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Reactions of Epoxides Derived from Internal Perfluoroolefins with *o*-Phenylenediamine and 2-Aminophenol

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Abstract—The reactions of epoxy derivatives of internal perfluoroolefins with *o*-phenylenediamine and 2-aminophenol in dioxane gave 23–67% of the corresponding 2,3-bis(perfluoroalkyl)quinoxalines and 2,3-bis-(perfluoroalkyl)-2*H*-1,4-benzoxazin-2-ols, respectively. When *N*,*N*-dimethylacetamide was used as a solvent, the main reaction pathway was anionic isomerization of epoxides into ketones which were then converted into 2-perfluoroalkylbenzimidazoles (in the reactions with *o*-phenylenediamine) or 2-hydroxy-*N*-perfluoroalkanoylanilines (in the reactions with 2-aminophenol). The reaction of 3,4-epoxydodecafluorohexane with 2-aminophenol in *N*,*N*-dimethylacetamide was accompanied by unusual cyclization to afford 2-pentafluoropropanoyl-2-pentafluoroethyl-1,3-benzoxazolidine.

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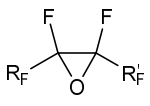
We previously showed that epoxy derivatives of internal perfluoroolefins can be converted into five- and six-membered N,O,S-containing heterocycles by the action of N,O,S-difunctional nucleophiles [1–3]. Reactions of perfluoro(2,3-epoxyalkanes) with ethylenediamine, 2-aminoethanol, thiourea, thiosemicarbazide, and aldehyde or ketone thiosemicarbazones gave perfluoroalkyl-substituted diazines, oxazines, 2-amino- and 2-hydrazinodihydrothiazoles, as well as ketone and camphor dihydrothiazolylhydrazones. There are no published data on reactions of internal perfluoro(epoxyalkanes) with aromatic difunctional nucleophilic reagents.

With the goal of obtaining perfluoroalkyl-substituted compounds having both heterocyclic and aromatic fragments, in the present work we examined reactions of 2,3-epoxyoctafluorobutane (**I**, *cis*/*trans* ≈ 1:9), 3,4-epoxydodecafluorohexane (**II**, *cis*/*trans* ≈ 1:9), and 2,3-epoxydodecafluorohexane (**III**, *cis*/*trans* ≈ 1:9) [4] with *o*-phenylenediamine (**IV**) and 2-aminophenol (**V**).



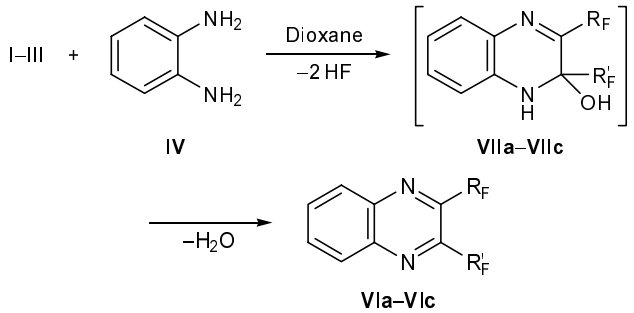
I–III

I, $R_F = R'_F = CF_3$; **II**, $R_F = R'_F = C_2F_5$; **III**, $R_F = CF_3$, $R'_F = C_3F_7$.

The reactions were performed in aprotic solvents capable of solvating cationic species but differing in their polarity, 1,4-dioxane and *N*,*N*-dimethylacetamide (DMA) with a view to estimate the regioselectivity of the observed transformations.

Unlike epoxyhexafluoropropane which is known to readily react with nucleophiles **IV** and **V** in a number of solvents [5], oxiranes **I**–**III** reacted with *o*-phenylenediamine (**IV**) in dioxane only at elevated temperature (sealed ampule, ~100°C); the reactions took several hours and led to formation of 2,3-bis(trifluoromethyl)quinoxaline (**VIa**), 2,3-bis(pentafluoroethyl)-

Scheme 1.



