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An Efficient Entry to Perfluoroalkyl Substituted Azoles Starting from β-Perfluoroalkyl-β-dicarbonyl Compounds.

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Abstract: 5-Perfluoroalkylpyrazoles **6**, 5-perfluoroalkylisoxazoles **11**, and 4-perfluoroacylisoxazoles **13** are obtained in high chemical yields and complete site and regioselectivity through the reaction of β-perfluoroalkyl-β-dicarbonyls **2** with hydrazonyl halides **1** and halooximes **8** in the presence of bases.

Interest in perfluoroalkyl substituted heterocycles comes from the useful applications that these compounds find mainly as agrochemicals, pharmaceuticals, components of polymers, but also as dyes, electrical insulating oils, high temperature lubricants.[1]

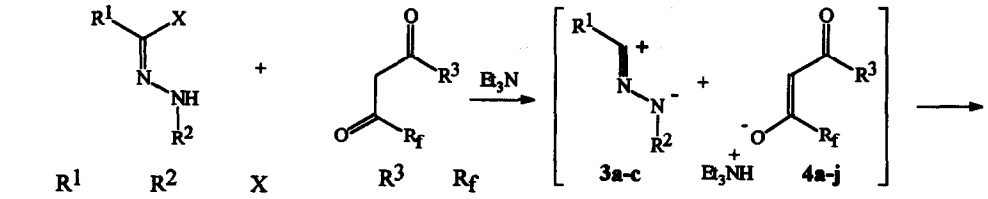
Many intriguing ring structures have been prepared by forming the heterocyclic ring starting from a fluorinated, open chain precursor. The reaction of 1,3-dipoles with a carbon-carbon or carbon-heteroatom multiple bond has emerged as a particularly versatile approach. In some cases the fluorinated chain is a part of the 1,3-dipole (trifluoromethyl nitrones,[2] polyfluoro nitrile oxides[3] and imines,[4] trifluorodiazoethane[5]), but usually it is a substituent in the alkene[6] or alkyne[7] dipolarophile. When this approach is employed, problems of regio and siteselectivity often arise.

In the search for new fluorinated dipolarophiles which are easily accessible and show both a manifold reactivity and a good selectivity, we have studied the reaction of β-perfluoroalkyl-β-dicarbonyl compounds **2** with hydrazonoyl halides **1** and halooximes **8**.[8] Here we describe how 5-perfluoralkylpyrazoles **6**, 5-perfluoroalkylisoxazoles **11**, and 4-perfluoroacylisoxazoles **13** are obtained in this way with complete selectivity.

Results and Discussion

When β-perfluoroalkyl-β-ketoesters **2a-d** and β-perfluoroalkyl-β-diketones **2e-j** are heated in benzene solution in the presence of hydrazonyl halides **1a-c** and of an excess of triethylamine, 5-perfluoro-

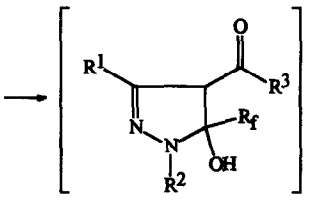
Scheme 1



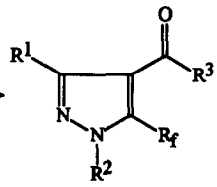
	R^1	R^2	X
1a	CO_2Et	C_6H_5	Cl
b	$COCH_3$	C_6H_5	Cl
c	C_6H_5	4-NO_2-C_6H_4	Br

	R^3	R_f
2a	OCH_3	CF_2Cl
b	OC_2H_5	CF_3
c	OC_2H_5	*n*-C_3F_7
d	OC_2H_5	*n*-C_3F_7
e	C_6H_5	CF_3
f	2-furyl	CF_3
g	2-thienyl	CF_3
h	CH_3	CF_3
i	C_2H_5	CF_3
j	CF_3	CF_3

3a-c Et_3NH **4a-j**



5a-m



6a-m

	R^1	R^2	R^3	R_f
6a	$CO_2C_2H_5$	C_6H_5	OC_2H_5	CF_2Cl
b	$COCH_3$	C_6H_5	OC_2H_5	CF_3
c	C_6H_5	4-NO_2-C_6H_4	OC_2H_5	CF_3
d	$CO_2C_2H_5$	C_6H_5	OCH_3	C_2F_5
e	$COCH_3$	C_6H_5	OC_2H_5	*n*-C_3F_7
f	$CO_2C_2H_5$	C_6H_5	C_6H_5	CF_3
g	C_6H_5	4-NO_2-C_6H_4	C_6H_5	CF_3
h	$CO_2C_2H_5$	C_6H_5	2-furyl	CF_3
i	$CO_2C_2H_5$	C_6H_5	2-thienyl	CF_3
j	$CO_2C_2H_5$	C_6H_5	CH_3	CF_3
k	$COCH_3$	C_6H_5	C_2H_5	CF_3
l	$CO_2C_2H_5$	C_6H_5	CH_3	CF_3
m	$CO_2C_2H_5$	C_6H_5	CF_3	CF_3

alkylpyrazoles **6a-m** are obtained exclusively in 74-86% yield (Scheme 1). It is reasonable to assume that, under adopted reaction conditions, nitrile imines **3** are formed and involved in a more or less concerted cycloaddition reaction with triethylammonium enolates **4** to give 5-hydroxy-2-pyrazolines **5**.

Alternatively, the reaction can be considered to proceed via a primary nucleophilic attack by the negatively charged α carbon of β-dicarbonyl enolates **4** on hydrazonyl halides **1**. Cyclization of the so formed intermediate affords the 5-hydroxy-2-pyrazolines **5**. In general, 5-hydroxy-5-alkyl-(or -aryl)-2-pyrazolines usually dehydrate spontaneously,[9] while corresponding 5-perfluoroalkyl analogues are much less prone to undergo aromatization via loss of water.[10] In our case intermediate pyrazolines **5** were never observed (TLC analyses), thus showing that dehydration to pyrazoles **6** occurred easily under adopted

reaction conditions. When the reactions were performed without base catalyses, the same complete regio and siteselectivity has been observed, but yields in products **6** were lower as formation of other compounds occurred.[11]

