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Reaction of 2-Perfluoroalkanoylcyclohexane-1,3-diones and 3-Chloro-2-perfluoroalkanoylcyclohex-2-ene-1-ones with Amines

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Abstract—Reactions of 2-perfluoroalkanoylcyclohexane-1,3-diones with primary and secondary amines involved acid cleavage of the substrate with formation of the corresponding 3-aminocyclohex-2-en-1-ones. Vinylogous nucleophilic substitution in 3-chloro-2-perfluoroalkanoylcyclohex-2-ene-1-ones with amines led to the formation of 3-amino-2-perfluoroalkanoylcyclohex-2-ene-1-ones.

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Recently synthesized 2-perfluoroalkanoylcyclohexane-1,3-diones [1] are reactive compounds due to the presence of three electrophilic centers (one exocyclic and two endocyclic carbonyl groups), and they can be used as starting compounds in the synthesis of a large series of new biologically active polyfluoroalkyl-containing carbo- and heterocyclic systems. 2-Perfluoroalkanoylcyclohexane-1,3-diones and the corresponding methyl enol ethers are known to react with difunctional nitrogen-containing nucleophiles such as phenylhydrazines to give regioisomeric 1-aryl-3-polyfluoroalkyl-6,7-dihydro-1*H*-indazol-4(5*H*)-ones and 2-aryl-3-perfluoroalkyl-6,7-dihydro-2*H*-indazol-4(5*H*)-ones, respectively [2]. There are no published data on reactions of fluoroalkyl-containing cyclic β,β′-triketones with nitrogen-centered mononucleophiles.

Reactions of both acyclic and alicyclic polyfluoroalkyl-containing β-dicarbonyl compounds with amines have been studied in sufficient detail [3]. Their regioselectivity depends on the amine nature, the presence or absence of fluoroalkyl substituents at the carbonyl groups, and reaction conditions, so that they may involve either one or both carbonyl groups. The main side processes in these transformations are acid cleavage and salt formation. Acid cleavage was observed exclusively for fluorine-containing acyclic β,β′-triketones [4].

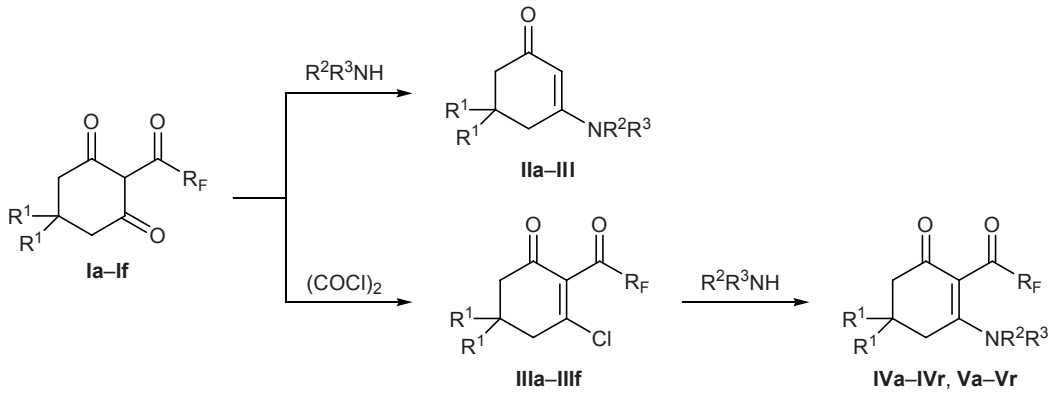
Depending on the ring and side chain structure, enamino derivatives of nonfluorinated analogs of 2-perfluoroalkanoylcyclohexane-1,3-diones exhibit various kinds of biological activity, such as antiinflammatory, antiaggregation, gastroprotective, etc. [5]; they are also used in agriculture as potent herbicides (Sethoxydim, Tralkoxydim, etc.) [6]. Taking into account specific properties of fluorine atom, replacement of hydrogen by fluorine could essentially affect physical, chemical, and biological properties of organic compounds [7].

In the present work we examined reactions of 2-perfluoroalkanoylcyclohexane-1,3-diones and 3-chloro-2-perfluoroalkanoylcyclohex-2-en-1-ones with primary (aniline, 4-fluoroaniline, benzylamine, 4-fluorobenzylamine) and secondary amines (pyrrolidine, piperidine) with a view to obtain new polyfluoroalkyl-containing enaminodiketones of the cyclohexane series.

Vinylogous amides at the exocyclic carbonyl group of nonfluorinated 2-acylcyclohexane-1,3-diones are generally synthesized by condensation of these compounds with amines [8]. However, like acyclic polyfluorinated β,β′-tricarbonyl compounds [4], 2-perfluoroalkanoylcyclohexane-1,3-diones **Ia**–**If** in reactions with primary and secondary amines even at room temperature underwent acid cleavage to cyclohexane-1,3-diones which were converted into enamino ketones **IIa**–**III** (Scheme 1).

To obtain enamino derivatives **IVa**–**IVr** and **Va**–**Vr** of 2-perfluoroalkanoylcyclohexane-1,3-diones it is

Scheme 1.



I, **III**, R^1 = Me, R_F = CF_3 (**a**), C_2F_5 (**b**), C_3F_7 (**c**); R^1 = H, R_F = CF_3 (**d**), C_2F_5 (**e**), C_3F_7 (**f**); **II**, R^1 = Me, R^2 = H, R^3 = Ph (**a**), 4-FC_6H_4 (**b**), $PhCH_2$ (**c**), 4-$FC_6H_4CH_2$ (**d**); R^2R^3 = $(CH_2)_4$ (**e**), $(CH_2)_5$ (**f**); R^1 = H, R^2 = H, R^3 = Ph (**g**), 4-FC_6H_4 (**h**), $PhCH_2$ (**i**), 4-$FC_6H_4CH_2$ (**j**); R^2R^3 = $(CH_2)_4$ (**k**), $(CH_2)_5$ (**l**); **IV**, **V**, R^2 = H, R^3 = Ph, R_F = CF_3 (**a**), C_2F_5 (**b**), C_3F_7 (**c**); R^3 = 4-FC_6H_4, R_F = CF_3 (**d**), C_2F_5 (**e**), C_3F_7 (**f**); R^3 = $PhCH_2$, R_F = CF_3 (**g**), C_2F_5 (**h**), C_3F_7 (**i**); R^3 = 4-$FC_6H_4CH_2$, R_F = CF_3 (**j**), C_2F_5 (**k**), C_3F_7 (**l**); R^2R^3 = $(CH_2)_4$, R_F = CF_3 (**m**), C_2F_5 (**n**), C_3F_7 (**o**); R^2R^3 = $(CH_2)_5$, R_F = CF_3 (**p**), C_2F_5 (**q**), C_3F_7 (**r**); **IV**, R^1 = Me; **V**, R^1 = H.

necessary that nucleophilic attack be directed at the trigonal C^3 center, which may be achieved via initial transformation of β,β′-triketones **Ia**–**If** into their enol derivatives and treatment of the latter with amines. We synthesized chlorovinyl diketones **IIIa**–**IIIf** by reaction of β,β′-triketones **Ia**–**If** with excess oxalyl chloride at room temperature. Unlike β,β′-triketones having no fluorine atoms (the corresponding vinylogous acid chlorides are formed in 3–5 h [9]), the reactions with compounds **Ia**–**If** lasted 3–4 days, the conversion of dimedone derivatives **Ia**–**Ic** was not complete, and the yield of β-chlorovinyl diketones **IIIa**–**IIIc** ranged from 60 to 68%. Presumably, the reason is the presence of electron-withdrawing perfluoroalkanoyl substituent; the formation of chlorocyclohexenones **IIIa**–**IIIc** is also hampered due to steric hindrances created by methyl groups in position *5* of the six-membered ring.