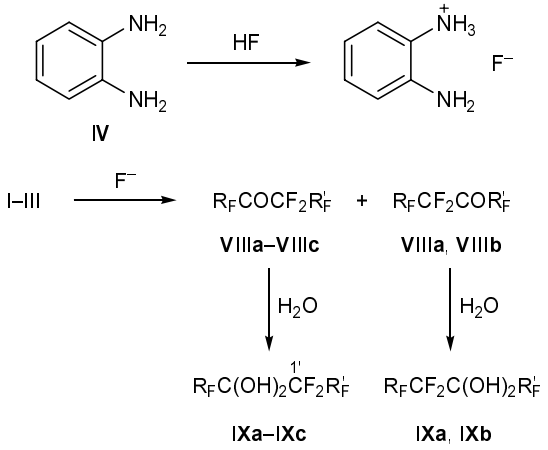
I, **VIa**, **VIIa**, $R_F = R'_F = CF_3$; **II**, **VIb**, **VIIb**, $R_F = R'_F = CF_2CF_3$; **III**, **VIc**, **VIIc**, $R_F = C^{1'}F_3$, $R'_F = C^{1''}F_2C^{2''}F_2C^{3''}F_3$.

quinoxaline (**VIb**), and 2-heptafluoropropyl-3-trifluoromethylquinoxaline (**VIc**), respectively (Scheme 1). Presumably, the process involves intermediate formation of 2,3-bis(perfluoroalkyl)-1,2-dihydro-1,4-benzodiazin-2-ols **VIIa**–**VIIc** which are converted into more stable aromatic quinoxaline system **VI** via elimination of water molecule (in contrast to diazinols synthesized by us previously by reaction of internal epoxyperfluoroalkanes with ethylenediamine [1]).

The structure of compounds **VIa**–**VIc** was confirmed by their IR and ^{1}H and ^{19}F NMR spectra and elemental analyses. The spectral parameters and physical constants of 2,3-bis(trifluoromethyl)quinoxaline (**VIa**) coincided with those reported in [6] for the product obtained from hexafluorobutane-2,3-dione and diamine **IV**.

Analysis of the ^{19}F NMR spectra of the reaction mixtures obtained from compounds **I**–**III** and diamine **IV** in dioxane showed the presence of ketones **VIIIa**–**VIIIc** (~25–28%) which were identified as the corresponding hydrates **IXa**–**IXc**. Ketones **VIII** are likely to be formed as a result of ionic isomerization of the initial oxiranes by the action of fluoride ion (Scheme 2, see table) [1, 7, 8].

Scheme 2.



I, **VIIIa**, **IXa**, $R_F = C^1F_3$, $R'_F = C^{2'}F_3$; **II**, **VIIIb**, **IXb**, $R_F = C^1F_2C^2F_3$, $R'_F = C^{2'}F_2C^{3'}F_3$; **III**, **VIIIc**, **IXc**, $R_F = C^1F_3$, $R'_F = C^{2'}F_2C^{3'}F_2C^{4'}F_3$.

The reactions of perfluorinated dialkyloxiranes **I** and **II** with diamine **IV** in a more polar solvent, *N*,*N*-dimethylacetamide were characterized by reduced yield of 2,3-bis(perfluoroalkyl)quinoxalines **VIa** and **VIb** and increased fraction of the isomerization products formed by the action of F^- on the initial oxirane. The formation of octafluorobutan-2-one (**VIIIa**) was

Reactions of perfluorinated oxiranes **I**–**III** with *o*-phenylenediamine (**IV**) and 2-aminophenol (**V**) (molar ratio oxirane–nucleophile 1:2)

