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Synthesis and Structure of 4-Hydroxy-4-fluoroalkyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazines

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Abstract—Azo coupling of fluorinated 1,3-diketones with 4-ethoxycarbonyl-1*H*-imidazole-5-diazonium chloride led to the formation of 4-hydroxy-4-polyfluoroalkyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazines. According to the ^{1}H and ^{19}F NMR data, these compounds in solution give rise to ring–chain tautomerism via opening of the C^4–N^5 bond, which is especially characteristic of dihydroimidazotriazines with a polyfluoroalkyl substituent longer than trifluoromethyl group.

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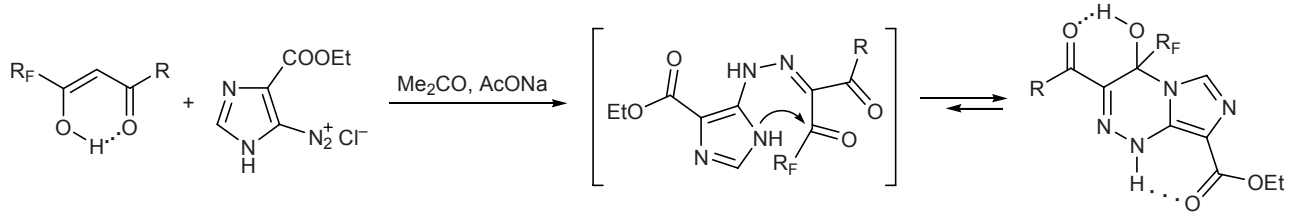
1,3-Diketones, including fluorinated derivatives, are known to react with arenediazonium salts to give the corresponding 1,2,3-triketone 2-arylhydrazones which are widely used as intermediate products in the synthesis of biologically active compounds, dyes, ligands for complex formation with metals, etc. [1]. Reactions of hetarenediazonium salts with nonfluorinated 1,3-diketones do not always lead to the formation of open-chain hydrazones; in some cases, the products are azolotriazines resulting from spontaneous intramolecular cyclization with participation of one carbonyl group [2].

We previously showed that the direction of azo coupling of fluorinated 1,3-diketones with hetarenediazonium salts is determined mainly by the hetarene structure. For example, azo coupling of fluorinated 1,3-diketones with 1,2,4-triazole-3-diazonium and 4-ethoxycarbonylpyrazole-3-diazonium chlorides gives the corresponding stable 4-fluoroalkyl-4-hydroxy-1,4-dihydroazolo[5,1-*c*]triazines instead of the expected 1,2,3-triketone 2-hetarylhydrazones [3]. In continuation of these studies, in the present work we examined azo coupling of fluorine-containing 1,3-diketones **Ia**–**Ih** with 4-ethoxycarbonyl-1*H*-imidazole-5-diazonium chloride. It is known that nonfluorinated 1,3-diketones react with imidazole-5-diazonium salts to afford 1,2,3-triketone 2-imidazolylhydrazones which undergo intramolecular condensation to imidazo[5,1-*c*][1,2,4]-triazines on heating in boiling acetic acid [4]. Imidazotriazines are isosteric to purine bases; therefore, they could be capable of inducing metabolic disorders and inhibiting protein biosynthesis [5]. Some imidazotriazines were reported to inhibit protein kinase [6] and phosphodiesterase [7].

We found that fluorinated 1,3-diketones **Ia**–**Ih** react with 4-ethoxycarbonyl-1*H*-imidazole-5-diazonium

Scheme 1.



Ia–Ih **A** **B**, **IIa–IIh**

R_F = CF_3, R = Me (**a**), *t*-Bu (**b**), Ph (**c**), 2-furyl (**d**), 1-naphthyl (**e**); R_F = $H(CF_2)_2$, R = Ph (**f**); R_F = C_3F_7, R = Me (**g**), Ph (**h**).

chloride in acetone in the presence of sodium acetate at reduced temperature to produce imidazo[5,1-*c*][1,2,4]-triazines **IIa**–**IIh** (Scheme 1). However, to distinguish between isomeric 1,2,3-triketone 2-imidazolylhydrazones **A** and 4-hydroxy-4-fluoroalkyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazines **B**, the structure of the isolated products was thoroughly studied by IR and NMR spectroscopy and X-ray analysis.

According to the X-ray diffraction data, compound **IIh** has the structure of ethyl 3-benzoyl-4-heptafluoropropyl-4-hydroxy-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (see figure). The O^1 and H^2 atoms are linked through intramolecular hydrogen bond with the following parameters: $O^1\cdots H^2$ 1.77(5) Å, $\angle O^1H^2O^2$ 156(2)°, $\angle C^4O^2H^2$ 100(1)°. The fused heterocyclic fragment is almost planar; the C^4 and N^1 atoms deviate from the $N^2C^3N^5C^6N^7C^8C^{8a}$ plane by 0.33(2) and 0.13(2) Å, respectively. The heptafluoropropyl group is oriented almost orthogonally to the triazine ring plane (85.4°), while the hydroxy group declines by an angle of 39.6°. One more intramolecular hydrogen bond is formed between the O^3 and H^1 atoms: $O^3\cdots H^1$ 2.40(7) Å, $\angle N^1H^1O^3$ 113(1)°, $\angle C^{19}O^3H^1$ 105(2)°. Judging by the O···H distances, the $O^3\cdots H^1$ hydrogen bond is weaker than $O^1\cdots H^2$.

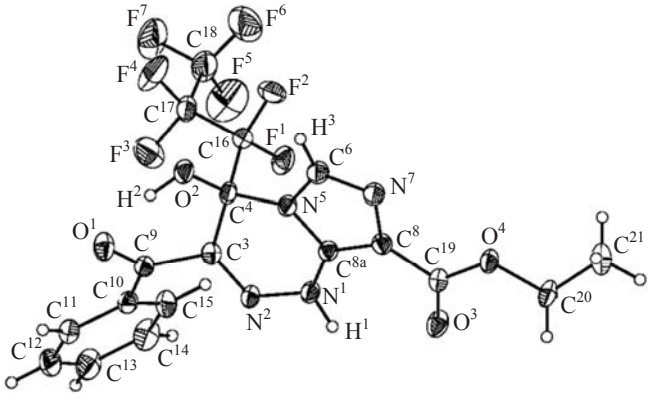
The presence of intramolecular bonds in dihydroimidazotriazine **IIh** also follows from the IR spectrum where the absorption band corresponding to stretching vibrations of two carbonyl groups is strongly broadened and displaced to lower frequencies (ν 1670 cm^{-1}) relative to its position typical of carbonyl groups conjugated with double C=C or C=N bond [8].

