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Synthesis and Structure of 2-Ethoxy- and 2-Aminomethylidene-3-fluoroalkyl-3-oxopropionates

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Abstract—Condensation of ethyl 3-polyfluoroalkyl-3-oxopropionates with excess triethyl orthoformate gave ethyl 3-polyfluoroalkyl-2-ethoxymethylidene-3-oxopropionates which reacted with primary aliphatic, aromatic, and heterocyclic amines to form ethyl 2-alkyl(aryl, hetaryl)aminomethylidene-3-polyfluoroalkyl-3-oxopropionates. According to the X-ray diffraction and IR data, the latter exist in the crystalline state as the corresponding *E* isomers, while in solution (NMR data), as mixtures of *Z* and *E* isomers. Condensation of ethyl 2-ethoxymethylidene-3-oxopropionates with secondary heterocyclic amines (morpholine and pyrrolidine) led to the formation of 2-morpholino(pyrrolidin-1-yl)methylidene-3-fluoroalkyl-3-oxopropionates which were shown to exist as *Z* isomers both in the crystalline state and in solution.

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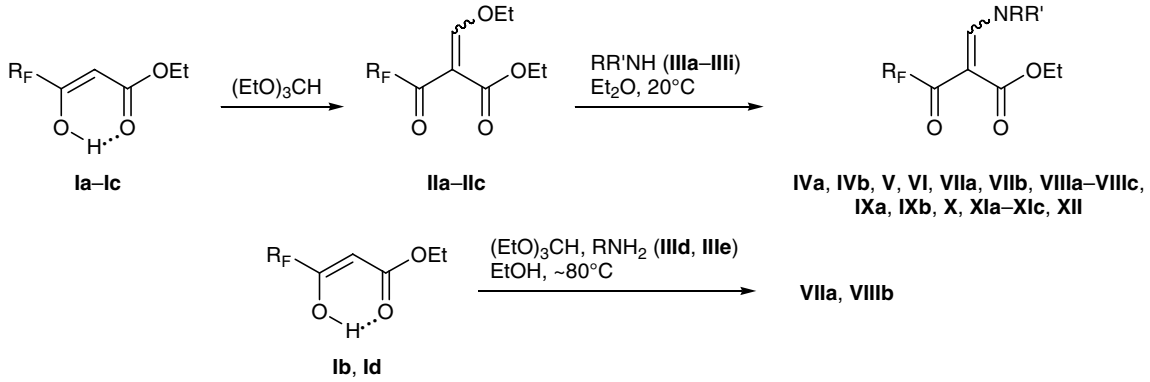
3-Oxopropionates, including those containing fluoroalkyl groups, are widely used in synthetic organic chemistry as convenient precursors of various acyclic, carbocyclic, and heterocyclic compounds some of which have found application in industry and medicine [1]. A promising approach to extension of the application scope of fluorinated 3-oxopropionates in organic synthesis is based on introduction into their molecules of additional functional groups. Such modification should increase the number of potential reaction centers and give rise to new competing reaction paths. For example, 3-oxo esters can be modified via introduction

Scheme 1.



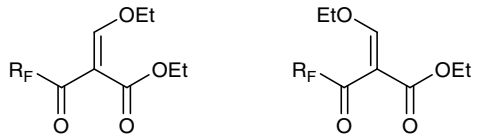
I, **II**, R_F = CF_3 (**a**), $H(CF_2)_2$ (**b**), C_3F_7 (**c**), HCF_2 (**d**); **III**, R′ = H, R = Me (**a**), $PhCH_2$ (**b**), Ph (**c**), 4-MeC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), pyridin-2-yl (**f**), pyrimidin-2-yl (**g**); RR′N = morpholino (**h**), pyrrolidin-1-yl (**i**); **IV**–**X**, R′ = H; **IV**, R = Me, R_F = CF_3 (a), C_3F_7 (**b**); **V**, R = $PhCH_2$, R_F = $H(CF_2)_2$; **VI**, R = Ph, R_F = CF_3; **VII**, R = 4-MeC_6H_4, R_F = HCF_2 (**a**), CF_3 (**b**); **VIII**, R = 4-$MeOC_6H_4$, R_F = CF_3 (**a**), $H(CF_2)_2$ (**b**), C_3F_7 (**c**); **IX**, R = pyridin-2-yl, R_F = CF_3 (**a**), C_3F_7 (**b**); **X**, R = pyrimidin-2-yl, R_F = CF_3; **XI**, RR′N = morpholino, R_F = CF_3 (**a**), $H(CF_2)_2$ (**b**), C_3F_7 (**c**); **XII**, RR′N = pyrrolidin-1-yl, R_F = CF_3.

into the 2-position of an alkoxy or aminomethylidene substituent capable of being involved in further transformations [2]. It is known that nonfluorinated 2-alkoxy- and 2-aminomethylidene-3-oxopropionates are widely used in organic chemistry due to their versatile synthetic potential. Available information on their fluorinated analogs is strongly limited. Jones [3] reported on the synthesis of ethyl 2-ethoxymethylidene-4,4,4-trifluoro-3-oxobutanoate for which only analytical data were given.

The present work was aimed at synthesizing 2-amino- and 2-ethoxymethylidene-3-polyfluoroalkyl-3-oxopropionates and studying their structure. We have found that ethyl 3-fluoroalkyl-3-oxopropionates **Ia–Ic** react with excess triethyl orthoformate to give ethyl 2-ethoxymethylidene-3-fluoroalkyl-3-oxopropionates **IIa–IIc** (Scheme 1). In the syntheses of nonfluorinated analogs of **II** [2] and ethyl 2-ethoxymethylidene-4,4,4-trifluoro-3-oxobutanoate [3] acetic anhydride was used to displace the reaction equilibrium via binding of the liberated ethanol to ethyl acetate. According to our results, compounds **II** can be obtained in satisfactory yields in the absence of acetic anhydride, by heating 3-oxo esters **Ia–Ic** with 4 equiv of triethyl orthoformate with simultaneous removal of the liberated ethanol by distillation.

Compounds **IIa–IIc** are light yellow oily substances; they were isolated and purified by vacuum distillation. The ^{1}H and ^{19}F NMR spectra of esters **IIa–IIc** in $CDCl_3$ contained two sets of signals, while all absorption bands belonging to characteristic groups in their IR spectra (neat) were broadened. These data led us to conclude that esters **IIa–IIc** exist as mixtures of *Z* and *E* isomers differing by orientation of substituents at the double C=C bond (Scheme 2).

Scheme 2.



Z-**II** *E*-**II**

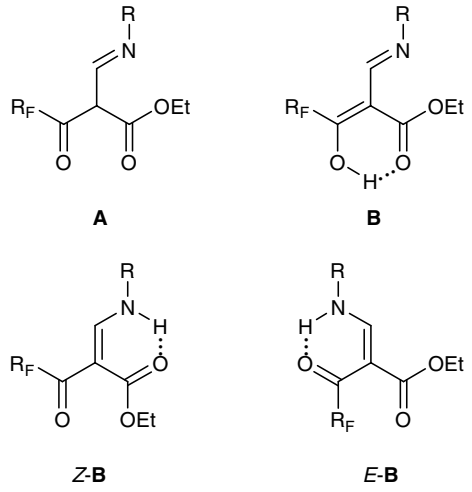
The *E* and *Z* isomers were distinguished by analysis of the CH= proton signals in the ^{1}H NMR spectrum of ester **IIa**. One CH= signal located at δ 7.73 ppm is a broadened singlet, presumably due to coupling with fluorine nuclei in the neighboring trifluoromethyl group; therefore, this signal was assigned to the *Z* isomer. Moreover, as shown in [4, 5], signals from the CH= protons of (*E*)-2-arylmethylidene-3-oxopropionates appear in a weaker field relative to the corresponding signals of their *Z* isomers. An analogous pattern was observed for compound **IIa**. In such a way we assigned signals for the *E* and *Z* isomers of esters **IIb** and **IIc**. It should be noted that the ratios of the *E* and *Z* isomers of **IIa–IIc** were approximately equimolar.

