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Reactions of Perfluoro(2-methylpent-2-ene) and Perfluoro(5-azanon-4-ene) with Primary Amines Containing a 2,6-Di-*tert*-butylphenol Fragment

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Abstract—Reactions of perfluoro(2-methylpent-2-ene) and perfluoro(5-azanon-4-ene) with 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol and 4-(3-aminopropyl)-2,6-di-*tert*-butylphenol in acetonitrile in the presence of triethylamine gave the corresponding azetidine, 1,2-dihydroazete, and 1,2-dihydro-1,3-diazete derivatives, respectively. The reaction mechanisms, role of triethylamine, and factors affecting the intramolecular nucleophilic cyclization process are discussed.

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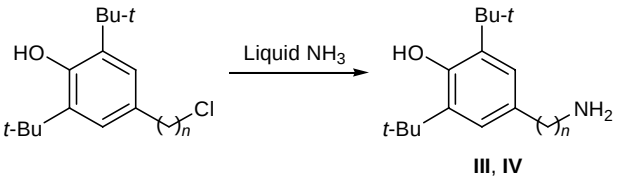
In the recent years, introduction of a fluorine atom or a perfluoroalkyl group into known biologically active compounds has become an important tool for their modification. The reason is that regioselective replacement of hydrogen in an aromatic or heterocyclic system by a perfluoroalkyl group could essentially change both physical and biological properties [1, 2]. In many cases, introduction of fluorine atoms enhances the biological activity of an existing medicine. Therefore, development of new and improvement of known methods for introduction of polyfluorinated fragments into organic substrates are strongly desirable [3]. Four-membered nitrogen-containing rings are structural fragments of a number of bioactive substances, and their modification via introduction of perfluoroalkyl groups attracts an appreciable interest.

We previously showed [4–6] that fluorine-containing azetes and dihydroazetes can be obtained from perfluoro(2-methylpent-2-ene) (**I**) and perfluoro(5-azanon-4-ene) (**II**) using primary aliphatic amines as nucleophiles. In continuation of our studies on the development of this approach, the goal of the present work was to synthesize such potential biologically active compounds in which a four-membered heteroring responsible for biological activity of the molecule as a whole would be linked to a fragment giving rise to antioxidant and anticarcinogenic activity typical of aminoalkyl-2,6-di-*tert*-butylphenol derivatives [7]. As such a fragment we used ω-(3,5-di-*tert*-butyl-4-hydroxyphenyl)alkyl groups [8].

4-(2-Aminoethyl)-2,6-di-*tert*-butylphenol (**III**) and 4-(3-aminopropyl)-2,6-di-*tert*-butylphenol (**IV**) were synthesized by amination of accessible 4-(ω-chloroalkyl)-2,6-di-*tert*-butylphenols with liquid ammonia at 70°C under pressure (Scheme 1).

Scheme 1.

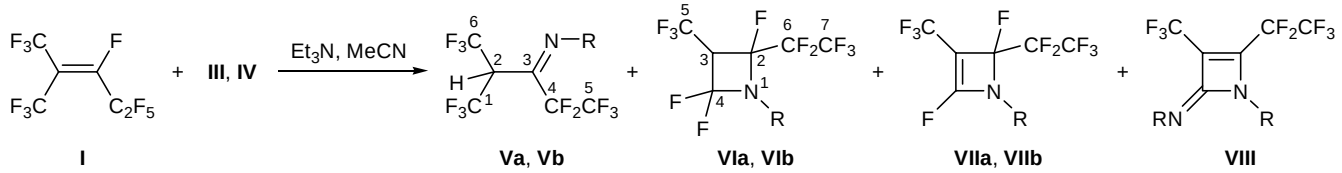


III, **IV**

III, $n = 2$; **IV**, $n = 3$.

