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N→N Acyl Group Migration in *N*-Acylpyrazoles: Isomerization of 1,4-Diacyl-5-methyl-1*H*-pyrazoles to 1,4-Diacyl-3-methyl-1*H*-pyrazoles

A. A. Petrov,* V. V. Pakal'nis, A. V. Zerov, and S. I. Yakimovich

St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia
**e-mail: aap1947@yandex.ru*

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Abstract—1,4-Diacyl-5-methyl-1*H*-pyrazoles on heating in toluene undergo isomerization to 1,4-diacyl-3-methyl-1*H*-pyrazoles via intermolecular N→N acyl group migration. 1,4,5-Trisubstituted pyrazoles obtained by reaction of 2-ethoxymethylidene derivatives of 1,3-diketones with 1,3-benzothiazol-2-ylhydrazine or phenylhydrazine failed to isomerize to 1,3,4-trisubstituted pyrazoles.

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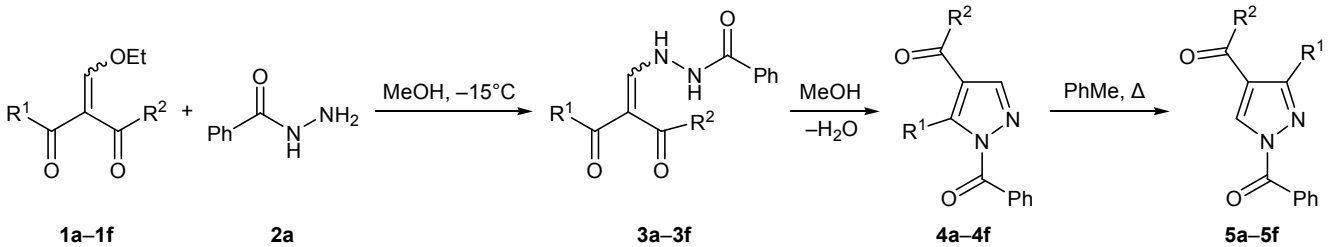
An important research line in organic chemistry is development of methods of synthesis of new functionalized heterocyclic compounds possessing useful properties. Among numerous chemical transformations, intra- and intermolecular migrations of functional groups from one part of a molecule (donor) to another (acceptor) occupy a particular place in organic and bioorganic chemistry. Studies of group migrations are important for elucidation of the mechanisms and extension of the scope of organic reactions, as well as for target-oriented organic synthesis [1–7]. Among acyl group transfer reactions leading to new positional isomers [8], N→O (pH <7), O→N (pH >7) [9–12], S→N [13, 14], and O→C migrations [15, 16] were reported. N→N Migration of acyl groups was described for aliphatic, aromatic, and heterocyclic diamines [3,4-diaminopentan-2-ol, pyridine-2,3-diamine, 5-(aminomethyl)-3-benzyl-3*H*-1,2,3-triazol-4-amine] [17–19] and diazabenzobicyclo[3.3.1]nonane [20] and spiro piperidine derivatives [21]. Miyaki and Shimizu [22, 23] reported N→N migrations of benzyl, allyl, 3-methylbut-2-en-1-yl, and glycosyl groups in purines. Kepe et al. [24] proved intermolecular N→N migrations of acyl and other groups (COMe, COAr, COHt, $COCH_2NHCOPh$, CONHPh, CSNHPh, CO_2CH_2Ph) in pyrazolones; however, only thermodynamically more stable isomer was isolated. Likewise, 5-amino-3-hydroxy-1*H*-pyrazole-1-carboxamide was converted to 3-amino-5-hydroxy isomer via migration of the carbamoyl group [25]. Bonacorso et al. [26] revealed 1,2-migration of the acyl group in the course of dehydration of 1-(hetarylcarbonyl)-5-hydroxy-3-phenyl-5-trifluoromethyl-4,5-dihydro-1*H*-pyrazoles in a mixture of $CHCl_3$ with P_2O_5 at 65°C.

Taking into account practical importance of pyrazole systems [27], search for alternative approaches to their selective functionalization is a topical problem in the chemistry of heterocyclic compounds. Alkoxy-

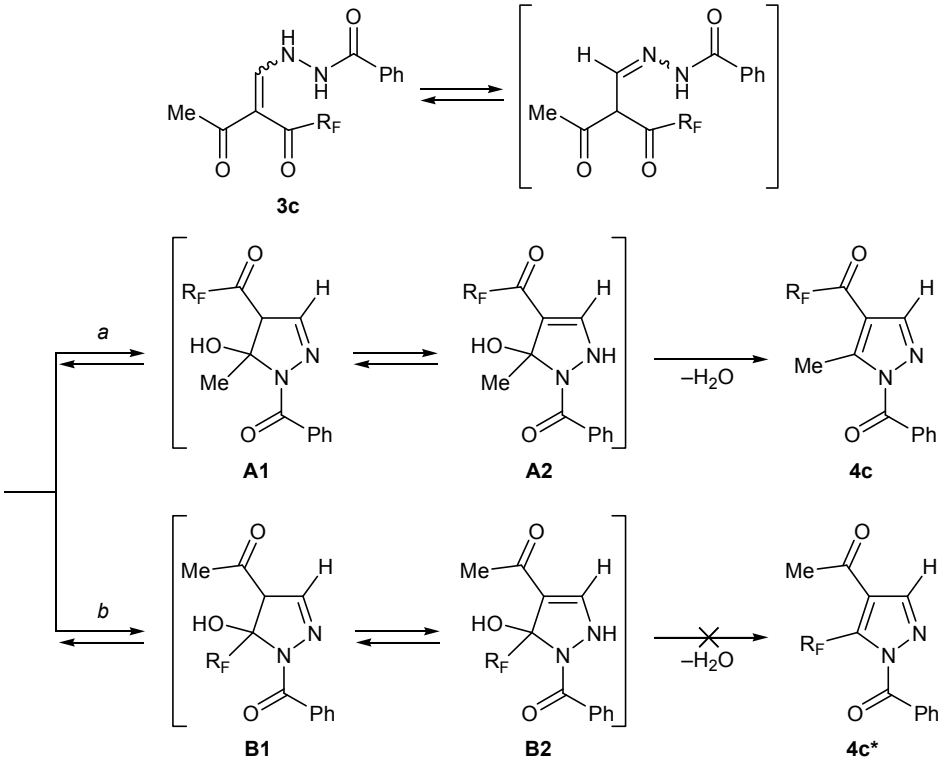
Scheme 1.



1a–1f **2a** **3a–3f** **4a–4f** **5a–5f**

$R^1 = R^2 = Me$ (**a**); $R^1 = Me$, $R^2 = EtO$ (**b**), CF_3 (**c**), C_3F_7 (**d**); $R^1 = R^2 = Et$ (**e**), Pr (**f**).

Scheme 2.



methylidene derivatives of 1,3-dicarbonyl compounds [28, 29] are known to react with carboxylic acid hydrazides to give *N*-acylpyrazoles [30–35] that are valuable building blocks in organic synthesis.

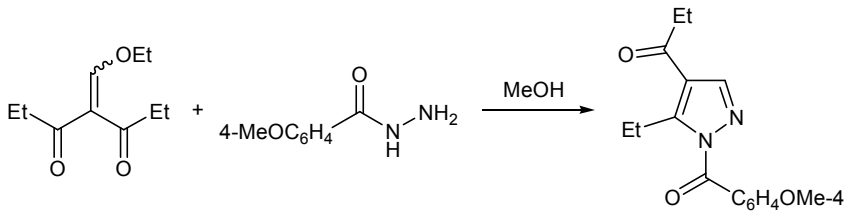
We previously showed that reactions of 3-(ethoxymethylidene)pentane-2,4-dione (**1a**) and ethyl 2-(ethoxymethylidene)-3-oxobutanoate (**1b**) with benzohydrazide (**2a**) in methanol initially give enehydrazines **3a** and **3b** which undergo cyclization to 4,5-disubstituted *N*-benzoylpyrazoles **4a** and **4b**; the latter rearrange to thermodynamically more stable 3,4-substituted *N*-benzoylpyrazoles **5a** and **5b** on heating in boiling toluene [31] (Scheme 1). According to the data of [30, 34], alkoxymethylidene derivatives of 1,3-dicarbonyl compounds reacted with acylhydrazines on heating to give 1,3,4-trisubstituted pyrazoles. On the other hand, 1,4,5-trisubstituted pyrazole, ethyl 1-carbamothioyl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1*H*-pyrazole-4-carboxylate, was isolated in the reaction of ethyl 2-(ethoxymethylidene)-4,4,4-trifluoro-3-oxobutanoate with thiosemicarbazide in ethanol at –15°C [35].

