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Regioselective Reduction of 2-Perfluoroalkanoylcyclohexane-1,3-diones and Their Enamino Derivatives

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Abstract—Ionic hydrogenation of 2-perfluoroalkanoylcyclohexane-1,3-diones and their endocyclic enamino derivatives containing a secondary amino group by the action of triethylsilane in trifluoroacetic acid in the presence of a catalytic amount of lithium perchlorate involved regioselective reduction of the side-chain carbonyl group to hydroxy with formation of the corresponding hydroxy diketones and hydroxy amino ketones, respectively. Under analogous conditions endocyclic enamino derivatives possessing a tertiary amino group underwent deacylation to give enamino ketones.

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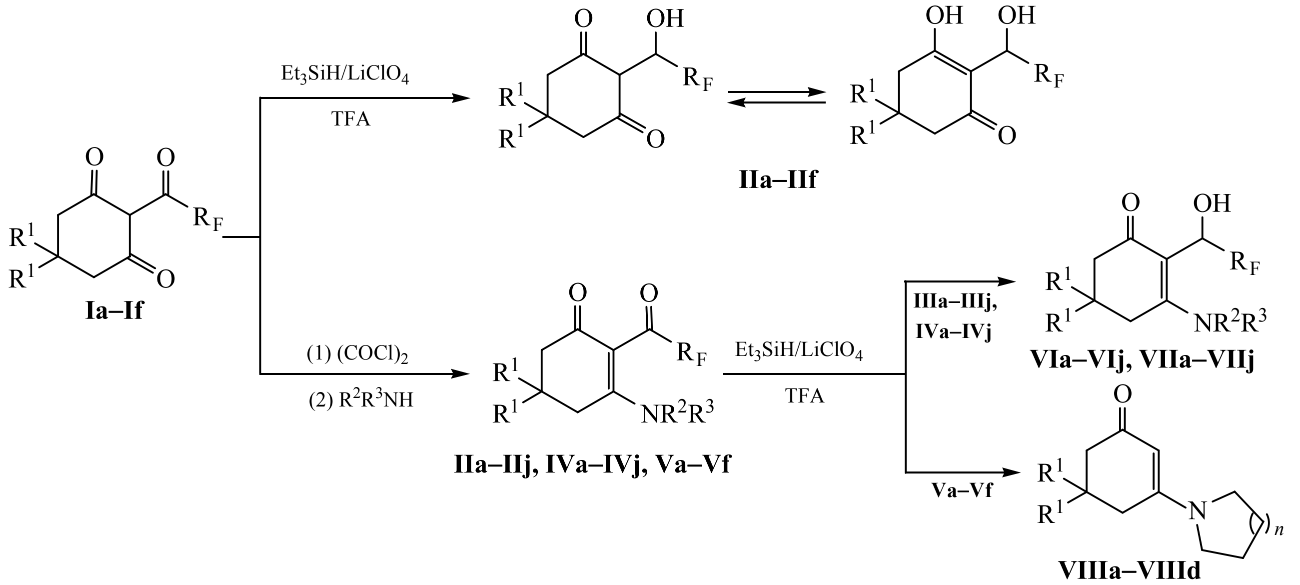
Due to the presence of polyfunctional β-tricarbonyl group 2-perfluoroalkanoylcyclohexane-1,3-diones are effective as building blocks in the synthesis of polyfluoroalkyl-containing carbo- and heterocyclic structures [1–3]. It is known that products of selective reduction of carbonyl group in cyclic β,β′-triketones and their derivatives are widely used in organic synthesis, in particular in syntheses of naturally occurring and related compounds [4, 5]. Catalytic hydrogenation of non-fluorinated 2-acylcycloalkane-1,3-diones is characterized by low selectivity; reduction products of both side-chain carbonyl group and one endocyclic carbonyl group are formed [6]. On the other hand, ionic hydrogenation conditions [7] ensured regioselective reduction of the side-chain carbonyl group to methylene group in both 2-acylcycloalkane-1,3-diones and their endocyclic enamino derivatives [8, 9], and this approach was followed in the synthesis of prostaglandins and phytoprostanes [10–13]. Taking into account specificity of fluorine, introduction of fluorine atoms into molecules of the above compounds could dramatically affect their physical, chemical, and biological properties [14]. In continuation of our studies on chemical modification of 2-perfluoroalkanoylcyclohexane-1,3-diones in the present work we examined their reductive transformations and analogous transformations of their endocyclic enamino derivatives, as well as the effect of fluorine atoms on the reaction direction and yield.

The behavior of 2-perfluoroalkanoylcyclohexane-1,3-diones **Ia**–**If** and their enamino derivatives at the endocyclic carbonyl group was examined under ionic hydrogenation conditions. We found that triethylsilane in trifluoroacetic acid in the presence of lithium perchlorate selectively reduces the exocyclic (side-chain perfluoroalkanoyl) carbonyl group to hydroxy [15]. Ionic hydrogenation of 2-perfluoroalkanoylcyclohexane-1,3-diones **Ia**–**If** was performed at room temperature (reaction time 5 h), and the yields of hydroxy diketones **IIa**–**IIf** thus obtained were 80–95% (Scheme 1). Increase of the reaction time to 24 h and more did not result in further reduction of compounds **IIa**–**IIf**.

By treatment of 2-perfluoroalkanoylcyclohexane-1,3-diones **Ia**–**If** with oxalyl chloride and subsequent vinylogous substitution in the resulting 3-chloro-2-perfluoroalkanoylcyclohex-2-en-1-ones by the action of primary and secondary amines we obtained in high yield enamino diketones **IIIa**–**IIIj**, **IVa**–**IVj**, and **Va**–**Vf** [3]. The behavior of secondary (**IIIa**–**IIIj**, **IVa**–**IVj**) and tertiary (**Va**–**Vf**) enamino derivatives under analogous ionic hydrogenation conditions was studied. Compounds **IIIa**–**IIIj** and **IVa**–**IVj** containing a secondary amino group were regioselectively reduced to polyfluoroalkyl-substituted enamino hydroxy ketones **VIa**–**VIj** and **VIIa**–**VIIj**, whereas enamino diketones **Va**–**Vf** having a tertiary amino group underwent

Scheme 1.