2-Alkyl(aryl, hetaryl)aminomethylidene-3-fluoroalkyl-3-oxopropionates **IV–XII** can be synthesized in two ways. The first of these is based on the condensation of 2-ethoxymethylidene-3-oxopropionates **IIa–IIc** with amines in diethyl ether at room temperature, and the second is three-component condensation of 3-oxo esters **I** with triethyl orthoformate and the corresponding amine in boiling ethanol (Scheme 1). As amine component we used primary aliphatic [methylamine (**IIIa**) and benzylamine (**IIIb**)], aromatic [aniline (**IIIc**), *p*-toluidine (**IIId**), and *p*-anisidine (**IIIe**)], and heterocyclic amines [2-aminopyridine (**IIIf**) and 2-aminopyrimidine (**IIIg**)] and secondary heterocyclic amines [morpholine (**IIIh**) and pyrrolidine (**IIIi**)]. In all cases, the products were those formed via condensation of amines **III** at the ethoxymethylidene fragment of esters **II**. The first procedure turned out to be more effective; it allowed preparation of 2-aminomethylidene-3-fluoroalkyl-3-oxopropionates having various alkyl, aryl, or hetaryl substituents on the nitrogen atom. The three-component condensation can be accomplished only with aromatic amines.

Compounds **IVa**, **IVb**, **VI**, **VIIa**, **VIIb**, **VIIIb**, **VIIIc**, **IXa**, **X**, and **XIa–XIc** are crystalline substances; they were isolated and purified by recrystallization. Oily esters **V**, **VIIIa**, **IXb**, and **XII** were purified by column chromatography using chloroform as eluent.

2-Aminomethylidene-3-oxopropionates **IVa**, **IVb**, **V**, **VI**, **VIIa**, **VIIb**, **VIIIa–VIIIc**, **IXa**, **IXb**, and **X** can be regarded as examples of a complex tautomeric system, for the NH proton therein is fairly labile and is capable of participating in various tautomeric transformations, as well as in hydrogen bonding (both inter- and intermolecular). Thus esters **IV–X** could give rise to keto–enol and amino–imine tautomerism, and they can exist as imino ketone (**A**), imino enol (**B**) and/or amino ketone (**C**) tautomers (Scheme 3). In addition, tautomer **C** may be *Z* or *E* isomer with respect to substituent configuration at the double C=C bond. Isomer *Z*-**C** should be stabilized via intramolecular hydrogen bond with the ester oxygen atom, while in isomer *E*-**C** analogous intramolecular hydrogen bond

Scheme 3.



can be formed with participation of the fluoroacyl carbonyl group.

The structure of esters **IV**–**X** was studied by IR and ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy, and X-ray analysis. In the IR spectra of compounds **IV**–**X** dispersed in mineral oil we observed strong absorption bands due to carbonyl stretching vibrations at 1725–1685 and 1668–1632 cm^{-1} and bands at 3278–3100 cm^{-1} belonging to stretching vibrations of amino group; these data suggest the presence of tautomer **C**. The low-frequency shift of the carbonyl absorption band results from conjugation of the carbonyl groups with the double C=C bond and intramolecular hydrogen bonding with the amino group. The IR spectra of 0.01 M solutions of compounds **IVa** and **VIIIc** in $CHCl_3$ were characterized by considerable broadening of absorption bands (see Experimental). Two sets of signals were present in the ^{1}H NMR spectra of **IVa** and **VIIIc**, recorded from solutions in $CDCl_3$. Signals from protons of the amino group and methylidene fragment appeared in a weak field (δ_{CH} ~8.15–9.36, δ_{NH} ~9.47–12.60 ppm) as doublets with a coupling constant of ~14 Hz, which indicates *trans* arrangement of these protons. Esters **IV**–**X** also showed doubled fluorine resonance signals in ^{19}F NMR spectra. The ^{1}H NMR spectra of **IVa** and **VI** in $(CD_3)_2CO$, $(CD_3)_2SO$, and CD_3OD also contained two sets of signals. Therefore, we concluded that esters **IV**–**X** in solution exist as mixtures of *Z* and *E* isomers of tautomer **C** and that in the crystalline state only one isomer of tautomer **C** is present. An exception was oily ester **V**; according to the IR data (neat), it is a mixture of *Z* and *E* isomers: the spectrum contains two sets of carbonyl absorption bands.

The structure of compounds **IVa** and **VIIa** in crystal was established by X-ray analysis. The crystalline structure of **IVa** and **VIIa** is formed by crystallographically independent molecules (Figs. 1, 2) occupying a common position. Esters **IVa** and **VIIa** in the crystalline state are *s-cis*,*s-cis* conformers of isomer *E*-**C**, where the trifluoroalkyl and ethoxy groups appear in neighboring positions. As shown in Fig. 1, translationally identical molecules of **VIIa** are stacked along the *b* crystallographic axis, giving rise to alternating layers along the *c* axis. The molecule is approximately planar. The maximal deviations from the mean-square plane are 0.03 Å (C^3) for the hexagon $H^1N^1C^5C^2C^3O^3$ and 0.003 Å (C^8) for the benzene ring C^8–C^{13}. The dihedral angle between the $H^1N^1C^5C^2C^3O^3$ and C^8–C^{13} planes is 4.3°. The intramolecular distance $O^3\cdots H^1$ is 1.90(3) Å, and the angles $N^1H^1O^3$ and $C^3O^3H^1$ are 136.5 and 102.7°,

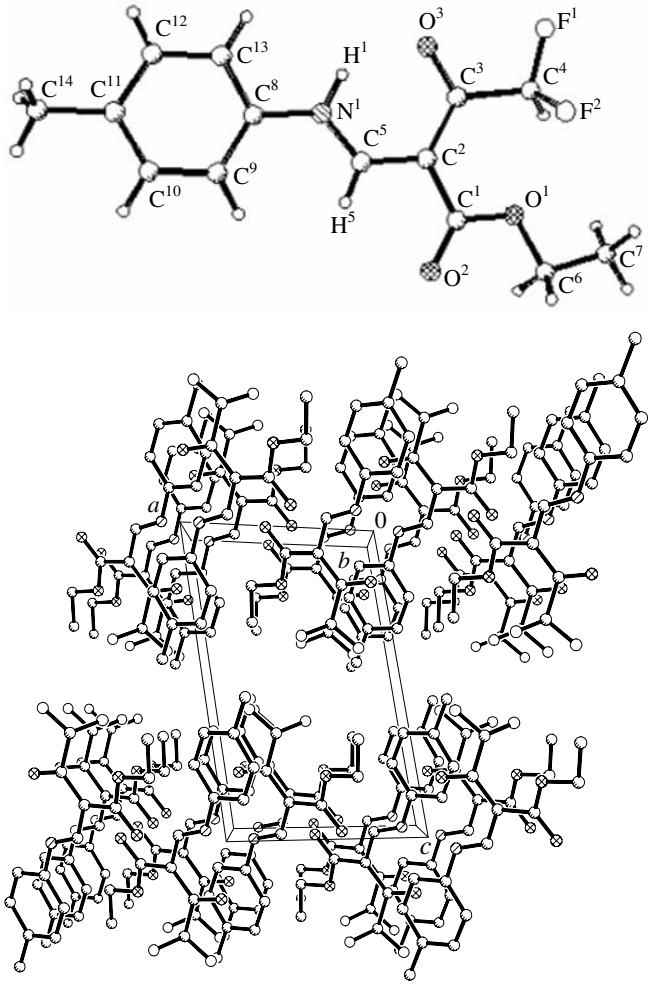


Fig. 1. Crystalline structure of ethyl 4,4-difluoro-2-(4-methylphenylaminomethylidene)-3-oxobutanoate (**VIIa**) according to the X-ray diffraction data.