Compounds **IIIa**–**IIIf** were treated with 2 equiv of the corresponding amine, 1 equiv of which was consumed for binding liberated hydrogen chloride. The reactions were carried out in chloroform at room temperature (reaction time 2–3 h), and the products were 3-amino-2-polyfluoroalkanoylcyclohex-2-en-1-ones **IVa**–**IVr** and **Va**–**Vr** (yield 73–94%; Scheme 1). As with fluorine-free analogs [8], the reaction was regioselective, and it followed vinylogous substitution mechanism with formation of only one product.

The structure of compounds **II**–**V** was confirmed by elemental analyses and IR, NMR, and mass spectra, as well as by comparing with published data. Chlorovinyl diketones **IIIa**–**IIIf** characteristically displayed in the IR spectra a set of absorption bands in the regions 1745–1750, 1680–1685, and 1615–1625 cm^{-1}, which belong to stretching vibrations of the unconjugated exocyclic carbonyl group, conjugated endocyclic carbonyl group, and double C=C bond, respectively. The presence of a band at 1745–1750 cm^{-1} indicates that the exocyclic carbonyl group is forced out from conjugation with the endocyclic C=C bond; analogous pattern was observed previously for nonfluorinated cyclic chlorovinyl diketones [9].

The IR spectra of 3-amino-2-perfluoroalkanoylcyclohex-2-en-1-ones **IVa**–**IVr** and **Va**–**Vr** contained absorption bands typical of endocyclic (1645–1690 cm^{-1}) and exocyclic carbonyl groups (1590–1640 cm^{-1}) and double C=C bond (1515–1585 cm^{-1}). The NH proton in compounds **IV** and **V** derived from primary amines is involved in strong intramolecular hydrogen bond with the exocyclic carbonyl group, and its signal appeared in the ^1H NMR spectra at δ 12.5–13.0 (**IVa**–**IVf**, **Va**–**Vf**) or 11.4–11.9 ppm (**IVg**–**IVk**, **Vg**–**Vk**). In the ^{13}C NMR spectra of **IVa**–**IVr** and **Va**–**Vr** signals from the endocyclic carbonyl carbon atom and CH atom at the double bond were located at δ_C 192.7–195.1 and 166.1–174.9 ppm, respectively. The exocyclic carbonyl carbon atom in trifluoroacetyl derivatives **IVa**, **IVd**, **IVg**, **IVj**, **IVm**, **IVp**, **Va**, **Vd**, **Vg**, **Vj**, **Vm**, and **Vp** resonated as a quartet at δ_C 178.1–183.9 ppm ($^2J_{CF}$ = 35–36 Hz), while the corresponding signal in the spectra of pentafluoropropionyl derivatives **IVb**, **IVe**, **IVh**, **IVk**, **IVn**, **IVq**, **Vb**, **Ve**, **Vh**, **Vk**, **Vn**, and **Vq** and hexafluorobutanoyl derivatives **IVc**, **IVf**, **IVi**, **IVl**, **IVo**, **IVr**, **Vc**, **Vf**, **Vi**,

Vl, **Vo**, and **Vr** was a triplet at δ_C 180.6–189.9 ppm ($^2J_{CF}$ = 26– 28 Hz). The ^{19}F NMR spectra of **IVa**, **IVd**, **IVg**, **IVj**, **IVm**, **IVp**, **Va**, **Vd**, **Vg**, **Vj**, **Vm**, and **Vp** contained a singlet at δ_F –72.5 to –73.5 ppm typical of trifluoroacetyl group. Compounds **IVb**, **IVe**, **IVh**, **IVk**, **IVn**, **IVq**, **Vb**, **Ve**, **Vh**, **Vk**, **Vn**, and **Vq** showed fluorine signals at δ_F –79.1 to –80.3 (CF_3) and –115.4 to –117.4 ppm (CF_2), and signals from fluorine atoms in hexafluorobutanoyl derivatives **IVc**, **IVf**, **IVi**, **IVl**, **IVo**, **IVr**, **Vc**, **Vf**, **Vi**, **Vl**, **Vo**, and **Vr** were located at δ_F –80.5 to –81.2 (CF_3), –110.6 to –113.0 (CF_2), and –121.8 to –123.1 ppm (CF_2).

EXPERIMENTAL

The NMR spectra were recorded on a Bruker Avance-500 spectrometer from solutions in $CDCl_3$ using tetramethylsilane (^{1}H, 500 MHz; ^{13}C, 125 MHz) and CCl_3F (^{19}F, 470 MHz) as internal references. The IR spectra were measured on a UR-20 instrument from samples prepared as KBr pellets (crystalline substances) or films (oily substances). The melting points were determined on a Boetius melting point apparatus. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent. Initial polyfluoroalkyl-containing β,β′-triketones **Ia**–**If** were prepared according to the procedure described in [1].

Reactions of 2-perfluoroalkanoylcyclohexane-1,3-diones Ia–If with amines (*general procedure***).** Triketone **Ia**–**If**, 1 mmol, was dissolved in 20 ml of chloroform, 1 mmol of the corresponding amine (aniline, 4-fluoroaniline, benzylamine, 4-fluorobenzylamine, pyrrolidine, or piperidine) was added, and the mixture was stirred for 7 h. The mixture was washed with water and dried over magnesium sulfate, the solvent was removed under reduced pressure, and the residue was recrystallized from diethyl ether–hexane to isolate individual enamino ketones **IIa**–**III**.

5,5-Dimethyl-3-phenylaminocyclohex-2-en-1-one (**IIa**) [10], 3-benzylamino-5,5-dimethylcyclohex-2-en-1-one (**IIc**) [10], 5,5-dimethyl-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (**IIe**) [11], 5,5-dimethyl-3-piperidinocyclohex-2-en-1-one (**IIf**) [12], 3-phenylaminocyclohex-2-en-1-one (**IIg**) [13], 3-benzylaminocyclohex-2-en-1-one (**IIi**) [10], 3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (**IIk**) [14], and 3-piperidinocyclohex-2-en-1-one (**III**) [15] were reported previously; their properties were consistent with published data.

3-(4-Fluorophenylamino)-5,5-dimethylcyclohex-2-en-1-one (IIb). Yield 90%, mp 191–194°C. IR spectrum, ν, cm^{-1}: 1585, 1535, 1515. ^{1}H NMR spectrum, δ, ppm: 1.04 s (6H, CH_3), 2.15 s (2H, CH_2), 2.35 s (2H, CH_2), 5.32 s (1H, 2-H), 6.97 m (2H, H_{arom}), 7.05 m (2H, H_{arom}), 7.86 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 29.7, 32.8, 43.0, 50.3, 97.2, 116.0 d (^2J = 23), 126.2 d (^3J = 8), 134.2 d (^4J = 2), 160.3 d (^1J = 246), 162.8, 198.1. ^{19}F NMR spectrum: δ_F –116.14 ppm.

3-(4-Fluorobenzylamino)-5,5-dimethylcyclohex-2-en-1-one (IId). Yield 92%, mp 142–145°C. IR spectrum, ν, cm^{-1}: 1605, 1575. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 s (6H, CH_3), 2.16 s (2H, CH_2), 2.28 s (2H, CH_2), 4.24 d (2H, CH_2, ^3J = 4.3), 5.19 s (1H, 2-H), 6.05 br.s (1H, NH), 7.01 m (2H, H_{arom}), 7.23 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 29.7, 32.9, 43.3, 46.5, 49.4, 97.7, 115.8 d (^2J = 22), 129.3 d (^3J = 8), 132.3, 162.3 d (^1J = 247), 164.3, 196.3. ^{19}F NMR spectrum: δ_F –114.46 ppm.