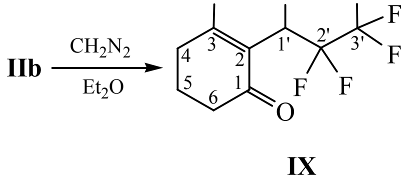
I, **II**, R^1 = H: R$_F$ = CF$_3$ (**a**), C$_2$F$_5$ (**b**), C$_3$F$_7$ (**c**); R^1 = Me: R$_F$ = CF$_3$ (**d**), C$_2$F$_5$ (**e**), C$_3$F$_7$ (**f**); **III, IV, VI, VII**, R^2 = H: R^3 = Ph, R$_F$ = CF$_3$ (**a**), C$_2$F$_5$ (**b**), C$_3$F$_7$ (**c**); R^3 = 4-FC$_6$H$_4$, R$_F$ = CF$_3$ (**d**), C$_2$F$_5$ (**e**), C$_3$F$_7$ (**f**); R^3 = C$_6$H$_5$CH$_2$, R$_F$ = CF$_3$ (**g**), C$_2$F$_5$ (**h**), C$_3$F$_7$ (**i**); R^3 = 4-FC$_6$H$_4$CH$_2$, R$_F$ = CF$_3$ (**j**); **III, VI**, R^1 = H; **IV, VII**, R^1 = Me; **V**, R^1 = H: R$_F$ = CF$_3$, R^{2}R^3 = (CH$_2$)$_4$ (**a**); R$_F$ = C$_2$F$_5$, R^{2}R^3 = (CH$_2$)$_4$ (**b**); R$_F$ = C$_3$F$_7$, R^{2}R^3 = (CH$_2$)$_4$ (**c**); R^1 = Me: R$_F$ = CF$_3$, R^{2}R^3 = (CH$_2$)$_5$ (**d**); R$_F$ = C$_2$F$_5$, R^{2}R^3 = (CH$_2$)$_5$ (**e**); R$_F$ = C$_3$F$_7$, R^{2}R^3 = (CH$_2$)$_5$ (**f**); **VIII**, R^1 = H: *n* = 1 (**a**), 2 (**b**); R^1 = Me: *n* = 1 (**c**), 2 (**d**).

deacylation to enamino ketones **VIIIa–VIIId**. Deacylation was also observed previously [9] in the course of ionic hydrogenation of endocyclic enamino derivatives of non-fluorinated β,β′-triketones [9].

The structure of the newly synthesized compounds was confirmed by their elemental analysis and IR and ^{1}H, ^{13}C, and ^{19}F NMR spectra. Previously described compounds were identified by comparison of their spectral parameters with published data. The IR spectra of hydroxy diketones **IIa**–**IIf** contained absorption bands belonging to stretching vibrations of the hydroxy group and conjugated carbonyl group and double bond in the regions 3410–3440, 1605–1615, and 1555–1585 cm^{-1}, respectively. In the ^{13}C NMR spectra of trifluoromethyl derivatives **IIa** and **IId**, the C–OH carbon atom appeared as a quartet at δ_C 67.7 and 67.4 ppm ($^2J_{CF}$ = 32 Hz), and the corresponding signal of pentafluoroethyl (**IIb**, **IIe**) and hexafluoropropyl derivatives (**IIc**, **IIf**) was a doublet of doublets at δ_C 67.8 (J_{CF} = 27, 23 Hz), 66.8 (J_{CF} = 28, 23 Hz) and 66.8 (J_{CF} = 29, 23 Hz), 66.5 ppm (J_{CF} = 28, 22 Hz), respectively. Hydroxy diketones **IIa** and **IId** displayed in the ^{19}F NMR spectra a signal from fluorine atoms in the trfluoromethyl group at δ_F –76.86 ($^3J_{FH}$ = 7 Hz) and –76.68 ppm ($^3J_{FH}$ = 7 Hz), respectively. Compounds **IIb–IIf** with a longer perfluoroalkyl chain were characterized by a complex ^{19}F NMR spectral pattern due to magnetic nonequivalence of fluorine atoms in the CF$_2$ groups.

In the ^{1}H NMR spectra of hydroxy diketones **IIa**–**IIf** we observed neither enol nor hydroxy proton signal, obviously because of fast exchange. Therefore, additional proofs for the assumed structure of these compounds were necessary. For this purpose, compound **IIb** was subjected to exhaustive methylation using a large excess of diazomethane. As a result, we isolated 90% of dimethoxy derivative **IX** (Scheme 2). Its formation seemed to be somewhat surprising taking into account that diazomethane generally does not alkylate alcoholic hydroxy groups in the absence of

Scheme 2.



IX

catalyst. Presumably, strong electron-withdrawing perfluoroalkyl group reduces the electron density on the oxygen atom and enhances the reactivity of the OH proton.

The structure dimethoxy derivative **IX** was examined by two-dimensional NMR spectroscopy. Quaternary carbon atoms were identified by analysis of their long-range couplings using HMBC technique. Although perfluorinated $C^{2'}$ and $C^{3'}$ carbon atoms displayed no cross peaks, they can be readily identified by coupling with fluorine nuclei. The CF_2 carbon atom gave a triplet of quartets at δ_C 113.08 ppm ($^1J = 259$, $^2J = 36$ Hz), and the CF_3 signal was a quartet of triplets at δ_C 118.99 ppm ($^1J = 287$, $^2J = 36$ Hz). The carbonyl carbon atom C^1 (δ_C 198.30 ppm) displayed a strong coupling with protons on C^6 and less intense cross peaks with protons on C^4 and C^5. The C^3 carbon atom (δ_C 180.72 ppm) showed strong cross peaks with protons in the methoxy group attached thereto and protons on C^4 and a weak cross peak with protons on C^5. The C^2 atom (δ_c 108.42 ppm) displayed couplings with protons on C^4 and C^6. Due to coupling with fluorine the $C^{1'}$ atom gave a triplet at δ_C 71.68 ppm ($^2J = 24$ Hz) in the ^{13}C NMR spectrum, and the HMBC spectrum contained a weak cross peak with protons in the methoxy group on $C^{1'}$.

In the IR spectra of hydroxy enamino ketones **VIa**–**VIj** and **VIIa**–**VIIj** we observed absorption bands typical of hydroxy group and conjugated carbonyl group and double bond in the regions 3290–3420, 1625–1690, and 1565–1585 cm^{-1}, respectively. In the ^1H NMR spectra of **VIa**–**VIj** and **VIIa**–**VIIj**, the NH proton is involved in intramolecular hydrogen bond with the OH group, and its signal appears in a weak field, at δ 9.29–10.48 ppm. Trifluoromethyl derivatives **VIa**, **VId**, **VIg**, **VIj**, **VIIa**, **VIId**, **VIIg**, and **VIIj** displayed in the ^{13}C NMR spectra a quartet at δ_C 66.0–66.4 ppm ($^2J_{CF} = 33$ Hz) from the C–OH carbon atom, and analogous signal of perfluoroethyl (**VIb**, **VIe**, **VIh**, **VIIb**, **VIIe**, **VIIh**) and perfluoropropyl derivatives (**VIc**, **VIf**, **VIi**, **VIIc**, **VIIf**, **VIIi**) was a doublet of doublets at δ_C 64.7–65.4 ppm ($J_{CF} = 27$–28, 22–23 Hz). The ^{19}F NMR spectra of **VIa**, **VId**, **VIg**, **VIj**, **VIIa**, **VIId**, **VIIg**, and **VIIj** indicated spin–spin coupling between fluorine atoms in the trifluoromethyl group and proton on the tertiary carbon atom: the CF_3 group gave a doublet at δ_F –77.70–78.24 ppm ($^3J_{F-H}$ 48 Hz). The ^{19}F NMR spectra of hydroxy enamino alcohols with a longer perfluorinated side chain showed a complex pattern.