In order to get a deeper insight into the above reaction, in this work we studied reactions of ethoxymethylidene derivatives **1c**–**1f** with benzohydrazide (**2a**) at –15°C in anhydrous methanol. In some cases we succeeded in isolating the primary product, enehydrazine **3**, in the pure state. The structure of enehydrazine (**3c**) isolated in the reaction of 3-(ethoxymethylidene)-1,1,1-trifluoropentane-2,4-dione (**1c**) with hydrazide **2a** (Scheme 1) was determined on the basis of its NMR and mass spectra with account taken of the spectral parameters of related compound **3a** which was synthesized by us previously [31].

Enehydrazine **3c** contains two nonequivalent carbonyl groups, so that its cyclization could give rise to isomeric dihydropyrazoles **A1**, **A2** and **B1**, **B2** (Scheme 2) whose subsequent dehydration might lead to the corresponding pyrazoles **4c** and **4c***. 5-Hydroxy-5-trifluoromethyl-4,5-dihydropyrazoles obtained by reaction of acid hydrazides with 1,3-diketones are usually stable and are not prone to lose water molecule [36–40]. Therefore, the rate of elimination of water from intermediates **A1** and **A2** should be higher than from **B1** and **B2** [41, 42], and the formation of pyrazole **4c** rather than **4c*** is readily understandable (Scheme 2).

The ^{13}C NMR spectrum of pyrazole **4c** showed a signal at δ_C 13.78 ppm due to methyl carbon atom (5-CH_3) and a quartet at δ_C 176.29 ppm ($^2J_{CF}$ = 36.9 Hz) due to carbonyl carbon atom of the trifluoroacetyl group (**C**OCF_3). Isomeric pyrazole **4c*** would

Scheme 3.



1e **2b** **4g**

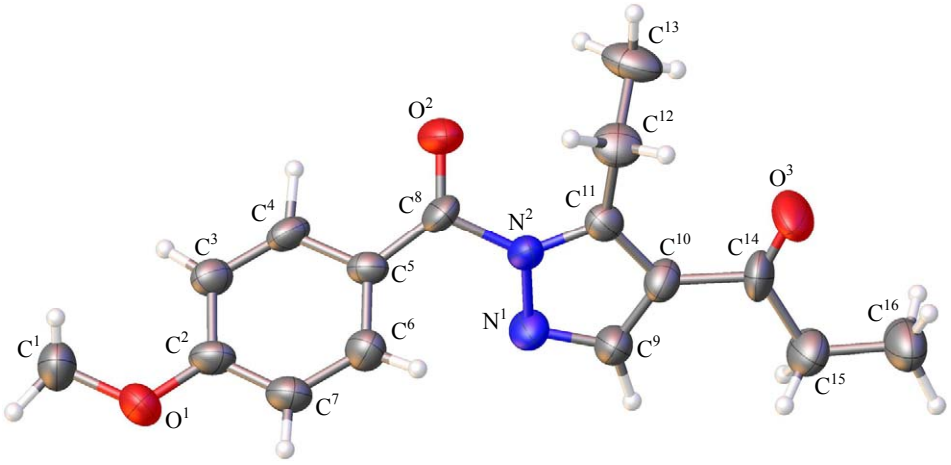
give rise to acetyl carbonyl signals in the regions δ_C 28–30 and 192–194 ppm [31]. The mass spectrum of the product contained a peak corresponding to the $[M - COCF_3]^+$ ion (M – 97), which also confirmed the proposed direction of intramolecular cyclization with formation of isomer **4c**. We failed to isolate intermediate enehydrazines **3** in the reactions of **1d**–**1f** with benzohydrazide, and the products were 1,4,5-trisubstituted pyrazoles **4d**–**4f** (Scheme 1).

Thus, the transformation sequence enehydrazine → 1,4,5-trisubstituted pyrazole → 1,3,4-trisubstituted pyrazole is intrinsic to reactions of benzoylhydrazine with 1,3-dicarbonyl compounds **1a**–**1f** containing both ester and alkyl or perfluoroalkyl ketone fragment.

Heating of pyrazoles **4c**–**4f** in boiling toluene or in melt resulted in their isomerization to 1,3,4-trisubstituted pyrazoles **5c**–**5f**. The reaction was complete in 6–8 h or 20–30 min, respectively (Scheme 1). The spectral characteristics of isomeric pyrazoles **4c**–**4f** and **5c**–**5f** are given in Experimental. The structure of 1,4,5-trisubstituted pyrazole **4g** obtained by reaction of ethoxymethylidene derivative **1e** with 4-methoxybenzohydrazide (**2b**) (Scheme 3) was proved by X-ray analysis (see figure), and the spectral characteristics of **4g** were used to determine the structure of isomeric 1,4,5- and 1,3,4-trisubstituted pyrazoles. The isomers were identified by comparing the chemical shifts of C^3 and C^5 and protons attached thereto in compounds **4c**–**4g** and **5c**–**5g**, as well as in pyrazoles described previously [31, 43].

The ^{1}H NMR spectra of 1,4,5-trisubstituted *N*-acylpyrazoles characteristically showed the 3-H signal at δ 7.91–8.30 ppm, whereas the 5-H signal of 1,3,4-trisubstituted isomers was located at δ 8.57–9.01 ppm. This difference may be used to distinguish isomeric pyrazoles **4** and **5**. Table contains characteristic chemical shifts of carbon nuclei in model compounds and 1,4,5- and 1,3,4-trisubstituted pyrazoles. In the ^{13}C NMR spectra of **4**, the carbon chemical shifts increase in the series $C^4 < C^3H < C^5$, $\Delta\delta_C = \delta_{C^5} - \delta_{C^3} \approx$ 5–11 ppm, and the corresponding series for isomers **5** is $C^4 < C^5H < C^3$, $\Delta\delta_C = \delta_{C^3} - \delta_{C^5} \approx$ 19–27 ppm. Thus, the ^{13}C data provide an additional criterion for distinguishing alternative structures.

We also studied the effect of substituents in the pyrazole ring on the N→N migration of the acyl group. For this purpose, 3-(ethoxymethylidene)pentane-2,4-dione (**1a**) was brought into reactions with hydrazides **2b**–**2e** containing acyl groups with different electronic and steric properties and with hydrazines **2f**–**2g** (Scheme 4). In some cases we succeeded in isolating intermediate enehydrazine as an individual compound



Structure of the molecule of 1-[5-ethyl-1-(4-methoxybenzoyl)-1*H*-pyrazol-4-yl]propan-1-one (**4g**) according to the X-ray diffraction data.