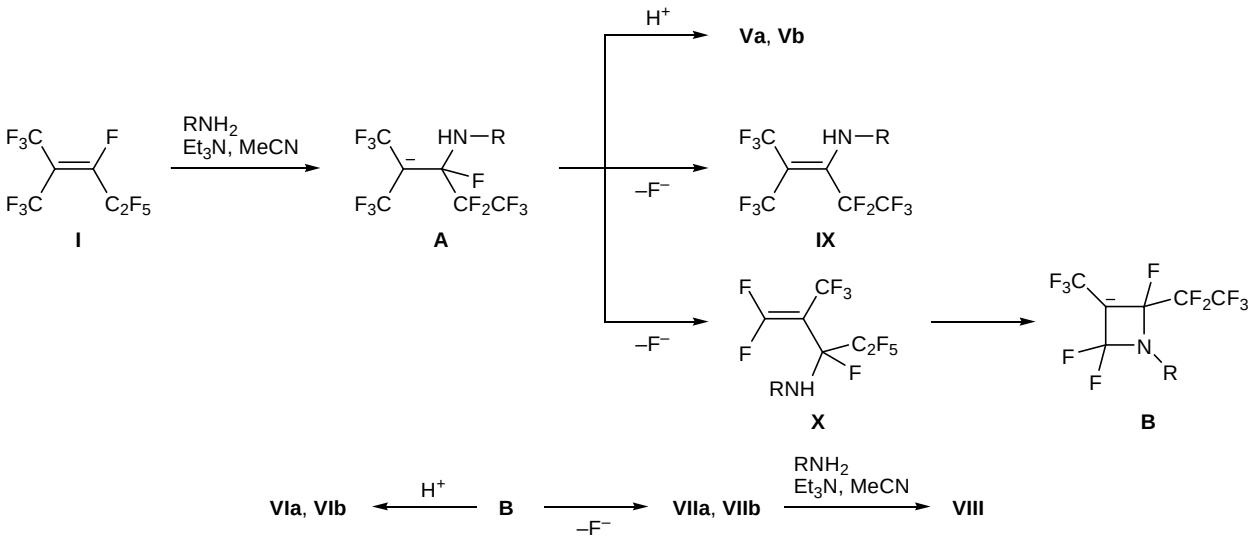
Reactions of equimolar amounts of compound **I** with aminophenols **III** and **IV** in acetonitrile in the presence of excess triethylamine gave mixtures of products resulting from addition at the double bond of alkene **I**, 2,6-di-*tert*-butyl-4-[2-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylideneamino)-ethyl]phenol (**Va**) and 2,6-di-*tert*-butyl-4-[3-(3,3,3-tri-

Scheme 2.



V–**VII**, R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_2$ (**a**), 4-HO-3,5-(*t*-Bu)$_2$(CH$_2$)$_3$ (**b**); **VIII**, R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_3$.

Scheme 3.



R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_n$; *n* = 2 (**a**), 3 (**b**).

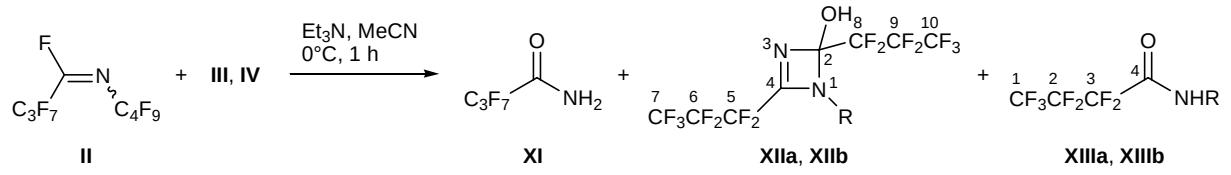
fluoro-1-pentafluoroethyl-2-trifluoromethylpropylideneamino)propyl]phenol (**Vb**), and those formed by four-membered ring closure, 1-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl]-2-pentafluoroethyl-3-trifluoromethylazetidine (**VIa**) or 1-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]-2-pentafluoroethyl-3-trifluoromethylazetidine (**VIb**) and 1-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl]-2-pentafluoroethyl-3-trifluoromethyl-1,2-dihydroazete (**VIIa**) or 1-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]-2-pentafluoroethyl-3-trifluoromethyl-1,2-dihydroazete (**VIIb**), respectively (Scheme 2). The formation of these products may be rationalized by Scheme 3.