Thus, unlike fluorine-free cyclic β,β-triketones, the reduction of 2-perfluoroacylcyclohexane-1,3-diones **Ia**–**If** and their secondary endocyclic enamino derivatives **IIIa**–**IIIj** and **IVa**–**IVj** under ionic hydrogenation conditions selectively gives hydroxy diketones **IIa**–**IIf** and hydroxy enamino ketones **VIa**–**VIj** and **VIIa**–**VIIj**, respectively; the reaction direction may be rationalized in terms of the effect of electron-withdrawing perfluoroalkyl substituent.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker Avance-500 spectrometer at 500 (^1H), 125 (^{13}C), and 470 MHz (^{19}F) from solutions in $CDCl_3$ unless otherwise stated; the chemical shifts were determined relative to tetramethylsilane (^1H, ^{13}C) or CCl_3F (^{19}F) as internal reference. The IR spectra were measured in KBr on a UR-20 spectrometer. The melting points were determined on a Boetius melting point apparatus. Initial 2-perfluoroalkanoylcyclohexane-1,3-diones **Ia**–**If** were synthesized according to the procedure reported in [16], and enamino derivatives **IIIa**–**IIIj**, **IVa**–**IVj**, and **Va**–**Vf** were obtained as described in [3]. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent.

Reduction of 2-perfluoroalkanoylcyclohexane-1,3-diones Ia–If and their enamino derivatives IIIa–IIIj, IVa–IVj, and Va–Vf (*general procedure*). Compound **Ia**–**If**, **IIIa**–**IIIj**, **IVa**–**IVj**, or **Va**–**Vf**, 1 mmol, was dissolved in 2 ml of trifluoroacetic acid, 2 ml of a 1% solution of lithium perchlorate in trifluoroacetic acid and 4 mmol of triethylsilane were added, and the mixture was stirred for 5 h at room temperature. Trifluoroacetic acid was distilled off under reduced pressure, the residue was washed with a small amount of *n*-hexane (4 × 4 ml) and treated with chloroform, the solution was filtered, and the solvent was removed to isolate compounds **IIa**–**IIf**, **VIa**–**VIj**, **VIIa**–**VIIj**, and **VIIIa**–**VIIId**. Hydroxy diketones **IIa**–**IIf** were purified by recrystallization from acetone–hexane, and hydroxy enamino ketones **VIa**–**VIj** and **VIIa**–**VIIj** were recrystallized from diethyl ether–hexane.

The physical constants and spectral parameters of 5,5-dimethyl-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohexane-1,3-dione (**IId**) [15], 5,5-dimethyl-2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohexane-1,3-dione (**IIe**) [15], 3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (**VIIIa**) [17], 3-piperidinocyclohex-2-en-1-one (**VIIIb**)

[18], 5,5-dimethyl-3-(pyrrolidin-1-yl)cyclohex-2-en-1-one (**VIIIc**) [19], and 5,5-dimethyl-3-piperidinocyclohex-2-en-1-one (**VIIId**) [20] were consistent with published data.

2-(2,2,2-Trifluoro-1-hydroxyethyl)cyclohexane-1,3-dione (IIa). Yield 88%, mp 89–92°C. IR spectrum, ν, cm^{-1}: 3410, 1610, 1585. ^1H NMR spectrum, δ, ppm: 2.00 q (2H, CH_2, ^3J = 6.5 Hz), 2.44 d. t (2H, CH_2, ^2J = 17.9, ^3J = 6.5 Hz), 2.50 d.t (2H, CH_2, ^2J = 17.4, ^3J = 6.5 Hz), 5.47 m (1H, C**H**OH). ^{13}C NMR spectrum (pyridine-*d*$_5$), δ_C, ppm: 21.0, 34.1, 67.7 q ($^2J_{CF}$ = 32 Hz), 107.4, 127.0 q (^1J = 285 Hz), 190.3. ^{19}F NMR spectrum (pyridine-*d*$_5$): δ_F –77.86 ppm (3F, CF_3, $^3J_{FH}$ = 7 Hz). Found, %: C 45.81; H 4.38. $C_8H_9F_3O_3$. Cal=culated, %: C 45.72; H 4.32.

2-(2,2,3,3,3-Pentafluoro-1-hydroxypropyl)cyclohexane-1,3-dione (IIb). Yield 92%, mp 93–96°C. IR spectrum, ν, cm^{-1}: 3425, 1605, 1555. ^1H NMR spectrum, δ, ppm: 2.00 q (2H, CH_2, ^3J = 6.3 Hz), 2.46 d.t (2H, CH_2, ^2J = 17.9, ^3J = 6.3 Hz), 2.51 d.t (2H, CH_2, ^2J = 17.7, ^3J = 6.3 Hz), 5.56 m (1H, C**H**OH). ^{13}C NMR spectrum (pyridine-*d*$_5$), δ_C, ppm: 21.1, 34.2, 67.8 d.d (J_{CF} = 27, 23 Hz), 106.8, 120.6 q.t (^1J = 288, ^2J = 36 Hz), 115.7 t.q (^1J = 258, ^2J = 34 Hz), 191.1. ^{19}F NMR spectrum (pyridine-*d*$_5$), δ_F, ppm: –81.6 s (3F, CF_3), –121.4 d (1F, $^2J_{FF}$ = 268 Hz), –129.1 d.d (1F, $^2J_{FF}$ = 269, $^3J_{FH}$ = 22 Hz). Found, %: C 41.62; H 3.53. $C_9H_9F_5O_3$. Calculated, %: C 41.55; H 3.49.