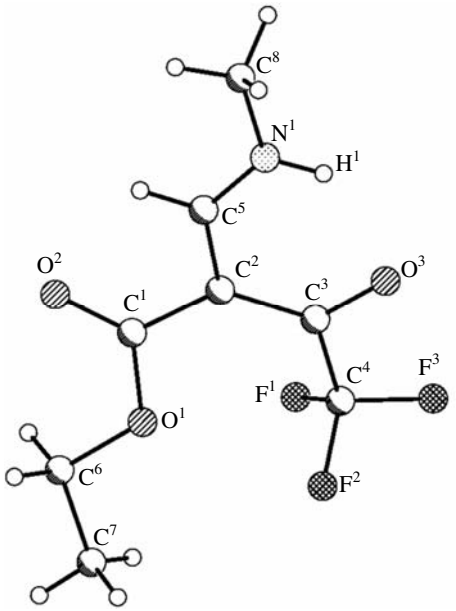
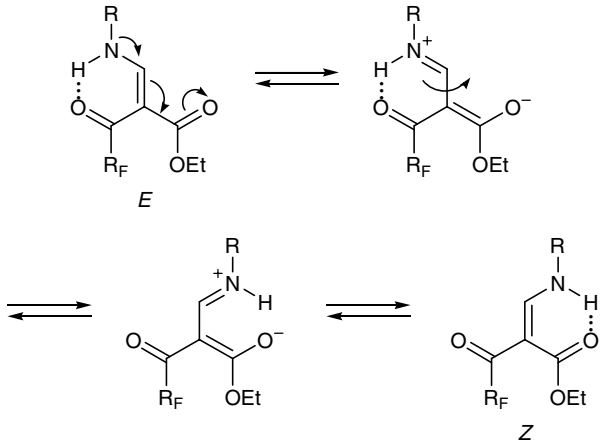


Fig. 2. Structure the molecule of ethyl 4,4,4-trifluoro-2-(methylaminomethylidene)-3-oxobutanoate (**IVa**) according to the X-ray diffraction data.

respectively. These data suggest formation of intramolecular hydrogen bond between O^3 and H^1. According to the X-ray diffraction data, molecules **IVa** are also approximately planar. The intramolecular distance $O^3\cdots H^1$ is 2.03(2) Å, and the angles $N^1H^1O^3$ and $C^3O^3H^1$ are 132.3 and 101.5°, respectively, indicating intramolecular hydrogen bonding $O^3\cdots H^1$.

It is known [6, 7] that the barrier to rotation about a double C=C bond considerably decreases if there exist neighboring functional groups polarizing that bond or the latter is a part of a conjugated system. This is especially typical of enamino ketones and so-called "push-pull" olefins in which one double-bonded carbon atom is attached to an electron-withdrawing group, and the other, to an electron-donor group. As a result of electron density delocalization, formally double carbon–carbon bond in such compounds becomes partially single, and the barrier to rotation about it decreases relative to normal olefins [7]. Presumably, in our case crystallization gives only one conformational *E* isomer. Dissolution is accompanied by isomerization to produce a mixture of *Z* and *E* isomers. Probably, the isomerization involves mesomeric structures shown in Scheme 4.

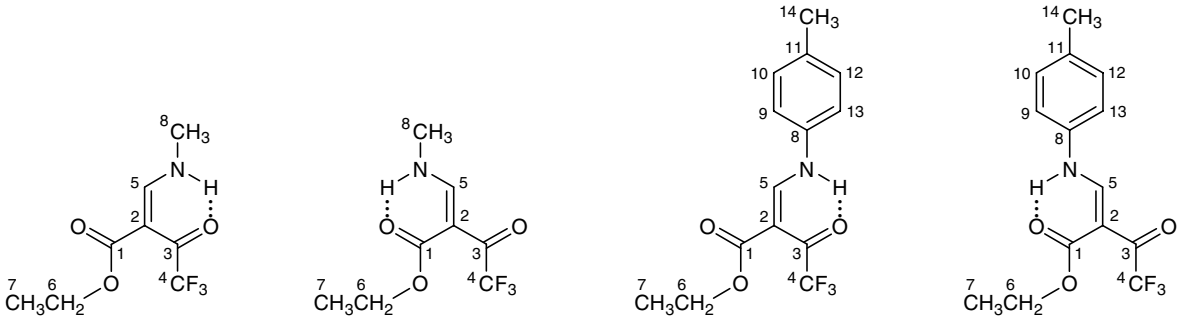
Scheme 4.



The *Z* and *E* isomers in solution were distinguished on the basis of the ^{13}C NMR spectra of esters **IVa** and **VIIb**. Analysis of the spectra allowed us to reveal some general relations. The major tautomer is characterized by a quartet signal from the C^3 carbonyl carbon atom neighboring to the trifluoromethyl group, which is located in a weaker field, as compared to the corresponding signal of the other isomer (Table 1), while the opposite pattern is observed for the ester carbonyl carbon atom (C^1). Taking into account that proton-donor solvents induce a downfield shift of the carbonyl carbon signal of acetone [8], we concluded that the downfield C^3 signal and upfield C^1 signal belong to the major *E* isomer and that the signals arranged in the reverse order arise from the *Z* isomer. This assignment is additionally confirmed by the fact that the C^5 signal (double-bonded carbon atom) of the *Z* isomer is a quartet ($J_{CF} \approx 1.3$ Hz for **IVa**) or broadened singlet (**VIIb**) due to long-range coupling with fluorine nuclei of the trifluoromethyl group.

In the ^1H NMR spectra of esters **IVa** and **VIIb** dissolved in $CDCl_3$, protons of the CH and NH groups of the predominant *E* isomer resonate in a weaker field relative to those of the *Z* isomer (see Experimental). Larger chemical shift of the NH proton in the *E* isomer indicate stronger intramolecular hydrogen bond therein and hence its higher stability. Signals from fluorine nuclei in the trifluoromethyl group of the *Z* isomers of **IVa** and **VIIb** appear in the ^{19}F NMR spectra ($CDCl_3$) in a weaker field relative to the CF_3 signals from the *E* isomers in which the trifluoroacetyl group is involved in intramolecular hydrogen bond. These findings are consistent with our previous data for fluoroalkyl-containing 1,2,3-triketone 2-arylhydrazones [9]. The above relations allowed us to assign signals to *Z* and *E* isomers of the other esters (**IVb**, **V**, **VI**, **VIIa**, **VIIIa**–**VIIIc**, **IXa**, **IXb**, and **X**). Almost all esters turned out to exist as equilibrium mixtures of *Z* and *E* isomers, the latter prevailing (as more stable).

Table 1. ^{13}C NMR spectra ($CDCl_3$) of compounds **IVa** and **VIb**, δ_C, ppm (J_{CF}, Hz)



E-**IVa** *Z*-**IVa** *E*-**VIIb** *Z*-**VIIb**

Atom	Compound **IVa**		Compound **VIIb**	
	E	*Z*	*E*	*Z*
C^1	165.29 s	167.95 s	165.11 s	167.74 s
C^2	97.37 s	96.11 s	99.25 s	98.24 s
C^3	178.46 q (J = 35.5)	177.5 q (J = 34.9)	179.18 q (J = 36.4)	178.43 q (J = 35.0)
C^4	117.08 q (J = 287.4)	117.29 q (J = 289.9)	116.92 q (J = 287.5)	117.12 q (J = 290.0)
C^5	164.07 s	162.72 br.s	155.94 s	154.00 q (J = 1.7)
S^6	60.53 s	60.36 s	60.90 s	60.81 s11
C^7	36.78 s	36.52 s	20.85 s	20.79 s
C^8	13.94 s	13.78 s	137.19 s	136.55 s
C^9, C^{13}	–	–	130.58 s	130.52 s
C^{10}, C^{12}	–	–	118.29 s	117.83 s
C^{11}	–	–	135.46 s	135.73 s
C^{14}	–	–	13.94 s	13.75 s

We examined isomeric composition of compounds **IVa** and **VI** in different solvents [$CDCl_3$, $(CD_3)_2CO$, $(CD_3)_2SO$, CD_3OD] and found that the isomer ratio almost does not depend on the solvent nature. The only observed effect was variation of the shape of signals. All signals were clearly resolved in weakly polar aprotic $CDCl_3$, in polar aprotic $(CD_3)_2SO$ all signals were broadened, and in polar proton-donor CD_3OD all CH= signals appeared as singlets, while signals from the NH protons were almost absent (due to exchange). The isomer ratio remained almost constant with time: the signal intensity ratio did not change in the NMR spectra recorded at equal time intervals. Exceptions were esters **IXa** and **X** containing heterocyclic fragments. The NMR spectra of these compounds revealed displacement of the equilibrium toward the *Z* isomer (Table 2).