The IR spectra of crystalline samples of compounds **IIa**–**IIg** were essentially similar to the spectrum of **IIh**. All compounds **IIa**–**IIh** displayed in the IR spectra two very strong absorption bands in the regions 3280–3230 and 3170–3100 cm^{-1} due to stretching vibrations of OH and NH groups, as well as one broadened or two strong absorption bands in the region 1695–1665 cm^{-1} due to vibrations of ester and ketone (acyl or aroyl) carbonyl groups. Analogous pattern was observed previously in the IR spectra of 4-fluoroalkyl-4-hydroxy-1,4-dihydroazolo[5,1-*c*][1,2,4]triazines [3]. In contrast, the IR spectra of 1,2,3-triketone 2-arylhydrazones [9] and 2-pyrazolylhydrazones [10] characteristically contain a very weak broadened absorption band in the region 3110–3040 cm^{-1}, which belongs to stretching vibrations of the NH group in the hydrazone fragment. The above data indicate that all compounds **IIa**–**IIh** in the crystalline state have the structure of cyclic isomer **B**.

The structure of compounds **IIa**–**IIh** in solution was studied by NMR spectroscopy. The ^1H and ^{19}F NMR spectra of trifluoromethyl derivatives **IIa**–**IIe** in $CDCl_3$, acetone-d_6, and DMSO-d_6 contained only one set of signals, indicating the presence of only one among possible isomers in solution. However, the ^1H and ^{19}F NMR patterns of polyfluoroalkyl-substituted compounds **IIf**–**IIh** in some cases implied the presence of more than one isomer.

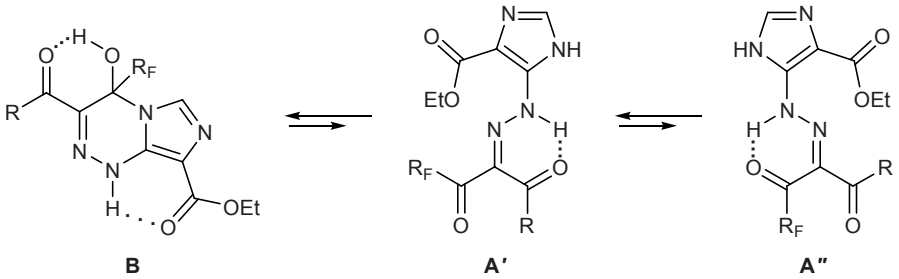
In the ^{13}C NMR spectrum of **IIa** in DMSO-d_6, the quartet signal from the trifluoromethyl carbon atom was located at δ_C ~79 ppm, which is typical of sp^3-hybridized carbon atom in heterocyclic structure **B** [3]. The ^1H NMR spectra did not allow us to reliably distinguish between cyclic and open-chain structures of compounds **IIa**–**IIh** because of similarity of supposed spectral parameters of imidazotriazines **B** and imidazolylhydrazones **A**.

The ^{19}F NMR data are more appropriate for this purpose. The chemical shifts of fluorine in CF_3 and α-CF_2 groups in open-chain 1,2,3-triketone 2-(het)arylhydrazones and cyclic azolotriazines differ considerably, depending on the nature of the neighboring carbon atoms. Fluorine atoms in CF_3 groups attached to sp^3-hybridized carbon atom in dihydroazolotriazines resonate in a stronger field (δ_F ~79 ppm in $CDCl_3$ and 85 ppm in DMSO-d_6) than do the corresponding fluorine nuclei in open-chain hydrazones (δ_F ~91 ppm in $CDCl_3$ and 93 ppm in DMSO-d_6), where the CF_3 group is attached to sp^2-hybridized carbon atom [9, 11]. The observed chemical shifts of fluorine atoms in the CF_3 groups of compounds **IIa**–**IIe** (δ_F 78.3–78.9 ppm in $CDCl_3$, 81.4–82.0 ppm in acetone-d_6, and 83.0–83.5 ppm in DMSO-d_6) suggest their cyclic structure. In most cases, the CF_3 signals are doublets (J_{FH} = 0.7–



Structure of the molecule of ethyl 3-benzoyl-4-heptafluoropropyl-4-hydroxy-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (**IIh**) according to the X-ray diffraction data.

Scheme 2.



B **A′** **A″**

1.2 Hz) due to coupling with 3-H in the imidazole ring; the 3-H proton resonates in the ^{1}H NMR spectra as a broadened quartet or singlet.

Interestingly, the ^{19}F NMR spectrum of compound **IIa** in DMSO-d_6, recorded repeatedly in 24 h after dissolution, contained low-intensity singlets at δ_F 93.07 (5%) and 89.10 ppm (1%) in addition to the doublet at δ_F 83.17 ppm (94%), belonging to cyclic structure **B** (see table). While studying steric structure of a large series of trifluoromethyl-containing 1,2,3-triketone 2-arylhydrazones, we previously showed [11] that fluorine signals of the CF_3CO group involved in intramolecular hydrogen bond with the NH proton of the arylhydrazone fragment appear in the ^{19}F NMR spectra (acetone-d_6) at δ_F ~89 ppm and that fluorine nuclei in the free CF_3CO group resonate at δ_F ~93 ppm. Taking these data into account, the new signals observed in the ^{19}F NMR spectrum of **IIa** in DMSO-d_6 should be assigned to geometric isomers of open-chain 1,1,1-trifluoropentane-2,3,4-trione 2-imidazolylhydrazone with free (**A′**) and H-bonded carbonyl group (**A″**) at the trifluoromethyl substituent (Scheme 2).

The ^{1}H and ^{19}F NMR spectra of tetrafluoroethyl derivative **IIf** in $CDCl_3$ contained one set of signals corresponding to cyclic structure **B**; fluorine atoms in the tetrafluoroethyl group gave rise to an *AB* spin system due to the presence of neighboring asymmetric carbon atom. However, the ^{1}H and ^{19}F NMR spectra of the same compound in DMSO-d_6 displayed two sets of signals, the major of which (95%) was assigned to cyclic isomer **B**. The minor set (5%) was characterized by a different pattern. The HCF_2 group gave a doublet of triplets ($^2J_{FH}$ = 52.8, $^3J_{FF}$ = 7.5 Hz), and the α-CF_2 signal was a doublet of multiplets ($^3J_{FF}$ = 7.5 Hz). This pattern is typical of tetrafluoroethyl group attached to a carbonyl carbon atom. In addition, fluorine atoms in the α-CF_2 group resonated in a weaker field (δ_F ~42 ppm) as compared to cyclic isomer **B** (δ_F ~37 ppm). The observed downfield shift is typical of α-CF_2 group attached to sp^2-hybridized carbon atom. Then the second set of signals should be assigned to open-chain tautomer **A**. The ^{1}H NMR spectra of **IIf** also contained doubled signals from most protons (see Experimental).