2-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutyl)cyclohexane-1,3-dione (IIc). Yield 95%, mp 72–75°C. IR spectrum, ν, cm^{-1}: 3435, 1605, 1555. ^1H NMR spectrum, δ, ppm: 2.00 q (2H, CH_2, ^3J = 6.1 Hz), 2.45 d.t (2H, CH_2, ^2J = 17.8, ^3J = 6.1 Hz), 2.51 d.t (2H, CH_2, ^2J = 17.7, ^3J = 6.1 Hz), 5.63 m (1H, C**H**OH). ^{13}C NMR spectrum (pyridine-*d*$_5$), δ_C, ppm: 21.0, 34.1, 66.8 d.d (J_{CF} = 29, 22 Hz), 106.8, 110.6 t.m (^1J = 266 Hz), 117.0 t.t (^1J = 260, ^2J = 29 Hz), 118.8 q.t (^1J = 288, ^2J = 34 Hz), 190.7. ^{19}F NMR spectrum (pyridine-*d*$_5$), δ_F, ppm: –79.95 s (3F, CF_3), –117.32 d.d (1F, $^2J_{FF}$ = 276, $^3J_{FH}$ = 4 Hz), –123.28 d (1F, $^2J_{FF}$ = 289 Hz), –125.47 d.m (1F, $^2J_{FF}$ = 276 Hz), –126.23 d (1F, $^2J_{FF}$ = 290 Hz). Found, %: C 38.65; H 2.90. $C_{10}H_9F_7O_3$. Calculated, %: C 38.72; H 2.92.

2-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutyl)-5,5-dimethylcyclohexane-1,3-dione (IIf). Yield 93%, mp 102–105°C. IR spectrum, ν, cm^{-1}: 3440, 1610, 1565. ^1H NMR spectrum (pyridine-*d*$_5$), δ, ppm: 1.09 s (6H, CH_3), 2.32 d (2H, CH_2, ^2J = 17.5 Hz), 2.36 d (2H, CH_2, ^2J = 17.5 Hz), 5.62 m (1H, C**H**OH). ^{13}C NMR spectrum (pyridine-*d*$_5$), δ_C, ppm: 27.7, 31.7, 47.4, 66.5 d.d (J_{CF} = 28, 22 Hz), 105.6, 110.3 t.m (^1J = 265 Hz), 116.8 t.t (^1J = 259, ^2J = 30 Hz), 118.5 q.t (^1J = 288, ^2J = 35 Hz), 189.1. ^{19}F NMR spectrum (pyridine-*d*$_5$), δ_F, ppm: –81.1 s (3F, CF_3), –118.2 d (1F, $^2J_{FF}$ = 277 Hz), –125.1 d (1F, $^2J_{FF}$ = 290 Hz), –126.6 d.m (1F, $^2J_{FF}$ = 279 Hz), –127.4 d.d (1F, $^2J_{FF}$ = 291, $^3J_{FH}$ = 6 Hz). Found, %: C 42.51; H 3.84. $C_{12}H_{13}F_7O_3$. Calculated, %: C 42.59; H 3.88.

3-Phenylamino-2-(2,2,2-trifluoro-1-hydroxyethyl)-cyclohex-2-en-1-one (VIa). Yield 75%, mp 169–172°C. IR spectrum, ν, cm^{-1}: 3320, 1675, 1565. ^1H NMR spectrum, δ, ppm: 1.90 m (2H, CH_2), 2.58 m (4H, CH_2), 5.73 m (1H, C**H**OH), 7.16 m (2H, H_{arom}), 7.36 m (1H, H_{arom}), 7.42 m (2H, H_{arom}), 10.32 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.6, 27.9, 32.5, 66.3 q (^2J = 33 Hz), 102.4, 125.4 q (^1J = 283 Hz), 125.7, 128.4, 129.8, 136.1, 173.5, 193.3. ^{19}F NMR spectrum: δ_F –78.01 ppm, d (3F, CF_3, $^3J_{FH}$ = 5 Hz). Found, %: C 58.85; H 4.91; N 4.85. $C_{14}H_{14}F_3NO_2$. Calculated, %: C 58.95; H 4.95; N 4.91.

2-(2,2,3,3,3-Pentafluoro-1-hydroxypropyl)-3-phenylaminocyclohex-2-en-1-one (VIb). Yield 77%, mp 92–95°C. IR spectrum, ν, cm^{-1}: 3310, 1675, 1565. ^1H NMR spectrum, δ, ppm: 1.89 m (2H, CH_2), 2.59 m (4H, CH_2), 5.90 m (1H, C**H**OH), 7.57 m (2H, H_{arom}), 7.39 m (3H, H_{arom}), 10.48 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.4, 28.0, 32.3, 65.2 d.d (J_{CF} = 28, 23 Hz), 102.2, 114.6 t.q (^1J = 256, ^2J = 35 Hz), 119.2 q.t (^1J = 287, ^2J = 36 Hz), 125.8, 128.6, 129.9, 136.0, 174.6, 193.0. ^{19}F NMR spectrum, δ_F, ppm: –82.25 s (3F, CF_3), –122.52 d.m (1F, $^2J_{FF}$ = 275 Hz), –127.65 d.d (1F, $^2J_{FF}$ = 275, $^3J_{FH}$ = 20 Hz). Found, %: C 53.81; H 4.25; N 4.24. $C_{15}H_{14}F_5NO_2$. Calculated, %: C 53.74; H 4.21; N 4.18.

2-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutyl)-3-phenylaminocyclohex-2-en-1-one (VIc). Yield 79%, mp 95–98°C. IR spectrum, ν, cm^{-1}: 3300, 1675, 1570. ^1H NMR spectrum, δ, ppm: 1.92 m (2H, CH_2), 2.61 m (4H, CH_2), 5.98 m (1H, C**H**OH), 7.18 m (2H, H_{arom}), 7.42 m (3H, H_{arom}), 10.34 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.5, 28.1, 32.3, 65.3 d.d (J_{CF} = 28, 23 Hz), 102.3, 109.5 t.m (^1J = 266 Hz), 116.2 t.t (^1J = 255, ^2J = 30 Hz), 118.0 q.t (^1J = 288, ^2J = 34 Hz), 125.8, 128.6, 129.9, 136.0, 174.6, 193.1. ^{19}F NMR spectrum, δ_F, ppm: –81.07 m (3F, CF_3), –118.82 d.m (1F, $^2J_{FF}$ = 282 Hz), –125.15 d.m (1F, $^2J_{FF}$ = 282 Hz), –125.62 d.m (1F, $^2J_{FF}$ = 292 Hz), –127.45 d.d (1F, $^2J_{FF}$ = 292, $^3J_{FH}$ = 11 Hz). Found, %: C 49.79; H 3.60;

N 3.58. $C_{16}H_{14}F_7NO_2$. Calculated, %: C 49.88; H 3.66; N 3.64.

