^3J 7.1 Hz), 4.12 q (2H, $\underline{CH_2}CH_3$, ^3J 7.1 Hz), 6.43–7.51 m (9H, C_6H_5, C_6H_4); 9.72 s, 10.57 s, 11.34 s (1H each, NH, NH_2). ^{19}F NMR spectrum, δ, ppm: –8.24 m, 2.07 m, 6.21 m, 19.23 m (1F each). Found, %: C 61.05; H 3.74; F 16.33; N 5.58. $C_{24}H_{18}F_4N_2O_4$. Calculated, %: C 60.76; H 3.82; F 16.02; N 5.90.

1*H*-Benzimidazol-2-yl(2-hydroxy-3,4,5-trifluorophenyl)methanone (XIII). Yield 0.222 g (76%), colorless powder, t.subl. 333°C (from ethanol). IR spectrum, ν, cm^{-1}: 3076, 2921, 2593 (NH, OH), 1620 (C=O), 1593, 1566, 1507, 1464 (C=C, CN, NH), 1022 (CF). ^{1}H NMR spectrum, δ, ppm: 6.58–7.20 m (4H, C_6H_4), 8.01 m (1H, =C–H), 10.11 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 5.89 m, 9.07 m, 14.51 m (1F each). Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 290 $[M - 2H]^+$ (100), 262 $[M - 2H - CO]^+$ (73). Found, %: C 57.98; H 2.72; F 19.78; N 9.25. $C_{14}H_7F_3N_2O_2$. Calculated, %: C 57.74; H 2.41; F 19.50; N 9.59.

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