3-(4-Fluorophenylamino)cyclohex-2-en-1-one (IIh). Yield 88%, mp 164–167°C. IR spectrum, ν, cm^{-1}: 1600, 1580. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.99 quint (2H, CH_2, ^3J = 6.2), 2.32 t (2H, CH_2, ^3J = 6.2), 2.53 t (2H, CH_2, ^3J = 6.2), 5.37 s (1H, 2-H), 6.99 m (2H, H_{arom}), 7.10 m (2H, H_{arom}), 7.54 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 21.8, 29.4, 36.2, 98.7, 116.1 d (^2J = 23), 126.3 d (^3J = 8), 133.9, 160.4 d (^1J = 246), 164.4, 198.4. ^{19}F NMR spectrum: δ_F –115.92 ppm.

3-(4-Fluorobenzylamino)cyclohex-2-en-1-one (IIj). Yield 90%, mp 114–117°C. IR spectrum, ν, cm^{-1}: 1600, 1555. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.96 quint (2H, CH_2, ^3J = 6.4), 2.28 t (2H, CH_2, ^3J = 6.4), 2.39 t (2H, CH_2, ^3J = 6.4), 4.19 d (2H, CH_2, ^3J = 5.1), 5.11 s (1H, 2-H), 5.59 br.s (1H, NH), 7.02 m (2H, H_{arom}), 7.23 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 22.0, 29.6, 36.4, 46.4, 97.3, 115.8 d (^2J = 22), 129.4 d (^3J = 8), 132.6, 162.3 d (^1J = 247), 164.5, 197.5. ^{19}F NMR spectrum: δ_F –114.66 ppm.

3-Chloro-2-polyfluoroalkanoylcyclohex-2-en-1-ones IIIa–IIIf (*general procedure***).** A mixture of 1 mmol of compound **Ia**–**If** and 10 mmol of oxalyl chloride was kept for 3–4 days at room temperature. Excess oxalyl chloride was removed under reduced pressure, the residue was dissolved in 15 ml of chloroform, the solution was washed with a saturated solution of sodium hydrogen carbonate and water and dried over magnesium sulfate, and the solvent was removed on a rotary evaporator.

3-Chloro-5,5-dimethyl-2-trifluoroacetylcyclohex-2-en-1-one (IIIa). Yield 60%, mp 67–70°C. IR spec-

trum, ν, cm^{-1}: 1750, 1680, 1625. ^1H NMR spectrum, δ, ppm: 1.26 s (6H, CH_3), 2.40 s (2H, CH_2), 2.73 s (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 27.8, 33.8, 48.3, 50.0, 114.8 q (^1J = 291), 133.8, 157.2, 184.1 q (^2J = 40), 193.4. ^{19}F NMR spectrum: δ_F –77.24 ppm (CF_3).

3-Chloro-5,5-dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (IIIb). Yield 63%, colorless oily substance. IR spectrum, ν, cm^{-1}: 1750, 1685, 1625. NMR spectrum ^1H, δ, ppm : 1.16 s (6H, $2CH_3$), 2.40 s (2H, CH_2), 2.73 s (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 27.7, 33.7, 48.3, 50.0, 106.3 t.q (^1J = 268, ^2J = 38), 117.7 q.t (^1J = 288, ^2J = 34), 134.1, 157.1, 187.0 t (^2J = 30), 193.34. ^{19}F NMR spectrum, δ_F, ppm: –81.59 (CF_3), –121.41 (CF_2).

3-Chloro-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-5,5-dimethylcyclohex-2-en-1-one (IIIc). Yield 68%, colorless oily substance. IR spectrum, ν, cm^{-1}: 1750, 1685, 1625. ^1H NMR spectrum, δ, ppm: 1.16 s (6H, CH_3), 2.40 s (2H, CH_2), 2.73 s (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 27.8, 33.8, 48.5, 50.1, 107.9 t.t (^1J = 269, ^2J = 33), 108.7 t.m (^1J = 267), 117.5 q.t (^1J = 289, ^2J = 33), 134.3, 157.2, 186.9 t (^2J = 31), 193.4. ^{19}F NMR spectrum, δ_F, ppm: –80.77 (CF_3), –118.45 (CF_2), –126.16 (CF_2).

3-Chloro-2-trifluoroacetylcyclohex-2-en-1-one (IIId). Yield 97%, mp 83–86°C. IR spectrum, ν, cm^{-1}: 1745, 1680, 1615. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.18 quint (2H, CH_2, ^3J = 6.5), 2.55 t (2H, CH_2, ^3J = 6.5), 2.87 t (2H, CH_2, ^3J = 6.5). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 21.4, 34.5, 36.1, 114.8 q (^1J = 291), 134.8, 159.0, 184.2 q (^2J = 40), 193.3. ^{19}F NMR spectrum: δ_F –77.36 ppm (CF_3).

3-Chloro-2-(2,2,3,3,3-pentafluoropropanoyl)-cyclohex-2-en-1-one (IIIe). Yield 90%, colorless oily substance. IR spectrum, ν, cm^{-1}: 1745, 1685, 1620. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.18 quint (2H, CH_2, ^3J = 6.2), 2.55 t (2H, CH_2, ^3J = 6.2), 2.87 t (2H, CH_2, ^3J = 6.2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 21.4, 34.6, 36.2, 106.3 t.q (^1J = 268, ^2J = 38), 117.9 q.t (^1J = 288, ^2J = 34), 135.1, 159.0, 187.2 t (^2J = 31), 193.3. ^{19}F NMR spectrum, δ_F, ppm: –81.65 (CF_3), –121.47 (CF_2).

3-Chloro-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-cyclohex-2-en-1-one (IIIf). Yield 88%, colorless oily substance. IR spectrum, ν, cm^{-1}: 1745, 1680, 1615. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.17 quint (2H, CH_2, ^3J = 6.1), 2.55 t (2H, CH_2, ^3J = 6.1), 2.87 t (2H, CH_2, ^3J = 6.1). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 21.4, 34.8, 36.2, 107.9 t.t (^1J = 269, ^2J = 33), 108.6 t.m (^1J = 267), 117.5 q.t (^1J = 288, ^2J = 33), 135.2, 159.1, 187.1 t (^2J = 31), 193.3. ^{19}F NMR spectrum, δ_F, ppm: –80.87 (CF_3), –118.53 (CF_2), –126.22 (CF_2).

Reactions of chlorovinyl diketones IIIa–IIIf with amines (*general procedure*). Compound **IIIa**–**IIIf**, 1 mmol, was dissolved in 15 ml of chloroform, 2 mmol of the corresponding amine was added, and the mixture was stirred for 2–3 h, the progress of the reaction being monitored by TLC. When the reaction was complete, the mixture was washed with water and dried over magnesium sulfate, the solvent was distilled off under reduced pressure, and the residue was recrystallized from diethyl ether–hexane. Compounds **IVa**–**IVr** and **Va**–**Vr** were isolated as colorless crystalline substances.