3-(4-Fluorophenylamino)-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VId). Yield 76%, mp 134–137°C. IR spectrum, ν, cm^{-1}: 3290, 1675, 1570. ^{1}H NMR spectrum, δ, ppm: 1.91 m (2H, CH_2), 2.56 m (4H, CH_2), 5.71 m (1H, C**H**OH), 7.14 m (4H, H_{arom}), 10.27 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.5, 27.9, 32.4, 66.3 q (^2J = 33 Hz), 102.9, 116.8 d (^2J = 23 Hz), 125.4 q (^1J = 284 Hz), 127.9 d (^3J = 9 Hz), 132.1, 162.2 d (^1J = 250 Hz), 174.0, 193.6. ^{19}F NMR spectrum, δ_F, ppm: –78.15 d (3F, CF_3, $^3J_{FH}$ = 4 Hz), –112.36 m (1F). Found, %: C 55.51; H 4.37; N 4.69. $C_{14}H_{13}F_4NO_2$. Calculated, %: C 55.45; H 4.32; N 4.62.

3-(4-Fluorophenylamino)-2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohex-2-en-1-one (VIe). Yield 76%, mp 78–81°C. IR spectrum, ν, cm^{-1}: 3290, 1675, 1575, 1515. ^{1}H NMR spectrum, δ, ppm: 1.81 m (2H, CH_2), 2.45 m (4H, CH_2), 5.78 m (1H, C**H**OH), 7.02 m (2H, H_{arom}), 7.07 m (2H, H_{arom}), 10.04 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.3, 27.8, 32.8, 65.0 d.d (J_{CF} = 27, 22 Hz), 102.2, 114.5 t.q (^1J = 257, ^2J = 37 Hz), 116.62 d (^2J = 23 Hz), 119.03 q.t (^1J = 285, ^2J = 35 Hz), 127.89 (^3J = 9 Hz), 132.1, 162.0 d (^1J = 249 Hz), 173.5, 194.0. ^{19}F NMR spectrum, δ_F, ppm: –82.26 s (3F, CF_3), –112.55 m (1F), –122.65 d.m (1F, $^2J_{FF}$ = 275 Hz), –127.62 d.d (1F, $^2J_{FF}$ = 275, $^3J_{FH}$ = 14 Hz). Found, %: C 50.91; H 3.65; N 3.91. $C_{15}H_{13}F_6NO_2$. Calculated, %: C 51.00; H 3.71; N 3.96.

3-(4-Fluorophenylamino)-2-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl)cyclohex-2-en-1-one (VIf). Yield 77%, mp 89–92°C. IR spectrum, ν, cm^{-1}: 3290, 1675, 1570. ^{1}H NMR spectrum, δ, ppm: 1.91 m (2H, CH_2), 2.54 m (2H, CH_2), 5.95 m (1H, C**H**OH), 7.15 m (4H, H_{arom}), 10.00 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.5, 28.0, 33.0, 65.4 d.d (J_{CF} = 28, 23 Hz), 102.5, 109.5 t.m (^1J = 266 Hz), 116.3 t.t (^1J = 255, ^2J = 30 Hz), 116.8 d (^2J = 23 Hz), 118.1 q.t (^1J = 288, ^2J = 34 Hz), 128.1 d (^3J = 8 Hz), 132.4, 162.2 d (^1J = 249 Hz), 173.9, 194.2. ^{19}F NMR spectrum, δ_F, ppm: –81.40 m (3F, CF_3), –112.73 s (1F), –119.31 d.m (1F, $^2J_{FF}$ = 282 Hz), –125.17 d.m (1F, $^2J_{FF}$ = 278 Hz), –125.71 d.m (1F, $^2J_{FF}$ = 286 Hz), –127.49 d.d (1F, $^2J_{FF}$ = 292, $^3J_{FH}$ = 11 Hz). Found, %: C 47.74; H 3.32; N 3.54. $C_{16}H_{13}F_8NO_2$. Calculated, %: C 47.65; H 3.25; N 3.47.

3-Benzylamino-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIg). Yield 79%, mp 91–94°C. IR spectrum, ν, cm^{-1}: 3290, 1680, 1580. ^{1}H NMR spectrum, δ, ppm: 1.91 m (2H, CH_2), 2.63 m (4H, CH_2), 4.60 d (2H, CH_2, ^3J = 5.9 Hz), 5.64 m (1H, C**H**OH), 7.22 m (2H, H_{arom}), 7.35 m (3H, H_{arom}), 9.82 br.t (1H, NH, ^3J = 5.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.5, 26.6, 30.2, 48.6, 66.0 q (^2J = 33 Hz), 101.7, 125.1 q (^1J = 283 Hz), 127.1, 128.7, 129.4, 134.2, 176.9, 188.8. ^{19}F NMR spectrum: δ_F –78.24 ppm, d (3F, CF_3, $^3J_{FH}$ = 6 Hz). Found, %: C 60.29; H 5.43; N 4.74. $C_{15}H_{16}NO_2F_3$. Calculated, %: C 60.20; H 5.39; N 4.68.

3-Benzylamino-2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohex-2-en-1-one (VIh). Yield 80%, mp 86–89°C. IR spectrum, ν, cm^{-1}: 3300, 1675, 1575. ^{1}H NMR spectrum, δ, ppm: 1.79 m (2H, CH_2), 2.50 m (4H, CH_2), 4.49 m (2H, CH_2), 5.74 m (1H, C**H**OH), 7.14 m (2H, H_{arom}), 7.24 m (3H, H_{arom}), 9.64 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 19.3, 26.6, 30.4, 48.35, 64.7 d.d (J_{CF} = 28, 22 Hz), 101.3, 114.2 t.q (^1J = 256, ^2J = 36 Hz), 118.9 q.t (^1J = 287, ^2J = 36 Hz), 126.9, 128.4, 129.2, 134.3, 176.7, 189.3. ^{19}F NMR spectrum, δ_F, ppm: –82.30 s (3F, CF_3), –122.55 d.m (1F, $^2J_{FF}$ = 275 Hz), –127.72 d.d (1F, $^2J_{FF}$ = 275, $^3J_{FH}$ = 20 Hz). Found, %: C 55.11; H 4.66; N 4.05. $C_{16}H_{16}NO_2F_5$. Calculated, %: C 55.02; H 4.62; N 4.01.