In the ^{19}F NMR spectrum of a solution of **IIf** in acetone-d_6 we observed three sets of signals. The major set (72%) was assigned to cyclic isomer **B**, whereas the two minor sets corresponded to open-chain isomers **A**. The α-CF_2 fluorine nuclei in **A″** (25%) and **A′** (3%) had different chemical shifts (δ_F ~41.9 and ~42.2 ppm, respectively). It may be presumed that the tetrafluoroethyl group in **A″** is contiguous to the carbonyl group involved in intramolecular hydrogen bond with the hydrazone fragment and that the same group in **A′** is linked to free carbonyl group (Scheme 2). Most proton signals of isomer **A′** are difficult to distinguish because of their low intensity and superposition of signals from other isomers.

It remained to determine which of the open-chain isomers of compound **IIf** is observed in the ^{19}F NMR spectrum recorded in DMSO-d_6. Taking into account similarity of the chemical shifts of fluorine nuclei in the α-CF_2 group linked to H-bonded carbonyl group in the ^{19}F NMR spectrum in $(CD_3)_2CO$ (**A″**, δ_F 41.95 ppm) and those observed in DMSO-d_6 (δ_F 41.98 ppm), structure **A″** was presumed.

According to the ^{1}H and ^{19}F NMR data, compound **IIg** having heptafluoropropyl and methyl groups in $CDCl_3$ exists as single cyclic tautomer **B**, while in DMSO-d_6 and acetone-d_6 mixture of three isomers **B**, **A′**, and **A″** at different ratios is present (see Experimental and table). Isomers **A′** and **A″** can be distinguished in the ^{1}H NMR spectra on the basis of chemical shifts of protons in the acetyl methyl group. It is known [11] that signal from acetyl group involved in intramolecular hydrogen bond with NH group is displaced downfield. Signals in the ^{19}F NMR spectrum of **IIg** were assigned to isomers **A′**, **A″**, and **B** by analysis of chemical shifts of fluorine nuclei in the α-CF_2 group. The fractions of cyclic structure **B** in

DMSO-d_6 and acetone-d_6 were almost equal (60 and 62%, respectively), whereas the ratio of open-chain isomers **A′** and **A″** strongly depended on the solvent. Isomer **A″** with the H-bonded fluoroacyl fragment predominated in DMSO-d_6, while in going to acetone-d_6 the fractions of isomers **A′** and **A″** leveled (see table).

In the ^{1}H and ^{19}F NMR spectra of **IIh** in $CDCl_3$, a minor set of signals due to open-chain isomer **A″** (3%) was present in addition to signals belonging to isomer **B** (97%). The fraction of isomer **A″** increased to 20% in going to DMSO-d_6 (**B**, 80%), and the spectra of a solution in acetone-d_6 contained signals from three isomers **B** (82%), **A′** (5%), and **A″** (13%; see table). The α-CF_2 signals in the ^{19}F NMR spectra of **IIh** in $CDCl_3$ (δ_F 47.02 ppm) and DMSO-d_6 (δ_F 50.48 ppm) were observed in a weaker field than those found for isomers **A′** (δ_F 51.50 ppm) and **A″** (δ_F 51.21 ppm) in acetone-d_6. Therefore, these signals were assigned to isomer **A″** in which intramolecular hydrogen bond is formed between the fluorinated acyl group and hydrazone fragment.

Thus the data of IR and ^{1}H and ^{19}F NMR spectroscopy and X-ray analysis showed that azo coupling of fluorinated 1,3-diketones **Ia**–**Ih** with 4-ethoxycarbonyl-1*H*-imidazole-5-diazonium chloride leads to the formation of 4-fluoroalkyl-4-hydroxy-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazines **IIa**–**IIh** which give rise to ring–chain isomerism in solution via dissociation of the C^4–N^5 bond. We can also state that, unlike analogous transformations of nonfluorinated 1,3-diketones, compounds **Ia**–**Ih** having electron-withdrawing polyfluoroalkyl substituents are converted into hydrated heterocyclic structures. Presumably, open-chain 1,2,3-triketone 2-imidazolylhydrazones **A** are unstable, and they tend to undergo intramolecular cyclization via addition of the hydrazone NH group at the carbonyl group linked to electron-withdrawing polyfluoroalkyl residue. We failed to effect dehydration of compounds **IIa**–**IIh** by heating in acetic acid, acetic anhydride, or boiling toluene in the presence of dehydrating agents.

With a view to examine solvent effect on the ring–chain isomerism of compounds **IIa**–**IIh**, ^{19}F NMR spectra of imidazotriazines **IIa**, **IId**, **IIf**, and **IIh** in CD_3CN, CD_3OD, and pyridine-d_5 were recorded. ^{19}F NMR spectroscopy was selected as the most appropriate method for identification of cyclic (**B**) and open-chain isomers (**A**). We found that in all cases open-chain structure **A″** appeared in pyridine-d_5. Open-chain isomers **A′** and **A″** were present in CD_3OD and CD_3CN only for compounds having a polyfluoroalkyl group with more than one carbon atom (see Experimental and table).