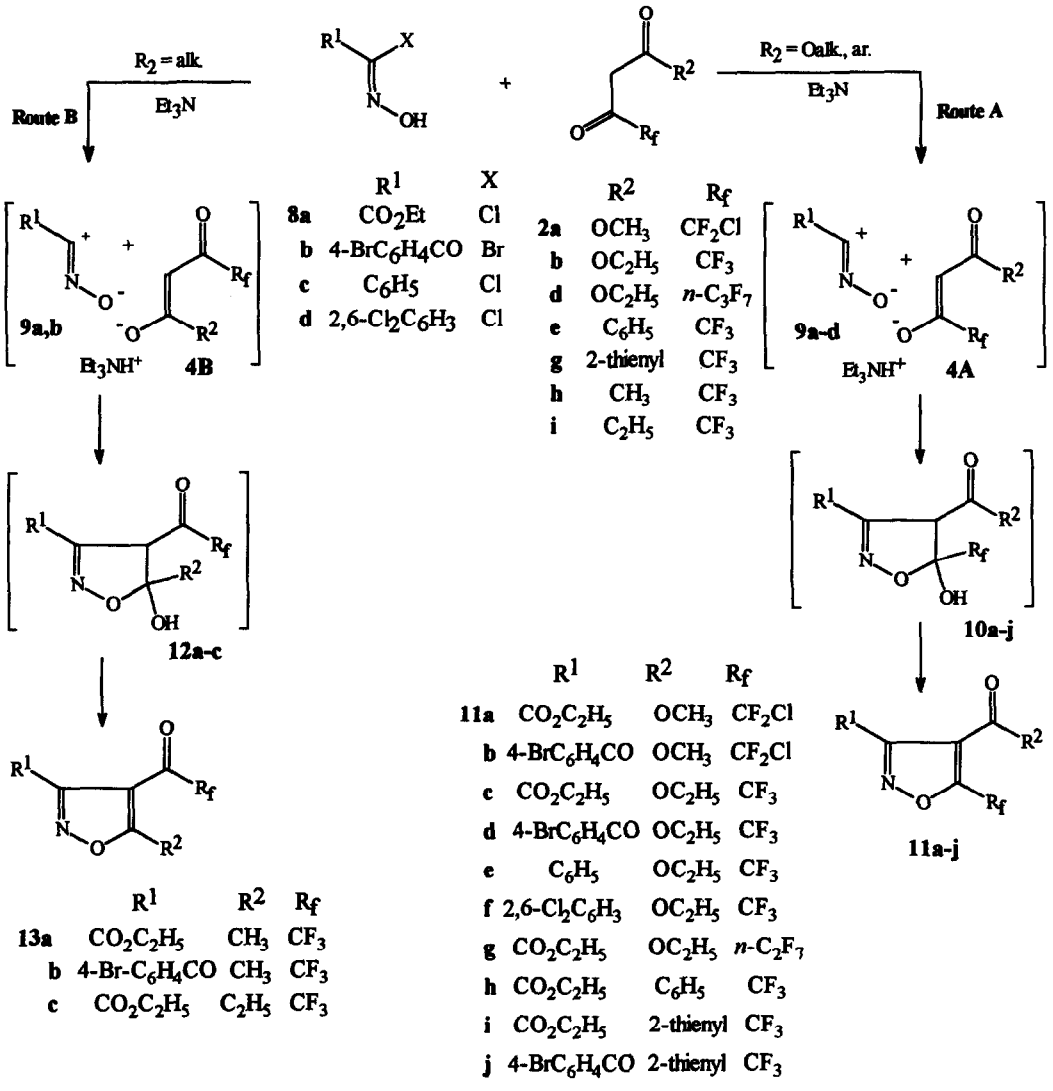
The regio and siteselectivity observed with fluoro substituted substrates **2** parallels that reported for corresponding hydrogenated compounds.[12] A quite varied set of hydrazonyl halides **1** and β-perfluoroalkyl-β-dicarbonyls **2** have been used without these selectivities being affected. Differently, when trifluoroacetylacetonitrile has been used as a dipolarophile, either 4-cyano-5-trifluoromethylpyrazoles or 5-amino-4-trifluoroacetylpyrazoles have been isolated depending on the basicity of the nitrogen atom of the nitrile imine.[6c]

When the triethylammonium salt of β-perfluoroalkyl-β-ketoesters **2a,b,d** are treated with nitrile oxides **9a-d** (generated in situ from corresponding chlorooximes by treatment with triethylamine in toluene or tetrahydrofuran), the 5-perfluoroalkylisoxazoles **11a-g** are formed in good yields (Scheme 2). Under the same reaction conditions, 1,1,1-trifluoro-2,4-butandiones **2e,g** carrying a phenyl or 2-thienyl residue on C-4, undergo a similar reaction pathway and 5-trifluoromethylisoxazoles **11h-j** are formed exclusively. Differently, the cyclization reaction of 1,1,1-trifluoro-2,4-butandiones **2h,i**, which bear an alkyl chain on C-4, occurs with a different regioselectivity and 5-alkyl-4-trifluoroacetylisoxazoles **13a-c** are produced cleanly and with complete site and regioselectivity. Other reaction conditions have also been studied (sodium hydride in tetrahydrofuran or dimethylformamide, sodium ethylate in ethanol) but yields in products **11** or **13** are lower.

Similarities exist between reactions reported in Schemes 1 and 2. In some cases, trace amounts of furoxans, formed through dimerization of chloroximes **8**, were isolated so that formation of isoxazoles **11** and **13** can be envisaged to occur through a 1,3-dipolar cycloaddition reation between nitrile oxide intermediates **9** and enolates **4**. However, the involvement of a stepwise mechanism with the initial nucleophilic attack of enolates **4** on 1,3-dipoles **9** can not be ruled out. Independently from the reaction mechanism which is followed, 5-hydroxy-2-isoxazolines **10** and **12** are probably the reaction products formed initially. Their presence has never been detected, thus showing that dehydration of these compounds to isoxazoles **11** and **13** takes place very easily. It is interesting to observe that dehydration of 5-perfluoroalkyl-5-hydroxy-2-isoxazolines is reported to occur only under severe conditions.[10] As a rule, corresponding 5-alkyl analogues lose water spontaneously,[13] but we have recently reported[14] that the isolation of structurally similar 5-hydroxy-2-isoxazolines is possible when the alkyl chain on C-5 is particularly demanding from the steric point of view.