Characteristic ^{13}C chemical shifts of the $CC^3H=N$, $C=C^5(Alk)N$, $CC^3(Alk)=N$, and $C=C^5HN$ fragments of pyrazoles **4**, **5**, **7**, and **8** in comparison with published data

Compound no.	δ_{C3}, ppm	δ_{C5}, ppm	$\Delta\delta_C$, ppm
4c–**4h** (5-Me)	142.3–142.7	152.6–154.3	~11
7b–**7e** (5-Me)	142.1–144.0	147.5–150.3	~5
1,5-Dialkylpyrazole [44]	140.3–143.3	136.2–136.3	~7
5c–**5h** (3-Me)	156.1–160.0	133.4–136.9	~ 23
8b–**8e** (3-Me)	153.0–154.7	134.2–135.4	~19
1,3-Dialkylpyrazole [44]	150.2–152.9	125.8–126.3	~27
3,5-Dimethyl-1-phenylpyrazole [45]	152.1	145.1	7

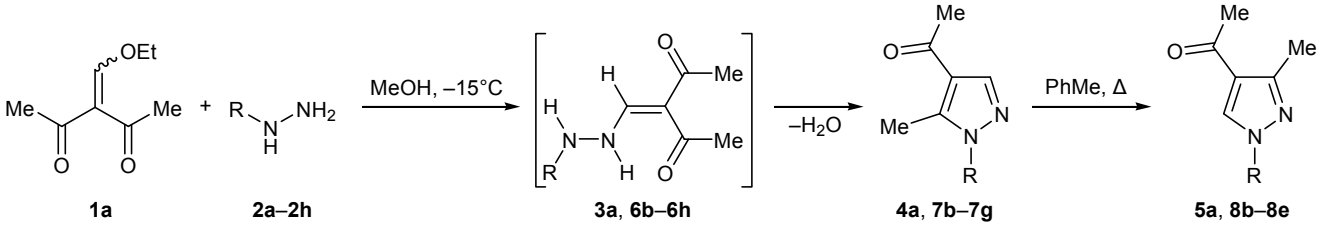
or in a mixture with 1,4,5-trisubstituted pyrazole (see Experimental). It was found that only *N*-acylpyrazoles **4a** [31] and **7b**–**7e** underwent isomerization in boiling benzene, as was observed for fluorinated derivatives. The rates of formation of 1,3,4-trisubstituted pyrazoles **5a** and **8b**–**8d** were approximately similar, and the migration process was complete in 6–8 h in boiling toluene or in 20–30 min in melt. Increase of the effective volume of the *N*-acyl group (compound **7e**) was accompanied by reduction of the isomerization rate (48 h in toluene or 1.5 h in melt). 1,4,5-Trisubstituted pyrazoles **7f** and **7g** failed to isomerize in $CDCl_3$ at 20–25°C, in toluene under reflux, or in melt.

In addition, we synthesized 1,4,5-trisubstituted pyrazoles **9a**–**9d** by reaction of polyfluorinated 1,3-diketones **1c** and **1d** with 1,3-benzothiazol-2-ylhydrazine (**2f**) and phenylhydrazine (**2g**) (Scheme 5). Compounds **9a**–**9d** did not undergo isomerization on heating in toluene or in melt.

The reaction of 2-(*N*,*N*-dimethylaminomethylidene)-5,5-dimethylcyclohexane-1,3-dione with benzoylhydrazine in acetic acid gave compound **10a** which is likely to exist in $CDCl_3$ solution as an equilibrium mixture of tautomers **A** and **B** (Scheme 6). The downfield region of the ^1H NMR spectrum of **10a** recorded at –50°C contained a doublet signal at δ 9.02 (J = 12.1 Hz), a doublet at δ 12.68 (J = 7.1 Hz), and a doublet of doublets at δ 13.90 ppm (J = 12.1, 7.1 Hz). This pattern is fully consistent with enehydrazine structure **B**, which is likely to predominate at reduced temperature. No cyclization of **10a** was observed on prolonged heating in boiling toluene.

According to DFT B3LYP/6-31G(*d*) quantum chemical calculations of pyrazoles **4a** and **5a**, the

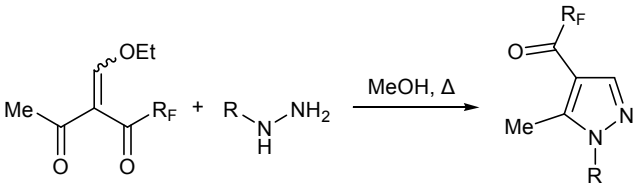
Scheme 4.



1a **2a–2h** **3a**, **6b–6h** **4a**, **7b–7g** **5a**, **8b–8e**

R = PhCO (**a**), 4-MeC_6H_4CO (**b**), thiophen-2-ylcarbonyl (**c**), EtOC(O) (**d**), 1-AdCO (**e**), 1,3-benzothiazol-2-yl (**f**), Ph (**g**).

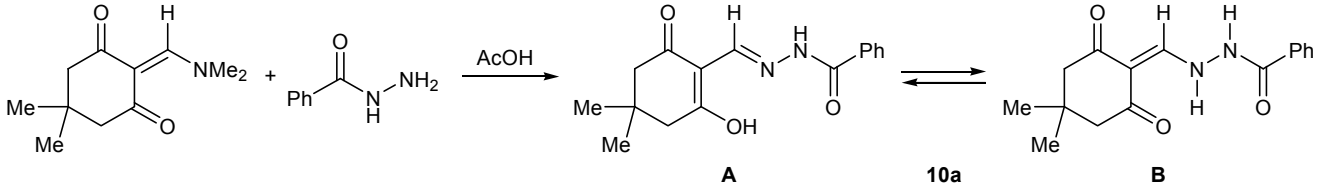
Scheme 5.



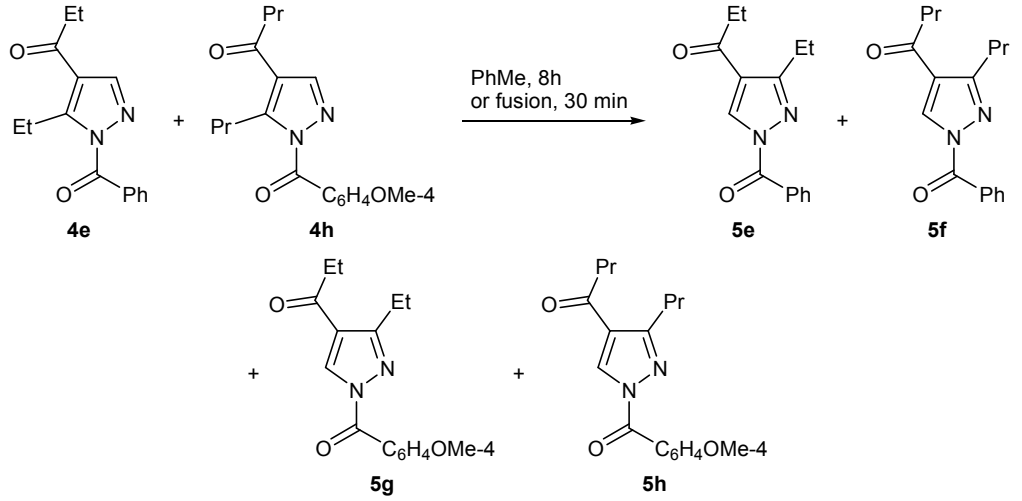
1c, **1d** **2f**, **2g** **9a–9d**

1, R_F = CF_3 (**c**), C_3F_7 (**d**); **2**, R = 1,3-benzothiazol-2-yl (**f**), Ph (**g**); **9**, R_F = CF_3, R = 1,3-benzothiazol-2-yl (**a**), Ph (**b**); R_F = C_3F_7, R = 1,3-benzothiazol-2-yl (**c**), Ph (**d**).

Scheme 6.



Scheme 7.



driving force of the isomerization **4a**→**5a** is higher stability of the 1,3,4-trisubstituted isomer. The difference in the energies of isomers **4a** and **5a** is 2.5 kcal× mol^{-1}. Presumably, the lower stability of pyrazole **4a** is related to steric interactions between the neighboring substituents in positions *1*, *4*, and *5* of the pyrazole ring.

The acyl group migration may be intra- or intermolecular. As follows from the dependence of the isomerization rate on the substrate concentration (6–8 h in toluene and 20–30 min in melt), the intermolecular mechanism is more probable. An additional proof for the intermolecular mechanism was obtained by special experiment. A mixture of equimolar amounts of 1,4,5-trisubstituted pyrazoles **4e** and **4h** in toluene was refluxed for 8 h; in parallel, a 1:1 mixture of the same compounds was fused for 30 min under reduced pressure (Scheme 7). In both cases, the products were four 1,3,4-trisubstituted pyrazoles **5e**–**5h** which were identified by ^{1}H and ^{13}C NMR spectroscopy, as well as by mass spectrometry (molecular ion peaks corresponding to four pyrazoles were present in the mass spectrum of the product mixture). The formation of "crossed" structures **5g** and **5h** is possible only for intermolecular migration of the acyl groups.

