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Synthesis, Structure and Complexation of the Fluorinated 1,3-Enaminoketones Containing at the Nitrogen Atom Substituents with a Terminal C≡C Bond

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Abstract—The reaction of fluorinated lithium 1,3-diketonates with propargylamine hydrochloride and 1,1,1-trifluorpentane-2,4-dione or 1,1,1-trifluoro-4-methoxypent-3-en-2-one with propargylamine and 3-aminophenylacetylene were performed to obtain fluorinated 1,3-enaminones containing at a nitrogen atom substituents with terminal C≡C bonds: (*Z*)-1,1,1-trifluoro-4-(2-propynylamino)-3-pentene-2-one, (*Z*)-1,1,2,2-tetrafluoro-5-(2-propynylamino)-4-hexen-3-one, and 4-(3-ethynylphenylamino)-1,1,1-trifluoropentyl-3-en-2-one. Reactions of 4-(3-ethynyl-phenylamino)-1,1,1-trifluoro-pentyl-3-en-2-one with Cu(II) acetate or nanosized powder of copper or its oxides led to the respective chelate complex. The structure of (*Z*)-1,1,2,2-tetrafluoro-5-(2-propynylamino)-4-hexen-3-one and a copper complex of 4-(3-etinilphenylamino)-1,1,1-trifluoropenta-3-en-2-one was determined by XRD.

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1,3-Enaminoketones containing at the nitrogen atom substituents with triple bonds are widely used in the synthesis of heterocycles. Thus, on the basis of the enaminoketones with terminal or internal C≡C bonds a series of substituted pyrroles and pyridines was synthesized [1]. In the reaction of β-alkoxyenones with secondary propargylamines a series of enaminoketones containing CF_3 group was obtained which were then subjected to cyclization to form substituted 1,2-dihydropyridines [2]. An exception is the (*E*)-1,1,1-trifluoro-4-[propyl(2-propynyl)amino]-3-penten-2-one, which under similar conditions isomerizes into 2,4-dimethyl-1-propyl 3-trifluoracetylpyrrole [3].

The acetylation of ethyl vinyl ether with chlorodifluoroacetic acid anhydride followed by treatment of the crude (*E*)-1,1-difluoro-1-chloro-4-ethoxybut-3-en-2-one with propargylamine resulted in (*Z*)-1,1-difluoro-1-chloro-4-(2-propynylamino)-3-butene-2-one in 89% yield [4]. This process requires cooling the reaction mixture and the use of anhydrous solvents. We did not found other examples of the synthesis and investigation of the properties of fluorine-containing enaminoketones with a propargyl substituent at the nitrogen atom.

Enaminones containing fluorinated substituents differ significantly from non-fluorinated analogs by the reactivity and physical properties due, first of all, to a strong electron-acceptor effect of the fluorine atom [5–7]. The presence in the structure of a fluorinated enaminoketone of a group with a triple bond opens new possibilities for the synthesis of metal complexes, heterocyclic systems, and products of cross-coupling [8, 9]. In this connection the search for a more simple approach to the synthesis of fluorinated enaminoketones having at the nitrogen atom a substituent with the C≡C bond is expedient.

In this paper we describe an effective way of the synthesis of fluorinated enaminoketones **IV**–**VI** (Schemes 1, 2) that are of interest not only for the synthesis of heterocycles, but also as ligands capable of forming chelate rings with donor atoms of nitrogen and oxygen. Additional coordination and synthetic possibilities of these ligands can be realized due to the presence in their structure of the terminal acetylene group. Note that the enaminoketones containing trifluoromethyl group described in [2, 3] are not capable of chelating at the enaminone fragment

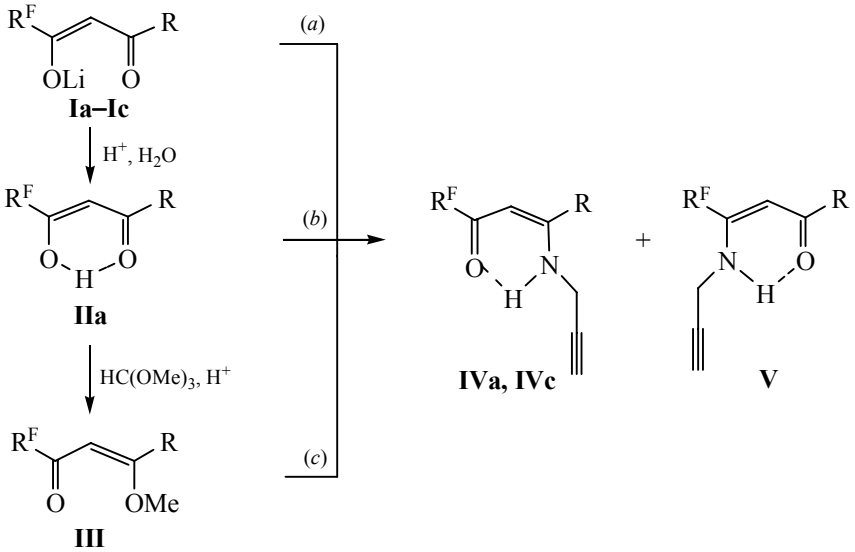
because of the lack of a hydrogen atom at the nitrogen atom, and the complexation of (*Z*)-1,1-difluoro-1-chloro-4-(2-propynylamino)-3-butene-2-one described in [4] has not been investigated.