We also examined by ^1H NMR spectroscopy the isomeric composition of ester **IVa** in $(CD_3)_2SO$ in the temperature range from 30 to 100°C. At 70°C, signals from the *Z* and *E* isomers coalesced, presumably due to increased rate of rotation about the C–N bond. An analogous behavior is typical of *N*,*N*-dialkyl enamino ketones and *N*,*N*-dialkyl enamino acids [7].

2-Hetarylmethylidene-substituted 3-oxopropionates **XIa**–**XIc** and **XII** have no NH group; therefore, they

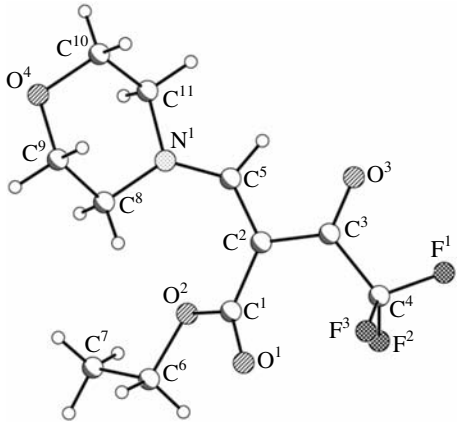


Fig. 3. Structure the molecule of ethyl 4,4,4-trifluoro-2-(morpholinomethylidene)-3-oxobutanoate (**XIa**) according to the X-ray diffraction data.

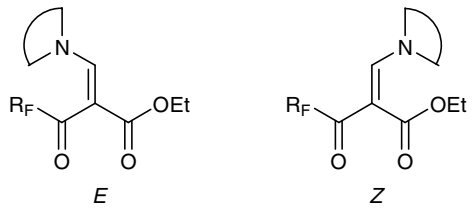
Table 2. *E*/*Z* Isomer ratios (%) of compounds **IVa**, **IVb**, **V**, **VI**, **VIIa**, **VIIb**, **VIIIa**–**VIIIc**, **IXa**, **IXb**, and **X** in solution according to the NMR data ($CDCl_3$)

Comp. no.	R_F	R	*E*	*Z*
IVa	CF_3	Me	73 (73)	27 (27)
IVb[a]	C_3F_7	Me	87	13
V	$H(CF_2)_2$	CH_2Ph	75	25
VI	CF_3	Ph	65	35
VIIa	HCF_2	4-MeC_6H_4	90	10
VIIb[a]	CF_3	4-MeC_6H_4	62	38
VIIIa	CF_3	4-$MeOC_6H_4$	67	33
VIIIb	$H(CF_2)_2$	4-$MeOC_6H_4$	73	27
VIIIc	C_3F_7	4-$MeOC_6H_4$	60	40
IXa[b]	CF_3	Pyridin-2-yl	71 (66)	29 (44)
IXb	C_3F_7	Pyridin-2-yl	44	56
X[b]	CF_3	Pyrimidin-2-yl	94 (75)	6 (25)

[a] In DMSO-d_6.
[b] In parentheses are given the isomer ratios after storage for 10 days at 20°C.

could give rise to only *Z*,*E* isomerism (Scheme 5). However, the ^1H and ^{19}F NMR spectra of these compounds in $CDCl_3$ showed that they exist as a single isomer. According to the X-ray diffraction data, ester **XIa** in crystal is *Z*-isomer in *s-trans*,*s-cis* conformation (Fig. 3). The IR spectra of a crystalline sample of **XIa** (mineral oil) and its solution in $CHCl_3$ revealed no considerable differences. Therefore, we concluded that ester **XIa** in $CDCl_3$ also has the structure of *Z* isomer. Comparison of the ^1H NMR and IR data for compounds **XIa**–**XIc** and **XII** showed that they have similar structures. Unlike esters **VI**–**X** stabilized by intramolecular hydrogen bond, compounds **XI** and **XII** are unstable, and they readily undergo decomposition in chloroform solution on storage.

Scheme 5.



EXPERIMENTAL

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from samples dispersed in mineral oil, thin films (neat), or 0.01 M solutions in chloroform. The ^1H NMR spectra were measured on a Bruker DRX-400 spectrometer at 400 MHz relative to tetramethylsilane. The ^{19}F NMR spectra were recorded on Tesla BS-587A (75.3 MHz) and Bruker DRX-400 instruments (376 MHz) using C_6F_6 as reference. The ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (100 MHz) relative to tetramethylsilane. The elemental compositions were determined on a Carlo Erba CHNS-O EA 1108 analyzer.

X-Ray diffraction study of a single crystal of compound **VIIa** was performed at room temperature on an Enraf–Nonius CAD-4 diffractometer (MoK_α irradiation, graphite monochromator, ω/2θ scanning); and single crystals of **IVa** and **XIa** were analyzed on an Xcalibur 3 diffractometer at 295(2) K (MoK_α irradiation, graphite monochromator, CCD detector, ω/2θ scanning). The structures were solved by the direct methods, followed by Fourier synthesis, using SHELXS-97 software [10] and were refined by the least-squares procedure in anisotropic full-matrix approximation for all non-hydrogen atoms using SHELXL-97 program [10]. The coordinates of hydrogen atoms were determined experimentally and were refined in isotropic approximation.

The principal crystallographic parameters of compounds **IVa**, **VIIa**, and **XIa** are collected in Table 3; the complete sets of crystallographic data were deposited to the Cambridge Crystallographic Data Center (entry nos. CCDC 612574, CCDC 620487, and CCDC 612575, respectively).

Ethyl 2-ethoxymethylidene-4,4,4-trifluoro-3-oxobutanoate (IIa). A mixture of 9.2 g (0.05 mol) of ester **Ia** and 29.6 g (0.2 mol) of triethyl orthoformate was heated under reflux for 1 h with simultaneous removal of ethanol by distillation. The mixture was then subjected to fractional distillation under reduced pressure. Yield 7.1 g (59%), bp 125–127°C (15–17 mm); published data [3]: bp 115–120°C (10 mm). IR spectrum (film), ν, cm^{-1}: 2987 (C–H), 1730–1712 (C=O), 1618–1580 (C=C), 1202–1108 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 1.32 t and 1.41 t (3H each, OCH_2CH_3, J = 7.2 Hz), 4.25 q and 4.30 q (2H each, OCH_2, J = 7.2 Hz), 7.83 s (1H, CH); *Z* isomer: 1.29 t and 1.45 t (3H each, OCH_2CH_3, J = 7.0 Hz), 4.29 q and 4.35 q (2H each, OCH_2, J = 7.0 Hz), 7.73 br.s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 86.16 s (CF_3, *E* isomer), 89.23 br.s (CF_3, *Z* isomer). Found, %: C 45.30; H 4.71; F 23.65. $C_9H_{11}F_3O_4$. Calculated, %: C 45.01; H 4.62; F 23.73.