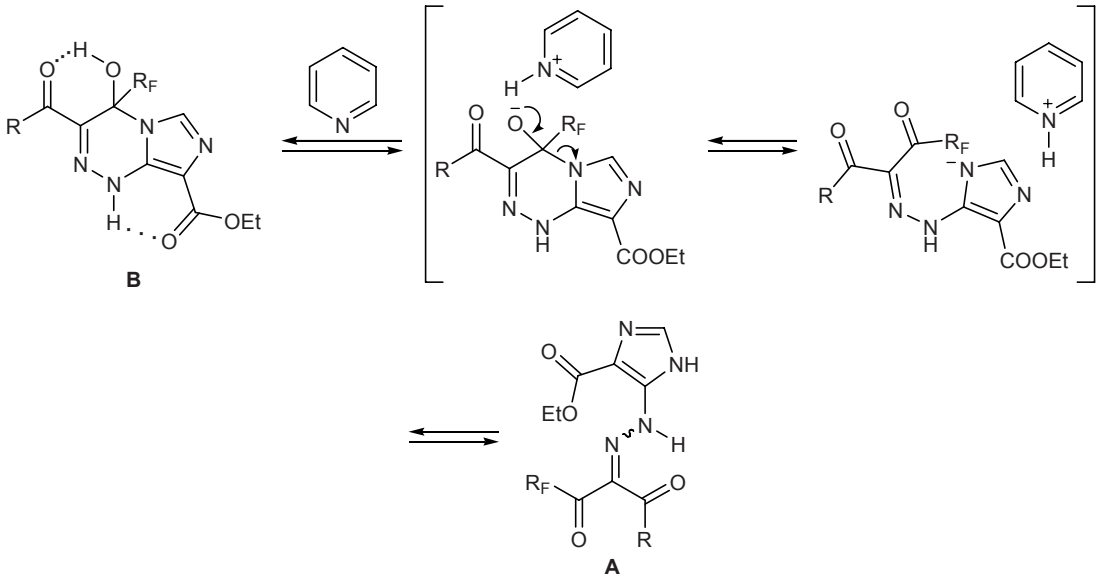
Isomeric compositions of compounds **IIa**–**IIh** in different solvents according to the ^{19}F NMR data

Comp. no.	Solvent	Isomer fraction, %		
		A′	**A″**	**B**
IIa	$CDCl_3$, acetone-d_6, CD_3OD, DMSO-d_6	–	–	100
	DMSO-d_6[a]	5	1	94
	Pyridine-d_5		9	91
IIb	$CDCl_3$, DMSO-d_6, acetone-d_6	–	–	100
IIc	$CDCl_3$, DMSO-d_6, acetone-d_6	–	–	100
IId	$CDCl_3$, DMSO-d_6, acetone-d_6, CD_3OD	–	–	100
	Pyridine-d_5	–	3	97
IIe	$CDCl_3$, DMSO-d_6, acetone-d_6	–	–	100
IIf	$CDCl_3$	–	–	100
	DMSO-d_6	–	5	95
	Acetone-d_6	3	25	72
	CD_3OD	2	7	91
	CD_3CN	16	5	79
	Pyridine-d_5	6	3	91
IIg	$CDCl_3$	–	–	100
	DMSO-d_6	3	35	62
	Acetone-d_6	21	19	60
IIh	$CDCl_3$	–	3	97
	DMSO-d_6	–	20	80
	Acetone-d_6	5	13	82
	CD_3OD	–	17	83
	CD_3CN	7	8	85
	Pyridine-d_5	–	18	82

[a] The ^{19}F NMR spectrum was recorded in 24 h after dissolution.

We can conclude that compounds **II** in the crystalline state have the structure of dihydroimidazotriazines **B** which are capable of undergoing ring–chain isomerism in solution as a result of cleavage of the C^4–N^5 bond. Ring–chain transformations are especially typical of dihydroimidazotriazines having more than one carbon atom in the polyfluoroalkyl substituent. The possibility for ring–chain isomerism is determined by reversible character of nucleophilic addition of the imidazole NH group at the polyfluoroacyl fragment.

Scheme 3.



More facile formation of open-chain structures from dihydroimidazotriazines **IIe**–**IIh** may be rationalized as follows. Longer polyfluoroalkyl groups induce more negative electrostatic field which favors expulsion of the neighboring nucleophilic nitrogen atom. Polar solvents such as DMSO-d_6, acetone-d_6, CD_3CN, and CD_3OD, are likely to enhance the effect of electrostatic field. Pyridine is a fairly strong base (pK_a = 5.23 [12]) which is capable of abstracting proton from the hydroxy group of dihydroimidazotriazine **B**, and anionic intermediate thus formed is stabilized via opening of the triazine ring (Scheme 3). Therefore, open-chain structures **A** are observed in pyridine-d_5 for all the examined compounds, regardless of the length of the polyfluoroalkyl chain.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from samples dispersed in mineral oil or using a diffuse reflectance adapter (DRA). The NMR spectra were obtained on a Bruker DRX-400 spectrometer at 400.13, 100.6, and 376 MHz for ^1H, ^{13}C, and ^{19}F, respectively; the chemical shifts were measured relative to tetramethylsilane (^1H, ^{13}C) or hexafluorobenzene (^{19}F). The elemental compositions were determined using a Perkin–Elmer 2400 Series II analyzer. Column chromatography was performed on Merck 60 silica gel (0.063–0.200 mm). The melting points were determined in open capillaries on a Stuart SMP3 melting point apparatus.

Single crystals of compound **IIh** were obtained by crystallization from chloroform–hexane (4 : 1). The X-ray diffraction data were acquired on an Xcalibur 3 diffractometer equipped with a CCD detector [graphite monochromator, λ(MoK_α) 0.71073 Å, temperature 102(2) K, ψ/ω-scanning]. Correction for absorption was introduced analytically using a multifaceted crystal model (CrysAlis RED 1.171.29.9). The structure was solved by the direct method from the Fourier difference syntheses using SHELXS-97 software [13]. The positions and temperature factors of non-hydrogen atoms were refined by the least-square procedure in full-matrix anisotropic approximation using SHELXL-97 software [13]. Crystallographic data for compound **IIh**: $C_{18}H_{13}F_7N_4O_4$; M 482.32; monoclinic crystals with the following unit cell parameters: a = 25.033(3), b = 11.312(3), c = 14.207(3) Å; β = 106.79(7)°; V = 3851.6(6) Å^3; Z = 8; d_{calc} = 1.664 g/cm^3; μ = 0.163 mm^{-1}; space group $C2/c$. Total of 3875 reflection intensities were measured; number of independent reflections 2659, R factor 0.040, number of refined parameters 306. The complete set of crystallographic data for compound **IIh** was deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 688635; *www.ccdc.cam.ac.uk/conts/retrieving.html*; CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: *deposit@ccdc.cam.ac.uk*).

Initial fluorinated 1,3-diketones **Ia**–**Ih** were synthesized according to the procedure described in [14].

4-Hydroxy-4-polyfluoroalkyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazines IIa–IIh (*general proce-*

dure). A two-necked flask equipped with a stirrer and a dropping funnel was charged with 10 mmol of ethyl 5-amino-1*H*-imidazole-4-carboxylate, a mixture of 3 ml of concentrated hydrochloric acid and 10 ml of water was added, the mixture was cooled to 0°C, and a solution of 0.70 g of sodium nitrite in 3 ml of water was slowly added dropwise under vigorous stirring, maintaining the temperature at 0°C. The resulting solution of imidazolediazonium salt was added dropwise to a solution of 4.55 g of sodium acetate and 10 mmol of 1,3-diketone **Ia**–**Ih** in 31 ml of acetone under stirring at 10°C. By the end of the addition procedure, crystals began to separate from the solution. The precipitate was filtered off and purified by column chromatography using chloroform as eluent.