As starting compounds for the synthesis of the enaminoketones **IV**–**VI** we used the available fluorinated reagents, lithium1,3-diketonates (**I**) [10] (Scheme 1). In the reactions of the diketonates **Ia** and **Ic** (R = Me) with propargylamine hydrochloride exclusively isomers **IV** are formed. In a similar reaction of diketonate **Ib** (R = Ph) with propergylamine hydrochloride two products were isolated: enaminoketone **V** and diketone **IIb** in a ratio of 9:1. The formation of isomeric compounds **IV** and **V** in these reactions is caused by the nature of the substituents R^F and R in the initial diketonate **I,** and it is consistent with the regularities found previously [11]. The synthesis of diketone **IIb** requires a prolonged heating of the reaction mixture due to the decrease in the reactivity of diketonates **I** in going from R = Me to R = Ph. The consequence of this is the partial hydrolysis of the diketonate **Ib** [12] or the enaminoketone **V** [13].

In addition, (*Z*)-1,1,1-trifluoro-4-(2-propynylamino)-3-penten-2-one (**IVa**) was synthesized by reacting diketone **IIa** or methoxyenone **III** with propargylamine. These reactions do not require heating, and the yield of enaminoketone **IVa** was 60 and 90%, respectively (Scheme 1). As diketonate **Ia** is the initial compound in the synthesis of diketone **IIa** [12], which in turn serves as the starting compound for methoxyenone **III** [14], the yields of the target enaminoketone **IVa** in all three methods of synthesis are close.

Earlier only the non-fluorinated 1,3diketones were involved in the reaction with propargylamine, and the catalyst for these reactions was $NaAuCl_4$ [3]. In the reaction of trifluoracetylacetone **IIa** with propergylamine we used the available triethyl borate, which greatly accelerated the amination reaction and increased its selectivity [15]. It is also noteworthy that the methoxyenone **III** was synthesized according to [14] that did not require the use of the halides sensitive to moisture (see the synthesis of alkoxyenones in [1–4]).

Scheme 1.

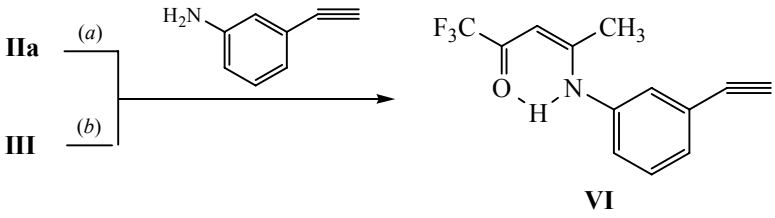


(*a*) $CH{\equiv}CCH_2NH_2{\cdot}HCl$, MeOH; (*b*) $CH{\equiv}CCH_2NH_2$, $B(OEt)_3$, $CHCl_3$; (*c*) $CH{\equiv}CCH_2NH_2$, $CHCl_3$; $R^F = CF_3$ (**Ia, IIa, III, IVa**); HCF_2 (**Ib, V**); $H(CF_2)_2$ (**Ic, IVc**); R = Me (**Ia, Ic, IIa, III, IVa, IVc**); Ph (**Ib, V**).

The reaction of diketone **IIa** or methoxyenone **III** with an aromatic amine containing an acetylene fragment, namely, with the 3-aminophenylacetylene, resulted in enaminoketone **VI** with 89 and 67% yield, respectively.

The composition and structure of compounds **IV**–**VI** was confirmed by elemental analysis, IR, ^1H and ^{19}F NMR spectroscopy, and gas chromatography–mass spectrometry. In favor of the formation of isomer **V** with geminal arrangement of the amino group and R^F

Scheme 2.



(*a*) $CHCl_3$, $B(OEt)_3$; (*b*) $CHCl_3$.

evidences the presence in the mass spectrum of intense peaks of fragments $[PhCO]^+$ (100%), $[M - PhCO]^+$ fragment, and the absence of a peak of $[HCF_2CO]^+$ ion. In the mass spectra of compounds **IVa** and **VI** the peaks with relative intensity 100% correspond to the fragment ions $[M - CF_3]^+$, while the peaks of ions $[M - CF_3CO]^+$, $[M - CF_3CO–CH_3]^+$, $[M - CF_3COCH_2]^+$ have the intensity from 1.4 to 35.9%.

We succeeded to prepare crystalline samples of the enaminoketones **IVa** and **IVc**, but the layered crystals of compound **IVa** were not suitable for the study by the method of the single crystal X-ray diffraction. The structure of (*Z*)-1,1,2,2-tetrafluoro-5-(2-propynylamino)-4-hexen-3-one (**IVc**) was confirmed by XRD.