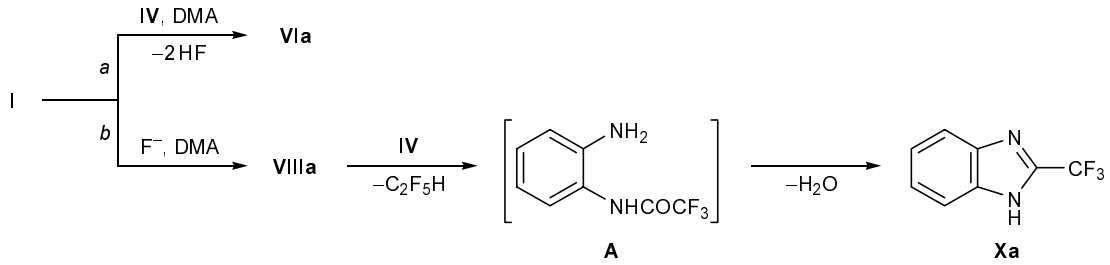
Initial reactant nos.	Solvent	Reaction time, h	Products (molar ratio,[a] %)
I, **IV**	Dioxane	8.5	**VIa**, **VIIIa** (~75:25)
I, **IV**	DMA	1.5	**VIa**, **Xa**, **VIIIa** (~8:15:77)
II, **IV**	Dioxane	4.5	**VIb**, **VIIIb** (~72:28)
II, **IV**	DMA	2.5	**VIb**, **Xb**, **Xc**, **XI**, **VIIb** (~8:72:14:6)
III, **IV**	Dioxane	6	**VIc**, **VIIIb**, **VIIIc** (~82:9:9)
I, **V**	Dioxane	3.5	**XIIa**
I, **V**	DMA	1	**XIIa**, **VIIIa**, **XIIIa** (~32:61:7)
II, **V**	Dioxane	4	**XIIb**
II, **V**	DMA	1	**XIV**, **XIIIb**, **XIIIc** (~15:73:12)
III, **V**	Dioxane	4.5	**XIIc**, **XIId** (~51:49)

[a] According to the ^{19}F NMR data.

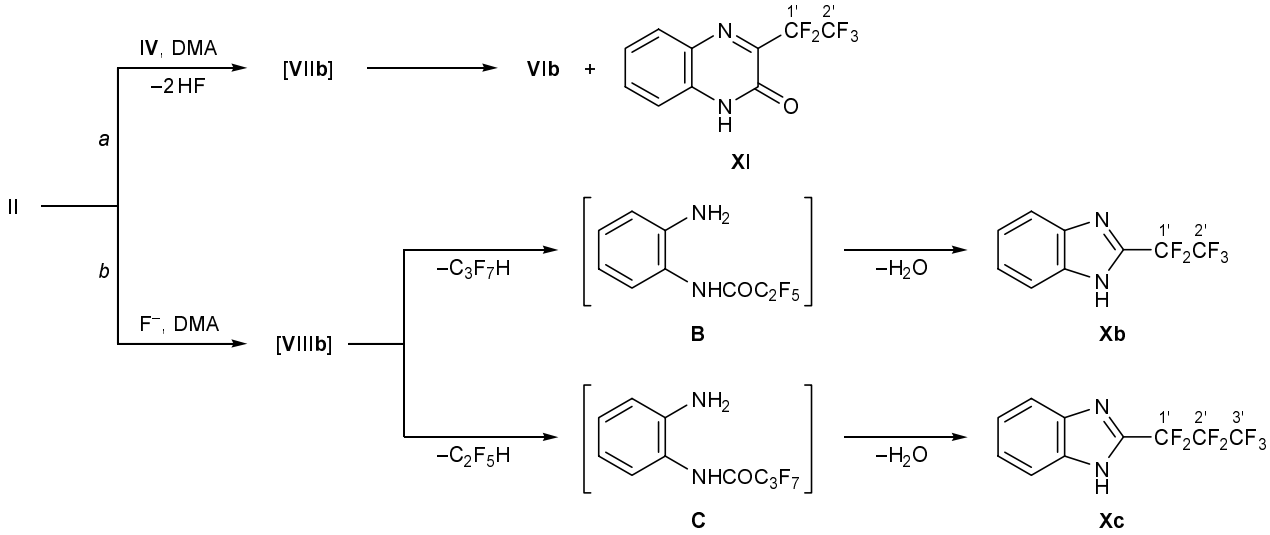
the main pathway in the reaction with oxirane **I**; in the presence of diamine **IV**, compound **VIIIa** underwent partial haloform cleavage to pentafluoroethane and 2-amino-*N*-trifluoroacetylaniline **A**. The latter turned out to be unstable under the given conditions, and it lost water molecule to give 2-trifluoromethylbenzimidazole (**Xa**) (Scheme 3, pathway *b*); 2,3-bis(trifluoromethyl)quinoxaline (**VIa**, pathway *a*) was the minor product: its yield was as poor as ~8%.