Ethyl 3-acetyl-4-hydroxy-4-trifluoromethyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIa). Yield 72%, light brown powder, mp 160–161°C. IR spectrum (mineral oil), ν, cm^{-1}: 3270, 3170 (NH, OH); 1685 br. (C=O); 1610, 1545 (δNH, C=C, C=N); 1220–1100 (C–F). ^{1}H NMR spectrum, δ, ppm, isomer **B** (100%): in $CDCl_3$: 1.44 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 2.58 s (3H, Me), 4.45 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.65 br.q (1H, 6-H, $^5J_{HF}$ = 0.9 Hz), 7.73 s (1H, NH), 10.36 br.s (1H, OH); in DMSO-d_6: 1.30 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.0 Hz), 2.42 s (3H, Me), 4.30 q (2H, OCH_2, $^3J_{HH}$ = 7.0 Hz), 7.89 br.s (1H, 6-H), 9.33 s (1H, NH), 12.65 s (1H, OH); in acetone-d_6: 1.35 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 2.51 s (3H, Me), 4.38 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.79 br.q (1H, 6-H, $^5J_{HF}$ = 1.1 Hz), 8.06 s (1H, NH), 11.91 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm, **B** (100%): 14.44 ($CH_2\mathbf{C}H_3$), 26.90 (OCH_2), 59.78 ($CO\mathbf{C}H_3$), 79.06 q (C^4, $^2J_{CF}$ = 35.7 Hz), 111.31 (C^3), 122.11 q (CF_3, $^3J_{CF}$ = 290.1 Hz), 129.59 (C^8), 130.20 (C^{8a}), 131.78 (C^6), 161.46 ($\mathbf{C}O_2Et$), 192.87 ($\mathbf{C}OCH_3$). ^{19}F NMR spectrum, δ_F, ppm: **B** (100%): in $CDCl_3$: 78.57 d (CF_3, $^5J_{FH}$ = 0.9 Hz); in DMSO-d_6: 83.17 d (CF_3, $^5J_{FH}$ = 1.0 Hz); in acetone-d_6: 81.75 d (CF_3, $^5J_{FH}$ = 1.1 Hz); in CD_3OD: 82.47 d (CF_3, $^5J_{FH}$ = 0.7 Hz); in pyridine-d_5: **B** (91%): 82.13 br.s (CF_3); **A″** (9%): 88.86 s (CF_3). Found, %: C 41.20; H 3.44; F 17.58; N 17.69. $C_{11}H_{11}F_3N_4O_4$. Calculated, %: C 41.26; H 3.46; F 17.80; N 17.50.

Ethyl 4-hydroxy-3-(2,2-dimethyl-1-oxopropyl)-4-trifluoromethyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIb). Yield 65%, bright yellow crystals, mp 75–76°C. IR diffuse reflectance spectrum, ν, cm^{-1}: 3260, 3145 (NH, OH); 1730, 1685 br (C=O); 1640, 1610, 1550 (δNH, C=C, C=N); 1200–1100 (C–F). ^{1}H NMR spectrum, δ, ppm, **B** (100%): in $CDCl_3$: 1.39 s (9H, CMe_3), 1.43 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.43 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.63 br.s (1H, 6-H), 8.22 br.s (1H, NH), 10.10 br.s (1H, OH); in DMSO-d_6: 1.30 s (9H, CMe_3), 1.30 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.0 Hz), 4.30 m (2H, OCH_2, $^3J_{HH}$ = 7.0 Hz), 7.85 br.s (1H, 6-H), 9.30 s (1H, NH), 12.41 s (1H, OH); in acetone-d_6: 1.34 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 1.37 s (9H, CMe_3), 4.38 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.77 br.q (1H, 6-H, $^5J_{HF}$ = 1.0 Hz), 8.29 s (1H, NH), 11.81 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm, **B** (100%): in $CDCl_3$: 78.52 d (CF_3, $^5J_{FH}$ = 0.9 Hz); in DMSO-d_6: 83.00 d (CF_3, $^5J_{FH}$ = 0.9 Hz); in acetone-d_6: 81.40 d (CF_3, $^5J_{FH}$ = 1.0 Hz). Found, %: C 46.04; H 4.82; F 15.69; N 15.59. $C_{14}H_{17}F_3N_4O_4$. Calculated, %: C 46.41; H 4.73; F 15.73; N 15.46.

Ethyl 3-benzoyl-4-hydroxy-4-trifluoromethyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIc). Yield 62%, yellow crystals, mp 112–113°C. IR spectrum (mineral oil), ν, cm^{-1}: 3280, 3135 (NH, OH); 1685 br, 1665 (C=O); 1605, 1590, 1550 (δNH, C=C, C=N); 1180–1150 (C–F). ^{1}H NMR spectrum, δ, ppm, **B** (100%): in $CDCl_3$: 1.33 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.36 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.50–7.70 m, 7.93–7.95 m (5H, Ph), 7.71 br.s (1H, 6-H), 8.30 s (1H, NH), 10.54 br.s (1H, OH); in DMSO-d_6: 1.30 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1), 4.29 m (2H, OCH_2, $^3J_{HH}$ = 7.1), 7.50–7.76 m (5H, Ph), 7.94 br.s (1H, 6-H), 9.66 s (1H, NH), 12.58 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm, **B** (100%): in $CDCl_3$: 78.79 d (CF_3, $^5J_{FH}$ = 0.8 Hz); in DMSO-d_6: 83.22 br.s (CF_3). Found, %: C 50.20; H 3.61; F 14.89; N 14.59. $C_{16}H_{13}F_3N_4O_4$. Calculated, %: C 50.27; H 3.43; F 14.91; N 14.66.