According to XRD data, crystals of compound **IVc** belong to the centrosymmetric space group of monoclinic crystal system. The enaminone fragment $O^1C^4C^3C^2N^1$ is planar (maximum deviation from the mean plane 0.017 Å) and has the U-shaped conformation fixed by the intramolecular hydrogen bond with $d(N^1\cdots O^1)$ = 2.705(1) Å. The lengths of C–C bonds of the enaminone fragment are largely leveled: $d(C^2–C^3)$ = 1.4027(13) Å, $d(C^3–C^4)$ = 1.3952(13) Å. However, the position of the hydrogen atom at the nitrogen atom found by the direct method [$d(N^1–H^1)$ = 0.867(13) Å, $d(H^1\cdots O^1)$ = 2.029(13) Å, angle $N^1H^1O^1$ = 134(1)°] indicates the enaminone rather than imino-enol structure. The measured C–F bond lengths range from 1.3548(12) to 1.363(11) Å (average 1.358 Å). In the crystal the molecules form centrosymmetric dimers through intermolecular H-bonds of NH···O type, $d(N^1–H^1)$ = 0.867(13) Å, $d(H^1\cdots O^1)$ [$–x, –y + 1, –z + 1$] = 2.321(13) Å, $d(N^1\cdots O^1)$ [$–x, –y + 1, –z + 1$] = 3.030(1) Å, angle $N^1H^1O^1$ [$–x, –y + 1, –z + 1$] = 139(1)° (Fig. 2). The N···O distance in this H-bond is larger than that of the intramolecular hydrogen bond by ~0.3 Å. Nevertheless, the system of these bonds can be considered as a bifurcate. Another feature of the molecular packing is the shortened bifurcate contact of C–H···O between the acetylene group and oxygen atom of the carbonyl group, $d(C^9–H^9)$ = 0.907(15) Å, $d(H^9\cdots O^1)$ [$x, y, 1 + z$] = 2.651(15) Å, $d(H^9\cdots O^1)$ [$–x, 1 – y, 2 – z$] = 2.602(15) Å, which, however, is significantly larger than the expected value of the hydrogen bond in the CH-acid compounds.

The study of complex compounds **IV**–**VI** showed that they do not react with nickel acetate or nanoscale nickel powders. Reaction of **IVa** with copper acetate leads to a mixture of products, from which complex **VII** was isolated. We failed to establish unambiguously the structure of this complex due to its extremely low solubility in organic solvents and the absence of a single crystal suitable for X-ray diffraction

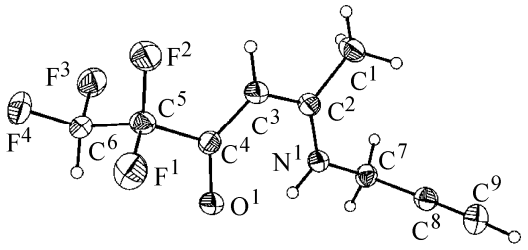


Fig. 1. General view of compound **IVc** shown with the thermal ellipsoids with 50% probability.

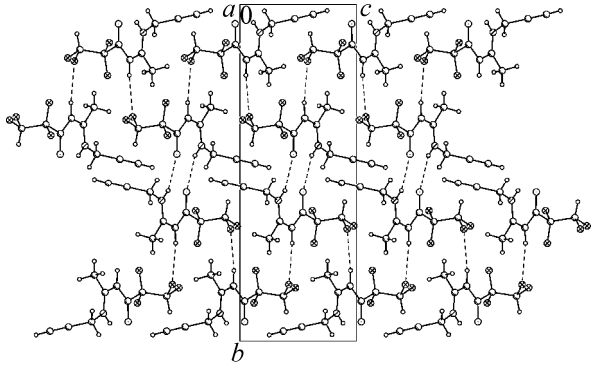
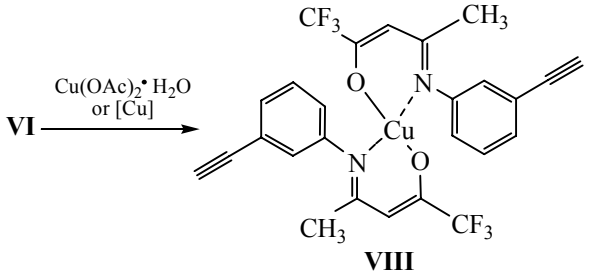


Fig. 2. Fragment of molecular packing of compound **IVc**.

analysis. In the IR spectrum of complex **VII** there is no absorption bands in the ranges of 3340–3290 cm^{-1} and 681–625 cm^{-1}, characteristic of the stretching and bending vibrations of C–H and C≡C bonds, respectively. In the IR spectrum of the original ligand **IVa** these bands are observed at 3312, 682 and 636 cm^{-1}, respectively. This indicates the complexation with the involvement of the terminal acetylene group. The comparison of IR spectra of complex **VII** and the initial ligand **IVa** showed a significant difference in the absorption bands of the system of conjugated O=C–C= C bonds (1700–1580 cm^{-1}). In addition, in the IR spectrum of complex **VII** there is no absorption band ν(NH) existing in the spectrum of the enaminoketone **IVa** at 3170 cm^{-1}, which confirms the chelation of the enaminone fragment. Probably, complex **VII** is a coordination polymer as a result of complexation at both enaminone fragment and terminal acetylene group.

The interaction of ligand **VI** with Cu(II) acetate leads to the formation of chelate **VIII** in ~20% yield. In the IR spectrum of complex **VIII** there is an absorption band at 3275 cm^{-1} characteristic of stretching vibrations of the ≡C–H bond, while the absorption band of stretching vibrations of NH at 3500–3400 cm^{-1} is absent. The use of nano-sized powders of copper or copper oxides instead of Cu(II) acetate allows enhancing the yield of complex **VIII** to 70%. (Scheme 3). Despite an excess of [Cu] in the reaction mixture, the complexation occurs at the enaminone fragment only without affecting the acetylene moiety. It should be noted that in the reaction in similar conditions of phenylacetylene and [Cu] occurs the oxidative condensation of phenylacetylene and the subsequent complex formation [16].

Scheme 3.