5,5-Dimethyl-2-trifluoroacetyl-3-phenylaminocyclohex-2-en-1-one (IVa). Yield 92%, mp 110–113°C. IR spectrum, ν, cm^{-1}: 1665, 1615, 1580. ^1H NMR spectrum, δ, ppm: 1.04 s (6H, CH_3), 2.39 s (2H, CH_2), 2.49 s (2H, CH_2), 7.19 m (2H, H_{arom}), 7.43 m (1H, H_{arom}), 7.49 m (2H, H_{arom}), 12.97 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 27.9, 31.5, 41.8, 51.5, 105.7, 117.3 q (^1J = 287), 125.9, 128.6, 129.9, 135.8, 173.1, 180.4 q (^2J = 36), 193.0. ^{19}F NMR spectrum: δ_F –72.75 ppm (CF_3). Found, %: C 61.59; H 5.11; N 4.42. $C_{16}H_{16}F_3NO_2$. Calculated, %: C 61.71; H 5.18; N 4.50.

5,5-Dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)-3-phenylaminocyclohex-2-en-1-one (IVb). Yield 89%, mp 126–129°C. IR spectrum, ν, cm^{-1}: 1665, 1595, 1565. ^1H NMR spectrum, δ, ppm: 1.02 s (6H, CH_3), 2.38 s (2H, CH_2), 2.49 s (2H, CH_2), 7.16 m (5H, H_{arom}), 12.83 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.0, 31.7, 41.9, 51.6, 107.0, 109.0 t.q (^1J = 271, ^2J = 35), 119.1 q.t (^1J = 288, ^2J = 36), 126.0, 128.6, 129.9, 135.8, 172.7, 183.9 t (^2J = 27), 193.0. ^{19}F NMR spectrum, δ_F, ppm: –79.53 (CF_3), –116.24 (2F, CF_2). Found, %: C 56.61; H 4.86; N 3.93. $C_{17}H_{16}F_5NO_2$. Calculated, %: C 56.49; H 4.77; N 3.88.

2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-5,5-dimethyl-3-phenylaminocyclohex-2-en-1-one (IVc). Yield 88%, mp 56–59°C. IR spectrum, ν, cm^{-1}: 1665, 1595, 1565. ^1H NMR spectrum, δ, ppm: 1.03 s (6H, CH_3), 2.38 s (2H, CH_2), 2.50 s (2H, CH_2), 7.17 m (3H, H_{arom}), 7.48 m (2H, H_{arom}), 12.68 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.0, 31.8, 41.8, 51.4, 107.1, 109.9 t.m (^1J = 269), 110.8 t.t (^1J = 269, ^2J = 31), 118.1 q.t (^1J = 288, ^2J = 34), 126.0, 128.6, 129.9, 135.8, 172.3, 184.3 t (^2J = 27), 193.1. ^{19}F NMR spectrum, δ_F, ppm: –80.78 (CF_3), –111.44

(CF_2), –121.80 (CF_2). Found, %: C 52.63; H 3.98; N 3.47. $C_{18}H_{16}F_7NO_2$. Calculated, %: C 52.54; H 3.92; N 3.41.

3-(4-Fluorophenylamino)-5,5-dimethyl-2-trifluoroacetylcyclohex-2-en-1-one (IVd). Yield 90%, mp 97–100°C. IR spectrum, ν, cm^{-1}: 1680, 1610, 1570. ^1H NMR spectrum, δ, ppm: 1.04 s (6H, CH_3), 2.38 s (2H, CH_2), 2.44 s (2H, CH_2), 7.18 m (4H, H_{arom}), 12.85 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 27.9, 31.6, 41.8, 51.5, 105.9, 117.0 d (^2J = 23), 117.3 q (^1J = 288), 128.0 d (^3J = 9), 131.9 d (^4J = 2), 162.2 d (^1J = 250), 173.4, 180.5 q (^2J = 36), 193.0. ^{19}F NMR spectrum, δ_F, ppm: –72.80 (CF_3), –111.91 (1F). Found, %: C 58.21; H 4.54; N 4.19. $C_{16}H_{15}F_4NO_2$. Calculated, %: C 58.36; H 4.59; N 4.25.

3-(4-Fluorophenylamino-5,5-dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (IVe). Yield 92%, mp 108–111°C. IR spectrum, ν, cm^{-1}: 1665, 1605, 1565. ^1H NMR spectrum, δ, ppm: 1.02 s (6H, CH_3), 2.38 s (2H, CH_2), 2.49 s (2H, CH_2), 7.17 m (4H, H_{arom}), 12.83 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.0, 31.7, 41.9, 51.5, 107.1, 109.0 t.q (^1J = 271, ^2J = 35), 117.0 d (^2J = 23), 119.1 q.t (^1J = 288, ^2J = 36), 128.0 d (^3J = 9), 131.8 (^4J = 2), 162.2 d (^1J = 250), 173.1, 184.0 t (^2J = 28), 192.9. ^{19}F NMR spectrum, δ_F, ppm: –79.58 (CF_3), –111.96 (F), –116.30 (CF_2). Found, %: C 53.75; H 4.14; N 3.61. $C_{17}H_{15}F_6NO_2$. Calculated, %: C 53.83; H 3.99; N 3.69.

3-(4-Fluorophenylamino)-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-5,5-dimethylcyclohex-2-en-1-one (IVf). Yield 87%, mp 51–54°C. IR spectrum, ν, cm^{-1}: 1670, 1605, 1565. ^1H NMR spectrum, δ, ppm: 1.03 s (6H, CH_3), 2.37 s (2H, CH_2), 2.45 s (2H, CH_2), 7.18 m (4H, H_{arom}), 12.57 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.0, 31.8, 41.8, 51.4, 107.2, 109.8 t.m (^1J = 269), 110.8 t.t (^1J = 269, ^2J = 31), 117.0 d (^2J = 23), 118.3 q.t (^1J = 288, ^2J = 34), 128.0 d (^3J = 9), 131.8 (^4J = 2), 162.2 d (^1J = 250), 172.6, 184.4 t (^2J = 27), 193.0. ^{19}F NMR spectrum, δ_F, ppm: –80.80 (CF_3), –111.52 (CF_2), –111.93 (F), –121.86 (CF_2). Found, %: C 50.46; H 3.59; N 3.31. $C_{18}H_{15}F_8NO_2$. Calculated, %: C 50.36; H 3.52; N 3.26.

3-Benzylamino-5,5-dimethyl-2-trifluoroacetylcyclohex-2-en-1-one (IVg). Yield 93%, mp 62–65°C. IR spectrum, ν, cm^{-1}: 1665, 1605, 1575. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.04 s (6H, CH_3), 2.30 s (2H, CH_2), 2.57 s (2H, CH_2), 4.62 d (2H, CH_2, ^3J = 5.8), 7.27 m (2H, H_{arom}), 7.37 m (3H, H_{arom}), 11.88 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 31.0, 40.6, 47.9, 51.2, 105.3, 117.4 q (^1J = 288), 127.1, 128.5, 129.3, 135.0, 174.1, 179.7 q (^2J = 36), 192.7. ^{19}F NMR spectrum: δ_F –72.51 (CF_3). Found, %: C 62.66; H 5.54; N 4.25. $C_{17}H_{18}F_3NO_2$. Calculated, %: C 62.76; H 5.58; N 4.31.

3-Benzylamino-5,5-dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (IVh). Yield 94%, mp 94–97°C. IR spectrum, ν, cm^{-1}: 1665, 1590, 1565. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.04 s (6H, CH_3), 2.30 s (2H, CH_2), 2.54 s (2H, CH_2), 4.60 d (2H, CH_2, ^3J = 5.7), 7.26 m (3H, H_{arom}), 7.33 m (2H, H_{arom}), 11.71 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 31.1, 40.6, 47.8, 51.1, 106.6, 109.1 t.q (^1J = 269, ^2J = 35), 119.2 q.t (^1J = 288, ^2J = 36), 127.0, 128.5, 129.3, 135.0, 173.8, 183.2 t (^2J = 27), 192.7. ^{19}F NMR spectrum, δ_F, ppm: –79.55 (CF_3), –116.15 (CF_2). Found, %: C 57.71; H 4.89; N 4.80. $C_{18}H_{18}F_5NO_2$. Calculated, %: C 57.60; H 4.83; N 3.73.