Ethyl 3-(furan-2-ylcarbonyl)-4-hydroxy-4-trifluoromethyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IId). Yield 68%, bright yellow crystals, mp 167–168°C. IR spectrum (mineral oil), ν, cm^{-1}: 3265, 3120 (NH, OH); 1695, 1680 (C=O); 1650, 1610, 1565, 1550 (δNH, C=C, C=N); 1220–1180 (C–F). ^{1}H NMR spectrum, δ, ppm, **B** (100%): in $CDCl_3$: 1.44 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.44 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.66 d.d (1H, 4′-H, $^3J_{4',3'}$ = 3.69, $^3J_{4',5'}$ = 1.68 Hz), 7.69 br.s (1H, 6-H), 7.71 d.d (1H, 3′-H, $^3J_{3',4'}$ = 3.69, $^4J_{3',5'}$ = 0.66 Hz), 7.80 d.d (1H, 5′-H, $^3J_{5',4'}$ = 1.68, $^4J_{5',3'}$ = 0.66 Hz), 8.21 br.s (1H, NH), 10.28 br.s (1H, OH); in DMSO-d_6: 1.31 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.32 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.77 d.d (1H, 4′-H, $^3J_{4',3'}$ = 3.58, $^3J_{4',5'}$ = 1.68 Hz), 7.50 d.d (1H, 3′-H, $^3J_{3',4'}$ = 3.58, $^4J_{3',5'}$ = 0.69 Hz), 7.92 br.s (1H, 6-H), 8.09 d.d (1H, 5′-H, $^3J_{5',4'}$ = 1.68, $^4J_{5',3'}$ = 0.69 Hz), 9.61 br.s (1H, NH),

12.61 br.s (1H, OH); in acetone-d_6: 1.35 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.38 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.76 d.d (1H, 4′-H, $^3J_{4',3'}$ = 3.64, $^3J_{4',5'}$ = 1.68 Hz), 7.71 d.d (1H, 3′-H, $^3J_{3',4'}$ = 3.64, $^4J_{3',5'}$ = 0.69 Hz), 7.83 br.q (1H, 6-H, $^5J_{HF}$ = 1.2 Hz), 8.00 d.d (1H, 5′-H, $^3J_{5',4'}$ = 1.68, $^4J_{5',3'}$ = 0.69 Hz), 8.41 br.s (1H, NH), 11.92 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm, **B** (100%): $CDCl_3$: 78.89 d (CF_3, $^5J_{FH}$ = 0.7 Hz); in DMSO-d_6: 83.16 s (CF_3); in acetone-d_6: 82.04 d (CF_3, $^5J_{FH}$ = 1.2 Hz); in CD_3OD: 82.61 d (CF_3, $^5J_{FH}$ = 1.0 Hz); in CD_3CN: 82.34 d (CF_3, $^5J_{FH}$ = 1.0 Hz); in pyridine-d_5: **B** (97%): 82.46 d (CF_3, $^5J_{FH}$ = 1.1 Hz); **A″** (3%): 88.29 s (CF_3). Found, %: C 45.08; H 3.10; F 15.24; N 15.21. $C_{14}H_{11}F_3N_4O_5$. Calculated, %: C 45.17; H 2.98; F 15.31; N 15.05.

Ethyl 4-hydroxy-3-(naphthalen-1-ylcarbonyl)-4-trifluoromethyl-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIe). Yield 63%, yellow crystals, mp 137–138°C. IR spectrum (mineral oil), ν, cm^{-1}: 3230, 3100 (NH, OH); 1670 br (C=O); 1635, 1615, 1610, 1560 (δNH, C=C, C=N); 1200–1150 (C–F). ^{1}H NMR spectrum, δ, ppm, **B** (100%): in $CDCl_3$: 1.31 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.37 m (2H, $C\mathbf{H}_2CH_3$, $^3J_{HH}$ = 7.1 Hz), 7.59–7.73 m (3H, H_{arom}), 7.91–8.01 m (4H, H_{arom}), 8.40 s (1H, NH), 8.53 br.q (1H, 6-H, $^5J_{HF}$ = 0.7 Hz), 10.44 br.s (1H, OH); in DMSO-d_6: 1.29 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.30 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.61–8.14 m (7H, H_{arom}), 8.40 s (1H, 6-H), 9.73 br.s (1H, NH), 12.60 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm, **B** (100%), in $CDCl_3$: 78.93 d (CF_3, $^5J_{FH}$ = 0.7 Hz); in DMSO-d_6: 83.47 s (CF_3). Found, %: C 55.40; H 3.58; F 13.06; N 13.01. $C_{20}H_{15}F_3N_4O_4$. Calculated, %: C 55.56; H 3.50; F 13.18; N 12.96.