VIII

According to the XRD, complex **VIII** forms crystals corresponding to the centrosymmetric space group P-1 of triclinic crystal system with the following unit cell parameters: a = 7.3828(14) Å, b = 9.4560(13) Å, c = 9.6054(14) Å, α = 95.562(12)°, β = 98.279(14)°, γ = 110.990(15)°. In complex **VIII** the copper ion is in the inversion center, and it coordinates two ligand **VI** molecules in the trans position (Fig. 3). The coordination environment of copper is a distorted square, the Cu–O bond length is 1.879(9) Å, Cu–N 2.000(26) Å, the angle N–Cu–O 91.12(2)°. The distribution of the C–C bond lengths in the chelate node suggests the iminoenolate structure of the complex **VIII**: the length of C^4–C^3 bond is 1.338(18) Å, C^3–C^2 bond 1.419(8) Å.

The atoms of the N_2O_2 coordination center are located in a plane (Δ_{max} = 0.000 Å), which forms an angle of 12.66º with the planes of iminoenol fragments (Δ_{max} = 0.017 Å) that in turn are situated parallel to each other forming a *ladder* architecture of the complex. The plane of the benzene ring (Δ_{max} = 0.012 Å) is turned at 89.57(3)º to the mean plane of the chelate $Cu^1N^1C^2C^3C^4O^1$ node.

The molecules of the complex in the crystal are connected in infinite chains along the b axis through the truncated polar contacts between the hydrogen atom of the ≡CH group of one molecule and the oxygen atom of the neighboring molecule of the complex **VIII**: $\equiv CH^{13}\cdots O^1$ [1 – x, 1 – y, 1 – z] = 2.690(35) Å (Fig. 4).

Thus, by reacting fluorinated lithium 1,3-diketonates with propargylamine hydrochloride and 1,1,1-trifluorpentan-2,4-dione or 1,1,1-trifluoro-4-methoxypent-3-en-2-one with propargylamine and 3-aminophenylacetylene we prepared fluorinated 1,3-enaminone containing at the nitrogen atom a substituent with the terminal C≡C bond. The reactions performed are simple and do not require anhydrous or anaerobic conditions. On the basis of (*Z*)-1,1,1-trifluoro-4-(2-propynylamino)-3-penten-2-one **IVa** and 4-(3-etinilphenylamino)-1,1,1-trifluorpent-3-en-2-one **VI** copper complexes were obtained.

EXPERIMENTAL

The lithium diketonates **Ia**–**Ic**, 1,1,1-trifluorpentan-2,4-dione **IIa**, and 1,1,1-trifluoro-4-methoxypent-3-en-2-one **III** were obtained by the methods of [10, 12, 14], respectively.

The reaction progress was monitored by TLC (plates Silufol UV-254, eluent $CHCl_3$), development with water solutions of copper acetate and $KMnO_4$. The NMR spectra were recorded on a Bruker DRX-

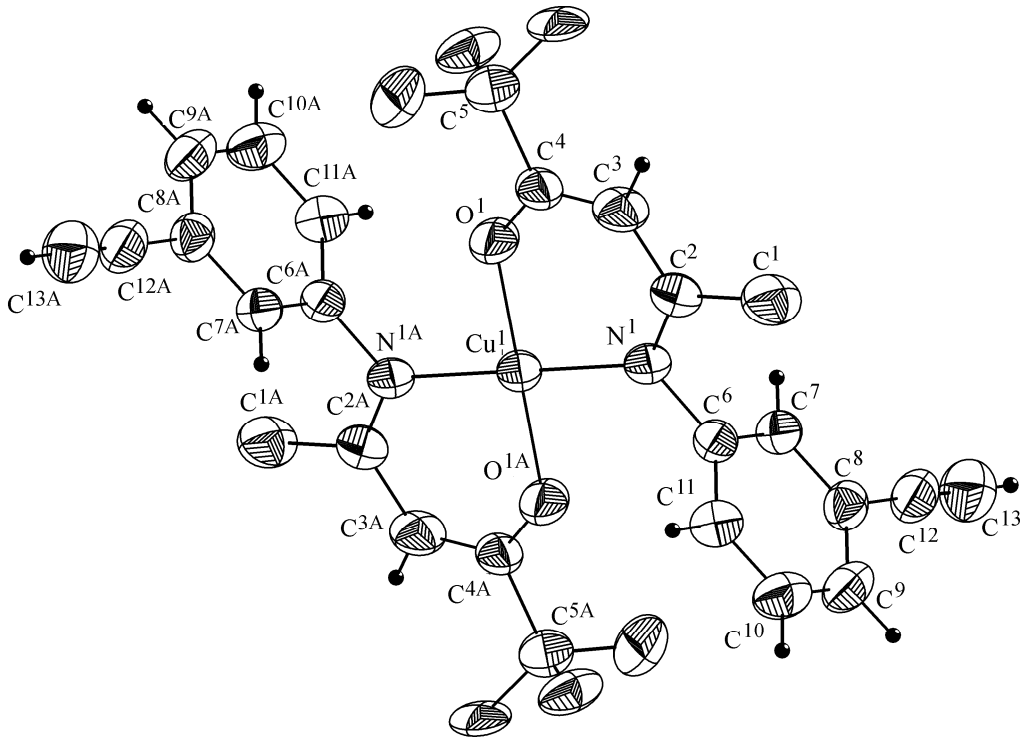


Fig. 3. The structure of complex **VIII** according to the XRD shown with the thermal ellipsoids of 50% probability.