In the prevailing enol form of all the β-dicarbonyl compounds **2** the carbonyl group adjacent to the perfluoroalkyl chain enolizes preferentially.[15] The unique exemption is 1,1,1-trifluoro-3-(2-thenoyl)acetone **2g** for which the enolized carbonyl is that adjacent to the thienyl residue.[16] 5-Perfluoroalkylisoxazoles **11** are formed (Route A) through a completely site and regioselective reaction involving enolates **4A**, in which the carbonyl adjacent to the *perfluoroalkyl chain* is enolized. The same selectivities are observed when dipoles **9** are reacted with corresponding unfluorinated dipolarophiles, for instance ethyl acetoacetate and benzoylacetone.[17] Formation of 4-trifluoroacetylisoxazoles **13** (Route B) occurs with the same regioselectivity discussed above (the positive site of dipoles **9** reacts with the α-carbon of β-dicarbonyls **2**) but with different siteselectivity, as the alternative enolates **4B**, in which the

Scheme 2



	R^1	X
8a	CO_2Et	Cl
b	4-BrC_6H_4CO	Br
c	C_6H_5	Cl
d	2,6-$Cl_2C_6H_3$	Cl

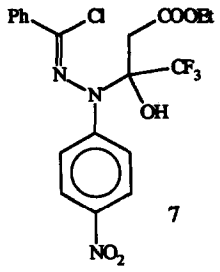
	R^2	R_f
2a	OCH_3	CF_2Cl
b	OC_2H_5	CF_3
d	OC_2H_5	*n*-C_3F_7
e	C_6H_5	CF_3
g	2-thienyl	CF_3
h	CH_3	CF_3
i	C_2H_5	CF_3

	R^1	R^2	R_f
13a	$CO_2C_2H_5$	CH_3	CF_3
b	4-Br-C_6H_4CO	CH_3	CF_3
c	$CO_2C_2H_5$	C_2H_5	CF_3

	R^1	R^2	R_f
11a	$CO_2C_2H_5$	OCH_3	CF_2Cl
b	4-BrC_6H_4CO	OCH_3	CF_2Cl
c	$CO_2C_2H_5$	OC_2H_5	CF_3
d	4-BrC_6H_4CO	OC_2H_5	CF_3
e	C_6H_5	OC_2H_5	CF_3
f	2,6-$Cl_2C_6H_3$	OC_2H_5	CF_3
g	$CO_2C_2H_5$	OC_2H_5	*n*-C_2F_7
h	$CO_2C_2H_5$	C_6H_5	CF_3
i	$CO_2C_2H_5$	2-thienyl	CF_3
j	4-BrC_6H_4CO	2-thienyl	CF_3

carbonyl adjacent to the *alkyl chain* is enolized, are involved. A perfluoroalkyl residue is therefore able to direct the course of a 1,3-dipolar cycloaddition reaction and the difference between Route A and Route B is connected with the differential effect on the reaction of a perfluoroalkyl group compared with aroyl (Route A) or acyl (Route B) residues.

The assignment of the structures of pyrazoles **6** and isoxazoles **11** and **13** comes from spectroscopic properties and chemical transformations. The chemical shifts of C-3, C-4, and C-5 in ^{13}C NMR spectra proved the formation of the heterocyclic rings. The $^2J_{C,F}$ (30 - 45 Hz) shown by C-5 signal of **6** and **11**



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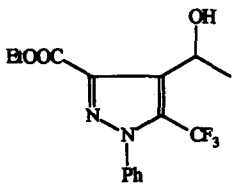

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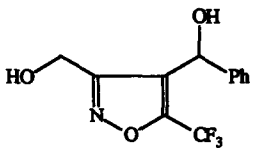

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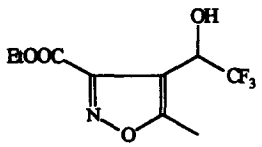

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revealed the presence of the perfluorinated chain on this carbon and ruled out the formation of the possible isomeric products, i. e. 4-perfluoroacyl-pyrazoles and -isoxazoles. Differently, for compounds **13** both C-4 and C-5 appeared as singlets and a $^{2}J_{C\text{-}F}$ was shown by the signal of a carbonyl group. Furthermore, reduction of the keto groups of 4-acetylpyrazole **6j** and 4-benzoylisoxazole **11h** by treatment with sodium borohydride afforded 3-ethoxycarbonyl-4-(1-hydroxyethyl)-1-phenyl-5-trifluoromethylpyrazole **14** and 4-hydroxybenzyl-3-hydroxymetyl-5-trifluoromethylisoxazole **15**, respectively, while reduction of 4-trifluoroacetylisoxazole **13a** gave 3-ethoxycarbonyl-4-(1-hydroxy-2,2,2-trifluoethyl)-5-methylisoxazole **16**. The structures of these 4-hydroxyalkylazoles was proven mainly by $^{3}J_{H\text{-}F}$ and $^{3}J_{H,H}$ shown by carbinol protons.

In conclusion, reported approaches to perfluoroalkyl substituted pyrazoles **6** and isoxazoles **11** and **13** are particularly attractive as a consequence of the high chemical yields and complete site and regioselectivities. Furthermore, β-perfluoroalkyl-β-dicarbonyl compounds appear to be particularly convenient fluorinated dipolarophiles as they can be easily prepared in one step and large quantities from cheap and commercially available products.[18] Traditional perfluoroalkyl substituted dipolarophiles, such as alkenes and alkynes, are sometimes less easy to be synthesized on a laboratory scale and give rise to non regioselective reactions.[6,7] Finally, prepared compounds are particularly interesting as, for instance, the substitution pattern of isoxazoles **13** is quite similar to that of some semisynthetic penicillins (e. g. and oxacillin, cloxacillin, and dicloxacillin).[13]

Experimental

Melting points were determined on a Büchi apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 177 spectrophotometer. Mass spectra were registered with a VG-70EQ apparatus. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with a Bruker AC 250 spectrometer in chloroform-*d* solution, using TMS and C_6F_6 (δ_F -162.90 ppm) as internal and external standards, respectively.

Reaction of hydrazonyl halides 1 with β-perfluoroalkyl-β-dicarbonyl compounds 2. General procedure. To a solution of β-perfluoroalkyl-β-dicarbonyl compound **2** (7.5 mmol) and triethylamine (1.38 mL, 9.9 mmol) in benzene (7.5 mL) was added a solution of hydrazonyl halide **1** (1.5 mmol) in benzene (1.5 mL). The reaction mixture was refluxed for a period varying from 1 to 12 hours, then it was quenched with a saturated water solution of ammonium chloride. The aqueous layer was acidified to pH = 1 with diluted hydrochloric acid and was extracted with ethyl acetate. The collected organic layers were dried over sodium sulphate, the solvent was removed under reduced pressure, and the residue was flash chromatographed on a silica gel.