Ethyl 3-benzoyl-4-hydroxy-4-(1,1,2,2-tetrafluoroethyl)-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIf). Yield 69%, bright yellow crystals, mp 159–160°C. IR diffuse reflectance spectrum, ν, cm^{-1}: 3255, 3145 (NH, OH); 1675 br (C=O); 1610, 1555 (δNH, C=C, C=N); 1220–1080 (C–F). ^{1}H NMR spectrum, δ, ppm, **B** (100%): in $CDCl_3$: 1.33 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.37 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.14 t.t (1H, HCF_2, $^2J_{HF}$ = 52.4, $^3J_{HF}$ = 5.1 Hz); 7.50–7.54 m, 7.67–7.69 m, and 7.95–7.97 m (5H, Ph); 7.66 br.s (1H, 6-H), 8.69 s (1H, NH), 10.46 br.s (1H, OH); in DMSO-d_6: 4.37 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.49–7.75 m (5H, Ph); **B** (95%): 1.29 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1), 6.87 t.t (1H, HCF_2, $^2J_{HF}$ = 51.4, $^3J_{HF}$ = 6.3), 7.86 d (1H, 6-H, $^5J_{HH}$ = 2.7 Hz), 9.45 d (1H, NH, $^5J_{HH}$ = 2.7 Hz), 12.53 s (1H, OH); **A″** (5%): 1.32 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 6.94 t.t (1H, HCF_2, $^2J_{HF}$ = 52.8, $^3J_{HF}$ = 5.6 Hz), 7.37 s (1H, 2-H), 8.52 s (1H, 1-H), 12.91 br.s (1H, 5-NH); in acetone-d_6: 7.34–7.74 m and 7.86–7.92 m (5H, Ph); **B** (72%): 1.34 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.37 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.76 t.t (1H, HCF_2, $^2J_{HF}$ = 51.8, $^3J_{HF}$ = 6.0 Hz), 7.79 br.s (1H, 6-H), 8.50 br.s (1H, NH), 11.74 br.s (1H, OH); **A″** (25%): 1.45 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 4.44 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.86 t.t (1H, HCF_2, $^2J_{HF}$ = 53.2, $^3J_{HF}$ = 6.0 Hz), 7.97 s (1H, 2-H), 8.01 s (1H, 1-H), 13.88 br.s (1H, 5-NH); **A′** (3%): 1.25 t (3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.1 Hz), 13.52 br.s (1H, 5-NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$: **B** (100%): 26.43 m (2F, HCF_2, *AB* system, Δ_{AB} = 3.34, $^2J_{AB}$ = 309.6, $^2J_{FH}$ = 54.2, $^3J_{FF}$ = 8.6, $^3J_{FH}$ = 5.1 Hz), 34.57 m (2F, CF_2, *AB* system, Δ_{AB} = 2.42, $^2J_{AB}$ = 274.2 Hz); in DMSO-d_6: **B** (95%): 27.78 m (2F, HCF_2, *AB* system, Δ_{AB} = 2.74, $^2J_{AB}$ = 298.9, $^2J_{FH}$ = 51.4, $^3J_{FF}$ = 10.4, $^3J_{FH}$ = 6.3 Hz), 37.54 m (2F, CF_2, *AB* system, Δ_{AB} = 3.04, $^2J_{AB}$ = 268.0 Hz); **A″** (5%): 25.77 d.t (2F, HCF_2, $^2J_{FH}$ = 52.8, $^3J_{FF}$ = 7.5 Hz), 41.98 d.m (2F, CF_2, $^3J_{FF}$ = 7.5 Hz); in acetone-d_6: **B** (72%): 28.22 m (2F, HCF_2, *AB* system, Δ_{AB} = 3.42, $^2J_{AB}$ = 304.5, $^2J_{FH}$ = 51.8, $^3J_{FF}$ = 9.4, $^3J_{FH}$ = 6.0 Hz), 37.39 m (2F, CF_2, *AB* system, Δ_{AB} = 2.84, $^2J_{AB}$ = 269.7 Hz); **A″** (25%): 27.99 d.t (2F, HCF_2, $^2J_{FH}$ = 53.4, $^3J_{FF}$ = 7.2 Hz), 41.95 m (2F, CF_2), 41.93 m (2F, CF_2); **A′** (3%): 26.68 d.t (2F, HCF_2, $^2J_{FH}$ = 52.5, $^3J_{FF}$ = 7.5 Hz), 42.23 m (2F, CF_2); in CD_3OD: **B** (91%): 26.88 m (1F, HCF_2, $^2J_{AB}$ = 303.3, $^2J_{FH}$ = 52.4, $^3J_{FF}$ = 9.5 Hz), 29.75 m (1F, HCF_2, $^2J_{AB}$ = 303.4, $^2J_{FH}$ = 51.8, $^3J_{FF}$ = 10.5 Hz), 36.34 m (1F, CF_2, $^2J_{AB}$ = 267.8 Hz), 36.82 m (1F, CF_2, $^2J_{AB}$ = 268.5 Hz); **A″** (7%): 27.36 d.m (2F, HCF_2, $^2J_{FH}$ = 53.4, $^3J_{FF}$ = 8.3 Hz), 42.03 m (2F, CF_2); **A′** (2%): 26.35 d.m (2F, HCF_2, $^2J_{FH}$ = 53.7 Hz), 42.14 m (2F, CF_2); in CD_3CN: **B** (79%): 27.82 m (2F, HCF_2, *AB* system, Δ_{AB} = 2.57, $^2J_{AB}$ = 306.1, $^2J_{FH}$ = 51.7, $^3J_{FF}$ = 9.0 Hz), 36.83 m (2F, CF_2, *AB* system, Δ_{AB} = 2.07, $^2J_{AB}$ = 271.4 Hz); **A′** (16%): 27.71 d.m (2F, HCF_2, $^2J_{FH}$ = 53.3, $^3J_{FF}$ = 7.2 Hz), 41.81 m (2F, CF_2); **A″** (5%): 26.32 d.m (2F, HCF_2, $^2J_{FH}$ = 53.4 Hz), 41.69 m (2F, CF_2); in pyridine-d_5: **B** (92%): 26.66 m (1F, HCF_2, $^2J_{AB}$ = 295.4, $^2J_{FH}$ = 52.4, $^3J_{FF}$ = 10.3 Hz), 29.23 m (1F, HCF_2, $^2J_{AB}$ = 300.2, $^2J_{FH}$ = 51.9, $^3J_{FF}$ = 11.4 Hz), 35.85 m (1F, CF_2, $^2J_{AB}$ = 260.5 Hz), 38.38 m (1F, CF_2, $^2J_{AB}$ = 265.7 Hz); **A′** (6%): 26.67 d.m (2F, HCF_2, $^2J_{FH}$ = 52.7 Hz), 41.70 m (2F, CF_2); **A″** (3%): 27.62 d.m (2F, HCF_2, $^2J_{FH}$ = 53.0 Hz), 41.50 m (2F, CF_2). Found, %: C 49.61; H 3.48; F 18.20; N 13.55. $C_{17}H_{14}F_4N_4O_4$. Calculated, %: C 49.56; H 3.41; F 18.34; N 13.52.