3-Benzylamino-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-5,5-dimethylcyclohex-2-en-1-one (IVi). Yield 88%, mp 72–75°C. IR spectrum, ν, cm^{-1}: 1665, 1595, 1575. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.05 s (6H, CH_3), 2.31 s (2H, CH_2), 2.54 s (2H, CH_2), 4.60 d (2H, CH_2, ^3J = 5.9), 7.26 m (3H, H_{arom}), 7.41 m (2H, H_{arom}), 11.58 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.3, 31.2, 40.6, 47.8, 50.9, 106.8, 109.8 t.m (^1J = 269), 110.8 t.t (^1J = 269, ^2J = 31), 118.1 q.t (^1J = 288, ^2J = 34), 127.0, 128.6, 129.4, 134.9, 173.3, 183.7 t (^2J = 26), 192.7. ^{19}F NMR spectrum, δ_F, ppm: –80.83 (CF_3), –111.37 (CF_2), –121.79 (CF_2). Found, %: C 53.73; H 4.21; N 3.23. $C_{19}H_{18}F_7NO_2$. Calculated, %: C 53.65; H 4.27; N 3.29.

3-(4-Fluorobenzylamino)-5,5-dimethyl-2-trifluoroacetylcyclohex-2-en-1-one (IVj). Yield 93%, mp 79–82°C. IR spectrum, ν, cm^{-1}: 1665, 1605, 1580. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.06 s (6H, CH_3), 2.30 s (2H, CH_2), 2.58 s (2H, CH_2), 4.62 d (2H, CH_2, ^3J = 5.7), 7.09 m (2H, H_{arom}), 7.27 m (2H, H_{arom}), 11.84 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 31.0, 40.6, 47.2, 51.2, 105.3, 116.3 d (^2J = 22), 117.4 q (^1J = 288), 129.1 d (^3J = 8), 130.8, 162.6 d (^1J = 248), 174.0, 179.7 q (^2J = 36), 192.7. ^{19}F NMR spectrum, δ_F, ppm: –72.53 (CF_3), –113.40 (F). Found, %: C 59.39; H 4.94; N 4.06. $C_{17}H_{17}F_4NO_2$. Calculated, %: C 59.47; H 4.99; N 4.08.

3-(4-Fluorobenzylamino)-5,5-dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (IVk). Yield 80%, mp 87–90°C. IR spectrum, ν, cm^{-1}: 1650, 1600, 1570. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.05 s (6H, CH_3), 2.31 s (2H, CH_2), 2.55 s

(2H, CH_2), 4.59 d (2H, CH_2, ^3J = 5.7), 7.09 m (2H, H_{arom}), 7.24 m (2H, H_{arom}), 11.66 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.2, 31.1, 40.6, 47.2, 51.1, 106.7, 109.1 t.q (^1J = 271, ^2J = 35), 116.4 d (^2J = 22), 119.2 q.t (^1J = 288, ^2J = 36), 130.0 d (^3J = 8), 130.8 d (^4J = 3), 162.7 d (^1J = 248), 173.7, 183.2 t (^2J = 27), 192.7. ^{19}F NMR spectrum, δ_F, ppm: –79.62 (CF_3), –113.35 (F), –116.22 (CF_2). Found, %: C 54.90; H 4.29; N 3.51. $C_{18}H_{17}F_6NO_2$. Calculated, %: C 54.97; H 4.36; N 3.56.

3-(4-Fluorobenzylamino)-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)-5,5-dimethylcyclohex-2-en-1-one (IVl). Yield 83%, mp 65–68°C. IR spectrum, ν, cm^{-1}: 1660, 1605, 1575. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.07 s (6H, CH_3), 2.33 s (2H, CH_2), 2.54 s (2H, CH_2), 4.59 d (2H, CH_2, ^3J = 5.8), 7.10 m (2H, H_{arom}), 7.25 m (2H, H_{arom}), 11.54 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 28.3, 31.2, 40.6, 47.2, 50.9, 106.8, 109.8 t.m (^1J = 269), 110.8 t.t (^1J = 269, ^2J = 31), 116.4 d (^2J = 22), 118.1 q.t (^1J = 288, ^2J = 34), 128.9 d (^3J = 8), 130.7 d (^4J = 3), 162.7 d (^1J = 248), 173.2, 183.8 t (^2J = 27), 192.7. ^{19}F NMR spectrum, δ_F, ppm: –80.86 (CF_3), –111.41 (CF_2), –113.20 (F), –121.82 m (CF_2). Found, %: C 51.59; H 3.93; N 3.20. $C_{19}H_{17}F_8NO_2$. Calculated, %: C 51.47; H 3.87; N 3.16.

5,5-Dimethyl-3-(pyrrolidin-1-yl)-2-trifluoroacetylcyclohex-2-en-1-one (IVm). Yield 83%, mp 151–154°C. IR spectrum, ν, cm^{-1}: 1690, 1620, 1525. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.09 s (6H, CH_3), 2.02 m (4H, CH_2), 2.27 s (2H, CH_2), 2.55 s (2H, CH_2), 2.76 m (2H, CH_2), 3.65 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 24.6, 25.9, 28.3, 31.1, 44.5, 50.8, 51.5, 55.8, 107.2, 116.3 q (^1J = 290), 166.1, 183.9 q (^2J = 35), 195.0. ^{19}F NMR spectrum: δ_F –73.73 ppm (CF_3). Found, %: C 58.00; H 6.21; N 4.78. $C_{14}H_{18}F_3NO_2$. Calculated, %: C 58.12; H 6.27; N 4.84.

5,5-Dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (IVn). Yield 78%, mp 143–146°C. IR spectrum, ν, cm^{-1}: 1660, 1625, 1520. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.09 s (6H, CH_3), 2.01 m (4H, CH_2), 2.28 s (2H, CH_2), 2.55 s (2H, CH_2), 2.79 m (2H, CH_2), 3.64 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 24.6, 25.9, 28.3, 31.0, 44.9, 51.0, 51.7, 55.6, 107.7 t.q (^1J = 269, ^2J = 35), 108.0, 119.0 q.t (^1J = 288, ^2J = 36), 166.5, 185.9 t (^2J = 27), 194.7. ^{19}F NMR spectrum, δ_F, ppm: –79.42 (CF_3), –115.46 (CF_2). Found, %: C 53.23; H 5.39; N 4.20. $C_{15}H_{18}F_5NO_2$. Calculated, %: C 53.10; H 5.35; N 4.13.

2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-5,5-dimethyl-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (IVo). Yield 79%, mp 87–90°C. IR spectrum, ν, cm^{-1}: 1665, 1630, 1520. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.09 s (6H, CH_3), 2.01 m (4H, CH_2), 2.28 s (2H, CH_2), 2.54 s (2H, CH_2), 2.81 m (2H, CH_2), 3.64 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 24.6, 25.9, 28.4, 31.1, 44.8, 50.9, 51.7, 55.7, 107.8, 109.5 t.t (^1J = 268, ^2J = 31), 109.7 t.m (^1J = 268), 118.0 q.t (^1J = 288, ^2J = 34), 166.2, 186.4 t (^2J = 27), 194.7. ^{19}F NMR spectrum, δ_F, ppm: –81.22 (CF_3), –110.58 (CF_2), –122.37 (CF_2). Found, %: C 49.48; H 4.52; N 3.65. $C_{16}H_{18}F_7NO_2$. Calculated, %: C 49.36; H 4.66; N 3.60.