The reaction of oxirane **II** with *o*-phenylenediamine (**IV**) in DMA (Scheme 4) was accompanied by formation of a small amounts of 2,3-bis(pentafluoroethyl)-quinoxaline (**VIb**) and 3-pentafluoroethylquinoxalin-2(1*H*)-one (**XI**); obviously, the latter was formed via ring closure of intermediate **VIIb** to 1,4-diazine (pathway *a*) with elimination of pentafluoroethane. It should be noted that intermediate **VIIb** was detected by GC–MS analysis of the reaction mixture, which supports the proposed scheme for the reaction of **II** with **IV**. However, the main reaction pathway is anionic isomerization of oxirane **II** to dodecafluorohexan-2-one (**VIIIb**) (pathway *b*) which undergoes haloform cleavage by the action of diamine **IV**, following both possible directions; as a result, 1*H*-heptafluoropropane, pentafluoroethane, and amides **B** and **C** are obtained. The latter are converted, respectively, into 2-pentafluoroethylbenzimidazole (**Xb**) and 2-heptafluoropropylbenzimidazole (**Xc**) via elimination of water

Scheme 3.



Scheme 4.

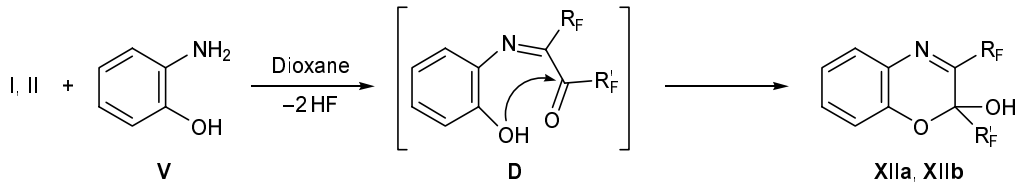


molecule. Quinoxaline **VIb** can be isolated from the product mixture by sublimation, and benzimidazole **Xb** can be isolated by crystallization of the residue from aqueous ethanol. The spectral parameters and physical constants of compound **Xb** coincided with those reported in [9]. Benzimidazoles **Xa**–**Xc** were also synthesized independently, by the Phillips reaction from the corresponding perfluorocarboxylic acids and *o*-phenylenediamine (**IV**) in the presence of hydrochloric acid [9, 10], and were then used for identification by ^{19}F NMR spectroscopy. Compound **XI** was identified by the IR [11], ^{19}F NMR, and GC–MS data.

The reactions of oxiranes **I** and **II** with 2-aminophenol (**V**) in dioxane were carried out under analogous conditions (sealed ampule, ~100°C). As a result, the corresponding cyclization products, 2,3-bis(trifluoromethyl)-2*H*-1,4-benzoxazin-2-ol (**XIIa**) and 2,3-bis(pentafluoroethyl)-2*H*-1,4-benzoxazin-2-ol (**XIIb**) were formed with high selectivity (Scheme 5). Presumably, the lower basicity of 2-aminophenol (**V**) compared to *o*-phenylenediamine (**IV**) is responsible for the lack of isomerization of the initial epoxy compounds into ketones.

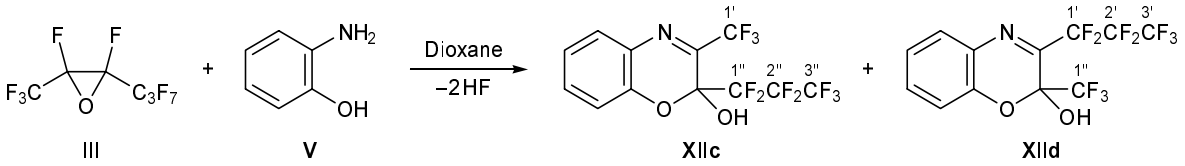
Pure compounds **XIIa** and **XIIb** were isolated, respectively, by crystallization and vacuum distillation, and their structure was confirmed by the IR and ^{1}H and ^{19}F NMR spectra. In addition, compound **XIIa** was characterized by ^{13}C NMR spectroscopy.