In summary, 2-ethoxymethylidene derivatives of 1,3-dicarbonyl compounds react with acylhydrazines to give intermediate enehydrazines which undergo cyclization to 1,4,5-trisubstituted pyrazoles. Thermal isomerization of the latter leads to 1,3,4-substituted pyrazoles via intermolecular N→N migration of the acyl group. No analogous transformation is observed for 1,4,5-trisubstituted pyrazoles obtained from 2-ethoxymethylidene derivatives of 1,3-diketones and 1,3-benzothiazol-2-ylhydrazine or phenylhydrazine.

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer Spectrum BX FT-IR System in KBr. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III spectrometer at 400 and 100 MHz, respectively. The mass spectra were obtained on MKh-1321 (electron impact, 70 eV) and Bruker Daltonics microTOF instruments (ESI, acetonitrile, 0.1% HCOOH). The elemental compositions were determined on a Hewlett Packard 185B CHN-analyzer. The progress of reactions was monitored, and the purity of the isolated compounds was checked, by TLC on Silufol UV-254 plates using ethyl acetate as eluent; spots were visualized by treatment with iodine vapor. The reaction mixtures were separated by column chromatography on Chemapol silica gel (100–160 μm). Ethoxymethylidene derivatives **1a**–**1f** were synthesized according to

the procedure described in [46] from the corresponding 1,3-dicarbonyl compounds and triethyl orthoformate in the presence of acetic anhydride at a molar ratio of 1:1.75:2.85. The X-ray diffraction data for compound **4g** were acquired on a Bruker SMART 1000 CCD diffractometer (Mo K_α radiation, graphite monochromator, ω-scanning). The structure was solved by the direct method and was refined first in isotropic and then in anisotropic approximation using SHELXL [47]. Hydrogen atoms were placed in geometrically calculated positions which were refined according to the riding model. The crystallographic data for compound **4g** were deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1519262).

Reaction of ethoxymethylidene derivatives 1a–1f with acylhydrazines 2a–2e (*general procedure*). A solution of 3 mmol of compound **1a**–**1f** in 5 mL of anhydrous methanol was cooled to –15°C, and a solution of 3 mmol of hydrazide **2a**–**2e** in 5 mL of anhydrous methanol was added dropwise with vigorous stirring. The mixture was stirred for 1 h, the solvent was removed under reduced pressure without heating, and the crystalline product (enehydrazine, 1,4,5-trisubstituted pyrazole, or their mixture) was filtered off and dried in air.

***N′*-(2-Acetyl-4,4,4-trifluoro-3-oxobut-1-en-1-yl)-benzohydrazide (3c).** Yield 0.567 g (63%), mp 152–153°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.43 s (3H, Me), 7.56 t (2H, H_{arom}, J = 7.1 Hz), 7.65 t (1H, H_{arom}, J = 7.1 Hz), 7.90 d (2H, H_{arom}, J = 7.1 Hz), 8.21 br.s (1H, C=CH), 12.33 br.s (1H, NH), 13.29 br.s (1H, NH). Found, %: C 51.94; H 3.75; N 9.21. $C_{13}H_{11}F_3N_2O_3$. Calculated, %: C 52.01; N 3.69; N 9.33.

***N′*-(2-Acetyl-3-oxobut-1-en-1-yl)-4-methoxybenzohydrazide (6b).** Yield 0.811 g (98%), mp 152–154°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s (3H, Me), 2.37 s (3H, Me), 3.84 s (3H, OCH_3), 7.08 d (2H, H_{arom}, J = 8.7 Hz), 7.87 d (2H, H_{arom}, J = 8.7 Hz), 8.16 d (1H, C=CH, J = 10.9 Hz), 11.56 br.s (1H, NH), 12.23 br.d (1H, NH, J = 11.6 Hz). Found, %: C 60.72; H 5.80; N 10.03. $C_{14}H_{16}N_2O_4$. Calculated, %: C 60.86; H 5.84; N 10.14.

***N′*-(2-Acetyl-3-oxobut-1-en-1-yl)thiophene-2-carbohydrazide (6c)** was isolated as a mixture with 1-[5-methyl-1-(thiophen-2-ylcarbonyl)-1*H*-pyrazol-4-yl]ethan-1-one (**7c**) at a ratio of 3:2. Pyrazole **7c** was separated by column chromatography (hexane–ethyl acetate, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.22 s (3H, Me), 2.36 s (3H, Me), 7.23 t (1H, H_{Th}, J = 4.4 Hz), 7.82 br.d (1H, H_{Th}, J = 2.9 Hz), 7.90 d (1H, H_{Th}, J = 4.4 Hz), 8.10 d (1H, C=CH, J = 10.9 Hz), 11.63 br.s (1H, NH), 11.99 br.d (1H, NH, J = 10.1 Hz).

Ethyl 2-(2-acetyl-3-oxobut-1-en-1-yl)hydrazinecarboxylate (6d) was isolated as a mixture with ethyl 4-acetyl-5-methyl-1*H*-pyrazole-1-carboxylate (**7d**) at a ratio of 4:5. Pyrazole **7d** was separated by column chromatography (hexane–ethyl acetate, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.3 Hz), 2.28 s (3H, Me), 2.49 s (3H, Me), 4.24 q (2H, OCH_2, J = 7.3 Hz), 7.64 br.s (1H, NH), 7.77 d (1H, C=CH, J = 10.2 Hz), 11.50 d (1H, NH, J = 10.2 Hz).

***N′*-(2-Acetyl-3-oxobut-1-en-1-yl)adamantane-1-carbohydrazide (6e)** was isolated as a mixture with 1-[1-(adamantan-1-ylcarbonyl)-5-methyl-1*H*-pyrazol-4-yl]ethan-1-one (**7e**) at a ratio of 1:1. Pyrazole **7e** was separated by column chromatography (hexane–ethyl acetate, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.74 br.s (6H, CH_2), 2.09 br.s (3H, CH), 2.26 s (6H, CH_2), 2.27 s (3H, Me), 2.50 s (3H, Me), 7.70 d (1H, C=CH, J = 10.2 Hz), 8.35 br.s (1H, NH), 11.62 br.d (1H, NH, J = 10.2 Hz).

1,4,5-Trisubstituted pyrazoles (*general procedure*). A mixture of 1.5 mmol of the corresponding enehydrazine and 5 mL of anhydrous methanol was kept at room temperature until complete dissolution. The solvent was removed under reduced pressure, and the crystalline product was filtered off and washed with cold methanol.

1-(1-Benzoyl-5-methyl-1*H*-pyrazol-4-yl)-2,2,2-trifluoroethanone (4c). Yield 0.376 g (89%), mp 87°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.04 s (3H, Me), 7.55 t (2H, H_{arom}, J = 7.3 Hz), 7.69 br.t (1H, H_{arom}, J = 8.0 Hz), 7.98 d (2H, H_{arom}, J = 7.3 Hz), 8.09 br.q (1H, 3-H, J_{HF} = 2.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.78 (5-CH_3), 116.05 (C^4), 116.53 q (CF_3, $^1J_{CF}$ = 290.2 Hz), 128.74 (2C, CH_{arom}), 131.73 (C_{arom}), 132.07 (2C, CH_{arom}), 134.47 (CH_{arom}), 142.34 q (C^3, J_{CF} = 4.0 Hz), 153.44 (C^5), 168.38 (**C**OPh), 176.29 q (**C**OCF_3, $^2J_{CF}$ = 36.9 Hz). Mass spectrum (EI), m/z (I_{rel}, %): 282 (11) $[M]^+$, 213 (2) $[M - CF_3]^+$, 185 (2) $[M - COCF_3]^+$, 122 (25), 109 (74), 105 (100) $[COPh]^+$, 77 (56) $[Ph]^+$, 51 (29), 42 (5). Found, %: C 55.30; H 3.15; N 9.90. $C_{13}H_9F_3N_2O_2$. Calculated, %: C 55.33; H 3.21; N 9.93.