5,5-Dimethyl-3-piperidino-2-trifluoroacetylcyclohex-2-en-1-one (IVp). Yield 80%, mp 109–112°C. IR spectrum, ν, cm^{-1}: 1665, 1625, 1535. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.13 s (6H, CH_3), 1.75 m (6H, CH_2), 2.28 s (2H, CH_2), 2.53 s (2H, CH_2) 3.36 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 23.2, 26.2, 28.7, 31.5, 44.3, 50.5, 53.3, 106.4, 116.9 q (^1J = 290), 171.8, 179.9 q (^2J = 35), 194.1. ^{19}F NMR spectrum: δ_F –73.17 ppm (CF_3). Found, %: C 59.25; H 6.59; N 4.53. $C_{15}H_{20}F_3NO_2$. Calculated, %: C 59.40; H 6.65; N 4.62.

5,5-Dimethyl-2-(2,2,3,3,3-pentafluoropropanoyl)-3-piperidinocyclohex-2-en-1-one (IVq). Yield 78%, mp 136–139°C. IR spectrum, ν, cm^{-1}: 1655, 1615, 1515. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.13 s (6H, CH_3), 1.74 m (6H, CH_2), 2.30 s (2H, CH_2), 2.52 s (2H, CH_2), 3.37 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 23.3, 26.3, 28.8, 31.4, 44.5, 50.5, 53.2, 107.4, 108.2 t.q (^1J = 271, ^2J = 35), 119.0 q.t (^1J = 288, ^2J = 36), 171.8, 182.7 t (^2J = 27), 193.5. ^{19}F NMR spectrum, δ_F, ppm: –80.06 (CF_3), –117.32 (CF_2). Found, %: C 54.28; H 5.65; N 3.89. $C_{16}H_{20}F_5NO_2$. Calculated, %: C 54.39; H 5.71; N 3.96.

2-(2,2,3,3,4,4,4-Hexafluorobutanoyl)-5,5-dimethyl-3-piperidinocyclohex-2-en-1-one (IVr). Yield 77%, mp 80–83°C. IR spectrum, ν, cm^{-1}: 1670, 1625, 1520. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.12 s (6H, CH_3), 1.73 m (6H, CH_2), 2.28 s (2H, CH_2), 2.51 s (2H, CH_2), 3.36 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 23.3, 26.3, 28.8, 31.5, 44.5, 50.4, 53.1, 107.4, 109.7 t.m (^1J = 268), 109.9 t.t (^1J = 270, ^2J = 30), 118.0 q.t (^1J = 288, ^2J = 35), 171.5, 183.9 t (^2J = 27), 193.4. ^{19}F NMR spectrum, δ_F, ppm: –80.94 (CF_3), –113.02 (CF_2), –123.11 (CF_2). Found, %: C 50.73; H 5.06; N 3.55. $C_{17}H_{20}F_7NO_2$. Calculated, %: C 50.62; H 5.00; N 3.47.

3-Phenylamino-2-trifluoroacetylcyclohex-2-en-1-one (Va). Yield 87%, mp 125–128°C. IR spectrum, ν,

cm^{-1}: 1670, 1620, 1570. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 quint (2H, CH_2, ^3J = 6.4), 2.47 t (2H, CH_2, ^3J = 6.4), 2.63 t (2H, CH_2, ^3J = 6.4), 7.20 m (2H, H_{arom}), 7.40 m (1H, H_{arom}), 7.47 m (2H, H_{arom}), 12.85 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.1, 28.9, 37.8, 106.7, 117.3 q (^1J = 288), 125.9, 128.6, 129.8, 135.9, 174.3, 180.8 q (^2J = 36), 193.4. ^{19}F NMR spectrum: δ_F –72.61 ppm (CF_3). Found, %: C 59.28; H 4.22; N 4.89. $C_{14}H_{12}F_3NO_2$. Calculated, %: C 59.37; H 4.27; N 4.94.

2-(2,2,3,3,3-Pentafluoropropanoyl)-3-phenylaminocyclohex-2-en-1-one (Vb). Yield 88%, mp 109–112°C. IR spectrum, ν, cm^{-1}: 1665, 1600, 1565. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.94 quint (2H, CH_2, ^3J = 6.3), 2.50 t (2H, CH_2, ^3J = 6.3), 2.63 t (2H, CH_2, ^3J = 6.3), 7.20 m (2H, H_{arom}), 7.44 m (3H, H_{arom}), 12.75 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.2, 28.9, 37.8, 107.8, 109.0 t.q (^1J = 271, ^2J = 35), 119.1 q.t (^1J = 288, ^2J = 36), 125.9, 128.6, 129.8, 135.8, 174.1, 184.2 t (^2J = 27), 193.4. ^{19}F NMR spectrum, δ_F, ppm: –79.56 (CF_3), –116.21 (CF_2). Found, %: C 54.17; H 3.70; N 4.26. $C_{15}H_{12}F_5NO_2$. Calculated, %: C 54.06; H 3.63; N 4.20.

2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-3-phenylaminocyclohex-2-en-1-one (Vc). Yield 89%, mp 98–101°C. IR spectrum, ν, cm^{-1}: 1670, 1605, 1570. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.94 quint (2H, CH_2, ^3J = 6.4), 2.49 t (2H, CH_2, ^3J = 6.4), 2.62 t (2H, CH_2, ^3J = 6.4), 7.20 m (2H, H_{arom}), 7.41 m (1H, H_{arom}), 7.47 m (2H, H_{arom}), 12.62 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.2, 28.8, 37.6, 108.0, 109.9 t.m (^1J = 268), 110.7 t.t (^1J = 269, ^2J = 31), 118.1 q.t (^1J = 288, ^2J = 34), 125.9, 128.6, 129.9, 135.8, 173.7, 184.6 t (^2J = 27), 193.5. ^{19}F NMR spectrum, δ_F, ppm: –80.85 (CF_3), –111.49 (CF_2), –121.91 (CF_2). Found, %: C 50.26; H 3.23; N 3.69. $C_{16}H_{12}F_7NO_2$. Calculated, %: C 50.14; H 3.16; N 3.65.

3-(4-Fluorophenylamino)-2-trifluoroacetylcyclohex-2-en-1-one (Vd). Yield 86%, mp 104–107°C. IR spectrum, ν, cm^{-1}: 1670, 1620, 1580. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.94 quint (2H, CH_2, ^3J = 6.3), 2.47 t (2H, CH_2, ^3J = 6.3), 2.60 t (2H, CH_2, ^3J = 6.3), 7.16 m (2H, H_{arom}), 7.23 m (2H, H_{arom}), 12.73 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.1, 28.8, 37.8, 106.8, 116.9 d (^2J = 23), 117.3 q (^1J = 288), 128.0 d (^3J = 9), 132.0 d (^4J = 3), 162.2 d (^1J = 250), 174.7, 180.9 q (^2J = 36), 193.3. ^{19}F NMR spectrum, δ_F, ppm: –72.66 (CF_3), –112.35 (F). Found, %: C 55.70; H 3.61; N 4.59. $C_{14}H_{11}F_4NO_2$. Calculated, %: C 55.82; H 3.68; N 4.65.