5-Chlorodifluoromethyl-3-ethoxycarbonyl-4-methoxycarbonyl-1-phenylpyrazole (6a). Eluent: *n*-hexane-ethyl acetate 77:23. Yield 78 %. mp 45 °C (*n*-hexane). IR (KBr): 1740 cm^{-1}. ^1H NMR δ: 1.39 (3H, t, CH_3); 3.98 (3H, s, OCH_3); 4.43 (2H, q, CH_2); 7.4-7.7 (5H, m, Ph). ^{19}F NMR δ: -46.7 (s). ^{13}C NMR δ: 14.2; 53.3; 62.0; 117.6 (C-4); 119.4 (t, $J_{C,F}$ = 289 Hz, CF_2Cl); 126.8, 129.2, 130.6, 138.1 (Ph); 136.3 (t, $^2J_{C,F}$ = 31 Hz, C-5); 141.2 (C-3); 160.2, 162.5 (CO_2Et, CO_2Me). MS: 358 (M^+). Anal. calcd. for $C_{15}H_{13}ClF_2N_2O_2$: C 50.22, H 3.65, N 7.81; found: C 50.13, H 3.58, N 7.76.

4-Ethoxycarbonyl-3-methylcarbonyl-1-phenyl-5-trifluoromethylpyrazole (6b). Eluent: *n*-hexane-ethyl acetate 85:15. Yield 78 %. mp 56 °C (*n*-hexane). IR (KBr): 1740; 1700 cm^{-1}. ^1H NMR δ: 1.40 (3H, t, CH_3); 2.63 (3H, s, CH_3); 4.43 (2H, q, CH_2); 7.4-7.7 (5H, m, Ph). ^{19}F NMR δ: -58.2 (s). ^{13}C NMR δ: 13.9; 26.7; 62.6; 118.1 (C-4); 118.8 (q, $J_{C,F}$ = 270 Hz, CF_3); 126.0, 129.5, 130.6, 138.1 (Ph); 131.9 (q, $^2J_{C,F}$ = 40 Hz, C-5); 147.9 (C-3); 162.1 (CO_2Et); 191.9 (*C*OMe).

4-Ethoxycarbonyl-1-(4-nitrophenyl)-3-phenyl-5-trifluoromethylpyrazole (6c). Eluent: *n*-hexane-ethyl acetate 87:13. Yield 74 %. mp 111 °C (diisopropyl ether). IR (KBr): 1730 cm^{-1}. ^1H NMR δ: 1.31 (3H, t, CH_3); 4.37 (2H, q, CH_2); 7.4-7.8, 8.3-8.5 (9H, m, CH ar.). ^{19}F NMR δ: -56.8 (s). ^{13}C NMR δ: 13.8; 62.2; 116.6 (C-4); 124.8, 126.6, 128.3, 128.6, 130.3, 132.8, 148.0, 152.5 (C and CH ar.); 132.6 (q, $^2J_{C,F}$ = 40 Hz, C-5); 143.6 (C-3); 162.2 (CO_2Et).

3-Ethoxycarbonyl-4-methoxycarbonyl-1-phenyl-5-pentafluoroethylpyrazole (6d). Eluent: *n*-hexane-ethyl acetate 82:18. Yield 86 %. mp 87 °C (diisopropyl ether). IR (KBr): 1740; 1720 cm^{-1}. ^1H NMR δ: 1.38 (3H, t, CH_3); 3.98 (3H, s, OCH_3); 4.43 (2H, q, CH_2); 7.3-7.6 (5H, m, Ph). ^{19}F NMR δ: -84.5 (3F, CF_3); -109.3 (2F, CF_2). ^{13}C NMR δ: 14.2; 53.3; 62.1; 121.0 (C-4); 127.3, 129.0, 130.7, 138.4 (Ph); 130.1 (t, $^2J_{C,F}$ = 30 Hz, C-5); 141.8 (C-3); 160.0, 162.3 (CO_2Et, CO_2Me). Anal. calcd. for $C_{16}H_{13}F_5N_2O_4$: C 48.99, H 3.34, N 7.14; found: C 49.78, H 3.46, N 6.95.

4-Ethoxycarbonyl-5-(heptafluoro-*n*-propyl)-3-methylcarbonyl-1-phenylpyrazole (6e). Eluent: *n*-hexane-ethyl acetate 83:17. Yield 76 %. mp 73 °C (*n*-hexane). IR (KBr): 1745; 1705 cm^{-1}. ^1H NMR δ: 1.38 (3H, t, CH_3); 2.61 (3H, s, CH_3); 4.45 (2H, q, CH_2); 7.4-7.7 (5H, m, Ph). ^{19}F NMR δ: -81.4 (3F, CF_3); -106.2 (2F, CF_2); -125.5 (2F, CF_2). ^{13}C NMR δ: 13.7; 26.5; 62.4; 120.4 (C-4); 127.1, 128.9, 130.5, 138.5 (Ph); 130.2 (t, $^2J_{C,F}$ = 30 Hz, C-5); 148.0 (C-3); 162.0 (CO_2Et); 191.7 ($COCH_3$).

3-Ethoxycarbonyl-1-phenyl-4-phenylcarbonyl-5-trifluoromethylpyrazole (6f). Eluent: *n*-hexane-ethyl acetate 78:22. Yield 85 %. mp 79 °C (*n*-hexane). IR (KBr): 1735; 1670 cm^{-1}. ^1H NMR δ: 1.08 (3H, t, CH_3); 4.23 (2H, q, CH_2); 7.4-7.7, 7.8-8.0 (10H, m, CH ar.). ^{19}F NMR δ: -57.2 (s). ^{13}C NMR δ: 13.7; 61.9; 118.8 (q, $J_{C,F}$ = 270 Hz, CF_3); 125.0 (C-4); 126.1, 128.8, 129.4, 130.6, 134.1, 136.8, 141.8, (C and CH ar.); 131.8 (q, $^2J_{C,F}$ = 40 Hz, C-5); 138.1 (C-3); 160.0 (CO_2Et); 188.6 (*C*OPh). Anal. calcd. for $C_{20}H_{15}F_3N_2O_3$: C 61.86, H 3.89, N 7.22; found: C 61.98, H 4.04, N 7.07.