The reactions of compound **I** with nucleophiles **III** and **IV** begin with attack by the amino nitrogen atom on the double-bonded carbon atom in alkene **I** to give carbanion **A**. The latter undergoes further transformations along different pathways. Addition of a proton (from the reaction medium) leads to compound **Va** or **Vb**. Elimination of fluoride ion from the CF fragment gives enamine **IX**. We failed to isolate compound **IX** as individual substance, but it was detected by ^{1}H and ^{19}F NMR spectroscopy in the reaction of **I** with aminophenol **IV**. Elimination of fluoride ion from the CF_3 group yields terminal olefin **X** which undergoes intramolecular nucleophilic cyclization to carbanion **B**. Proton addition to **B** gives compound **VIa** or **VIb**, while elimination of fluoride ion leads to dihydroazete **VII**. The fluorine atom at the double bond in **VII** is fairly labile, and it is readily replaced by amino group via reaction with the initial nucleophile; as a result, compound **VIII** is obtained.

Compound **II** reacted with amines **III** and **IV** in a more complicated fashion. The products were heptafluorobutanamide (**XI**) and diazete derivatives, 1-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl]-2,4-bis(heptafluoropropyl)-1,2-dihydro-1,3-diazet-2-ol (**XIIa**) or 1-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]-2,4-bis(heptafluoropropyl)-1,2-dihydro-1,3-diazet-2-ol (**XIIb**) and *N*-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-ethyl]heptafluorobutanamide (**XIIIa**) or *N*-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]heptafluorobutanamide (**XIIIb**), respectively (Scheme 4).

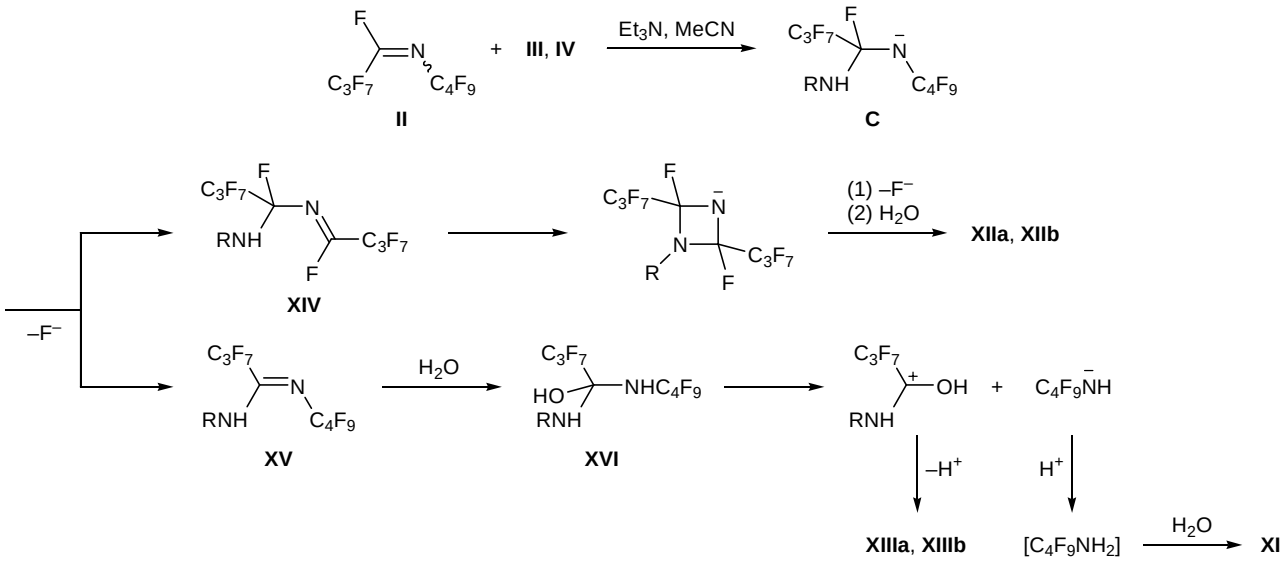
A probable mechanism of this reaction is shown in Scheme 5. Initial attack by the N-nucleophilic center of aminophenol **III** or **IV** on the N=C carbon atom

Scheme 4.



R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_2$ (**a**), 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_3$ (**b**).

Scheme 5.



R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_n$; *n* = 2 (**a**), 3 (**b**).

generates nitrogen-centered anion **C**. Elimination of fluoride ion from anion **C** may occur either from the CF_2 or CF fragment. In the first case, a new azaalkene **XIV** is formed, and it undergoes intramolecular nucleophilic cyclization to give compounds **XIIa** and **XIIb**. Elimination of fluoride ion from the CF fragment gives azaalkene **XV** whose hydrolysis leads to α-hydroxy amine **XVI**; the latter is likely to be unstable, and it decomposes into amide **XI** and compound **XIIIa** or **XIIIb**. The product ratio strongly depends on the reaction conditions and the amount of triethylamine.