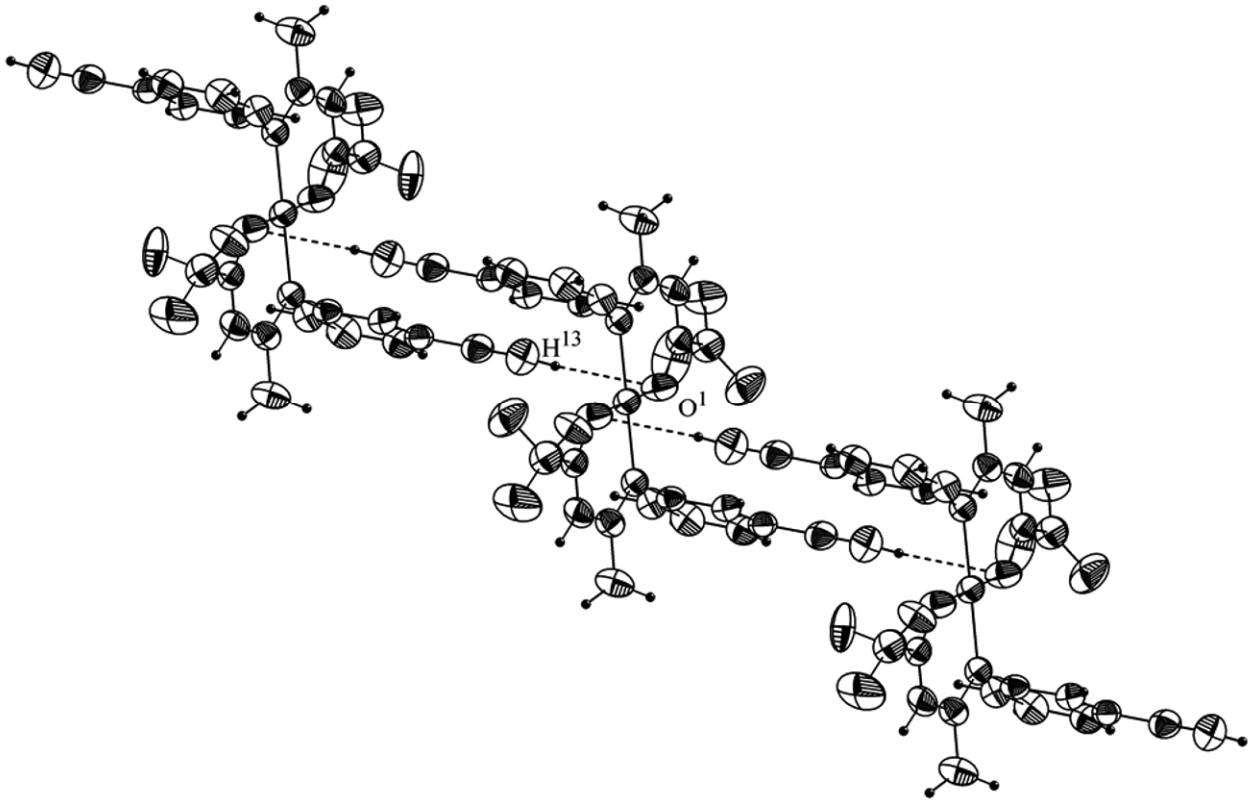


Fig. 4. Packing of molecules **VIII** in the crystal along the *c* axis.

400 spectrometer [400 MHz (^{1}H), 376 MHz (^{19}F)], internal references $SiMe_4$ and C_6F_6. The IR spectra were recorded on a Spectrum One B FT-IR spectrometer (Perkin Elmer) using diffuse reflectance attachment.

The XRD analysis of compounds **IVc** and **VIII** was performed on an automatic four-circle diffractometer Xcalibur 3 with CCD detector along the usual procedure (MoK_α-radiation, graphite monochromator, ω-scannning, the scan step 1°, T = 150(2) K. Corrections for extinction were not introduced. The structures were solved and refined using the SHELXTL software [17, 18].

For the XRD analysis of compound **IVc** a fragment of a colorless crystal of the size 0.24×0.15×0.20 mm was used. The crystals are monoclinic, space symmetry group $P2_1/c$, unit cell parameters: a = 6.8154(3) Å, b = 20.4264(7) Å, c = 7.1008 (3) Å, β = 94.069 (4)°, V = 986.04(7) Å^3, Z = 4 for the empirical formula $C_9H_9F_4NO$. d_{calc} = 1.503 g cm^{-3}, μ = 0.149 mm^{-1}, F(000) = 456, the angle of scanning θ: 3.00° < θ < 30.50°. 6243 reflections were collected, of which 2948 were independent (R_{int} = 0.0133), including 2166 reflections with $I > 2\sigma(I)$. The completeness of scanning for θ = 30.50° is 97.9%. The structure was solved by the direct method and refined by the full-matrix least-squares method with respect to F^2. All non-hydrogen atoms were refined in the anisotropic approximation, the hydrogen atoms of CH_3 and CF_2H groups were placed in the geometrically calculated positions and included in the refinement using the *rider* model with the dependent thermal parameters, the other hydrogen atoms were solved and refined independently in the isotropic approximation. The final refinement parameters are as follows: R_1 = 0.0317, wR_2 = 0.0880 [for reflections with $I > 2\sigma(I)$], R_1 = 0.0480, wR_2 = 0.0932 (for all reflections) with the Q parameter S = 1.005. Maximum and minimum residual electron density peaks are 0.313 and –0.216 ē Å^{-3}.