3-(4-Fluorophenylamino)-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (Ve). Yield 85%, mp 123–126°C. IR spectrum, ν, cm^{-1}: 1665, 1615, 1570. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 quint (2H, CH_2, ^3J = 6.4), 2.50 t (2H, CH_2, ^3J = 6.4), 2.59 t (2H, CH_2, ^3J = 6.4), 7.18 m (4H, H_{arom}), 12.64 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.1, 28.8, 37.7, 108.0, 108.9 t.q (^1J = 271, ^2J = 35), 116.9 d (^2J = 23), 119.1 q.t (^1J = 288, ^2J = 36), 127.9 d (^3J = 9), 131.8, 162.2 d (^1J = 250), 174.3, 184.4 t (^2J = 28), 193.2. ^{19}F NMR spectrum, δ_F, ppm: –79.61 (CF_3), –112.06 (F), –116.29 (CF_2). Found, %: C 51.17; H 3.11; N 3.92. $C_{15}H_{11}F_6NO_2$. Calculated, %: C 51.29; H 3.16; N 3.99.

3-(4-Fluorophenylamino)-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)cyclohex-2-en-1-one (Vf). Yield 86%, mp 56–59°C. IR spectrum, ν, cm^{-1}: 1665, 1620, 1560. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 quint (2H, CH_2, ^3J = 6.3), 2.49 t (2H, CH_2, ^3J = 6.3), 2.59 t (2H, CH_2, ^3J = 6.3), 7.19 m (4H, H_{arom}), 12.50 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 20.1, 28.7, 37.5, 108.1, 109.9 t.m (^1J = 268), 110.7 t.t (^1J = 269, ^2J = 31), 116.9 d (^2J = 23), 118.2 q.t (^1J = 288, ^2J = 35), 128.0 d (^3J = 9), 131.8 d (^4J = 2), 162.2 d (^1J = 250), 174.0, 184.8 t (^2J = 26), 193.4. ^{19}F NMR spectrum, δ_F, ppm: –80.87 (CF_3), –111.60 (CF_2), –112.18 (F), –121.99 (CF_2). Found, %: C 47.75; H 2.70; N 3.42. $C_{16}H_{11}F_8NO_2$. Calculated, %: C 47.89; H 2.76; N 3.49.

3-Benzylamino-2-trifluoroacetylcyclohex-2-en-1-one (Vg). Yield 90%, mp 67–69°C. IR spectrum, ν, cm^{-1}: 1670, 1600, 1580. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.97 quint (2H, CH_2, ^3J = 6.4), 2.42 t (2H, CH_2, ^3J = 6.4), 2.69 t (2H, CH_2, ^3J = 6.4), 4.61 d (2H, CH_2, ^3J = 5.8), 7.27 m (2H, H_{arom}), 7.38 m (3H, H_{arom}), 11.80 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.5, 27.4, 37.4, 47.9, 106.3, 117.3 q (^1J = 287), 127.2, 128.6, 129.4, 134.8, 175.0, 180.4 q (^2J = 36), 193.0. ^{19}F NMR spectrum: δ_F –72.76 ppm (CF_3). Found, %: C 60.76; H 4.82; N 4.79. $C_{15}H_{14}F_3NO_2$. Calculated, %: C 60.61; H 4.75; N 4.71.

3-Benzylamino-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (Vh). Yield 89%, mp 70–73°C. IR spectrum, ν, cm^{-1}: 1660, 1595, 1575. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.97 quint (2H, CH_2, ^3J = 6.4), 2.42 t (2H, CH_2, ^3J = 6.4), 2.67 t (2H, CH_2, ^3J = 6.4), 4.60 d (2H, CH_2, ^3J = 5.8), 7.26 m (2H, H_{arom}), 7.37 m (3H, H_{arom}), 11.60 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.5, 27.4, 37.3, 47.9, 107.6, 109.0 t.q (^1J = 271, ^2J = 35), 119.1 q.t (^1J = 288, ^2J = 36), 127.1, 128.6, 129.4, 134.9, 174.9, 183.8 t

(^2J = 27), 193.2. ^{19}F NMR spectrum, δ_F, ppm: –79.57 (CF_3), –116.21 (CF_2). Found, %: C 55.48; H 4.11; N 4.10. $C_{16}H_{14}F_5NO_2$. Calculated, %: C 55.34; H 4.06; N 4.03.

3-Benzylamino-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)cyclohex-2-en-1-one (Vi). Yield 88%, mp 80–83°C. IR spectrum, ν, cm^{-1}: 1665, 1595, 1575. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.97 quint (2H, CH_2, ^3J = 6.4), 2.39 t (2H, CH_2, ^3J = 6.4), 2.67 t (2H, CH_2, ^3J = 6.4), 4.59 d (2H, CH_2, ^3J = 5.8), 7.25 m (2H, H_{arom}), 7.37 m (3H, H_{arom}), 11.46 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.6, 27.3, 37.1, 47.9, 107.6, 109.9 t.m (^1J = 268), 110.7 t.t (^1J = 269, ^2J = 31), 118.1 q.t (^1J = 288, ^2J = 34), 127.2, 128.6, 129.4, 134.9, 174.6, 184.2 t (^2J = 26), 193.3. ^{19}F NMR spectrum, δ_F, ppm: –80.90 (CF_3), –111.55 (CF_2), –121.91 (CF_2). Found, %: C 51.30; H 3.49; N 3.46. $C_{17}H_{14}F_7NO_2$. Calculated, %: C 51.39; H 3.55; N 3.53.

3-(4-Fluorobenzylamino)-2-trifluoroacetylcyclohex-2-en-1-one (Vj). Yield 92%, mp 133–135°C. IR spectrum, ν, cm^{-1}: 1660, 1620, 1585. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.99 quint (2H, CH_2, ^3J = 6.4), 2.44 t (2H, CH_2, ^3J = 6.4), 2.69 t (2H, CH_2, ^3J = 6.4), 4.59 d (2H, CH_2, ^3J = 5.7), 7.10 m (2H, H_{arom}), 7.26 m (2H, H_{arom}), 11.75 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.6, 27.4, 37.4, 47.3, 106.5, 116.4 d (^2J = 22), 117.3 q (^1J = 287), 129.1 d (^3J = 8), 130.6 d (^4J = 3), 162.7 d (^1J = 248), 174.8, 180.7 q (^2J = 36), 192.8. ^{19}F NMR spectrum, δ_F, ppm: –72.76 (CF_3), –113.15 (F). Found, %: C 57.27; H 4.22; N 4.51. $C_{15}H_{13}F_4NO_2$. Calculated, %: C 57.15; H 4.16; N 4.44.

3-(4-Fluorobenzylamino)-2-(2,2,3,3,3-pentafluoropropanoyl)cyclohex-2-en-1-one (Vk). Yield 93%, mp 69–72°C. IR spectrum, ν, cm^{-1}: 1660, 1595, 1515. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.99 quint (2H, CH_2, ^3J = 6.4), 2.42 t (2H, CH_2, ^3J = 6.4), 2.68 t (2H, CH_2, ^3J = 6.4), 4.59 d (2H, CH_2, ^3J = 5.7), 7.09 m (2H, H_{arom}), 7.26 m (2H, H_{arom}), 11.55 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.5, 27.4, 37.3, 47.2, 107.6, 108.9 t.q (^1J = 271, ^2J = 35), 116.4 d (^2J = 22), 119.1 q.t (^1J = 288, ^2J = 36), 129.1 d (^3J = 8), 130.7 d (^4J = 2), 162.7 d (^1J = 250), 174.8, 183.9 t (^2J = 27), 193.1. ^{19}F NMR spectrum, δ_F, ppm: –79.63 (CF_3), –113.30 (F), –116.26 (CF_2). Found, %: C 52.49; H 3.51; N 3.79. $C_{16}H_{13}F_6NO_2$. Calculated, %: C 52.61; H 3.59; N 3.83.