Thus we have synthesized new dihydroazete and dihydro-1,3-diazete derivatives containing perfluoroalkyl groups and sterically hindered phenol fragments.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200, 50, and 188 MHz, respectively. The chemical shifts were measured relative to HMDS (^{1}H and ^{13}C, internal) and C_6F_6 (^{19}F, internal); ^{1}H–^{13}C coupling constants were not measured. The IR spectra were obtained from 5% solutions in CCl_4 on a Specord M-80 spectrometer. The electronic absorption spectra were measured on a Specord UV-Vis spectrophotometer using ethanol as solvent. The molecular weights were determined by mass spectrometry (Finnigan MAT-8200 GC–MS system, electron impact, 70 eV).

4-(2-Aminoethyl)-2,6-di-*tert*-butylphenol (III). A mixture of 26.9 g (0.1 mol) of 4-(2-chloroethyl)-2,6-di-*tert*-butylphenol and 100 ml of liquid ammonia was heated for 8 h at 70°C in a steel high-pressure reactor. The reactor was cooled to room temperature and opened, excess ammonia was evaporated, and the residue (28.2 g of a gray powder) was shaken with 200 ml of toluene in a separatory funnel. The organic phase was washed with 200 ml of a 5% aqueous solution of sodium carbonate and water, dried over $MgSO_4$, and distilled. Yield 10 g (97%), bp 160°C (1 mm), mp 104–106°C (from hexane); published data [7]: mp 106–107°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 s (18H, *t*-Bu), 2.55 m (2H, CH_2), 2.82 m (2H, CH_2), 4.87 s (1H, OH), 6.83 m (2H, H_{arom}).

4-(3-Aminopropyl)-2,6-di-*tert*-butylphenol (IV) was synthesized in a similar way. Yield 29 g (98%), bp 196–200°C (5 mm), mp 122–123°C; published data [7]: mp 122–122.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 s (18H, *t*-Bu), 1.55–1.70 m (2H, CH_2-C**H**$_2$CH$_2$), 2.48 t (2H, CH_2), 2.70 t (2H, CH_2), 6.85 s (2H, H_{arom}).

Reaction of perfluoro(2-methylpent-2-ene) (I) with aminophenol (III). Compound **I**, 3.0 g (0.01 mol), was added over a period of 10 min to a solution of 2.6 g (0.01 mol) of aminophenol **III** and 3.03 g (0.03 mol) of triethylamine in 20 ml of anhydrous acetonitrile under stirring and cooling with ice water. The mixture was allowed to warm up to 18–20°C, stirred for 3 h at that temperature, heated for 0.5 h at 45°C, and left overnight. It was then poured into water and extracted with methylene chloride. The extract was washed with 5% hydrochloric acid and water, dried over $CaCl_2$, and evaporated, and the residue was subjected to column chromatography on silica gel. The column was eluted first with hexane (fraction *I*) and then with hexane–methylene chloride (2:1) (fractions *II* and *III*). According to the ^{19}F NMR and GLC data, fraction *I* contained 2,6-di-*tert*-butyl-4-[2-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylprop-2-enylamino)ethyl]phenol (**IX**) [^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 101.4 (3F, 6-F), 100.6 (3F, 1-F), 82.2 (3F, 5-F), 48.3 (2F, 4-F)] and 2,6-di-*tert*-butyl-4-[2-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylideneamino)ethyl]phenol (**Va**) [^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 98.5 (6F, 1-F, 6-F), 79.6 (3F, 5-F), 47.2 (2F, 4-F)] at a ratio of 2:2.8. Fractions *II* and *III* contained compounds **VIa** and **VIIa**, respectively.