Table 3. Crystallographic data for compounds **IVa**, **VIIa**, and **XIa**

Parameter	**IVa**	**VIIa**	**XIa**
Formula	$C_8H_{10}F_3NO_3$	$C_{14}H_{15}F_2NO_3$	$C_{11}H_{14}F_3NO_4$
Molecular weight	225.17	283.27	281.23
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.0923(16)	7.983(2)	7.9855(16)
b, Å	11.472(3)	8.288(1)	8.7560(15)
c, Å	8.8067(13)	12.139(3)	10.375(4)
α, deg	90.00	108.02(2)	66.02(2)
β, deg	100.878(14)	91.10(2)	89.65(3)
γ, deg	90.00	114.07(2)	80.540(15)
V, Å^3	1001.3(3)	687.5(3)	652.3(3)
Z	4	2	2
λ, Å	0.71073	0.71073	0.71073
d_{calc}, g/cm^3	1.494	1.37	1.432
μ, cm^{-1}	0.148	0.114	0.135
Total reflection number	16223	2082	10725
Number of independent reflections	3158	1977	3949
Number of reflections with $F_0 > 4\sigma(F_0)$	1057	1692	1539
Number of parameters	176	242	228
$2\theta_{max}$, deg	63.60	46.94	63.44
Range of h	$-14 \le h \le 14$	$-8 \le h \le 8$	$-11 \le h \le 11$
Range of k	$-16 \le k \le 16$	$-9 \le k \le 8$	$-12 \le k \le 12$
Range of l	$-12 \le l \le 12$	$0 \le l \le 13$	$-15 \le l \le 14$
R-Factor [$F_0 > 4\sigma(F_0)$], wR_2	0.039, 0.068	0.032, 0.086	0.0372, 0.0644

Ethyl 2-ethoxymethylidene-3-oxoalkanoates **IIb** and **IIc** were synthesized in a similar way.

Ethyl 2-ethoxymethylidene-4,4,5,5-tetrafluoro-3-oxopentanoate (**IIb**) was synthesized from 10.8 g (0.05 mol) of ester **Ib**. Yield 8.9 g (66%), bp 135–140°C (115–117 mm). IR spectrum (film), ν, cm^{-1}: 2989 (=C–H), 1725–1711 br (C=O), 1616–1591 (C=C), 1209–1111 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 1.29 t and 1.39 t (3H each, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.24 q and 4.29 q (2H each, OCH_2, J = 7.2 Hz), 6.27 t.t.t (1H, HCF_2, J = 52.9, 5.8 Hz), 7.78 s (1H, CH); *Z* isomer: 1.32 t and 1.44 t (3H each, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.27 q and 4.35 q (2H each, OCH_2, J = 7.2 Hz), 6.24 t.t.t [1H, $H(CF_2)_2$, J = 53.0, 5.8 Hz], 7.77 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *E* isomer: 23.10 d.m (2F, HCF_2, J = 52.9 Hz), 37.87 m (2F, CF_2); *Z* isomer: 22.87 d.m (2F, HCF_2, J = 52.9 Hz), 40.79 m (2F, CF_2). Found, %: C 42.60; H 4.43; F 25.40. $C_{10}H_{12}F_4O_4$. Calculated, %: C 42.67; H 4.48; F 25.31.

Ethyl 2-ethoxymethylidene-4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate (IIc) was synthesized from 14.2 g (0.05 mol) of ester **Ic**. Yield 9.7 g (57%), bp 142–144°C (15–17 mm). IR spectrum (film), ν, cm^{-1}: 2989 (=C–H), 1732–1719 br (C=O), 1621 (C=C), 1231–1128 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer (57%): 1.26 t and 1.32 t (3H each, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 4.05 q and 4.18 q (2H each, OCH_2, J = 7.0 Hz), 8.00 s (1H, CH); *E* isomer (43%): 1.17 t and 1.34 t (3H each, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.14 q and 4.37 q (2H each, OCH_2, J = 7.2 Hz), 8.04 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *Z* isomer (57%): 44.94 m (2F, CF_2), 46.68 m (2F, CF_2), 82.14 t (3F, CF_3, J = 8.5 Hz); *E* isomer (43%): 42.17 m (2F, CF_2), 47.69 m (2F, CF_2), 81.98 t (3F, CF_3, J = 8.5 Hz). Found, %: C 38.82; H 3.11; F 39.14. $C_{11}H_{11}F_7O_4$. Calculated, %: C 38.84; H 3.26; F 39.09.

Ethyl 2-alkyl(aryl, hetaryl)aminomethylidene-3-oxoalkanoates IV–XII. *a*. Gaseous methylamine was passed over a period of 30 min through a solution of

0.01 mol of the corresponding ethyl 2-ethoxymethylidene-3-oxoalkanoate **II** in 10 ml of diethyl ether at 20°C until complete conversion of the initial ester (TLC). The mixture was evaporated, and the residue was recrystallized from hexane.

b. A mixture of 0.01 mol of ester **II** and 0.01 mol of amine **IIIb**–**IIIi** in 10 ml of diethyl ether was stirred at room temperature for 15–40 min in the synthesis of esters **VI**, **VIIa**, **VIIb**, **VIIIb**, **XIb**, and **XIc** and for 2–4 h in the synthesis of esters **IXa**–**IXb** and **XII**. The mixture was evaporated, and the residue was recrystallized from hexane. Compounds **V**, **VIIIa**, **IXb**, **XIa**, and **XII** were purified by flash chromatography on silica gel (0.063–0.200 mm) using $CHCl_3$ as eluent.

c. A mixture of 0.01 mol of ester **I**, 0.02 mol of triethyl orthoformate, and 0.01 mol of amine **IIId** or **IIIe** in 15 ml of ethanol was heated for 12 h under reflux. The mixture was evaporated, and the residue was recrystallized from hexane.

Ethyl (2*E*)-4,4,4-trifluoro-2-methylaminomethylidene-3-oxobutanoate (IVa). Yield 1.39 g (62%) (*a*), mp 92–94°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3252 (N–H); 1693 (C=O, ester); 1638 (C=O, ketone); 1607, 1582 (C=C, N–H); 1236–1143 (C–F); in $CHCl_3$: 1688 v.br (C=O, ester); 1648 br (C=O, ketone); 1602, 1522 (C=C, δN–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 1.31 t (3H, OCH_2CH_3, *J* = 7.2 Hz), 3.27 d.d (3H, NCH_3, *J* = 5.1, 0.6 Hz), 4.24 q (2H, OCH_2, *J* = 7.2 Hz), 8.15 br.d (1H, CH, *J* = 14.4 Hz), 10.53 br.s (1H, NH); *Z* isomer: 1.33 t (3H, OCH_2CH_3, *J* = 7.2 Hz), 3.24 d.d (3H, NCH_3, *J* = 5.1, 0.6 Hz), 4.25 q (2H, OCH_2, *J* = 7.2 Hz), 8.03 br.d (1H, CH, *J* = 14.4 Hz), 9.63 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 89.15 s (CF_3, *E* isomer), 90.07 s (CF_3, *Z* isomer). Found, %: C 42.60; H 4.46; F 25.59; N 6.23. $C_8H_{10}F_3NO_3$. Calculated, %: C 42.67; H 4.48; F 25.31; N 6.22.

Ethyl (2*E*)-4,4,5,5,6,6,6-heptafluoro-2-methylaminomethylidene-3-oxohexanoate (IVb). Yield 1.75 g (54%) (*a*), mp 104–105°C. IR spectrum (mineral oil), ν, cm^{-1}: 3250 (N–H); 1695 (C=O, ester); 1640 (C=O); 1600, 1578 (C=C, δN–H); 1270–1116 (C–F). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: *E* isomer: 1.25 t (3H, OCH_2CH_3, *J* = 7.0 Hz), 4.11 q (2H, OCH_2, *J* = 7.0 Hz), 8.09 d (1H, CH, *J* = 14.1 Hz), 10.42 br.s (1H, NH); *Z* isomer (13%): 1.27 t (3H, OCH_2CH_3, *J* = 7.0 Hz), 3.67 q (2H, OCH_2, *J* = 7.0 Hz), 7.97 d (1H, CH, *J* = 14.1 Hz), 9.47 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: *E* isomer: 39.06 m (2F, 5-F), 49.39 m (2F, 4-F, *J* = 9.8 Hz), 82.55 t (3F, 6-F, *J* = 9.8 Hz); *Z* isomer: 38.80 m (2F, 5-F), 49.39 m (2F, 4-F, *J* = 9.8 Hz), 82.42 t (3F, 6-F, *J* = 9.8 Hz). Found, %: C 36.90; H 3.16; F 40.87; N 4.25. $C_{10}H_{10}F_7NO_3$. Calculated, %: C 36.94; H 3.10; F 40.90; N 4.31.