1-(4-Nitrophenyl)-3-phenyl-4-phenylcarbonyl-5-trifluoromethylpyrazole (6g). Eluent: cyclohexane-diisopropyl ether 78:22. Yield 75 %. mp 159 °C (diisopropyl ether). IR (KBr): 1675 cm^{-1}. ^1H NMR δ: 7.3-8.0, 8.3-8.5 (m, CH ar.). ^{19}F NMR δ: -56.0 (s). ^{13}C NMR δ: 122.6 (C-4); 124.8, 126.4, 127.7, 128.8, 128.9, 129.4, 129.8, 130.1, 134.4, 136.7, 148.0, 151.6 (C and CH ar.); 143.6 (C-3); 190.1 (*C*O).

3-Ethoxycarbonyl-4-(2-furyl)carbonyl-1-phenyl-5-trifluoromethylpyrazole (6h). Eluent: *n*-hexane-ethyl acetate 73:27. Yield 75 %. mp 127 °C (diisopropyl ether). IR (KBr): 1720; 1655 cm^{-1}. ^1H NMR δ: 1.19 (3H, t, CH_3); 4.29 (2H, q, CH_2); 6.62, 7.23, 7.67 (3H, dd each, C_4H_3O); 7.4-7.6 (5H, m, Ph). ^{19}F NMR δ: -57.4 (s). ^{13}C NMR δ: 13.9; 61.9; 113.0, 119.8, 126.1, 129.4, 130.6, 138.1, 147.8, 152.8 (C and CH ar.); 118.7 (q, $J_{C,F}$ = 270 Hz, CF_3); 123.6 (C-4); 132.1 (q, $^2J_{C,F}$ = 40 Hz, C-5); 142.0 (C-3); 160.1 (CO_2Et); 175.4 (COC_4H_3O). MS: 378 (M^+).

3-Ethoxycarbonyl-1-phenyl-4-(2-thienyl)carbonyl-5-trifluoromethylpyrazole (6i). Eluent: *n*-hexane-ethyl acetate 72:27. Yield 70 %. mp 104 °C (diisopropyl ether). IR (KBr): 1730; 1650 cm^{-1}. ^1H NMR δ: 1.16 (3H, t, CH_3); 4.28 (2H, q, CH_2); 7.16, 7.51, 7.79 (3H, dd each, C_4H_3S); 7.4-7.6 (5H, m, Ph). ^{19}F NMR δ: -57.2 (s). ^{13}C NMR δ: 13.8; 62.0; 118.7 (q, $J_{C,F}$ = 270 Hz, CF_3); 124.6 (C-4); 126.1, 128.5, 129.4, 130.6, 134.9, 135.8, 138.0, 144.3 (C and CH ar.); 131.8 (q, $^2J_{C,F}$ = 40 Hz, C-5); 141.7 (C-3); 160.0 (CO_2Et); 180.3 (COC_4H_3S). Anal. calcd. for $C_{18}H_{13}F_3N_2O_3S$: C 54.82, H 3.32, N 7.10; found: C 55.02, H 3.51, N 7.03.

3-Ethoxycarbonyl-4-methylcarbonyl-1-phenyl-5-trifluoromethylpyrazole (6j). Eluent: *n*-hexane-ethyl acetate 77:23. Yield 73 %. mp 48 °C (from diisopropyl ether). IR (KBr): 1710 cm^{-1}. ^1H NMR δ: 1.40 (3H, t, CH_3); 2.65 (3H, s, CH_3); 4.44 (2H, q, CH_2); 7.4-7.6 (5H, m, Ph). ^{19}F NMR δ: -57.2 (s). ^{13}C NMR δ: 14.2; 32.2; 62.2; 118.8 (q, $J_{C,F}$ = 270 Hz, CF_3); 126.1, 129.4, 130.6, 138.0 (Ph); 127.9 (C-4); 130.3 (q, $^2J_{C,F}$ = 40 Hz, C-5); 140.4 (C-3); 160.4 (CO_2Et); 195.8 ($COCH_3$). Anal. calcd. for $C_{15}H_{13}F_3N_2O_3$: C 55.22, H 4.02, N 8.59; found: C 55.13, H 3.91, N 8.47.

3,4-Di(methylcarbonyl)-1-phenyl-5-trifluoromethylpyrazole (6k). Eluent: *n*-hexane-ethyl acetate 83:17. Yield 74 %. mp 111 °C (diisopropyl ether). IR (KBr): 1710; 1695 cm^{-1}. ^1H NMR δ: 2.60 (3H, t, CH_3); 2.62 (3H, s, CH_3); 7.4-7.6 (5H, m, Ph). ^{19}F NMR δ: -57.4 (s). ^{13}C NMR δ: 26.5; 31.8; 118.9 (q, $J_{C,F}$ = 270 Hz, CF_3); 125.9, 129.5, 130.3, 138.2 (Ph); 126.6 (C-4); 147.5 (C-3); 192.8, 196.3 (two $COCH_3$).

4-Ethylcarbonyl-3-ethoxycarbonyl-1-phenyl-5-trifluoromethylpyrazole (6l). Eluent: *n*-hexane-ethyl acetate 81:19. Yield 65 %. Oil. IR (KBr): 1740; 1720 cm^{-1}. ^1H NMR δ: 1.25 (3H, t, CH_2CH_3); 1.38 (3H, s, OCH_2CH_3) 2.91 (2H, q, CH_2CH_3); 4.42 (2H, q, OCH_2CH_3); 7.4-7.6 (5H, m, Ph). ^{19}F NMR δ: -57.3 (s). ^{13}C NMR δ: 7.6; 14.2; 38.4; 62.1; 126.1, 129.4, 130.6, 138.1 (Ph); 127.8 (C-4); 140.6 (C-3); 160.5 (CO_2Et); 195.8 ($COEt$).