2,6-Di-*tert*-butyl-4-[2-(2,2,4-trifluoro-4-pentafluoroethyl-3-trifluoromethylazetidin-1-yl)ethyl]-phenol (VIa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.96 (1H, OH), 6.90 m (1H, 9-H), 4.12 m (1H, 2-H), 3.39 m (1H, 7-H), 2.54 m (1H, 8-H), 1.36 m (3H, 14-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 106.2 q (1F, 4-F, J = 23 Hz), 105.3 d (3F, 5-F, J = 23 Hz), 81.6 s (3F, 7-F), 52.8 and 48.1 (2F, 6-F, *AB* system, J_{FF} = 287 Hz), 49.4 (1F, 2-F). Mass spectrum, *m*/*z* (I_{rel}, %): 529 (22.00) $[M]^+$, 514 (19.94) $[M - CH_3]^+$, 310 (0.81) $[M - CH_2C_{14}H_{20}OH]^+$, 233 (3.05) $[CH_2CH_2C_{14}H_{20}OH]^+$, 219 (100) $[CH_2C_{14}H_{20}OH]^+$, 205 (1.02) $[C_{14}H_{20}OH]^+$, 119 (2.36) $[C_2F_5]^+$, 69 (1.17) $[CF_3]^+$, 57 (25.72) $[C(CH_3)_3]^+$. Found: $[M]^+$ 529.1842. $C_{22}H_{26}F_{11}NO$. Calculated: *M* 529.1838.

2,6-Di-*tert*-butyl-4-{2-[2,4-difluoro-2-pentafluoroethyl-3-trifluoromethylazet-1(2*H*)-yl]ethyl}-phenol (VIIa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.96 (1H, OH), 6.90 (1H, 10-H), 3.39 (1H, 8-H), 2.54 (1H, 9-H), 1.36 (3H, 14-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 106.2 q (1F, 4-F, J = 23 Hz), 105.3 d (3F, 5-F, J = 23 Hz), 81.6 s (3F, 7-F), 52.8 and 48.1 (2F, 6-F, *AB* system, J_{FF} = 290 Hz), 49.4 s (1F, 2-F).

The reaction of compound **I** with aminophenol **IV** was carried out in a similar way.

2,6-Di-*tert*-butyl-4-[3-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylideneamino)-propyl]phenol (Vb). IR spectrum, ν, cm^{-1}: 3647 (OH); 2959, 2926, 2874 (C–H); 1683–1661 (C=N); 1551 (C=C_{arom}); 1310, 1361 (C–O); 1229–1179 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.32 (1H, OH), 6.97 m (1H, 11-H), 3.78 m (1H, 2-H), 3.21 m (1H, 7-H), 2.63 m (1H, 8-H), 2.54 (1H, 9-H), 1.39 (3H, 15-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 101.3 (6F, 1-F, 6-F), 82.8 (3F, 5-F), 49.1 (2F, 4-F). Mass spectrum, *m*/*z* (I_{rel}, %): 543 (49.73) $[M]^+$, 528 (43.40) $[M - CH_3]^+$, 524 (3.06) $[M - F]^+$, 508 (3.64) $[M - F - CH_4]^+$, 486 (2.74) $[M - C(CH_3)_3]^+$, 311 (0.92) $[M - CH_2CHCC_{14}H_{20}OH]^+$, 246 (16.19) $[CH_2CHCH_2-C_{14}H_{20}O]^+$, 232 (100) $[CH_2=CHC_{14}H_{20}OH]^+$, 231 (24.56) $[CH_2=CHC_{14}H_{20}O]^+$, 219 (22.72) $[CH_2C_{14}H_{20}-OH]^+$, 217 (32.66) $[HCC_{14}H_{20}O]^+$, 205 (2.66) $[C_{14}H_{20}-OH]^+$, 189 (19.28) $[C_{14}H_{20}]^+$, 145 (6.88) $[C_2F_5CN]^+$, 131 (4.81) $[CF_2=CCF_3]^+$, 119 (4.27) $[C_2F_5]^+$, 94 (17.42) $[C_6H_5OH]^+$, 69 (2.42) $[CF_3]^+$, 57 (78.43) $[C(CH_3)_3]^+$. Found: $[M]^+$ 543.2002. $C_{23}H_{28}F_{11}NO$. Calculated: *M* 543.1995.