Ethyl (2*E*)-2-benzylaminomethylidene-4,4,5,5-tetrafluoro-3-oxopentanoate (V). Yield 2.39 g (72%) (*b*), oily substance. IR spectrum (film), ν, cm^{-1}: 3250 (N–H); 1705 (C=O, ester); 1645 (C=O, ketone); 1594, 1582 (C=C, δN–H); 1267–1091 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.23–7.43 m (5H, C_6H_5); *E* isomer: 1.31 t (3H, OCH_2CH_3, *J* = 7.2 Hz), 4.23 q (2H, OCH_2, *J* = 7.2 Hz), 4.60 d (2H, OCH_2, *J* = 5.9 Hz), 6.68 t.t (1H, HCF_2, *J* = 53.8, 5.8 Hz), 8.16 d (1H, CH, *J* = 14.2 Hz), 10.89 br.s (1H, NH); *Z* isomer: 1.32 t (3H, OCH_2CH_3, *J* = 7.1 Hz), 4.26 q (2H, OCH_2, *J* = 7.1 Hz), 4.59 d (2H, OCH_2, *J* = 5.9 Hz), 6.34 t.t [1H, $H(CF_2)_2$, *J* = 53.3, 6.0 Hz], 8.06 d (1H, CH, *J* = 14.2 Hz), 9.80 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *E* isomer: 23.94 d.t (2F, 5-F, *J* = 53.8, 7.9 Hz), 39.58 m (2F, 4-F, *J* = 5.8 Hz); *Z* isomer: 22.09 d.m (2F, 5-F, *J* = 53.3 Hz), 41.23 m (2F, 4-F, *J* = 6.0 Hz). Found, %: C 54.13; H 4.35; F 22.78; N 4.27. $C_{15}H_{14}F_4NO_3$. Calculated, %: C 54.22; H 4.35; F 22.87; N 4.22.

Ethyl (2*E*)-4,4,4-trifluoro-3-oxo-2-(phenylaminomethylidene)butanoate (VI). Yield 1.58 g (55%) (*b*), mp 66–68°C. IR spectrum (mineral oil), ν, cm^{-1}: 3200, 3150 (N–H); 1715 (C=O, ester); 1644 (C=O); 1601, 1574 (C=C, δN–H); 1188–1125 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.46–7.19 m (5H, Ph); *E* isomer: 1.35 t (3H, OCH_2CH_3, *J* = 7.0 Hz), 4.30 q (2H, OCH_2, *J* = 7.0 Hz), 8.63 d (1H, CH, *J* = 14.1 Hz), 12.18 br.d (1H, NH, *J* = 14.1 Hz); *Z* isomer: 1.37 t (3H, OCH_2CH_3, *J* = 7.1 Hz), 4.33 q (2H, OCH_2, *J* = 7.1 Hz), 8.49 d (1H, CH, *J* = 14.1 Hz), 11.38 br.d (1H, NH, *J* = 14.1 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 89.03 s (CF_3, *E* isomer), 89.98 s (CF_3, *Z* isomer). Found, %: C 54.50; H 4.26; F 19.95; N 4.87. $C_{13}H_{12}F_3NO_3$. Calculated, %: C 54.36; H 4.21; F 19.84; N 4.88.

Ethyl (2*E*)-4,4-difluoro-2-(4-methylphenylaminomethylidene)-3-oxobutanoate (VIIa). Yield 1.89 g (67%) (*c*), mp 89–90°C. IR spectrum (mineral oil), ν, cm^{-1}: 3120 (N–H); 3000 (C–H); 1690 (C=O, ester); 1640 (C=O, ketone); 1600, 1570 (C=C, δN–H); 1100–1030 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.12–7.15 m, 7.23–7.25 m (2H, C_6H_4); *E* isomer: 1.36 t (3H, OCH_2CH_3, *J* = 7.1 Hz), 2.36 s (3H, CH_3), 4.33 q (2H, OCH_2, *J* = 7.1 Hz), 6.88 (1H, HCF_2, *J* = 54.5 Hz), 8.58 d (1H, CH, *J* = 13.9 Hz), 12.60 br.d

(1H, NH, J = 13.9 Hz); Z isomer: 1.39 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.35 s (3H, CH_3), 4.35 q (2H, OCH_2, J = 7.1 Hz), 6.60 t (HCF_2, J = 54.5), 8.62 d (1H, CH, J = 14.0 Hz), 11.29 br.d (1H, NH, J = 14.0 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 34.15 d (HCF_2, E isomer, J = 54.5 Hz), 35.17 d (HCF_2, Z isomer, J = 54.5 Hz). Found, %: C 59.21; H 5.36; F 13.13; N 4.95. $C_{14}H_{15}F_2NO_3$. Calculated, %: C 59.36; H 5.34; F 13.41; N 4.55.

Ethyl (2*E*)-4,4,4-trifluoro-2-(4-methylphenylaminomethylidene)-3-oxobutanoate (VIIb). Yield 2.11 g (70%) (*b*), mp 60–62°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3225, 3456 (N–H); 1691 (C=O, ester); 1633 (C=O, ketone); 1609, 1580 (C=C, δN–H); 1194–1144 (C–F); in $CHCl_3$: 1689 br (C=O, ester); 1637 br (C=O, ketone); 1604, 1577 (C=C, δN–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.08–7.15 m and 7.21–7.25 m (2H each, C_6H_4); E isomer: 1.34 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 2.37 s (3H, CH_3), 4.29 q (2H, OCH_2, J = 7.2 Hz), 8.60 d (1H, CH, J = 14.1 Hz), 12.21 br.d (1H, NH, J = 14.1 Hz); Z isomer: 1.37 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.36 s (3H, CH_3), 4.33 q (2H, OCH_2, J = 7.1 Hz), 8.47 d (1H, CH, J = 14.1 Hz), 11.38 br.d (1H, NH, J = 14.1 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 89.07 s (CF_3, E isomer), 89.99 s (CF_3, Z isomer). Found, %: C 55.93; H 4.73; F 18.93; N 4.67. $C_{14}H_{14}F_3NO_3$. Calculated, %: C 55.82; H 4.68; F 18.92; N 4.65.

Ethyl (2*E*)-4,4,4-trifluoro-2-(4-methoxyphenylaminomethylidene)-3-oxobutanoate (VIIIa). Yield 1.46 g (46%) (*b*), oily substance. IR spectrum (film), ν, cm^{-1}: 3226 (N–H); 2984 (C–H); 1724 (C=O, ester); 1701 (C=O); 1634, 1607, 1581, 1516 (C=C, δN–H); 1275–1158 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.93–6.97 m and 7.13–7.20 m (2H each, C_6H_4); E isomer: 1.34 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.83 s (3H, OCH_3), 4.29 q (2H, OCH_2, J = 7.0 Hz), 8.54 d (1H, CH, J = 14.1 Hz), 12.27 br.d (1H, NH, J = 14.1 Hz); Z isomer: 1.37 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.82 s (3H, OCH_3), 4.32 q (2H, OCH_2, J = 7.0 Hz), 8.41 d (1H, CH, J = 14.3 Hz), 11.39 br.d (1H, NH, J = 14.3 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 89.14 s (CF_3, E isomer), 90.04 s (CF_3, Z isomer). Found, %: C 52.85; H 4.32; F 17.68; N 4.35. $C_{14}H_{14}F_3NO_4$. Calculated, %: C 53.00; H 4.45; F 17.96; N 4.41.