XRD structural analysis of compound **VIII** was performed using a gray-green crystal of 0.18× 0.09×0.03 mm size. The crystal is triclinic, space symmetry group P-1, the unit cell parameters are: a = 7.383(1) Å, b = 9.456(1) Å, c = 9.605(1) Å, α = 95.56(1)°, β = 98.28(1)°, γ = 110.99(2)°, **V** = 611.49(17) Å^3, Z = 1 for the empirical formula $C_{26}H_{18}F_6N_2O_2Cu$. d_{calc} = 1.542 g cm^{-3}, μ = 0.965 mm^{-1}, the scanning angle θ: 2.92° < θ < 30.51°. 4992 reflections were collected, of which 3684 were independent (R_{int} = 0.0218), including 2202 with $I > 2\sigma(I)$. The final refinement parameters are as follows: R_1 = 0.0708, wR_2 = 0.0906 [for reflections with $I > 2\sigma(I)$], R_1 = 0.0708, wR_2 = 0.0864 (all reflections) with the Q parameter S = 1.004].

The results of X-ray diffraction studies are registered in Cambrodge Crystallographic Data Center [CCDC 864707 (**IVc**), CCDC 864703 (**VIII**)].

Chromatography–mass spectrometry analysis was performed using an Agilent GC 7890A MSD 5975C inert XL EI/CI gas chromatograph–mass spectrometer (USA) and a quartz capillary column HP5-MS (polydimethylsiloxane, 5 wt % of phenyl groups), 30 m long with a diameter of 0.25 mm, film thickness 0.25 μm. The initial column temperature 40°C (3 min keeping), then heating at the rate 10°C per minute to 290°C (keeping for 30 min). Evaporator temperature is 250°C. The temperature of the transition chamber 280°C, the temperature of the ion source 230°C, temperature of the quadrupole 250°C. The carrier gas helium, split ratio 1:50, flow rate through the column 1.0 ml min^{-1}. Scanning of the full ion current in the range of 20–1000 amu at the electron ionization energy 70 eV.

(*Z*)-1,1,1-Trifluoro-4-(2-propynylamino)-3-penten-2-one (IVa). *a*. To a solution of 0.10 g (0.62 mmol) of lithium diketonate **Ia** in 10 ml of MeOH was added 0.06 g (0.69 mmol) of propargylamine hydrochloride. The reaction mixture was refluxed for 1.5 h, and then evaporated to dryness. The product was purified by column chromatography on SiO_2 ($CHCl_3$). We obtained 0.05 g (44%) of white crystals of **IVa**, mp 86–87°C. Found, %: C 50.05; H 4.30; F 29.46; N 7.29. $C_8H_8F_3NO$. Calculated, %: C 50.27; H 4.22; F 29.82; N 7.33. IR spectrum, ν, cm^{-1}: 3312 (≡ CH), 3170 (NH), 2951, 2851 (CH), 2176 (C≡C), 1623, 1554, 1523 (O = CC = C), 1446, 1390 (δCH), 1342, 1302, 1268, 1233, 1183, 1168, 1149 (CF). ^{1}H NMR spectrum (δ, ppm, J, Hz): 2.18 s (3H, Me), 2.37 m (1H, ≡CH, ^4J = 2.50 Hz), 4.10 d.d (2H, CH_2, ^3J = 6.0 Hz, ^4J = 2.5 Hz), 5.41 s (1H, =CH–), 11.07 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 84.93 s (CF_3). Mass spectrum, *m/z*: 191 (51.3%) $[M]^+$, 122 (100%) $[M - CF_3]^+$, 176 (4.0%) $[M - CH_3]^{\bullet+}$, 107 (0.4%) $[M - CF_3, CH_3]^{\bullet+}$, 94 (35.9%) $[M - CF_3CO]^+$, 79 (1.4%) $[M - CF_3CO, CH_3]^+$, 80 (5.6%) $[M - CF_3COCH_2]^+$.

b. To 0.20 g (1.30 mmol) of 1,1,1-trifluorpentan-2,4-dione **IIa** was added a solution of 0.08 g (1.43 mmol) of propargylamine in 4 ml of $CHCl_3$, and then 0.21 g (1.43 mmol) of triethyl borate. The reaction mixture was kept at room temperature for 2 h, then 15 ml of distilled water was added, the lower chloroform layer

was separated and evaporated. The product was purified by column chromatography on SiO_2 ($CHCl_3$). We obtained 0.14 g (58%) of white crystals of **IVa**, mp 86–87°C.

c. To 0.20 g (1.19 mmol) of methoxyenone **III** was poured a solution of 0.06 g (1.19 mmol) of propargylamine in 4 ml of $CHCl_3$. The reaction mixture was kept at room temperature for 2 h, 15 ml of distilled water was added, the lower chloroform layer was separated and evaporated. The product was purified by column chromatography on SiO_2 ($CHCl_3$). We obtained 0.20 g (89%) of white crystals of **IVa**, mp 86–87°C.