2,6-Di-*tert*-butyl-4-[3-(2,2,4-trifluoro-4-pentafluoroethyl-3-trifluoromethylazetidin-1-yl)propyl]-phenol (VIb). mp 126–127°C. IR spectrum, ν, cm^{-1}: 3646 (OH); 2959, 2926, 2874 (C–H); 1664, 1645 (C=N); 1552 (C=C_{arom}); 1484, 1466 (C–N); 1362, 1337 (C–O); 1262–1192 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.61 (1H, OH), 6.97 (1H, 12-H), 3.21 (1H, 8-H), 2.63 (1H, 9-H), 2.54 (1H, 10-H), 1.39 (3H, 16-H). ^{19}F NMR spectrum, ($CDCl_3$), δ_F, ppm: 107.7 (2F, 5-F), 99.0 (2F, 4-F), 82.8 (3F, 7-F), 49.9 and 49.4 (2F, 6-F, *AB* system, J_{FF} = 240 Hz), 49.0 (1F, 2-F). Mass spectrum, *m*/*z* (I_{rel}, %): 543 (2.79) $[M]^+$, 528 (2.40) $[M - CH_3]^+$, 523 (0.89) $[M - HF]^+$, 310 (0.52) $[M - CH_2CH_2C_{14}H_{20}OH]^+$, 290 (0.73) $[C_7H_2F_{10}N]^+$, 259 (19.80) $[CF_3CFC(C_2F_5)NCH_2]^+$, 240 (3.79) $[CF_3C=C(C_2F_5)NCH_2]^+$, 232 (6.67) $[CH_2=CHC_{14}H_{20}-OH]^+$, 219 (4.07) $[CH_2C_{14}H_{20}OH]^+$, 217 (8.22) $[HCC_{14}H_{20}O]^+$, 159 (4.15) $[C_2F_5CNCH_2]^+$, 145 (1.09) $[C_2F_5CN]^+$, 131 (1.49) $[CF_3C=CF_2]^+$, 119 (2.02) $[C_2F_5]^+$, 69 (11.08) $[CF_3]^+$, 57 (100) $[C(CH_3)_3]^+$, 43 (68.62) $[HC(CH_3)_3]^+$, 42 (36.52) $[CH_3CH=CH_2]^+$, 41

(78.81) $[CH_3CCH_3]^+$. Found: $[M]^+$ 543.1975. $C_{23}H_{28}F_{11}NO$. Calculated: *M* 543.1995.

2,6-Di-*tert*-butyl-4-{3-[2,4-difluoro-2-pentafluoroethyl-3-trifluoromethylazet-1(2*H*)-yl]propyl}phenol (VIIb). mp 118–119°C. IR spectrum, ν, cm^{-1}: 3646 (OH); 2959, 2930, 2874 (C–H); 1669, 1645 (C=N); 1552 (C=C_{arom}); 1466, 1436 (C–N); 1362, 1337 (C–O); 1228–1160 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.58 (1H, OH), 6.87 (1H, 12-H), 4.12 (1H, 3-H), 3.21 (1H, 8-H), 2.63 (1H, 9-H), 2.54 (1H, 10-H), 1.39 (3H, 16-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 111.0 (1F, 4-F), 107.0 (3F, 5-F), 82.8 (3F, 7-F), 49.9 and 49.4 (2F, 6-F, *AB* system, J_{FF} = 240 Hz), 49.0 (1F, 2-F).