1-(1-Benzoyl-5-methyl-1*H*-pyrazol-4-yl)-2,2,3,3,4,4,4-heptafluorobutan-1-one (4d). Yield 1.008 g (88%), mp 42.5–44.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.02 s (3H, 5-Me), 7.55 t (2H, H_{arom},

J = 7.6 Hz), 7.69 t (1H, H_{arom}, *J* = 7.6 Hz), 7.98 d (2H, H_{arom}, *J* = 7.6 Hz), 8.10 br.s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.78 (5-CH_3), 101–137 (C_3F_7), 117.48 (C^4), 128.70 (2C, CH_{arom}), 131.71 (C_{arom}), 132.07 (2C, CH_{arom}), 134.45 (CH_{arom}), 142.27 t.t (C^3, J_{CF} = 8.0, 2.0 Hz), 153.70 (C^5), 168.33 (**C**OPh), 178.68 t (**C**OC_3F_7, $^2J_{CF}$ = 26.9 Hz). Found, %: C 47.01; H 2.35; N 7.34. $C_{15}H_9F_7N_2O_2$. Calculated, %: C 47.13; H 2.37; N 7.33.

1-(1-Benzoyl-5-ethyl-1*H*-pyrazol-4-yl)propan-1-one (4e). Yield 0.560 g (73%), mp 96–97°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.2 Hz), 1.35 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.3 Hz), 2.88 q (2H, CH_2, *J* = 7.3 Hz), 3.43 q (2H, CH_2, *J* = 7.2 Hz), 7.51 t (2H, H_{arom}, *J* = 8.0 Hz), 7.64 m (1H, H_{arom}), 7.92 br.d (2H, H_{arom}, *J* = 6.5 Hz), 7.98 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.22 (Me), 13.72 (Me), 20.12 (CH_2), 35.20 (CH_2), 121.81 (C^4), 128.57 (2C, CH_{arom}), 131.79 (2C, CH_{arom}), 132.77 (C_{arom}), 133.84 (CH_{arom}), 142.69 (C^3), 154.22 (C^5), 168.93 (**C**OPh), 196.58 (**C**OEt). Found, %: C 70.16; H 6.32; N 10.99. $C_{15}H_{16}N_2O_2$. Calculated, %: C 70.29; H 6.29; N 10.93.

1-(1-Benzoyl-5-propyl-1*H*-pyrazol-4-yl)butan-1-one (4f). Yield 0.247 g (29%), mp 69–70°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.04 t (6H, Me, *J* = 7.2 Hz), 1.69–1.80 m (4H, CH_2), 2.81 t (2H, CH_2, *J* = 7.3 Hz), 3.35–3.39 m (2H, CH_2), 7.53 br.t (2H, H_{arom}, *J* = 7.7 Hz), 7.63 m (1H, H_{arom}), 7.97 s (1H, 3-H), 8.14 d (2H, H_{arom}, *J* = 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.23 (Me), 14.43 (Me), 18.09 (CH_2), 21.89 (CH_2), 28.06 (CH_2), 43.87 (CH_2), 122.10 (C^4), 128.53 (2C, CH_{arom}), 131.80 (2C, CH_{arom}), 132.75 (C_{arom}), 133.88 (CH_{arom}), 142.67 (C^3), 154.28 (C^5), 168.99 (**C**OPh), 196.20 (**C**OPr). Found, %: C 71.73; H 7.03; N 9.96. $C_{17}H_{20}N_2O_2$. Calculated, %: C 71.81; H 7.09; N 9.85.

1-[5-Ethyl-1-(4-methoxybenzoyl)-1*H*-pyrazol-4-yl]propan-1-one (4g). Yield 0.618 g (72%), mp 121–122°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.3 Hz), 1.34 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.3 Hz), 2.88 q (2H, CH_2, *J* = 7.3 Hz), 3.39 q (2H, CH_2, *J* = 7.3 Hz), 3.91 s (3H, OMe), 6.99 d (2H, H_{arom}, *J* = 9.2 Hz), 7.96 d (2H, H_{arom}, *J* = 9.2 Hz), 7.98 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.24 (Me), 13.77 (Me), 20.05 (CH_2), 35.10 (CH_2), 55.98 (OMe), 114.03 (2C, CH_{arom}), 121.55 (C^4), 124.60 (C_{arom}), 134.55 (2C, CH_{arom}), 142.34 (C^3), 153.91 (C^5), 164.45 (C_{arom}), 167.86 (**C**OAr), 196.58 (**C**OEt). Found, %: C 67.06; H 6.30; N 9.78. $C_{16}H_{18}N_2O_3$. Calculated, %: C 67.12; H 6.34; N 9.78.

A single crystal of **4g** suitable for X-ray analysis was obtained by slow evaporation of its solution in toluene. Colorless crystals, $C_{16}H_{18}N_2O_3$, *M* 286.32; monoclinic crystal system, space group *Pc*; unit cell parameters (293 K): *a* = 4.1366, *b* = 21.5940, *c* = 33.9450 Å; β = 90.012°; *V* = 3032.2 $Å^3$; *Z* = 8; d_{calc} = 1.254 mg/mm^3; Final divergence factors: R_{all} = 0.0825, *wR* = 0.1229; total of 15760 reflection intensities were measured, including 4708 independent reflections.

1-[1-(4-Methoxybenzoyl)-5-propyl-1*H*-pyrazol-4-yl]butan-1-one (4h). Yield 0.754 g (80%), mp 79–80°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.03 t (6H, Me, *J* = 7.3 Hz), 1.70–1.81 m (4H, CH_2), 2.82 t (2H, CH_2, *J* = 7.3 Hz), 3.33–3.38 m (2H, CH_2), 3.91 s (3H, OCH_3), 6.99 d (2H, H_{arom}, *J* = 8.7 Hz), 7.95 d (2H, H_{arom}, *J* = 8.7 Hz), 7.98 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.22 (Me), 14.48 (Me), 17.85 (CH_2), 23.01 (CH_2), 28.03 (CH_2), 43.89 (CH_2), 55.99 (OMe), 114.04 (2C, CH_{arom}), 122.08 (C^4), 124.68 (C_{arom}), 134.53 (2C, CH_{arom}), 142.36 (C^3), 152.63 (C^5), 164.45 (C_{arom}), 168.03 (CON), 196.25 (4-CO). Found, %: C 68.66; H 7.03; N 8.83. $C_{18}H_{22}N_2O_3$. Calculated, %: C 68.77; H 7.05; N 8.91.

1,3,4-Trisubstituted pyrazoles (*general procedure*). *a*. A solution of 1.5 mmol of 1,4,5-trisubstituted pyrazole in 8 mL of anhydrous toluene was refluxed for 6–8 h. The progress of the isomerization was monitored by ^1H NMR. The solvent was distilled off under reduced pressure, and the residue was recrystallized from petroleum ether.

b. 1,4,5-Trisubstituted pyrazole, 1.5 mmol, was placed in a round-bottom flask and heated under reduced pressure (7–15 mm) until melting, and the melt was kept for 1 h. The product was cooled under reduced pressure, analyzed by NMR, and recrystallized from hexane.

1-(1-Benzoyl-3-methyl-1*H*-pyrazol-4-yl)-2,2,2-trifluoroethanone (5c). Yield 0.393 g (93%), mp 77–79°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 s (3H, 3-Me), 7.57 t (2H, H_{arom}, *J* = 7.3 Hz), 7.71 t (1H, H_{arom}, *J* = 7.3 Hz), 8.20 d (2H, H_{arom}, *J* = 8.0 Hz), 9.01 br.q (1H, 5-H, J_{HF} = 1.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.81 (3-CH_3), 116.01 (C^4), 116.57 q (CF_3, $^1J_{CF}$ = 291.2 Hz), 128.81 (2C, CH_{arom}), 130.30 (C_{arom}), 132.37 (2C, CH_{arom}), 134.53 (CH_{arom}), 136.91 m (C^5), 156.08 (C^3), 165.86 (**C**OPh), 175.65 q (**C**OCF_3, $^2J_{CF}$ = 36.9 Hz). Found, %: C 55.26; H 3.26; N 9.79. $C_{13}H_9F_3N_2O_2$. Calculated, %: C 55.33; H 3.21; N 9.93.