3-Benzylamino-2-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl)cyclohex-2-en-1-one (VIi). Yield 88%, mp 135–138°C. IR spectrum, ν, cm^{-1}: 3305, 1675, 1575. ^{1}H NMR spectrum, δ, ppm: 1.88 m (2H, CH_2), 2.23 m (1H), 2.40 m (2H, CH_2), 2.57 d.t (1H, ^2J = 17.1, ^3J = 5.0 Hz), 4.47 d.d (1H, ^2J = 15.9, ^3J = 6.1 Hz), 4.51 d.d (1H, ^2J = 15.9, ^3J = 6.1 Hz), 5.75 m (1H, C**H**OH), 7.25 m (2H, H_{arom}), 7.30 m (1H, H_{arom}), 7.37 m (2H, H_{arom}), 9.89 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.5, 26.5, 35.5, 47.14, 65.2 m, 101.4, 109.5 t.m (^1J = 266 Hz), 116.6 t.t (^1J = 254, ^2J = 25 Hz), 118.0 q.t (^1J = 288, ^2J = 34 Hz), 126.5, 127.8, 129.0, 137.1, 168.9 d (^3J = 2 Hz), 194.9. ^{19}F NMR spectrum, δ_F, ppm: –81.07 t (3F, CF_3, J = 10 Hz), –118.79 d.m (1F, $^2J_{FF}$ = 282 Hz), –124.34 d.m (1F, $^2J_{FF}$ = 282 Hz), –125.42 d.d (1F, $^2J_{FF}$ = 291, $^3J_{FH}$ = 7 Hz), –127.22 d.d (1F, $^2J_{FF}$ = 290, $^3J_{FH}$ = 9 Hz). Found, %: C 51.06; H 4.01; N 3.46. $C_{17}H_{16}NO_2F_7$. Calculated, %: C 51.14; H 4.04; N 3.51.

3-(4-Fluorobenzylamino)-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIj). Yield 78%, mp 92–95°C. IR spectrum, ν, cm^{-1}: 3290, 1675, 1585. ^{1}H NMR spectrum, δ, ppm: 1.94 m (2H, CH_2), 2.63 m (4H, CH_2), 4.59 d (2H, CH_2, ^3J = 4.7 Hz), 5.63 m (1H, C**H**OH), 7.07 m (2H, H_{arom}), 7.23 m (2H, H_{arom}), 9.62 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 19.6, 26.6, 30.6, 47.8, 66.0 q (^2J = 33 Hz), 101.7, 116.4 d (^2J = 22 Hz), 125.1 q (^1J = 284 Hz), 129.0 d (^3J = 8 Hz), 130.2 d (^4J = 1 Hz), 162.7 d (^1J = 248 Hz), 176.1, 189.74. ^{19}F NMR spectrum, δ_F, ppm: –78.18 d (3F, CF_3, $^3J_{FH}$ = 5 Hz), –113.27 m (1F). Found, %: C 56.87; H 4.81; N 4.47. $C_{15}H_{15}NO_2F_4$. Calculated, %: C 56.78; H 4.77; N 4.41.

5,5-Dimethyl-3-phenylamino-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIIa). Yield 77%, mp 65–68°C. IR spectrum, ν, cm^{-1}: 3280, 1675, 1565. ^{1}H NMR spectrum, δ, ppm: 1.01 s (3H, CH_3), 1.03 s (3H, CH_3), 2.35 d (1H, ^2J = 16.9 Hz), 2.43 s (2H, CH_2), 2.43 d (1H, ^2J = 16.9 Hz), 5.72 m (1H, C**H**OH), 7.14 m (2H, H_{arom}), 7.36 m (1H, H_{arom}), 7.43 m (2H, H_{arom}), 9.92 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 27.2, 28.1, 32.4, 41.0, 47.1, 66.4 q (^2J = 33 Hz), 101.5, 125.5 q (^1J = 284 Hz), 126.0, 128.0, 129.7, 136.5, 169.8, 193.5. ^{19}F NMR spectrum: δ_F –77.70 ppm, d ($^3J_{FH}$ = 7 Hz). Found, %: C 61.43; H 5.82; N 4.54. $C_{16}H_{18}NO_2F_3$. Calculated, %: C 61.34; H 5.79; N 4.47.

5,5-Dimethyl-2-(2,2,3,3,3-pentafluoro-1-hydroxy-propyl)-3-phenylaminocyclohex-2-en-1-one (VIIb). Yield 76%, mp 75–78°C. IR spectrum, ν, cm^{-1}: 3290, 1675, 1570, 1510. ^{1}H NMR spectrum, δ, ppm: 1.01 br.s (6H, CH_3), 2.37 d (1H, ^2J = 16.9 Hz), 2.43 s (2H, CH_2), 2.44 d (1H, ^2J = 16.9 Hz), 5.90 m (1H, C**H**OH), 7.15 m (2H, H_{arom}), 7.36 m (1H, H_{arom}), 7.43 m (2H, H_{arom}), 10.18 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.9, 27.9, 32.2, 41.0, 46.6, 65.1 d.d (J_{CF} = 28, 23 Hz), 101.3, 114.6 t.q (^1J = 255, ^2J = 36 Hz), 119.1 q.t (^1J = 287, ^2J = 36 Hz), 125.9, 128.1, 129.7, 136.3, 171.3, 193.0. ^{19}F NMR spectrum, δ_F, ppm: –82.21 s (3F, CF_3), –121.86 d.m (1F, $^2J_{FF}$ = 275 Hz), –127.95 d.d (1F, $^2J_{FF}$ = 275, $^3J_{FH}$ = 15 Hz). Found, %: C 56.11; H 4.95; N 3.80. $C_{17}H_{18}NO_2F_5$. Calculated, %: C 56.20; H 4.99; N 3.86.

2-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutyl)-5,5-dimethyl-3-phenylaminocyclohex-2-en-1-one (VIIc). Yield 78%, mp 52–55°C. IR spectrum, ν, cm^{-1}: 3305, 1675, 1565. ^{1}H NMR spectrum, δ, ppm: 1.02 br.s (6H, CH_3), 2.41 m (4H, CH_2), 6.00 m (1H, C**H**OH), 7.15 m (2H, H_{arom}), 7.39 m (3H, H_{arom}), 10.38 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.8, 27.9, 32.2, 41.0, 46.3, 65.2 d.d (J_{CF} = 28, 23 Hz), 101.4, 109.4 t.m (^1J = 266 Hz), 116.2 t.t (^1J = 255, ^2J = 31 Hz), 117.9 q.t (^1J = 288, ^2J = 34 Hz), 125.9, 128.2, 129.7, 136.2, 172.0, 192.6. ^{19}F NMR spectrum, δ_F, ppm: –81.28 t (3F, CF_3, J = 9.3), –118.57 d.m (1F, $^2J_{FF}$ = 282.3 Hz), –125.30 d.m (1F, $^2J_{FF}$ = 280.3 Hz), –125.55 d.m (1F, $^2J_{FF}$ = 292 Hz), –127.42 d.d (1F, $^2J_{FF}$ = 292, $^3J_{FH}$ = 12 Hz). Found, %: C 52.24; H 4.35; N 3.33. $C_{18}H_{18}NO_2F_7$. Calculated, %: C 52.31; H 4.39; N 3.39.