2,6-Di-*tert*-butyl-4-(3-{2-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propylimino]-4-pentafluoroethyl-3-trifluoromethylazet-1(2*H*)-yl}propyl)phenol (VIII). mp 110–112°C. IR spectrum, ν, cm^{-1}: 3646 (OH); 2959, 2930, 2874 (C–H); 1665, 1645 (C=N); 1552 (C=C_{arom}); 1466 (C=C); 1436 (C–N); 1362, 1337 (C–O); 1228–1160 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.11 (OH), 6.95 (4H, 12-H, 21-H), 3.15 (4H, 8-H, 17-H), 2.63 (4H, 9-H, 12-H), 2.46 (4H, 10-H, 19-H), 1.86 (4H, 15-H, 24-H), 1.38 (36H, 16-H, 25-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 106.4 s (3F, 5-F), 82.0 s (3F, 7-F), 48.8 d (2F, 6-F, *J* = 19 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 157.6 (C^4), 152.5 (C^{14}), 152.3 (C^{23}), 142.1 (C^2, $^2J_{CF}$ = 21.4 Hz), 136.1 (C^{13}), 136 (C^{13}, C^{22}), 131.7 (C^{20}), 131.6 (C^{11}), 123.8 (C^{12}, C^{21}), 121.6 (C^5, $^1J_{CF}$ = 282 Hz), 119.6 (C^7, $^1J_{CF}$ = 271.2, $^2J_{CF}$ = 30 Hz), 114.0 (C^3, $^2J_{CF}$ = 38 Hz), 108.6 (C^6, $^1J_{CF}$ = 266.9, $^2J_{CF}$ = 41.3 Hz), 53.2 (C^8), 52.9 (C^{17}), 50.6 (C^9, C^{18}), 34.2 (C^{10}), 34.5 (C^{19}), 32.3 (C^{16}, C^{25}), 30.1 (C^{15}, C^{24}). Mass spectrum, *m*/*z* (I_{rel}, %): 746 (45.28) $[M]^+$, 727 (3.56) $[M - F]^+$, 527 (8.77) $[M - CH_2C_{14}H_{20}OH]^+$, 514 (92.82) $[M - CH_2CH_2C_{14}H_{20}O]^+$, 513 (24.11) $[M - CH_2CH_2C_{14}H_{20}OH]^+$, 233 (7.09) $[CH_2CH_2C_{14}H_{20}OH]^+$, 219 (49.96) $[CH_2C_{14}H_{20}OH]^+$, 205 (1.64) $[C_{14}H_{20}OH]^+$, 119 (4.00) $[C_2F_5]^+$, 69 (3.15) $[CF_3]^+$, 57 (100) $[C(CH_3)_3]^+$.

The reactions of compound **II** with aminophenols **III** and **IV** were carried out as described above for compound **I**.

1-[2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)ethyl]-2,4-bis(heptafluoropropyl)-1,2-dihydro-1,3-diazet-2-ol (XIIa). mp 119–120°C (from heptane). IR spectrum, ν, cm^{-1}: 3646 (OH); 2958, 2921, 2874 (C–H); 1732, 1686 (C=N); 1551 (C=C_{arom}); 1471, 1435 (C–N); 1390, 1359 (C–O); 1232–1157 (C–F). UV spectrum (EtOH): λ_{max} 275 nm (ε 2000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.70 (1H, OH), 6.89 (1H, 14-H), 3.17 (1H, 11-H), 2.56 (1H, 12-H), 1.39 (3H, 19-H, CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.6 (6F, 7-F, 10-F), 47.5 (2F, 5-F), 48.3 and 46.5 (2F, 8-F, *AB* system, J_{FF} = 278 Hz), 37.4 (2F, 6-F), 36.7 (2F, 9-F). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 151.2 (C^{16}), 147.7 (C^4, $^2J_{CF}$ = 23.4 Hz), 142.5 (C^2, $^2J_{C-F}$ = 23.4 Hz), 135.9 (C^{15}), 131.0 (C^{14}), 123.1 (C^{13}), 117.5 (C^7, C^{10}, $^1J_{CF}$ = 290.7, $^2J_{CF}$ = 28.5 Hz), 109.1 (C^5, C^8, $^1J_{CF}$ = 259.9, $^2J_{CF}$ = 31.3 Hz), 107.7 (C^6, C^9, $^1J_{CF}$ = 267.9, $^2J_{CF}$ = 32.8 Hz), 48.2 (C^{11}), 41.1 (C^{12}), 32.4 (C^{13}), 33.4 (C^{17}), 29.9 (C^{18}). Found, %: C 45.65; F 40.34; N 4.66. $[M]^+$ 654. $C_{25}H_{28}F_{14}N_2O_2$. Calculated, %: C 45.87; F 40.67; N 4.28. *M* 654.