Ethyl (2*E*)-4,4,5,5-tetrafluoro-2-(4-methoxyphenylaminomethylidene)-3-oxopentanoate (VIIIb). Yield 2.06 g (59%) (*b*), 1.50 g (43%) (*c*), mp 89–91°C. IR spectrum (mineral oil), ν, cm^{-1}: 2986 (C–H); 1700 (C=O, ester); 1637 (C=O, ketone); 1603, 1583, 1517 (C=C, δN–H); 1230–1147 (C–F). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.78 s (3H, OCH_3), 7.00–7.02 m and 7.43–7.52 m (2H each, C_6H_4); E isomer: 1.28 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 4.19 q (2H, OCH_2, J = 7.0 Hz), 6.99 t (1H, HCF_2, J = 53.0, 6.6 Hz), 8.44 d (1H, CH, J = 14.5 Hz), 12.10 br.d (1H, NH, J = 14.5 Hz); Z isomer: 1.15 t (3H, $OCH_2C\mathbf{H}_3$, J = 6.0 Hz), 4.27 q (2H, OCH_2, J = 6.0 Hz), 6.83 t (1H, HCF_2, J = 52.0 Hz), 8.26 br.d (1H, CH, J = 14.5 Hz), 10.97 br.d (1H, NH, J = 14.5 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: E isomer: 41.53 d.d (2F, 4-F, J = 14.8, 7.7 Hz), 25.35 d.t (2F, 5-F, J = 53.0, 7.7 Hz); Z isomer: 42.39 m (2F, 4-F), 24.11 d.m (2F, 5-F, J = 52.0 Hz). Found, %: C 51.18; H 4.14; F 21.33; N 3.88. $C_{15}H_{15}F_4NO_4$. Calculated, %: C 51.58; H 4.33; F 21.76; N 4.01.

Ethyl (2*E*)-4,4,5,5,6,6,6-heptafluoro-2-(4-methoxyphenylaminomethylidene)-3-oxohexanoate (VIIIc). Yield 2.59 g (62%) (*b*), mp 60–62°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3206 (C–H); 1685 (C=O, ester); 1653 (C=O, ketone); 1601, 1582, 1516 (C=C, δN–H); 1274–1136 (C–F); in $CHCl_3$: 1680 br (C=O, ester); 1631 br (C=O, ketone); 1604, 1579 (C=C, δN–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: E isomer: 1.33 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 3.83 s (3H, OCH_3), 4.29 q (2H, OCH_2, J = 7.2 Hz), 6.95 d.m (2H, C_6H_4, J = 8.9 Hz), 7.16 d.m (2H, C_6H_4, J = 8.9 Hz), 8.45 d (1H, CH, J = 14.0 Hz), 12.18 br.d (1H, NH, J = 14.0 Hz); Z isomer: 1.35 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 3.82 s (3H, OCH_3), 4.32 q (2H, OCH_2, J = 7.1 Hz), 6.94 d.m (2H, C_6H_4, J = 8.9 Hz), 7.13 d.m (2H, C_6H_4, J = 8.9 Hz), 8.30 d (1H, CH, J = 14.2 Hz), 11.27 br.d (1H, NH, J = 14.2 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: E isomer: 38.26 m (2F, 5-F), 48.61 q.m (2F, 4-F, J = 9.9 Hz), 81.56 t (3F, 6-F, J = 9.9 Hz); Z isomer: 37.58 m (2F, 5-F), 49.22 q.m (2F, 4-F, J = 9.6 Hz), 81.68 t (3F, 6-F, J = 9.6 Hz). Found, %: C 46.10; H 3.40; F 31.61; N 3.25. $C_{16}H_{14}F_7NO_4$. Calculated, %: C 46.05; H 3.38; F 31.87; N 3.36.

Ethyl (2*E*)-4,4,4-trifluoro-3-oxo-2-(pyridin-2-ylaminomethylidene)butanoate (IXa). Yield 1.61 g (56%) (*b*), mp 72–73°C. IR spectrum (mineral oil), ν, cm^{-1}: 3251 (N–H); 1702 (C=O, ester); 1633 (C=O, ketone); 1607, 1591, 1561 (C=C, C=N, δN–H); 1198–1113 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: E isomer: 1.36 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 4.32 q (2H, OCH_2, J = 7.0 Hz), 7.08 br.d (1H, 3′-H, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 0.8 Hz), 7.19 d.d.d (1H, 5′-H, $J_{5',4'}$ = 7.4, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 0.8 Hz), 7.76 d.d.d (1H, 4′-H, $J_{4',3'}$ =

8.0, $J_{4',5'}$ = 7.4, $J_{4',6'}$ = 1.2 Hz), 8.44 d.d (1H, 6′-H, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.8 Hz), 9.36 d (1H, CH, J = 13.3 Hz), 12.08 br.d (1H, NH, J = 13.3 Hz); *Z* isomer: 1.38 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 4.35 q (2H, OCH_2, J = 7.0 Hz), 6.96 br.d (1H, 3′-H, $J_{3',4'}$ = 8.2, $J_{3',5'}$ = 0.8 Hz), 7.14 d.d.d (1H, 5′-H, $J_{5',4'}$ = 7.4, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 0.8 Hz), 7.73 d.d.d (1H, 4′-H, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.4, $J_{4',6'}$ = 1.2 Hz), 8.41 d.d (1H, 6′-H, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.2 Hz), 9.23 d (1H, CH, J = 13.1 Hz), 11.41 br.d (1H, NH, J = 13.1 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 88.79 s (CF_3, *E* isomer), 90.15 s (CF_3, *Z* isomer). Found, %: C 49.99; H 3.79; F 19.75; N 9.63. $C_{12}H_{11}F_3N_2O_3$. Calculated, %: C 50.01; H 3.85; F 19.77; N 9.72.

Ethyl (2*E*)-4,4,5,5,6,6,6-heptafluoro-3-oxo-2-(pyridin-2-ylaminomethylidene)hexanoate (IXb). Yield 2.39 g (62%) (*b*), mp 65–67°C. IR spectrum (film), ν, cm^{-1}: 3271 (N–H); 1668 (C=O, ester); 1668 (C=O, ketone); 1608, 1562, 1476 (C=C, C=N, δN–H); 1230–1120 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 1.35 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.31 q (2H, OCH_2, J = 7.2 Hz), 6.99 br.d (1H, 3′-H, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 0.8 Hz), 7.13 d.d.d (1H, 5′-H, $J_{5',4'}$ = 7.0, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 0.7 Hz), 7.76 d.d.d (1H, 4′-H, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.0, $J_{4',6'}$ = 1.7 Hz), 8.44 d.d (1H, 6′-H, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.7 Hz), 9.28 d (1H, CH, J = 13.2 Hz), 11.95 d (1H, NH, J = 13.2 Hz); *Z* isomer: 1.36 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.34 q (2H, OCH_2, J = 7.2 Hz), 6.94 br.d (1H, 3′-H, $J_{3',4'}$ = 8.0, $J_{3',5'}$ = 0.8 Hz), 7.12 d.d.d (1H, 5′-H, $J_{5',4'}$ = 7.1, $J_{5',6'}$ = 4.8, $J_{5',3'}$ = 0.7 Hz), 7.72 d.d.d (1H, 4′-H, $J_{4',3'}$ = 8.0, $J_{4',5'}$ = 7.1, $J_{4',6'}$ = 1.7 Hz), 8.40 d.d (1H, 6′-H, $J_{6',5'}$ = 4.8, $J_{6',4'}$ = 1.4 Hz), 9.14 d (1H, CH, J = 13.0 Hz), 11.28 d (1H, NH, J = 13.0 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *E* isomer: 38.17 m (2F, 5-F), 48.25 q.m (2F, 4-F, J = 9.8 Hz), 81.52 t (3F, 6-F, J = 9.8 Hz); *Z* isomer: 37.24 m (2F, 5-F), 49.03 q.m (2F, 4-F, J = 9.5 Hz), 81.61 t (3F, 6-F, J = 9.5 Hz). Found, %: C 43.43; H 2.67; F 34.10; N 7.18. $C_{14}H_{10}F_7N_2O_3$. Calculated, %: C 43.42; H 2.60; F 34.34; N 7.23.