Ethyl 3-acetyl-4-heptafluoropropyl-4-hydroxy-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIg). Yield 74%, yellow crystals, mp 119–120°C. IR spectrum (mineral oil), ν, cm^{-1}: 3230, 3140 (NH, OH); 1685, 1665 (C=O); 1605, 1550 (δNH, C=C, C=N); 1230–1125 (C–F). ^1H NMR spectrum, δ, ppm: in $CDCl_3$: **B** (100%): 1.44 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 2.58 s (3H, $COCH_3$), 4.45 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.64 br.s (1H, 6-H), 8.07 s (1H, NH), 10.28 br.s (1H, OH); in DMSO-d_6: **B** (62%): 1.30 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.0 Hz), 2.42 s (3H, $COCH_3$), 4.30 m (2H, OCH_2, $^3J_{HH}$ = 7.0 Hz), 7.87 s (1H, 6-H), 9.44 s (1H, NH), 12.68 br.s (1H, OH); **A′** (3%): 1.41 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.2 Hz), 2.53 s (3H, $COCH_3$), 4.40 q (2H, OCH_2, $^3J_{HH}$ = 7.2 Hz), 7.93 s (1H, 2-H), 9.38 s (1H, 1-H), 13.48 s (1H, 5-NH); **A″** (35%): 1.27 t (3H, CH_2CH_3, $^3J_{HH}$ = 6.7 Hz), 2.11 s (3H, $COCH_3$), 4.31 q (2H, OCH_2, $^3J_{HH}$ = 6.7 Hz), 7.70 s (1H, 2-H), 8.46 s (1H, 1-H), 12.94 s (1H, 5-NH); in acetone-d_6: **B** (60%): 1.35 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 2.53 s (3H, $COCH_3$), 4.38 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.79 br.s (1H, 6-H), 7.99 br.s (1H, NH), 11.90 br.s (1H, OH); **A′** (21%): 1.49 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 2.60 s (3H, $COCH_3$), 4.45 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.56 br.s (1H, 1-H), 7.99 s (1H, 2-H), 12.10 br.s (1H, 5-NH); **A″** (19%): 1.32 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 2.30 s (3H, $COCH_3$), 4.32 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.36 br.s (1H, 1-H), 7.85 s (1H, 2-H), 11.90 br.s (1H, 5-NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$, **B** (100%): 36.01 m (2F, β-CF_2), 41.04 m (2F, α-CF_2), 81.11 m (3F, CF_3); in DMSO-d_6: **B** (62%): 36.88 m (2F, β-CF_2), 43.90 m (2F, α-CF_2), 82.44 m (3F, CF_3); **A′** (3%): 38.39 m (2F, β-CF_2), 51.92 m (2F, α-CF_2), 81.98 m (3F, CF_3); **A″** (35%): 38.90 m (2F, β-CF_2), 51.44 m (2F, α-CF_2), 82.80 m (3F, CF_3); in acetone-d_6: **B** (60%): 38.16 m (2F, β-CF_2), 44.01 m (2F, α-CF_2), 83.01 m (3F, CF_3); **A′** (21%): 39.74 m (2F, β-CF_2), 52.30 m (2F, α-CF_2), 83.41 m (3F, CF_3); **A″** (19%): 40.37 m (2F, β-CF_2), 51.91 m (2F, α-CF_2), 83.25 m (3F, CF_3). Found, %: C 37.24; H 2.64; F 31.75; N 13.25. $C_{13}H_{11}F_7N_4O_4$. Calculated, %: C 37.16; H 2.64; F 31.65; N 13.33.

Ethyl 3-benzoyl-4-heptafluoropropyl-4-hydroxy-1,4-dihydroimidazo[5,1-*c*][1,2,4]triazine-8-carboxylate (IIh). Yield 70%, yellow crystals, mp 77–78°C. IR diffuse reflectance spectrum, ν, cm^{-1}: 3250, 3170 (NH, OH); 1670 (C=O); 1605, 1550 (δNH, C=C, C=N); 1220–1120 (C–F). ^1H NMR spectrum, δ, ppm: in $CDCl_3$: 1.37 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.39 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.51–7.68 m and 8.71–8.74 m (5H, Ph); **B** (97%): 7.70 br.s (1H, 6-H), 8.74 s (1H, NH), 10.37 br.s (1H, OH); **A″** (3%): 7.20 br.s (1H, 2-H), 8.71 s (1H, 1-H), 12.03 br.s (1H, 5-NH); in DMSO-d_6: **B** (80%): 1.23 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.29 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.51–7.75 m (5H, Ph), 7.93 br.s (1H, 6-H), 9.80 s (1H, NH), 12.64 br.s (1H, OH); **A″** (20%): 1.31 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.34 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.34–7.47 m (5H, Ph), 7.39 s (1H, 2-H), 8.50 s (1H, 1-H), 13.23 s (1H, 5-NH); in acetone-d_6: 7.34–7.97 m (5H, Ph); **B** (82%): 1.34 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.37 m (2H, OCH_2), 7.85 br.s (1H, 6-H), 8.78 s (1H, NH), 11.97 br.s (1H, OH); **A′** (5%): 1.43 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.31 m (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.85 s (1H, 2-H), 8.19 s (1H, 1-H), 13.95 s (1H, 5-NH); **A″** (13%): 1.33 t (3H, CH_2CH_3, $^3J_{HH}$ = 7.1 Hz), 4.43 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 7.48 s (1H, 2-H), 8.74 s (1H, 1-H), 12.25 s (1H, 5-NH). ^{19}F NMR spectrum, δ_F, ppm: in $CDCl_3$: **B** (97%): 36.58 m (2F, β-CF_2), 40.90 m (2F, α-CF_2, *AB* system, Δ_{AB} = 1.92, J_{AB} = 286.6 Hz), 81.09 m (3F, CF_3); **A″** (3%): 36.60 m (2F, β-CF_2), 47.02 m (2F, α-CF_2), 81.27 m (3F, CF_3); in DMSO-d_6: **B** (80%): 37.58 m (2F, β-CF_2), 44.32 m (2F, α-CF_2), 82.41 m (3F, CF_3); **A″** (20%): 38.46 m (2F, β-CF_2), 50.48 m (2F, α-CF_2), 82.69 m (3F, CF_3); in acetone-d_6: **B** (82%): 38.78 m (2F, β-CF_2), 41.89 m (2F, α-CF_2), 82.99 m (3F, CF_3); **A′** (5%): 40.44 m (2F, β-CF_2), 51.50 m (2F, α-CF_2), 83.22 m (3F, CF_3); **A″** (13%): 39.54 m (2F, β-CF_2), 51.21 m (2F, α-CF_2), 83.16 m (3F, CF_3); in CD_3OD: **B** (83%): 38.95 m (2F, β-CF_2), 44.44 m (2F, α-CF_2), 82.90 m (3F, CF_3); **A″** (17%): 39.48 m (2F, β-CF_2), 51.10 m (2F, α-CF_2), 83.07 m (3F, CF_3); in CD_3CN: **B** (85%): 38.54 m (2F, β-CF_2), 43.40 m (2F, α-CF_2), 82.90 m (3F, CF_3); **A′** (7%): 38.95 m (2F, β-CF_2), 51.34 m (2F, α-CF_2), 83.15 m (3F, CF_3); **A″** (7%): 39.51 m (2F, β-CF_2), 50.93 m (2F, α-CF_2), 83.03 m (3F, CF_3); in pyridine-d_5: **B** (82%): 37.96 m (2F, β-CF_2), 43.83 m (2F, α-CF_2), 82.01 m (3F, CF_3); **A″** (18%): 38.41 m (2F, β-CF_2), 50.21 m (2F, α-CF_2), 82.14 m (3F, CF_3). Found, %: C 44.57; H 2.69; F 27.64; N 11.45. $C_{18}H_{13}F_7N_4O_4$. Calculated, %: C 44.82; H 2.72; F 27.57; N 11.62.

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