1-[3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propyl]-2,4-bis(heptafluoropropyl)-1,2-dihydro-1,3-diazet-2-ol (XIIb). mp 123–124°C (from heptane). IR spectrum, ν, cm^{-1}: 3646 (OH); 2958, 2921, 2874 (C–H); 1732, 1686 (C=N); 1551 (C=C_{arom}); 1471, 1435 (C–N); 1390, 1359 (C–O); 1232–1157 (C–F). UV spectrum (EtOH): λ_{max} 275 nm (ε 2000). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.70 (1H, OH), 6.99 (1H, 15-H), 3.17 (1H, 11-H), 2.56 (1H, 12-H), 2.22 (1H, 13-H), 1.39 (3H, 19-H, CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.6 (6F, 7-F, 10-F), 47.5 (2F, 5-F), 48.3 and 46.5 (2F, 8-F, *AB* system, J_{FF} = 278 Hz), 37.4 (2F, 6-F), 36.7 (2F, 9-F). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 151.2 (C^{17}), 147.7 (C^4, $^2J_{CF}$ = 23.4 Hz), 142.5 (C^2, $^2J_{CF}$ = 23.4 Hz), 135.9 (C^{16}), 131.0 (C^{14}), 123.1 (C^{15}), 117.5 (C^7, C^{10}, $^1J_{CF}$ = 290.7, $^2J_{CF}$ = 28.5 Hz), 109.1 (C^5, C^8, $^1J_{CF}$ = 259.9, $^2J_{CF}$ = 31.3 Hz), 107.7 (C^6, C^9, $^1J_{CF}$ = 267.9, $^2J_{CF}$ = 32.8 Hz), 48.2 (C^{11}), 41.1 (C^{12}), 32.4 (C^{13}), 33.4 (C^{18}), 29.9 (C^{19}). Found, %: C 44.87; F 41.34; N 4.26. $[M]^+$ 640. $C_{24}H_{26}F_{14}N_2O_2$. Calculated, %: C 45.00; F 41.56; N 4.38. *M* 640.

***N*-[2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)ethyl]-heptafluorobutanamide (XIIIa).** bp 162–163°C (0.2 mm). IR spectrum, ν, cm^{-1}: 3645 (OH); 3448 (NH); 2960, 2921, 2874 (C–H); 1732 (C=O); 1528 (C=C_{arom}); 1234–1187 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.44 (1H, OH), 6.97 (1H, 8-H), 5.31 (1H, NH), 3.53 (1H, 5-H), 2.78 (1H, 6-H), 1.38 (3H, 12-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.4 (3F, 1-F), 43.0 (2F, 3-F), 36.2 (2F, 2-F). Mass spectrum, *m*/*z* (I_{rel}, %): 445 (35.52) $[M]^+$, 388 (1.03) $[M - C(CH_3)_3]^+$, 374 (24.63) $[M - (CH_3)_3CCH_2]^+$, 232 (99.02) $[CH_2{=}CHC_{14}H_{20}OH]^+$, 226 (1.46) $[C_3F_7C(O)NHCH_2]^+$, 219 (100) $[CH_2C_{14}H_{20}OH]^+$, 205 (1.26) $[C_{14}H_{20}OH]^+$, 169 (3.18) $[C_3F_7]^+$, 119 (4.16) $[C_2F_5]^+$, 100 (0.39) $[CF_2{=}CF_2]^+$, 69 (5.29) $[CF_3]^+$, 57 (62.89) $[C(CH_3)_3]^+$. Found: $[M]^+$ 445.1855. $C_{20}H_{26}F_7NO_2$. Calculated: *M* 445.1852.

***N*-[3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propyl]-heptafluorobutanamide (XIIIb).** bp 150–152°C (0.4 mm). IR spectrum, ν, cm^{-1}: 3646 (OH); 3446 (NH); 2959, 2930, 2874 (C–H); 1732 (C=O); 1529 ($C=C_{arom}$); 1390 (C–O); 1234–1157 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.00 (1H, OH), 6.95 (1H, 9-H), 5.39 (1H, NH), 3.60 (1H, 5-H), 3.21 (1H, 6-H), 2.83 (1H, 7-H), 1.35 (3H, 13-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.7 (3F, 1-F), 43.3 (2F, 3-F), 36.5 (2F, 2-F). Mass spectrum, *m*/*z* (I_{rel}, %): 459 (33.69) $[M]^+$, 402 (0.69) $[M - C(CH_3)_3]^+$, 388 (43.81) $[M - (CH_3)_3CCH_2]^+$, 297 (5.97) $[M - C_6H_3O]^+$, 169 (6.12) $[C_3F_7]^+$, 119 (4.41) $[C_2F_5]^+$, 100 (2.29) $[CF_2=CF_2]^+$, 69 (14.21) $[CF_3]^+$, 57 (62.89) $[C(CH_3)_3]^+$. Found: $[M]^+$ 459.2005. $C_{21}H_{28}F_7NO_2$. Calculated: *M* 459.2008.

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