Ethyl (2*E*)-4,4,4-trifluoro-3-oxo-2-(pyrimidin-2-ylaminomethylidene)butanoate (X). A mixture of 2.40 g (0.01 mol) of ester **IIa** and 0.95 g (0.01 mol) of pyrimidin-2-amine in 10 ml of 1,4-dioxane was heated for 48 h under reflux. The mixture was evaporated, and the residue was recrystallized from hexane. Yield 1.30 g (45%), mp 108–110°C. IR spectrum (mineral oil), ν, cm^{-1}: 3278 (N–H); 3104 (C–H); 1716 (CO, ester); 1657 (C=O, ketone); 1596, 1574, 1553 (C=C, C=N, δN–H); 1220–1113 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 1.37 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.33 q (2H, OCH_2, J = 7.2 Hz), 7.11 t (1H, 5′-H, J = 4.9 Hz), 8.64 d (2H, 4′-H, 6′-H, J = 4.9 Hz), 9.29 d (1H, CH, J = 13.5 Hz), 11.68 d (1H, NH, J = 13.5 Hz); *Z* isomer: 1.38 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 4.36 q (2H, OCH_2, J = 7.2 Hz), 7.15 t (1H, 5′-H, J = 4.9 Hz), 8.61 d (2H, 4′-H, 6′-H, J = 4.9 Hz), 9.14 d (1H, CH, J = 13.1 Hz), 11.21 d (1H, NH, J = 13.1 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 88.53 s (CF_3, *E* isomer), 89.94 s (CF_3, *Z* isomer). Found, %: C 45.66; H 3.28; F 19.69; N 14.64. $C_{11}H_{10}F_3N_3O_3$. Calculated, %: C 45.68; H 3.49; F 19.71; N 14.53.

Ethyl (2*Z*)-4,4,4-trifluoro-2-(morpholinomethylidene)-3-oxobutanoate (XIa). Yield 2.08 g (74%) (*b*), mp 65–67°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3005 (C–H), 1699 (C=O, ester), 1644 (C=O, ketone), 1575 (C=C), 1205–1114 (C–F); in $CHCl_3$: 1701 (C=O, ester), 1665 (C=O, ketone), 1570 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 3.48 m and 3.81 m (4H each, CH_2CH_2), 4.22 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.2 Hz), 7.64 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$): δ_F 89.62 ppm, s (CF_3). Found, %: C 46.92; H 4.98; F 20.16; N 4.89. $C_{11}H_{14}F_3NO_4$. Calculated, %: C 46.98; H 5.02; F 20.27; N 4.98.

Ethyl (2*Z*)-4,4,5,5-tetrafluoro-2-(morpholinomethylidene)-3-oxopentanoate (XIb). Yield 1.96 g (70%) (*b*), mp 50–52°C. IR spectrum, ν, cm^{-1} (mineral oil): 3017 (C–H), 1691 (C=O, ester), 1653 (C=O), 1571 (C=C), 1214–1075 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 3.79 m and 3.45 m (4H each, CH_2CH_2), 4.23 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.2 Hz), 6.33 t.t (1H, HCF_2, J = 53.3, 5.9 Hz), 7.58 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 22.23 d.m (2F, 5-F, J = 53.3 Hz), 40.26 m (2F, 4-F). Found, %: C 51.09; H 5.32; F 26.92; N 4.74. $C_{12}H_{15}F_4NO_4$. Calculated, %: C 51.25; H 5.38; F 27.02; N 4.98.

Ethyl (2*Z*)-4,4,5,5,6,6,6-heptafluoro-2-(morpholinomethylidene)-3-oxohexanoate (XIc). Yield 2.44 g (64%) (*b*), mp 65–67°C. IR spectrum (mineral oil), ν, cm^{-1}: 3004 (C–H); 1724 (C=O, ester); 1703 (C=O); 1647, 1633, 1555 (C=C); 1256–1117 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 3.46 m and 3.80 m (4H each, CH_2CH_2), 4.23 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.2 Hz), 7.56 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 37.27 m (2F, 5-F), 48.18 m (2F, 4-F, J = 9.8 Hz), 81.42 t (3F, 6-F, J = 9.8 Hz). Found, %: C 40.90; H 3.68; F 34.80; N 3.69. $C_{13}H_{14}F_7NO_4$. Calculated, %: C 40.96; H 3.70; F 34.88; N 3.67.

Ethyl (2*Z*)-4,4,4-trifluoro-3-oxo-2-(pyrrolidin-1-ylmethylidene)butanoate (XII). Yield 1.54 g (58%) (*b*), oily substance. IR spectrum (film), ν, cm^{-1}: 3010 (C–H), 1706 (C=O, ester), 1654 (C=O), 1574 (C=C), 1200–1150 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 2.03 t (2H, CH_2, J = 6.7 Hz), 3.14 m (2H, CH_2), 3.29 t.t (2H, CH_2, J = 6.7, 7.2 Hz), 3.76 t (2H, CH_2, J = 7.2 Hz), 4.22 q (2H, OCH_2, J = 7.2 Hz), 7.89 s (1H, CH). ^{19}F NMR spectrum ($CDCl_3$): δ_F 89.55 ppm, s (CF_3). Found, %: C 49.62; H 5.65; F 21.30; N 5.53. $C_{13}H_{14}F_7NO_4$. Calculated, %: C 49.81; H 5.32; F 21.49; N 5.28.

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REFERENCES

1. Pashkevich, V.M. and Saloutin, V.I., *Usp. Khim*., 1985, vol. 54, p. 1997.
2. Klaizen, L., *Justus Liebigs Ann. Chem*., 1897, vol. 297, p. 164; Klaizen, L., *Justus Liebigs Ann. Chem*., 1897, vol. 297, p. 29; Ayyangar Nagaraj, R., Lahoti Rajgopal, J., and Thomas, D., *Org. Prep. Proced. Int*., 1982, vol. 15, p. 327; *Chem. Abstr*., 1982, vol. 97, no. 181887.
3. Jones, R.G., *J. Am. Chem. Soc*., 1951, vol. 73, p. 3684.
4. Danion-Bougot, R. and Carrie, R., *C.R. Acad. Sci., Ser. C*, 1967, vol. 264, p. 457; Currie, D.J., Lough, C.E., McClusky, F.K., and Holmes, H.L., *Can. J. Chem*., 1969, vol. 47, p. 3147.
5. Pryadeina, M.V., Kuzueva, O.G., Burgart, Ya.V., and Saloutin, V.I., *Russ. J. Org. Chem*., 2002, vol. 38, p. 224.
6. Potapov, V.M., *Stereokhimiya* (Stereochemistry), Moscow: Khimiya, 1988, p. 263.
7. Oki, M., *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, Deerfield Beach: VCH, 1985, pp. 77, 112.
8. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983, p. 46; Levy, G.C., Lichter, R.L., and Nelson, G.L., *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, New York: Wiley, 1980, p. 143.
9. Khudina, O.G., Shchegol'kov, E.V., Burgart, Ya.V., Kodess, M.I., Saloutin, V.I., Kazheva, O.N., Shilov, G.V., D'yachenko, O.A., Grishina, M.A., Potemkin, V.A., and Chupakhin, O.N., *Russ. J. Org. Chem*., 2007, vol. 43, p. 380.
10. Sheldrick, G.M., *SHELXS 97*, Göttingen: Univ. Göttingen, 1997.