1-(1-Benzoyl-3-methyl-1*H*-pyrazol-4-yl)-2,2,3,3,4,4,4-heptafluorobutan-1-one (5d). Yield

0.560 g (98%), light yellow oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.61 s (3H, Me), 7.57 t (2H, H_{arom}, J = 8.0 Hz), 7.71 t (1H, H_{arom}, J = 8.0 Hz), 8.20 d (2H, H_{arom}, J = 8.0 Hz), 9.01 br.t (1H, 5-H, J_{HF} = 2.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.94 (3-CH_3), 110.08–120.24 m (C_3F_7), 117.29 br.t (C^4, J_{CF} = 3.0 Hz), 128.78 (2C, CH_{arom}), 130.30 (C_{arom}), 132.39 (2C, CH_{arom}), 134.51 (CH_{arom}), 136.93 t.t (C^5, J_{CF} = 8.0, 2.0 Hz), 156.28 (C^3), 165.87 (**C**OPh), 178.60 t (**C**OC_3F_7, $^2J_{CF}$ = 26.9 Hz). Mass spectrum (ESI), *m/z* (I_{rel}, %): 382 (11.6) $[M + H]^+$, 405 (100) $[M + Na]^+$, 421 (16.6) $[M + K]^+$, 787 (24) $[2M + Na]^+$.

1-(1-Benzoyl-3-ethyl-1*H*-pyrazol-4-yl)propan-1-one (5e). Yield 0.234 g (61%), mp 97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (3H, $CH_2C\mathbf{H}_3$, J = 7.3 Hz), 1.29 t (3H, $CH_2C\mathbf{H}_3$, J = 7.3 Hz), 2.90 q (2H, CH_2, J = 7.3 Hz), 3.00 q (2H, CH_2, J = 7.3 Hz), 7.54 br.t (2H, H_{arom}, J = 7.3 Hz), 7.67 t (1H, H_{arom}, J = 8.0 Hz), 8.23 d (2H, H_{arom}, J = 8.0 Hz), 8.86 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.42 (Me), 12.75 (Me), 22.25 (CH_2), 34.48 (CH_2), 122.63 (C^4), 128.59 (2C, CH_{arom}), 131.08 (C_{arom}), 132.39 (2C, CH_{arom}), 133.93 (C^5), 134.66 (CH_{arom}), 159.97 (C^3), 166.35 (**C**OPh), 196.32 (**C**OEt). Found, %: C 70.20; H 6.22; N 10.84. $C_{15}H_{16}N_2O_2$. Calculated, %: C 70.29; H 6.29; N 10.93.

1-(1-Benzoyl-3-propyl-1*H*-pyrazol-4-yl)butan-1-one (5f). Yield 0.362 g (85%), mp 61°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (3H, Me, J = 7.6 Hz), 1.03 t (3H, Me, J = 7.7 Hz), 1.70–1.82 m (4H, CH_2), 2.82 t (2H, CH_2, J = 7.1 Hz), 2.95 t (2H, CH_2, J = 7.1 Hz), 7.51 t (2H, H_{arom}, J = 8.0 Hz), 7.64 t (1H, H_{arom}, J = 8.0 Hz), 8.21 d (2H, H_{arom}, J = 8.0 Hz), 8.84 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.24 (Me), 14.40 (Me), 18.17 (CH_2), 21.86 (CH_2), 30.59 (CH_2), 43.32 (CH_2), 122.67 (C^4), 128.63 (2C, CH_{arom}), 131.12 (C_{arom}), 132.32 (2C, CH_{arom}), 133.98 and 134.66 (C^5, CH_{arom}), 158.89 (C^3), 166.27 (**C**OPh), 195.90 (**C**OPr). Found, %: C 71.79; H 7.00; N 9.80. $C_{17}H_{20}N_2O_2$. Calculated, %: C 71.81; H 7.09; N 9.85.

1-[3-Ethyl-1-(4-methoxybenzoyl)-1*H*-pyrazol-4-yl]propan-1-one (5g). Yield 0.330 g (77%), mp 93–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (3H, $CH_2C\mathbf{H}_3$, J = 7.1 Hz), 1.30 t (3H, $CH_2C\mathbf{H}_3$, J = 7.3 Hz), 2.89 q (2H, CH_2, J = 7.1 Hz), 3.01 q (2H, CH_2, J = 7.3 Hz), 3.93 s (3H, OMe), 7.02 d (2H, H_{arom}, J = 8.7 Hz), 8.33 d (2H, H_{arom}, J = 8.7 Hz), 8.85 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.46 (Me), 12.80 (Me), 22.25 (CH_2), 34.42 (CH_2), 55.95 (OMe), 114.04 (2C, CH_{arom}), 122.22 (C_{arom}), 123.10 (C^4), 134.83 (C^5), 135.12 (2C, CH_{arom}), 159.64 (C^3), 164.43 (C_{arom}), 165.28 (**C**OAr), 196.41 (**C**OEt). Found, %: C 67.01; H 6.34; N 9.68. $C_{16}H_{18}N_2O_3$. Calculated, %: C 67.12; H 6.34; N 9.78.

1-[1-(4-Methoxybenzoyl)-3-propyl-1*H*-pyrazol-4-yl]butan-1-one (5h). Yield 0.254 g (54%), mp 54.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 t (3H, Me, J = 7.7 Hz), 1.03 t (3H, Me, J = 7.7 Hz), 1.71–1.81 m (4H, CH_2), 2.82 t (2H, CH_2, J = 7.1 Hz), 2.95 t (2H, CH_2, J = 7.1 Hz), 3.93 s (OMe), 7.02 d (2H, H_{arom}, J = 8.8 Hz), 8.32 d (2H, H_{arom}, J = 8.8 Hz), 8.84 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.23 (Me), 14.43 (Me), 18.13 (CH_2), 21.90 (CH_2), 30.63 (CH_2), 43.30 (CH_2), 55.95 (OMe), 114.06 (2C, CH_{arom}), 122.69 (C^4), 123.12 (C_{arom}), 134.88 (C^5), 135.10 (2C, CH_{arom}), 158.45 (C^3), 164.53 (C_{arom}), 165.33 (**C**OAr), 196.04 (**C**OPr). Found, %: C 68.71; H 7.03; N 8.86. $C_{18}H_{22}N_2O_3$. Calculated, %: C 68.77; H 7.05; N 8.91.

1-[1-(4-Methoxybenzoyl)-5-methyl-1*H*-pyrazol-4-yl]ethanone (7b) was obtained by keeping 0.03 g of *N*′-(2-acetyl-3-oxobut-1-en-1-yl)-4-methoxybenzohydrazide (**6b**) in DMSO-d_6. Yield 0.011 g (38%), mp 150–151°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.48 s (3H, Me), 2.79 s (3H, Me), 3.87 s (3H, OMe), 7.09 d (2H, H_{arom}, J = 8.9 Hz), 7.90 d (2H, H_{arom}, J = 8.9 Hz), 8.30 s (1H, 3-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.37 (5-CH_3), 30.30 (CO**C**H_3), 56.55 (OMe), 114.47 (2C, CH_{arom}), 122.90 (C^4), 124.55 (C_{arom}), 134.98 (2C, CH_{arom}), 144.00 (C^3), 147.53 (C^5), 164.47 (C_{arom}), 168.21 (**C**OAr), 194.58 (**C**OMe). Found, %: C 65.08; H 5.42; N 10.89. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.11; H 5.46; N 10.85.

1-[5-Methyl-1-(thiophen-2-ylcarbonyl)-1*H*-pyrazol-4-yl]ethanone (7c). Yield 0.207 g (59%), mp 118°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, Me), 3.00 s (3H, Me), 7.20 d.d (1H, H_{Th}, J = 3.3, 3.6 Hz), 7.82 br.d (1H, H_{Th}, J = 5.1 Hz), 8.04 s (1H, 3-H), 8.33 d.d (1H, H_{Th}, J = 4.3, 1.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.78 (5-CH_3), 29.94 (CO**C**H_3), 123.22 (C^4), 127.81 (CH_{Th}), 133.75 (C_{Th}), 138.35 (CH_{Th}), 139.27 (CH_{Th}), 143.18 (C^3), 148.68 (C^5), 161.43 (1-C=O), 193.85 (**C**OMe). Found, %: C 56.34; H 4.36; N 11.94. $C_{11}H_{10}N_2O_2S$. Calculated, %: C 56.40; H 4.30; N 11.96.