3-Ethoxycarbonyl-1-phenyl-5-trifluoromethyl-4-trifluoromethylcarbonylpyrazole (6m). Eluent: *n*-hexane-ethyl acetate (86:14 v/v). Yield 70 %. Oil. IR (KBr): 1755; 1720 cm^{-1}. ^1H NMR δ: 1.38 (3H, t, CH_3); 4.45 (2H, q, CH_2); 7.4-7.7 (5H, m, Ph). ^{19}F NMR δ: -57.8 (3F, s, CF_3); -77.7 (3F, s, $COCF_3$). ^{13}C NMR δ: 14.0; 62.8; 118.2 (q, $J_{C,F}$ = 270 Hz, CF_3); 118.8 (C-4); 126.1, 129.6, 131.1, 137.5 (Ph); 142.4. (C-3); 159.6 (CO_2Et); 179.8 ($COCF_3$).

***N'*-(Ethyl (3-hydroxy-4,4,4-trifluorobutanoate)3-yl)-*N'*-(4-nitrophenyl)benzenecarbohydrazonyl bromide (7).** To a solution of β-perfluoroalkyl-β-dicarbonyl compound **2b** (0.75 mmol) in benzene (1 mL) was added a solution of hydrazonyl bromide **1c** (0.15 mmol) in the same solvent (0.5 mL). The reaction mixture was refluxed for 4 hours, then the solvent was removed under reduced pressure and the residue was flash chromatographed on silica gel with *n*-hexane-ethyl acetate 9:1 as eluent to give pyrazole **6c** in 31% yield and the adduct **7** in 46% yield. Benzenecarbohydrazonyl bromide **7**: ^1H NMR: δ 0.94 (3H, t, OCH_2CH_3); 3.36, 3.62 (2H, AB system, CH_2CO); 3.92 (2H, q, OCH_2CH_3); 7.3-8.3 (9H, m, CH ar.). ^{19}F NMR: δ -96.0 (s). Anal. calcd. for $C_{19}H_{17}ClF_3N_3O_5$: C 49.56, H 7.30; N 9.13; found: C49.80, H, 7.53, N 8.89.

Reaction of hydroxyiminoyl halogenides 8 with β-perfluoroalkyl-β-dicarbonyl compounds 2. General procedure. To a stirred solution of β-perfluoroalkyl-β-dicarbonyl compound **2** (7.5 mmol) and triethylamine (1.38 ml, 9.9 mmol) in benzene (7.5 mL) was added a solution of hydroxyiminoyl halogenide **8** (1.5 mmol) in benzene (1.5 mL). After 36 hours at room temperature, a usual work-up was made and the residue was flash chromatographed on silica gel.

5-Chlorodifluoromethyl-3-ethoxycarbonyl-4-methoxycarbonylisoxazole (11a). Eluent: *n*-hexane-diisopropyl ether 8:2. Yield 81 %. Oil. IR (film): 1755 cm^{-1}. ^1H NMR δ: 1.42 (3H, t, CH_3); 3.95 (3H, s, OCH_3); 4.48 (2H, q, CH_2). ^{19}F NMR δ: -53.3 (s). ^{13}C NMR δ: 14.0; 53.5; 63.4; 112.2 (C-4); 118.0 (t, $J_{C,F}$ = 289 Hz, CF_2Cl); 155.4, 157.8, 158.7 (C-3, CO_2Et, CO_2CH_3); 162.2 (t, $^2J_{C,F}$ = 38 Hz, C-5). MS: 283 (M^+). Anal. calcd. for $C_9H_8ClF_2NO_5$: C 38.11, H 2.84, N 4.94; found: C 38.22, H 2.88, N 5.04.

3-(4-Bromophenyl)carbonyl-5-chlorodifluoromethyl-4-methoxycarbonylisoxazole (11b). Eluent: cyclohexane-diisopropyl ether 9:1. Yield 79 %. mp 53 °C (diisopropyl ether). IR (nujol): 1745; 1670 cm^{-1}. ^1H NMR δ: 3.86 (3H, s, OCH_3); 7.71, 7.94 (4H, dd each, BrC_6H_4). ^{19}F NMR δ: -53.1 (s). ^{13}C NMR δ: 53.4; 112.4 (C-4); 118.2 (t, $J_{C,F}$ = 289 Hz, CF_2Cl); 130.9, 131.7, 132.4, 133.5 (BrC_6H_4); 158.5, 160.3 (C-3, CO_2CH_3); 162.6 (t, $^2J_{C,F}$ 38 Hz, C-5); 182.8 (COC_6H_4Br). MS: 394 (M^+). Anal. calcd. for $C_{13}H_7BrClF_2NO_4$: C 39.57, H 1.79, N 3.55; found: C 39.57, H 1.89, N 3.55.

3,4-Di(ethoxycarbonyl)-5-trifluoromethylisoxazole (11c). Eluent: *n*-hexane-diisopropyl ether 85:15. Yield 80 %. Oil. IR (film): 1750 cm^{-1}. ^1H NMR δ: 1.37 (3H, t, CH_3); 1.43 (3H, s, CH_3); 4.41 (2H, q, CH_2); 4.49 (2H, q, CH_2). ^{19}F NMR δ: -64.0 (s). ^{13}C NMR δ: 13.8; 14.0; 63.0; 63.5; 114.1 (C-4); 117.1 (q, $J_{C,F}$ = 270 Hz, CF_3); 155.7, 157.8, 157.9 (C-3, two CO_2Et); 159.0 (q, $^2J_{C,F}$ = 45 Hz, C-5). MS: 281

(M^+). Anal. calcd. for $C_{10}H_{10}F_3NO_5$: C 42.71, H 3.58, N 4.98; found: C 42.76, H 3.54, N 5.07.

3-(4-Bromophenyl)carbonyl-4-ethoxycarbonyl-5-trifluoromethylisoxazole (11d). Eluent: cyclohexane-diisopropyl ether 91:9. Yield 77 %. Oil. IR (film): 1740; 1690 cm^{-1}. ^1H NMR δ: 1.25 (3H, s, CH_3); 4.32 (2H, q, CH_2); 7.70, 7.90 (4H, dd each, BrC_6H_4). ^{19}F NMR δ: -63.7 (s). ^{13}C NMR δ: 13.6; 62.9; 114.3 (C-4); 117.2 (q, $J_{C,F}$ = 270 Hz, CF_3); 130.9, 131.6, 132.5, 133.6 (BrC_6H_4); 157.7, 160.5 (C-3, CO_2Et); 159.5 (q, $^2J_{C,F}$ = 44 Hz, C-5); 183.0 (COC_6H_4Br). MS: 392 (M^+). Anal. calcd. for $C_{14}H_9BrF_3NO_4$: C 42.88, H 2.31, N 3.57; found: C 42.76, H 2.34, N 3.55.