3-(4-Fluorophenylamino)-5,5-dimethyl-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIId). Yield 75%, mp 98–101°C. IR spectrum, ν, cm^{-1}: 3300, 1675, 1570. ^{1}H NMR spectrum, δ, ppm: 0.98 s (3H, CH_3), 1.01 s (3H, CH_3), 2.31 d (1H, ^2J = 17.1 Hz), 2.35 d (1H, ^2J = 17.1 Hz), 2.42 d (2H, CH_2, ^2J = 14.0 Hz), 5.69 m (1H, C**H**OH), 7.12 m (4H, H_{arom}), 10.04 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.9, 28.2, 32.3, 41.0, 46.7, 66.3 q (^2J = 33 Hz), 101.54, 116.77 d (^2J = 23 Hz), 125.5 q (^1J = 284 Hz), 128.1 d (^3J = 9 Hz), 132.4, 162.0 d (^1J = 249 Hz), 171.1, 193.3. ^{19}F NMR spectrum, δ_F, ppm: –77.96 d (3F, CF_3, $^3J_{FH}$ = 8 Hz), –112.70 m (1F). Found, %: C 58.00; H 5.17; N 4.23. $C_{16}H_{17}NO_2F_4$. Calculated, %: C 58.00; H 5.17; N 4.23.

3-(4-Fluorophenylamino)-5,5-dimethyl-2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohex-2-en-1-one (VIIe). Yield 75%, mp 78–81°C. IR spectrum, ν, cm^{-1}: 3305, 1675, 1570. ^{1}H NMR spectrum, δ, ppm: 0.99 br.s (6H, CH_3), 2.30 d (1H, ^2J = 17.6 Hz), 2.35 d (1H, ^2J = 17.6 Hz), 2.36 s (2H, CH_2), 5.85 m (1H, C**H**OH), 7.11 m (4H, H_{arom}), 9.84 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.8, 28.1, 32.1, 41.0, 47.1, 65.0 d.d (J_{CF} = 28, 22 Hz), 101.4, 114.6 t.q (^1J = 255, ^2J = 36 Hz), 116.6 d (^2J = 23 Hz), 119.1 q.t (^1J = 287, ^2J = 36 Hz), 128.1 (^3J = 8 Hz), 132.6, 161.8 d (^1J = 249 Hz), 170.5, 193.9. ^{19}F NMR spectrum, δ_F, ppm: –82.26 s (3F, CF_3), –113.16 m (1F), –121.95 d.m (1F, $^2J_{FF}$ = 273 Hz), –127.92 d.m ($^2J_{FF}$ = 277 Hz). Found, %: C 53.48; H 4.45; N 3.62. $C_{17}H_{17}NO_2F_6$. Calculated, %: C 53.55; H 4.49; N 3.67.

3-(4-Fluorophenylamino)-2-(2,2,3,3,4,4,4-hepta-fluoro-1-hydroxybutyl)-5,5-dimethylcyclohex-2-en-1-one (VIIf). Yield 77%, mp 87–90°C. IR spectrum, ν, cm^{-1}: 3290, 1685, 1575. ^{1}H NMR spectrum, δ, ppm: 1.00 s (3H, CH_3), 1.01 s (3H, CH_3), 2.30 d (1H, ^2J = 16.9 Hz), 2.36 d (1H, ^2J = 16.9 Hz), 2.38 s (2H, CH_2), 5.94 m (1H, C**H**OH), 7.12 m (4H, H_{arom}), 9.96 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.8, 28.1, 32.1, 41.0, 47.1, 65.2 d.d (J_{CF} = 27, 23 Hz), 101.5, 109.4 t.m (^1J = 266 Hz), 116.3 t.t (^1J = 254, ^2J = 30 Hz), 116.6 d (J = 23 Hz), 117.9 q.t (^1J = 288, ^2J = 34 Hz), 128.1 d (^3J = 8 Hz), 132.6, 161.9 d (^1J = 249 Hz), 170.7, 193.8. ^{19}F NMR spectrum, δ_F, ppm: –81.30 t (3F, CF_3, J = 8), –113.12 s (1F), –118.63 d.m

(1F, $^{2}J_{FF}$ = 283 Hz), –125.29 d.m (1F, $^{2}J_{FF}$ = 286 Hz), –125.58 d.m (1F, $^{2}J_{FF}$ = 292 Hz), –127.44 d.d (1F, $^{2}J_{FF}$ = 292, $^{3}J_{FH}$ = 11 Hz). Found, %: C 50.20; H 3.99; N 3.31. $C_{18}H_{17}NO_2F_8$. Calculated, %: C 50.12; H 3.97; N 3.25.

3-Benzylamino-5,5-dimethyl-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIIg). Yield 78%, mp 72–75°C. IR spectrum, ν, cm^{-1}: 3420, 1675, 1580. ^{1}H NMR spectrum, δ, ppm: 0.96 s (3H, CH_3), 1.05 s (3H, CH_3), 2.48 d (1H, ^{2}J = 17.2 Hz), 2.50 s (2H, CH_2), 2.54 d (1H, ^{2}J = 17.2 Hz), 2.62 d (2H, CH_2, ^{3}J = 5.7 Hz), 5.67 m (1H, C**H**OH), 7.23 m (2H, H_{arom}), 7.32 m (2H, H_{arom}), 7.38 m (1H, H_{arom}), 9.29 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.9, 28.7, 31.8, 39.9, 44.9, 48.2, 66.2 q (^{2}J = 33 Hz), 100.6, 125.3 q (^{1}J = 284 Hz), 126.8, 128.5, 129.3, 134.9, 173.7, 189.7. ^{19}F NMR spectrum, δ_F, ppm: –77.87 d (3F, CF_3, $^{3}J_{FH}$ = 7 Hz). Found, %: C 62.30; H 6.11; N 4.22. $C_{17}H_{20}NO_2F_3$. Calculated, %: C 62.38; H 6.16; N 4.28.