Ethyl 4-acetyl-5-methyl-1*H*-pyrazole-1-carboxylate (7d). Yield 0.068 g (23%), mp 49–50°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 t (3H,

$OCH_2C\mathbf{H}_3$, J = 7.3 Hz), 2.50 s (3H, Me), 2.93 s (3H, Me), 4.56 q (2H, OCH_2, J = 7.3 Hz), 7.99 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.40 (Me), 14.56 (Me), 29.86 ($CO\mathbf{C}H_3$), 65.43 (OCH_2), 122.91 (C^4), 143.88 (C^3), 150.35 (C^5), 154.92 ($\mathbf{C}O_2Et$), 193.78 ($\mathbf{C}OMe$). Found, %: C 54.98; H 6.13; N 14.21. $C_9H_{12}N_2O_3$. Calculated, %: C 55.10; H 6.16; N 14.28.

1-[1-(Adamantan-1-ylcarbonyl)-5-methyl-1*H*-pyrazol-4-yl]ethanone (7e). Yield 0.168 g (43%), mp 110–113°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 br.s (6H, CH_2), 2.10 br.s (3H, CH), 2.26 br.s (6H, CH_2), 2.49 s (3H, COMe), 2.84 s (3H, 5-Me), 7.91 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.03 (5-CH_3), 28.53 (CH_2), 29.88 ($CO\mathbf{C}H_3$), 36.88 (3C, CH), 38.78 (3C, CH_2), 45.81 (C_{Ad}), 121.77 (C^4), 142.09 (C^3), 148.40 (C^5), 178.86 (1-C=O), 193.96 ($\mathbf{C}OMe$). Found, %: C 71.15; H 7.67; N 9.70. $C_{17}H_{22}N_2O_2$. Calculated, %: C 71.30; H 7.74; N 9.78.

1-[1-(4-Methoxybenzoyl)-3-methyl-1*H*-pyrazol-4-yl]ethanone (8b). Yield 0.348 g (90%), mp 126–127°C; published data [48]: mp 97–99°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, Me), 2.56 s (3H, Me), 3.93 s (3H, OMe), 7.02 d (2H, H_{arom}, J = 8.7 Hz), 8.29 d (2H, H_{arom}, J = 8.7 Hz), 8.83 s (1H, 5-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.84 (3-CH_3), 29.02 ($CO\mathbf{C}H_3$), 55.96 (OMe), 114.11 (2C, CH_{arom}), 122.99 (C^4), 123.36 (C_{arom}), 135.00 (2C, CH_{arom}), 135.28 (C^5), 154.43 (C^3), 164.50 (C_{arom}), 165.28 ($\mathbf{C}OAr$), 193.35 ($\mathbf{C}OMe$). Found, %: C 65.10; H 5.46; N 10.79. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.11; H 5.46; N 10.85.

1-[3-Methyl-1-(thiophen-2-ylcarbonyl)-1*H*-pyrazol-4-yl]ethanone (8c). Yield 0.302 g (86%), mp 165–166°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, Me), 2.59 s (3H, Me), 7.23 br.t (1H, H_{Th}, J = 4.4 Hz), 7.86 d (1H, H_{Th}, J = 3.6 Hz), 8.50 d (1H, H_{Th}, J = 4.4 Hz), 8.82 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.89 (3-CH_3), 29.02 ($CO\mathbf{C}H_3$), 123.93 (C^4), 128.10 (CH_{Th}), 132.36 (C_{Th}), 134.22 (C^5), 138.49 (CH_{Th}), 139.51 (CH_{Th}), 154.61 (C^3), 158.98 (1-C=O), 193.24 ($\mathbf{C}OMe$). Found, %: C 56.32; H 4.26; N 11.88. $C_{11}H_{10}N_2O_2S$. Calculated, %: C 56.40; H 4.30; N 11.96.

Ethyl 4-acetyl-3-methyl-1*H*-pyrazole-1-carboxylate (8d). Yield 0.226 g (77%), mp 58–62°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.3 Hz), 2.49 s (3H, Me), 2.55 s (3H, Me), 4.58 q (2H, OCH_2, J = 7.3 Hz), 8.57 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.64 (Me), 14.73 (Me), 28.95 ($CO\mathbf{C}H_3$), 65.73 (OCH_2), 123.84 (C^4), 135.45 (C^5), 149.29 (C^3), 154.90 ($\mathbf{C}O_2Et$), 192.74 ($\mathbf{C}OMe$). Found, %: C 55.02; H 6.11; N 14.23. $C_9H_{12}N_2O_3$. Calculated, %: C 55.10; H 6.16; N 14.28.

1-[(Adamantan-1-ylcarbonyl)-3-methyl-1*H*-pyrazol-4-yl]ethanone (8e). Yield 0.324 g (83%), mp 115°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.80 br.s (6H, CH_2), 2.11 br.s (3H, CH), 2.29 br.s (6H, CH_2), 2.47 s (3H, Me), 2.51 s (3H, Me), 8.63 s (1H, 5-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.88 (CH_3), 28.54 (3C, CH), 28.89 ($CO\mathbf{C}H_3$), 36.88 (3C, CH_2), 38.64 (3C, CH_2), 44.30 (C_{Ad}), 122.33 (C^4), 134.78 (C^5), 153.17 (C^3), 176.05 ($\mathbf{C}OAd$), 193.33 ($\mathbf{C}OMe$). Found, %: C 71.10; H 7.65; N 9.71. $C_{17}H_{22}N_2O_2$. Calculated, %: C 71.30; H 7.74; N 9.78.

Reactions of 2-ethoxymethylidene derivatives 1a, 1c, and 1d with 1,3-benzothiazol-2-ylhydrazine and phenylhydrazine (*general procedure*). A solution of 3 mmol of compound **1a**, **1c**, or **1d** in 5 mL of anhydrous methanol was cooled to –15°C, and a solution of 0.495 g (3 mmol) of 1,3-benzothiazole-2-ylhydrazine or 0.324 g of phenylhydrazine in 3 mL of anhydrous methanol was slowly added with vigorous stirring. The mixture was stirred for 1 h, and the crystalline product was filtered off, dried, and recrystallized from hexane.

1-[1-(1,3-Benzothiazol-2-yl)-5-methyl-1*H*-pyrazol-4-yl]ethanone (7f). Yield 0.609 g (79%), mp 185–186°C [48]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, Me), 3.19 s (3H, Me), 7.41 t.d (1H, H_{arom}, J = 7.3, 1.5 Hz), 7.51 t.d (1H, H_{arom}, J = 7.3, 1.4 Hz), 7.87 br.d (1H, H_{arom}, J = 8.0 Hz), 7.96 br.d (1H, H_{arom}, J = 8.0 Hz), 8.03 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.62 (5-CH_3), 29.63 ($CO\mathbf{C}H_3$), 121.71 (CH_{arom}), 123.29 (C^4), 123.55 (CH_{arom}), 125.78 (CH_{arom}), 126.96 (CH_{arom}), 133.55 (C_{arom}), 143.83 (C^3), 145.98 (C^5), 151.52 (C_{arom}), 160.96 (C_{arom}), 193.48 (C=O). Found, %: C 60.60; H 4.26; N 16.23. $C_{13}H_{11}N_3OS$. Calculated, %: C 60.68; H 4.31; N 16.33.

1-(5-Methyl-1-phenyl-1*H*-pyrazol-4-yl)ethanone (7g). Yield 0.222 g (37%), mp 102.5–103°C [49]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 s (3H, Me), 2.59 s (3H, Me), 7.41–7.44 m (2H, H_{arom}), 7.47–7.56 m (3H, H_{arom}), 8.02 s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.78 (5-CH_3), 29.08 ($CO\mathbf{C}H_3$), 121.50 (C^4), 125.94 (2C, CH_{arom}), 129.20 (2C, CH_{arom}), 129.69 (CH_{arom}), 138.95 (C_{arom}), 142.32 (C^3), 143.38 (C^5), 193.92 ($\mathbf{C}OMe$). Found, %: C 71.87; H 6.00; N 13.91. $C_{12}H_{12}N_2O$. Calculated, %: C 71.98; H 6.04; N 13.99.