(*Z*)-1,1,2,2-Tetrafluoro-5-(2-propynylamino)-4-hexen-3-one (IVc). A solution of 0.50 g (2.6 mmol) of lithium diketonate **Ic** and 0.24 g (2.6 mmol) of propargylamine hydrochloride in 10 ml of methanol was refluxed until the disappearance of the initial compounds (TLC monitoring), the reaction mixture was cooled, filtered through a layer of silica gel, the solvent was evaporated, and the residue was crystallized from methanol. We obtained 0.5 g (43%) of **(*Z*)-1,1,2,2-tetrafluoro-5-(2-propynylamino)-4-hexen-3-one IVc,** mp 43–44°C. Found, %: C 48.26, H 4.03; F 34.09; N 6.25. $C_9H_9F_4NO$. Calculated, %: C 48.43, H 4.06; F 34.05; N 6.27. IR spectrum, ν, cm^{-1}): 3270 (NH), 2123 (≡CH), 2181, 2123 (C≡C), 1608, 1554 (O=CC=C). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 2.18 s (3H, Me), 2.37 t (1H, ≡CH, ^4J = 2.53 Hz), 4.10 d.d (2H, CH_2, ^3J = 5.99 Hz, ^4J = 2.53 Hz), 5.51 s (1H, =CH–), 6.11 t.t (1H, $H(CF_2)_2$, $^2J_{HF}$ = 53.2 Hz, $^3J_{HF}$ = 5.5 Hz), 11.18 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 22.44 d.t ($^2J_{FH}$ = 53.2 Hz, $^3J_{FH}$ = 7.6 Hz), 35.86 t.d.d ($^3J_{FF}$ = 7.6 Hz, $^3J_{FH}$ = 5.5 Hz, $^4J_{FH}$ = 1.2 Hz).

(*Z*)-1,1-Difluoro-2-(2-propynylamino)-2-butene-4-phenyl-4-one (V). Similarly, from 0.50 g (2.4 mmol) of lithium diketonate **Ic** and 0.22 g (2.4 mmol) of propargylamine hydrochloride was obtained 0.40 g of a mixture (9:1) of diketone **IIb** and enaminoketone **V** as an oil (chromatography–mass spectrometry analysis). The mixture was separated by column chromatography eluting the diketone **IIb** with hexane, and the enaminoketone **V** with $CHCl_3$. We obtained 0.35 g (57%) of compound **V** as an oil. Found, %: C 66.51, H 4.78; F 15.86; N 6.15. $C_{13}H_{11}F_2NO$. Calculated, %: C 66.38, H 4.71; F 16.15; N 5.95. IR spectrum, (ν, cm^{-1}): 3299 (NH), 2924, 2825 (C≡C), 1623, 1597 (O=CC=C). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 2.37 m (1H, ≡CH, ^4J = 2.52 Hz), 4.21 d.d (2H, CH_2, ^3J = 5.03 Hz, ^4J = 2.52 Hz), 6.07 s (1H, =CH–), 6.31 t (^{1}H, NCF_2, $^2J_{HF}$ = 53.40 Hz), 10.56 br.s (1H, NH). ^{19}F NMR spectrum (δ, ppm): 43.25 d ($^2J_{HF}$ 53.40 Hz). Mass spectrum, *m/z*: 235 (20%) $[M]^{\bullet+}$, 184 (4%) $[M - HCF_2]^{\bullet+}$, 130 (10%) $[M - PhCO]^{\bullet+}$, 105 (100%) $[PhCO]^{\bullet+}$, 77 (45%) $[Ph]^{\bullet+}$, 51 (7%) $[HCF_2]^{\bullet+}$.

4-(3-Ethynylphenylamino)-1,1,1-trifluorpent-3-en-2-one (VI). *a*. To 0.15 g (0.97 mmol) of 1,3-diketone **IIa** was added a solution of 3-aminophenylacetylene (0.13 g, 1.7 mmol) in 4 ml of $CHCl_3$ and 0.16 g (1.07 mmol) of triethyl borate. The reaction mixture was kept at room temperature for 1.5 h ad then 15 ml of distilled water was added, the bottom layer was separated, and chloroform was evaporated. The product was purified by column chromatography on SiO_2 ($CHCl_3$). We obtained 0.22 g (89%) of compound **VI** as a colorless oil.

b. To a solution of 1.51 g (8.96 mmol) of methoxyenone **III** was poured a solution of 1.00 g (8.54 mmol) of 3-aminophenylacetylene in 8 ml of $CHCl_3$. The reaction mixture was kept at room temperature for a day, then the solvent was removed and the residue was purified by column chromatography on SiO_2 (eluent $CHCl_3$). We obtained 1.46 g (67%) of colorless oil of compound **VI**. Found, %: C 61.30, H 4.04, F 22.24, N 5.60. $C_{13}H_{10}F_3NO$. Calculated, %: C 61.66, H 3.98, F 22.51, N 5.53. IR spectrum (ν, cm^{-1}): 3298 {≡CH, 2924 (CH_3), 1617, 1573, 1525, 1484, 1436, 1385 [δ(N–H), ν(O=CC=C, C–C)] (Ph)}, 1302, 1246, 1190, 1139, 1117 (CF). ^{1}H NMR spectrum, δ, ppm: 2.12 s (3H, Me), 3.15 s (1H, ≡CH), 5.56 s (1H, =CH–), 7.15–7.17 m (1H), 7.29–7.30 m (1H), 7.36–7.40 m (1H), 7.43–7.45 m (1H), C_6H_4], 12.53 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: 84.98 s (CF_3). Mass spectrum, *m/z*: 253 (38.1%) $[M]^+$, 184 (100%) $[M - CF_3]^+$, 238 (3.1%) $[M - CH_3]^{\bullet+}$, 168 (3.2%) $[M - CF_3, CH_3]^{\bullet+}$, 156 (8.5%) $[M - CF_3CO]^{\bullet+}$, 141 (5.6%) $[M - CF_3CO, CH_3]^{\bullet+}$, 140 (2.0%) $[M - CF_3COCH_2]^{\bullet+}$.