4-Ethoxycarbonyl-3-phenyl-5-trifluoromethylisoxazole (11e). Eluent: cyclohexane-diisopropyl ether 9:1. Yield 82 %. Oil. IR (film): 1740 cm^{-1}. ^1H NMR δ: 1.30 (3H, s, CH_3); 4.35 (2H, q, CH_2); 7.4-7.8 (5H, m, Ph). ^{19}F NMR δ: -64.0 (s). ^{13}C NMR δ: 13.7; 62.4; 112.8 (C-4); 117.6 (q, $J_{C,F}$ = 270 Hz, CF_3); 126.4, 128.6, 129.1, 130.8 (Ph); 159.3, 163.0 (C-3, *C*OOEt); 160.0 (q, $^2J_{C,F}$ = 43 Hz, C-5).

3-(2,6-Dichlorophenyl)-4-ethoxycarbonyl-5-trifluoromethylisoxazole (11f). Eluent: *n*-hexane-diisopropyl ether 89:11. Yield 91 %. IR (film): 1735 cm^{-1}. ^1H NMR δ: 1.12 (3H, s, CH_3); 4.33 (2H, q, CH_2); 7.3-7.5 (3H, m, $C_6H_3Cl_2$). ^{19}F NMR δ: -63.7 (s). ^{13}C NMR δ: 13.5; 62.1; 113.6 (C-4); 117.4 (q, $J_{C,F}$ = 270 Hz, CF_3); 126.2, 128.1, 132.1, 135.5 ($C_6H_3Cl_2$); 157.9, 159.8 (C-3, *C*OOEt); 160.6 (q, $^2J_{C,F}$ = 42 Hz, C-5).

3,4-Di(ethoxycarbonyl)-5-(heptafluoro-*n*-propyl)isoxazole (11g). Eluent: *n*-hexane-diisopropyl ether 9:1. Yield 78 %. Oil. IR (film): 1750 cm^{-1}. ^1H NMR δ: 1.36 (3H, t, CH_3); 1.43 (3H, s, CH_3); 4.43 (2H, q, CH_2); 4.49 (2H, q, CH_2). ^{19}F NMR δ: -81.5 (3F, t, CF_3); -113.5 (2F, m, CF_2); -127.4 (2F, t, CF_2). ^{13}C NMR δ: 13.8; 14.0; 63.1; 63.4; 117.0 (C-4); 155.3, 157.7, 158.0 (C-3, two CO_2Et); 157.3 (t, $^2J_{C,F}$ = 31 Hz, C-5). MS: 381 (M^+). Anal. calcd. for $C_{12}H_{10}F_7NO_5$: C 37.81, H 2.64, N 3.68; found: C 37.79, H 2.62, N 3.59.

3-Ethoxycarbonyl-4-phenylcarbonyl-5-trifluoromethylisoxazole (11h). Eluent: cyclohexane-diisopropyl ether 8:2. Yield 81 %. Oil. IR (film): 1760; 1680 cm^{-1}. ^1H NMR δ: 1.16 (3H, s, CH_3); 4.29 (2H, q, CH_2); 7.4-7.9 (5H, m, Ph). ^{19}F NMR δ: -63.9 (s). ^{13}C NMR δ: 13.6; 63.3; 117.1 (q, $J_{C,F}$ = 270 Hz, CF_3); 120.2 (C-4); 129.1, 129.4, 135.0, 135.9 (Ph); 155.0, 157.4 (C-3, CO_2Et); 157.2 (q, $^2J_{C,F}$ = 44 Hz, C-5); 184.5 (*C*OPh). MS: 313 (M^+). Anal. calcd. for $C_{14}H_{10}F_3NO_4$: C 53.68, H 3.22, N 4.47; found: C 53.65, H 3.19, N 4.46.

3-Ethoxycarbonyl-4-(2-thienyl)carbonyl-5-trifluoromethylisoxazole (11i). Eluent: cyclohexane-diisopropyl ether 8:2. Yield 86 %. mp 58 °C (diisopropyl ether). IR (nujol): 1740; 1670 cm^{-1}. ^1H NMR δ: 1.26 (3H, s, CH_3); 4.35 (2H, q, CH_2); 7.1-7.9 (3H, m, C_4H_3S). ^{19}F NMR δ: -63.8 (s). ^{13}C NMR δ: 13.7; 63.3; 117.1 (q, $J_{C,F}$ = 270 Hz, CF_3); 119.9 (C-4); 128.8, 135.5, 137.1, 143.1 (C_4H_3S); 154.8, 157.3 (C-3, CO_2Et); 157.2 (q, $^2J_{C,F}$ = 44 Hz, C-5); 176.0 (COC_4H_3S). MS: 319 (M^+). Anal. calcd. for $C_{12}H_8F_3NO_4S$: C 45.14, H 2.53, N 4.39; found: C 45.09, H 2.58, N 4.37.

3-(4-Bromophenyl)carbonyl-4-(2-thienyl)carbonyl-5-trifluoromethylisoxazole (11j). Eluent: cyclohexane-diisopropyl ether 88:12. Yield 76 %. mp 117 °C (diisopropyl ether). IR (KBr): 1650 cm^{-1}. ^1H NMR δ: 7.1-7.9 (3H, m, C_4H_3S); 7.69 and 8.13 (4H, dd each, BrC_6H_4). ^{19}F NMR δ: -63.5 (s). ^{13}C NMR δ: 117.2 (q, $J_{C,F}$ = 270 Hz, CF_3); 120.8 (C-4); 128.8, 130.9, 132.1, 132.4, 133.1, 135.3, 136.9, 143.0 (C and CH ar.); 156.5 (q, $^2J_{C,F}$ = 44 Hz, C-5) 159.9 (C-3); 176.3 (COC_4H_3S); 181.9 (COC_6H_4Br). MS: 430 (M^+). Anal. calcd. for $C_{16}H_7BrF_3NO_3S$: C 44.67, H 1.64, N 3.26; found: C 44.71, H 1.78, N 3.27.