3-Benzylamino-5,5-dimethyl-2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohex-2-en-1-one (VIIh). Yield 82%, mp 79–82°C. IR spectrum, ν, cm^{-1}: 3410, 1680, 1565. ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H, CH_3), 1.01 s (3H, CH_3), 2.36 d (1H, ^{2}J = 17.9 Hz), 2.40 d (1H, ^{2}J = 17.9 Hz), 4.57 m (2H, CH_2), 5.84 m (1H, C**H**OH), 7.23 m (2H, H_{arom}), 7.30 m (1H, H_{arom}), 7.36 m (2H, H_{arom}), 9.37 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.4, 28.5, 31.4, 39.7, 44.9, 47.9, 64.8 d.d (J_{CF} = 28, 22 Hz), 100.3, 114.5 t.q (^{1}J = 255, ^{2}J = 36 Hz), 119.0 q.t (^{1}J = 287, ^{2}J = 36 Hz), 126.6, 128.2, 129.1, 135.2, 174.2, 189.6. ^{19}F NMR spectrum, δ_F, ppm: –82.20 s (3F, CF_3), –121.86 d.m (1F, $^{2}J_{FF}$ = 275 Hz), –127.78 d.m (1F, $^{2}J_{FF}$ = 277 Hz). Found, %: C 57.38; H 5.39; N 3.78. $C_{18}H_{20}F_5NO_2$. Calculated, %: C 57.29; H 5.34; N 3.71.

3-Benzylamino-2-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl)-5,5-dimethylcyclohex-2-en-1-one (VIIi). Yield 79%, mp 116–119°C. IR spectrum, ν, cm^{-1}: 3415, 1670, 1575. ^{1}H NMR spectrum, δ, ppm: 0.95 s (3H, CH_3), 1.01 s (3H, CH_3), 2.38 d (1H, ^{2}J = 17.8 Hz), 2.42 d (1H, ^{2}J = 17.8 Hz), 2.44 s (2H, CH_2), 4.57 m (2H, CH_2), 5.94 m (1H, C**H**OH), 7.23 m (2H, H_{arom}), 7.30 m (1H, H_{arom}), 7.36 m (2H, H_{arom}), 9.50 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.4, 28.5, 31.5, 39.8, 44.8, 47.9, 65.0 d.d (J_{CF} = 28, 22 Hz), 100.4, 109.3 t.m (^{1}J = 266 Hz), 116.1 t.t (^{1}J = 254, ^{2}J = 30 Hz), 117.8 q.t (^{1}J = 288, ^{2}J = 34 Hz), 126.6, 128.2, 129.1, 135.2, 174.4, 189.5. ^{19}F NMR spectrum, δ_F, ppm: –81.27 t (3F, CF_3, J = 9 Hz), –118.60 d.m (1F, $^{2}J_{FF}$ = 282 Hz), –125.12 d.m (1F, $^{2}J_{FF}$ = 277 Hz), –125.62 d.m (1F, $^{2}J_{FF}$ = 291 Hz), –127.44 d.d (1F, $^{2}J_{FF}$ = 292, $^{3}J_{FH}$ = 11 Hz). Found, %: C 53.48; H 4.75; N 3.45. $C_{19}H_{20}NO_2F_7$. Calculated, %: C 53.40; H 4.72; N 3.28.

3-(4-Fluorobenzylamino)-5,5-dimethyl-2-(2,2,2-trifluoro-1-hydroxyethyl)cyclohex-2-en-1-one (VIIj). Yield 76%, mp 84–87°C. IR spectrum, ν, cm^{-1}: 3420, 1690, 1625, 1575. ^{1}H NMR spectrum, δ, ppm: 0.97 s (3H, CH_3), 1.04 s (3H, CH_3), 2.42 s (2H, CH_2), 2.47 d (2H, CH_2, ^{2}J = 18.5 Hz), 4.57 d (2H, CH_2, ^{3}J = 5.6 Hz), 5.64 m (1H, C**H**OH), 7.06 m (2H, H_{arom}), 7.23 m (2H, H_{arom}), 9.30 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.7, 28.2, 31.5, 39.2, 45.1, 47.4, 66.1 q (^{2}J = 33 Hz), 100.6, 116.2 d (^{2}J = 22 Hz), 125.4 q (^{1}J = 284 Hz), 128.7 d (^{3}J = 8 Hz), 131.1 d (^{3}J = 2 Hz), 162.6 d (^{1}J = 247 Hz), 173.6, 189.9. ^{19}F NMR spectrum, δ_F, ppm: –77.88 d (3F, CF_3, $^{3}J_{FH}$ = 8 Hz), –113.72 m (1F). Found, %: C 59.21; H 5.59; N 4.12. $C_{17}H_{19}NO_2F_4$. Calculated, %: C 59.13; H 5.55; N 4.06.

Methylation of 2-(2,2,3,3,3-pentafluoro-1-hydroxypropyl)cyclohexane-1,3-dione (IIb). A solution of diazomethane in diethyl ether prepared as described [21], 15 ml, was added dropwise under stirring over a period of 30 min to a solution of 1 mmol of compound **IIb** in 10 ml of diethyl ether cooled to 0°C. The solvent was distilled off under reduced pressure, and the residue was recrystallized from diethyl ether–hexane to isolate 3-methoxy-2-(2,2,3,3,3-pentafluoro-1-methoxypropyl)cyclohex-2-en-1-one (**IX**) as a colorless crystalline substance. Yield 90%, mp 110–113°C. IR spectrum, ν, cm^{-1}: 1645, 1595. ^{1}H NMR spectrum, δ, ppm: 1.94 m (2H, 5-H), 2.31 d.d (2H, 6-H, ^{2}J = 17.7, ^{3}J 5.7 Hz), 2.66 m (2H, 4-H), 3.25 s (3H, 1′-OCH_3), 3.83 s (3H, 3-OCH_3), 5.05 m (1H, 1′-H). ^{13}C NMR spectrum, δ_C, ppm: 19.94 (C^5), 25.53 (C^4), 36.05 (C^6), 56.19 (3-OCH_3), 58.29 (1′-OCH_3), 71.68 t ($C^{1'}$, ^{2}J = 24 Hz), 108.42 (C^2), 113.08 t.q ($C^{2'}$, ^{1}J = 259, ^{2}J = 36 Hz), 118.99 q.t ($C^{3'}$, ^{1}J = 287, ^{2}J = 36 Hz), 180.72 (C^3), 198.30 (C^1). ^{19}F NMR spectrum, δ_F, ppm: –83.58 s (3F, CF_3), –121.36 d.m (1F, ^{1}J = 267 Hz), –124.80 d.d (1F, ^{1}J = 274, $^{3}J_{FH}$ = 20 Hz). Found, %: C 45.76; H 4.50. $C_{11}H_{13}F_5O_3$. Calculated, %: C 45.84; H 4.55.

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