Synthesis of complex VII. To a solution of 0.15 g (0.78 mmol) of **IVa** in 7 ml of MeCN was poured a solution of 0.08 g (0.39 mmol) of $Cu(CH_3COO)_2 \cdot H_2O$ in MeCN. The reaction mixture was kept for 30 min at room temperature, then 10 ml of water was added, the precipitate was filtered off and dried in air. We obtained 0.06 g of brown powder insoluble in organic solvents. IR spectrum, (ν, cm^{-1}): 2929, 2853 (CH_3, CH_2), 1615, 1585, 1531 (O=CC= C), 1472, 1388 [δ(CH_3), δ(CH_2)], 1303,1251, 1191, 1126, 1086 (CF).

Synthesis of complex VIII. *a*. To a solution of 0.01 g (0.39 mmol) of **VI** in 3 ml of MeOH was poured a solution of 0.04 g (0.20 mmol) of $Cu(CH_3COO)_2 \cdot H_2O$ in MeOH. The reaction mixture was kept at room temperature for three days, then evaporated to dryness. The product was purified by column chromatography on SiO_2 ($CHCl_3$). We obtained 0.02 g (19%) of brown oily complex **VIII**.

b. To a solution of 0.32 g (1.26 mmol) of compound **VI** in 5 ml of $CHCl_3$ was added 0.05 g 0.63 mmol) of nano-sized powder of copper and its oxides (calculated for CuO, particle size 40 nm), and the reaction mixture was kept at room temperature for three days. Unreacted [Cu] was filtered off and the filtrate was chromatographed ($CHCl_3$). We obtained 0.03 g (70%) of complex **VIII** as brown oil. Found, %: C 52.49, H 3.15, F 19.64, N 4.61; $C_{26}H_{18}F_6N_2O_2Cu \cdot 1/4CHCl_3$. Calculated, %: C 52.74, H 3.08, F 19.07, N 4.68. IR spectrum (ν, cm^{-1}): 3275 (≡CH), 2921 (CH_3), 1610, 1573, 1524, 1467, 1364 [δ(N–H, O=CC=C, C–C) phenyl ring], 1299, 1245, 1184, 1137, 1087 (CF). Crystals for X-ray diffraction were obtained by crystallization of oily complex **VIII** from hexane at –18ºC.

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REFERENCES

1. Cacchi, S., Fabrizi, G., and Filisti, E, *Org. Lett.*, 2008, vol. 10, no. 13, p. 2629.
2. Martins, M.A.P., Rossatto, M., Prola, L.D.T., Moreira, D.N., Campos, P.T., Zanatta, N., and Bonacorso, H.G, *ARKIVOC*, 2010, no. 9, p. 12.
3. Rossatto, M., *Doctoral (Chem.) Disseration*, Federal Universitate of Santa Maria., 2009, no. 10, p. 1286.
4. Fenain, F., Merdebielle, M., Rocher, M., Onomura, O., and Okada, E., *J. Fluor. Chem*., 2007, vol. 128, no. 10, p. 1286.
5. Ishikawa, N., *Syntheses and Functions of Fluorine Compounds*, Moscow: Mir, 1990.
6. *Fluorine Compounds. Modern Technology and Application*, Ishikawa, N., Ed., Moscow: Mir, 1984.
7. Kirsch, P., *Modern Fluoroorganic Chemistry: Synthesis*, *Reactivity*, *Applications*, Weinheim: Wiley-VCH, 2004.
8. Kollmen, J., Khigedas, L., Norton, J., and Finke, R., *Organometallic Chemistry of Transition Metals*, Moscow: Mir, 1989.
9. Mykhalichko, B.M., Temkin, O.N., and Myskiv, M.G, *Usp. Khim*., 2000, vol. 69, no.11, p. 1042.
10. Filyakova, V.I., Karpenko, N.S., Kuznetsova, O.A., and Pashkevich, K.I, *Zh. Org. Khim*., 1998, vol. 34, no. 3, p. 411.
11. Boltacheva, H.C., Filyakova, V.I., and Charushin, V.N, *Zh. Org. Khim*., 2005, vol. 41, no. 10, p. 1483.
12. Karpenko, N.S., *Candidate Sci. (Chem.) Dissertation*, Yekaterinburg, 2004.
13. Bazhenova, L.N., Filyakova, V.I., Kirichenko, V.E., and Pashkevich, K.I, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1991, no. 3, p. 664.
14. Mkrtchyan, E.G., Yachevskii, D.S., Chizhov, D.L., and Charushin, V.N, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, no. 9, p. 2086.
15. Chizhov, D.L., Pervova, M.G., Samorukova, M.A., Khmara, E.F., Filyakova, V.I., Saloutin, V.I., and Charushin, V.N, *J. Fluor. Chem*., 2011, vol. 132, no. 6, p. 394.
16. Khmara, E.F., Filyakova, V.I., Ermakov, A.E., Rhee, S.K., and Charushin, V.N, *Zh. Obshch. Khim.*, 2007, vol. 77, no.3, p. 439.
17. Sheldrick, G.M., *SHELXS97 Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1997.
18. Sheldrick, G.M., *SHELXL97 Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.