3-Ethoxycarbonyl-5-methyl-4-trifluoromethylcarbonylisoxazole (13a). Eluent: cyclohexane-diisopropyl ether 7:3. Yield 74 %. IR (KBr): 1695 cm^{-1}. *Keto-form*: ^1H NMR δ: 1.44 (3H, t, OCH_2CH_3); 2.71 (3H, s, CH_3); 4.47 (2H, q, CH_2). ^{19}F NMR δ: -70.6 (s). ^{13}C NMR δ: 13.0; 13.9; 64.2; 113.2 (C-4); 115.2 (q, $J_{C,F}$ = 289 Hz, CF_3); 152.5 (C-3); 163.6 (*C*OOEt); 173.6 (C-5); 176.5 (q, $^2J_{C,F}$ = 38 Hz, $COCF_3$). *Hydrated-form*: ^1H NMR δ: 1.46 (3H, t, OCH_2CH_3); 2.65 (3H, s, CH_3); 4.53 (2H, q, CH_2). ^{19}F NMR δ: -88.2 (s). ^{13}C NMR δ: 13.0; 13.1; 63.5; 90.9 (q, $^2J_{C,F}$ = 35 Hz, $C(OH)_2CF_3$); 112.9 (C-4); 123.0 (q, $J_{C,F}$ = 283 Hz, CF_3); 155.0 (C-3); 159.2 (*C*OOEt); 176.8 (C-5).

3-(4-Bromophenyl)carbonyl-5-methyl-4-trifluoromethylcarbonylisoxazole (13b). Eluent: cyclohexane-diisopropyl ether 7:3. Yield 70 %. *Keto-form*: ^1H NMR δ: 2.78 (3H, s, CH_3); 7.6-8.1 (BrC_6H_4). ^{19}F NMR δ: -76.1 (s). ^{13}C NMR δ: 12.9; 113.3 (C-4); 115.2 (q, $J_{C,F}$ = 289 Hz, CF_3); 131.1, 132.1 132.8, 134.0 (BrC_6H_4); 157.9 (C-3); 172.8 (C-5); 176.1 (q, $^2J_{C,F}$ = 38 Hz, $COCF_3$); 189.6 (COC_6H_4Br).

Hydrated-form: ^{1}H NMR δ: 2.72 (3H, s, CH_3); 7.6-8.1 (BrC_6H_4). ^{19}F NMR δ: -88.0 (s). ^{13}C NMR δ: 13.1; 90.6 (q, $^2J_{C,F}$ = 35 Hz, $COCF_3$); 111.9 (C-4); 130.8, 131.7 132.4, 133.5 (BrC_6H_4); 159.9 (C-3); 176.5 (C-5); 184.2 (COC_6H_4Br).

5-Ethyl-3-ethoxycarbonyl-4-trifluoromethylcarbonylisoxazole (13c). Eluent: *n*-hexane-ethyl acetate 77:23. Yield 64 %. Oil. IR (film): 1710 cm^{-1}. *Keto-form*: ^{1}H NMR δ: 1.23 and 1.48 (6H, m, two CH_3); 3.03 (2H, q, CH_2CH_3); 4.46 (2H, q, OCH_2CH_3). ^{19}F NMR δ: -76.5 (s). *Hydrated-form*: ^{1}H NMR δ: 1.23 and 1.48 (6H, m, two CH_3); 3.09 (2H, q, CH_2CH_3); 4.52 (2H, q, OCH_2CH_3). ^{19}F NMR δ: -88.2 (s).

3-Ethoxycarbonyl-4-(1-hydroxyethyl)1-phenyl-5-trifluoromethylpyrazole (14). To a cooled and stirred solution of pyrazole **6j** (130 mg, 0.4 mmol) in anhydrous THF (3.5 mL) was added sodium borohydride (46 mg, 1.2 mmol). After 36 hours at room temperature, a usual work-up was made and the residue was flash chromatographed on silica ge with *n*-hexane-ethyl acetate 78:22 to give the hydroxymethylpyrazole **14** in 83% yield. ^{1}H NMR δ: 1.44 (3H, s, OCH_2CH_3); 1.60 (3H, d, J = 6.5 Hz, $CHCH_3$); 4.50 (2H, q, CH_2); 5.19 (1H, q, J = 6.5 Hz, $OCHC$-4); 5.2 (1H, br. s, OH); 7.3-7.6 (5H, m, Ph). ^{19}F NMR δ: -56.2 (s).

4-Hydroxybenzyl-3-hydroxymethyl-5-trifluoromethylisoxazole (15). To a cooled (-30 °C) and stirred solution of isoxazole **11h** (125 mg, 0.4 mmol) in anhydrous THF (2.0 mL) was added a slurry of sodium borohydride (15 mg, 0.4 mmol) in the same solvent. After 16 hours at room temperature, a usual work-up was made and the residue was flash chromatographed on silica gel with *n*-hexane-ethyl acetate 72:28 to give the hydroxymethylisoxazole **15** in 78% yield. mp 57 °C (*n*-hexane-ethyl acetate). ^{1}H NMR δ: 4.33 and 4.70 (1H each, d each, OCH_2C-3); 6.17 (1H, s, $OCHC$-4); 7.2-7.5 (5H, m, Ph). ^{19}F NMR δ: -63.0 (s).

3-Ethoxycarbonyl-4-(1-hydroxy-2,2,2-trifluoroethyl)5-methylisoxazole (16). To a cooled (0 °C) and stirred solution of isoxazole **13a** (161 mg, 0.6 mmol) in anhydrous THF (3.5 mL) was added a solution of sodium borohydride (23 mg, 0.6 mmol) in the same solvent. After 16 hours at room temperature, a usual work-up was made and the residue was flash chromatographed on silica gel with *n*-hexane-ethyl acetate 75:25 to give the hydroxytrifluoroethylisoxazole in 80% yield. Oil. ^{1}H NMR δ: 1.47 (3H, t,); 2.52 (3H, s, CH_3C-5); 4.51 and 4.52 (2H each, dq, CH_2); 5.03 (1H, q, $OCHC$-4). ^{19}F NMR δ: -80.0 (d, CF_3, $^3J_{H,F}$ = 7 Hz).

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11. For instance, when trifluoroacetoacetate **2b** was refluxed with hydrazonyl bromide **1c** the *N'*-(ethyl (3-hydroxy-4,4,4-trifluorobutanoate)3-yl)-*N'*-(4-nitrophenyl)-benzenecarbohydrazonyl bromide was formed as main reaction product through the addition of the hydrazonyl nitrogen to the keto group of the dicarbonyl system.
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