1-[1-(1,3-Benzothiazol-2-yl)-5-methyl-1*H*-pyrazol-4-yl]-2,2,2-trifluoroethanone (9a). Yield 0.700 g (75%), mp 168–169°C; published data [50]: mp 170–172°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.16 s (3H, Me), 7.51 t.d (1H, H_{arom}, J = 7.3, 1.4 Hz), 7.59 t.d (1H, H_{arom}, J = 7.3, 1.4 Hz), 8.03 d (1H, H_{arom}, J = 7.3 Hz), 8.17 d (1H, H_{arom}, J = 7.3 Hz), 8.48 q (1H, 3-H, J_{HF} = 1.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.49 (Me), 116.62 (C^4), 116.09 q (CF_3, $^1J_{CF}$ = 289.7 Hz), 122.57 (CH_{arom}), 123.14 (CH_{arom}), 126.13 (CH_{arom}), 127.23 (CH_{arom}), 132.87 (C_{arom}), 143.57 (C^3), 150.14 and 150.52 (C^5, C_{arom}), 160.14 (C_{arom}), 174.82 q (**C**OCF_3, $^2J_{CF}$ = 36.4 Hz). Found, %: C 50.09; H 2.51; N 13.57. $C_{13}H_8F_3N_3OS$. Calculated, %: C 50.16; H 2.59; N 13.50.

2,2,2-Trifluoro-1-(5-methyl-1-phenyl-1*H*-pyrazol-4-yl)ethanone (9b). Yield 0.442 g (58%), mp 85°C [50]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.63 s (3H, 5-Me), 7.42 m (2H, H_{arom}), 7.53 m (3H, H_{arom}), 8.12 q (1H, 3-H, J_{HF} = 1.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.74 (5-CH_3), 116.54 q (CF_3, $^1J_{CF}$ = 290.8 Hz), 122.31 (C^4), 125.58 (2C, CH_{arom}), 129.52 (2C, CH_{arom}), 137.84 (C_{arom}), 142.04 (C^3), 147.39 (C^5), 175.95 q (**C**OCF_3, $^2J_{CF}$ = 29.9 Hz). Found, %: C 56.76; H 3.50; N 11.00. $C_{12}H_9F_3N_2O$. Calculated, %: C 56.70; H 3.57; N 11.02.

1-[1-(1,3-Benzothiazol-2-yl)-5-methyl-1*H*-pyrazol-4-yl]-2,2,3,3,4,4,4-heptafluorobutan-1-one (9c). Yield 1.196 g (97%), mp 111–112°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.24 s (3H, 5-Me), 7.43 t (1H, H_{arom}, J = 7.3 Hz), 7.52 t.d (1H, H_{arom}, J = 7.3, 1.4 Hz), 7.87 d (1H, H_{arom}, J = 8.0 Hz), 7.98 d (1H, H_{arom}, J = 8.0 Hz), 8.14 br.s (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.01 (5-CH_3), 105–125 m (C_3F_7), 117.82 (C^4), 121.80 (CH_{arom}), 123.81 (CH_{arom}), 126.24 (CH_{arom}), 127.19 (CH_{arom}), 133.67 (C_{arom}), 143.41 br.t.t (C^3, J_{CF} = 7.0, 2.0 Hz), 150.58 and 151.32 (C^5, C_{arom}), 160.19 (C_{arom}), 178.16 t (**C**OC_3F_7, $^2J_{CF}$ = 26.9 Hz). Found, %: C 43.76; H 1.93; N 10.22. $C_{15}H_8F_7N_3OS$. Calculated, %: C 43.80; H 1.96; N 10.22.

2,2,3,3,4,4,4-Heptafluoro-1-(5-methyl-1-phenyl-1*H*-pyrazol-4-yl)butan-1-one (9d). Yield 0.754 g (71%), light orange oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.65 s (3H, 5-Me), 7.44–7.47 m (2H, H_{arom}), 7.53–7.57 m (3H, H_{arom}), 8.16 br.t (1H, 3-H, J_{HF} = 2.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.27 (5-CH_3), 106.00–116.00 (C_3F_7), 166.08 (C^4), 120.43 (CH_{arom}), 125.98 (2C, CH_{arom}), 129.88 (2C, CH_{arom}), 138.12 (C_{arom}), 142.44 t.t (C^3, J_{CF} = 8.0, 2.0 Hz), 148.10 (C^5), 178.15 t (**C**OC_3F_7, $^2J_{CF}$ = 28.9 Hz). Mass spectrum (ESI), m/z (I_{rel}, %): 355 (100) $[M + H]^+$, 377 (12) $[M + Na]^+$, 393 (4) $[M + K]^+$.

***N′*-[(4,4-Dimethyl-2,6-dioxocyclohexyl)methylidene]benzohydrazide (10a).** Acetic acid, 1 mL, was added with stirring to a solution of 0.488 g (2.5 mmol) of 2-(dimethylaminomethylidene)-5,5-dimethylcyclohexane-1,3-dione in 5 mL of anhydrous methanol on cooling with ice, and a solution of 0.340 g (2.5 mmol) of benzohydrazide in 5 mL of anhydrous methanol was then added dropwise with stirring. A solid separated from the solution almost immediately after addition of benzolhydrazide and was filtered off. Yield 0.594 g (83%), mp 234–235°C; published data [51]: mp 220–222°C. IR spectrum, ν, cm^{-1}: 3450, 3185, 3049, 2954, 1665, 1647, 1563, 1531, 1491, 1431 1366, 1309, 1290, 1136, 1031, 1009, 979, 797, 713, 691, 618, 576. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: at 25°C: 1.09 s (6H, Me), 2.37 s (2H, CH_2), 2.47 s (2H, CH_2), 7.50 t (2H, H_{arom}, J = 7.3 Hz), 7.62 t (1H, H_{arom}, J = 7.3 Hz), 8.04 d (2H, H_{arom}, J = 7.3 Hz), 8.87 s (1H, C=CH), 11.92 s (1H, NHCO), 13.60–13.75 br.s (1H, NH or OH); at –50°C: 1.08 s (6H, Me), 2.41 s (2H, CH_2), 2.48 s (2H, CH_2), 7.53 t (2H, H_{arom}, J = 7.3 Hz), 7.67 m (1H, H_{arom}), 8.05 d (2H, H_{arom}, J = 8.0 Hz), 9.02 d (1H, C=CH, J = 12.1 Hz), 12.68 d (1H, NHCO, J = 7.1 Hz), 13.90 d.d (1H, NH, J = 12.1, 7.1 Hz); in DMSO-d_6 at 25°C: 0.99 s (6H, Me), 2.30 s (2H, CH_2), 2.37 s (2H, CH_2), 7.54 t (2H, H_{arom}, J = 7.3 Hz), 7.63 t (1H, H_{arom}, J = 7.3 Hz), 7.89 d (2H, H_{arom}, J = 7.3 Hz), 8.18 s (1H, C=CH), 11.50–13.50 br.s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 28.98 (2C, Me), 31.97 (**C**Me_2), 50.68 (CH_2), 51.33 (CH_2), 106.33 (**C**=CH); 128.10, 129.07, 131.16, 133.19 (C_{arom}); 148.81 (C=**C**H), 163.14 (**C**OPh), 198.00 (2C, C=O); in DMSO-d_6: 28.90 (2C, Me), 31.73 (**C**Me_2), 51.23 (2C, CH_2), 106.59 (**C**=CH); 128.34, 129.55, 132.04, 133.29 (C_{arom}); 152.02 (C=**C**H), 164.38 (**C**OPh), 195.35 (C=O), 197.62 (C=O). Mass spectrum (EI), m/z (I_{rel}, %): 286 (11) $[M]^+$, 166 (5) $[M – NHCOPh]^+$, 122 (24), 105 (100) $[COPh]^+$, 77 (24) $[Ph]^+$. Found, %: C 67.17; H 6.37; N 9.79. $C_{16}H_{18}N_2O_3$. Calculated, %: C 67.12; H 6.34; N 9.78.

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