3-(4-Fluorobenzylamino)-2-(2,2,3,3,4,4,4-heptafluorobutanoyl)cyclohex-2-en-1-one (Vl). Yield 90%, mp 69–72°C. IR spectrum, ν, cm^{-1}: 1665, 1580, 1515. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.00 quint (2H, CH_2, ^3J = 6.4), 2.42 t (2H, CH_2, ^3J = 6.4), 2.68 t (2H, CH_2, ^3J = 6.4), 4.59 d (2H, CH_2, ^3J = 5.7), 7.09 m (2H, H_{arom}), 7.26 m (2H, H_{arom}), 11.43 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.6, 27.3, 37.1, 47.2, 107.7, 109.9 t.m (^1J = 269), 110.7 t.t (^1J = 269, ^2J = 30), 116.4 d (^2J = 22), 118.1 q.t (^1J = 288, ^2J = 35), 129.1 d (^3J = 8), 130.7 d (^4J = 3), 162.7 d (^1J = 248), 174.4, 184.4 t (^2J = 26), 193.2. ^{19}F NMR spectrum, δ_F, ppm: –80.92 (CF_3), –111.59 (CF_2), –113.31 (F), –121.96 (CF_2). Found, %: C 49.31; H 3.22; N 3.46. $C_{17}H_{13}F_8NO_2$. Calculated, %: C 49.17; H 3.16; N 3.37.

3-(Pyrrolidin-1-yl)-2-trifluoroacetylcyclohex-2-en-1-one (Vm). Yield 80%, mp 103–105°C. IR spectrum, ν, cm^{-1}: 1655, 1625, 1525. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 quint (2H, CH_2, ^3J = 6.3), 2.04 m (4H, CH_2), 2.36 t (2H, CH_2, ^3J = 6.3), 2.73 t (2H, CH_2, ^3J = 6.3), 2.80 m (2H, CH_2), 3.66 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.8, 24.6, 25.8, 31.3, 37.5, 51.4, 55.9, 108.0, 116.5 q (^1J = 290), 167.9, 182.9 q (^2J = 35), 195.1. ^{19}F NMR spectrum: δ_F –73.65 ppm (CF_3). Found, %: C 55.31; H 5.47; N 5.45. $C_{12}H_{14}F_3NO_2$. Calculated, %: C 55.17; H 5.40; N 5.36.

2-(2,2,3,3,3-Pentafluoropropanoyl)-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (Vn). Yield 79%, mp 102–105°C. IR spectrum, ν, cm^{-1}: 1650, 1625, 1515. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 quint (2H, CH_2, ^3J = 6.4), 2.02 m (4H, CH_2), 2.37 t (2H, CH_2, ^3J = 6.4), 2.71 t (2H, CH_2, ^3J = 6.4), 2.81 m (2H, CH_2), 3.64 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.7, 24.6, 25.9, 31.6, 37.7, 51.5, 55.7, 108.8, 108.9 t.q (^1J = 269, ^2J = 35), 119.0 q.t (^1J = 288, ^2J = 36), 168.2, 185.1 t (^2J = 28), 194.8. ^{19}F NMR spectrum, δ_F, ppm: –79.12 (CF_3), –115.37 (CF_2). Found, %: C 50.02; H 4.48; N 4.43. $C_{13}H_{14}F_5NO_2$. Calculated, %: C 50.17; H 4.53; N 4.50.

2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (Vo). Yield 77%, mp 105–108°C. IR spectrum, ν, cm^{-1}: 1655, 1610, 1535. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.96 quint (2H, CH_2, ^3J = 6.4), 2.02 m (4H, CH_2), 2.38 t (2H, CH_2, ^3J = 6.4), 2.72 t (2H, CH_2, ^3J = 6.4), 2.83 m (2H, CH_2), 3.66 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.8, 24.6, 25.9, 31.5, 37.5, 51.6, 55.8, 108.7, 109.7 t.m (^1J = 269), 109.7 t.t (^1J = 268, ^2J = 31), 118.1 q.t (^1J = 288, ^2J = 35), 167.9, 185.9 t (^2J = 27), 194.8. ^{19}F NMR spectrum, δ_F, ppm: –81.18 (CF_3), –110.70 (CF_2), –122.32 (CF_2). Found, %: C 46.69; H 3.98; N 3.96. $C_{14}H_{14}F_7NO_2$. Calculated, %: C 46.55; H 3.91; N 3.88.

3-Piperidino-2-trifluoroacetylcyclohex-2-en-1-one (Vp). Yield 79%, mp 87–90°C. IR spectrum, ν, cm^{-1}: 1670, 1630, 1560. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.76 m (6H, CH_2), 1.96 quint (2H, CH_2, ^3J = 6.3), 2.32 t (2H, CH_2, ^3J = 6.3), 2.73 t (2H, CH_2, ^3J = 6.3), 3.41 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.0, 23.2, 26.0, 31.0, 37.0, 53.3, 106.8, 117.2 q (^1J = 290), 173.2, 178.1 q (^2J = 35), 194.5. ^{19}F NMR spectrum: δ –73.05 ppm (CF_3). Found, %: C 56.60; H 5.79; N 5.01. $C_{13}H_{16}F_3NO_2$. Calculated, %: C 56.72; H 5.86; N 5.09.

2-(2,2,3,3,3-Pentafluoropropanoyl)-3-piperidinocyclohex-2-en-1-one (Vq). Yield 76%, mp 104–107°C. IR spectrum, ν, cm^{-1}: 1645, 1625, 1520. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.75 m (6H, CH_2), 1.97 quint (2H, CH_2, ^3J = 6.4), 2.34 t (2H, CH_2, ^3J = 6.4), 2.72 t (2H, CH_2, ^3J = 6.4), 3.43 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 18.9, 23.2, 26.1, 31.1, 37.1, 53.2, 107.7, 108.5 t.q (^1J = 272, ^2J = 35), 119.0 q.t (^1J = 288, ^2J = 36), 173.1, 180.6 t (^2J = 27), 193.9. ^{19}F NMR spectrum, δ_F, ppm: –80.30 (CF_3), –117.39 (CF_2). Found, %: C 51.57; H 4.90; N 4.24. $C_{14}H_{16}F_5NO_2$. Calculated, %: C 51.70; H 4.96; N 4.31.

2-(2,2,3,3,4,4,4-Heptafluorobutanoyl)-3-piperidinocyclohex-2-en-1-one (Vr). Yield 73%, mp 85–88°C. IR spectrum, ν, cm^{-1}: 1660, 1615, 1535. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.75 m (6H, CH_2), 1.97 quint (2H, CH_2, ^3J = 6.4), 2.35 t (2H, CH_2, ^3J = 6.4), 2.72 t (2H, CH_2, ^3J = 6.4), 3.42 m (4H, CH_2). ^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz): 19.1, 23.3, 26.0, 31.0, 36.9, 53.1, 107.8, 109.6 t.m (^1J = 268), 110.2 t.t (^1J = 270, ^2J = 31), 118.0 q.t (^1J = 289, ^2J = 35), 172.8, 181.9 t (^2J = 26), 193.9. ^{19}F NMR spectrum, δ_F, ppm: –80.51 (CF_3), –112.98 (CF_2), –123.03 (CF_2). Found, %: C 48.16; H 4.38; N 3.80. $C_{15}H_{16}F_7NO_2$. Calculated, %: C 48.01; H 4.30; N 3.73.

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