Scheme 5.



$R_F = C^{1'}F_3$, $R'_F = C^{1''}F_3$ (**a**); $R_F = C^{2'}F_3C^{1'}F_AF_B$, $R'_F = C^{2''}F_3C^{1''}F_AF_B$ (**b**).

Scheme 6.

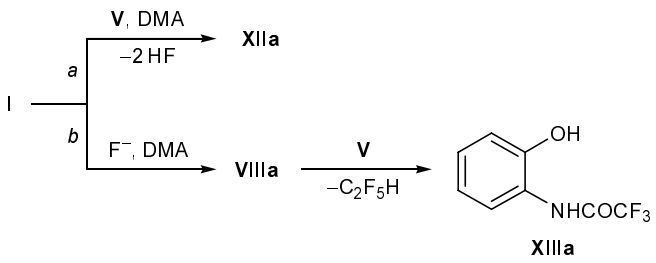


Under analogous conditions, nucleophilic opening of the oxirane ring in unsymmetrically substituted 2,3-epoxy dodecafluorohexane (**III**) by the action of 2-aminophenol (**V**) occurred in both possible directions to give a mixture of regioisomeric 2-heptafluoropropyl-3-trifluoromethyl-2*H*-1,4-benzoxazin-2-ol (**XIIc**) and 3-heptafluoropropyl-2-trifluoromethyl-2*H*-1,4-benzoxazin-2-ol (**XIId**) (Scheme 6). These products were formed in approximately equal amounts (see table), indicating equal probabilities for nucleophile to attack both carbon atom in the oxirane ring. This may be rationalized in terms of the determining effect of electronic factors on the stability of intermediate O-anions [1]. Different physical properties of compounds **XIIc** and **XIId** allowed us to isolate the former in the pure state by recrystallization of the product mixture.

When the reaction of 2,3-epoxyoctafluorobutane (**I**) with aminophenol (**V**) was performed in DMA, the major product was octafluorobutan-2-one (**VIIIa**, pathway *b*) which was likely to result from ionic isomerization of the substrate by the action of fluoride ion [7, 8]; in addition, small amounts of 2,3-bis(trifluoromethyl)-2*H*-1,4-benzoxazin-2-ol (**XIIa**, ~32%, pathway *a*) and 2-hydroxy-*N*-trifluoroacetylaniline (**XIIIa**, ~7%) were obtained (Scheme 7). Obviously, the latter resulted from haloform cleavage of ketone **VIIIa** by the action of aminophenol (pathway *b*). The formation of amides according to an analogous scheme was observed by us previously in the reactions of internal perfluoro(epoxyalkanes) with ethylenediamine and 2-aminoethanol in a polar aprotic solvent [1]).

It should be noted that increase in the length of fluoroalkyl substituents in the initial oxirane gives rise to an unusual pathway in the reaction with *o*-aminophenol (**V**) in DMA. Thus compound **II** reacted with aminophenol **V** in DMA to give amides **XIIIb** and **XIIIc** and 2-pentafluoroethyl-2-pentafluoropropanoyl-2,3-dihydro-1,3-benzoxazole (**XIV**) (Scheme 8). Presumably, the process begins with nucleophilic attack by the amino group of aminophenol **V** on the oxirane carbon atom in **II** to give intermediate **E** as a result of opening of the three-membered ring (Scheme 8, pathway *a*). However, the subsequent cyclization involves the imino carbon atom rather than carbonyl carbon atom [as in the reaction with compound **I** (Scheme 5)], which may be due to weaker solvation of the C=N group in DMA, as compared to the carbonyl group. The cyclization releases fluoride ion which promotes isomerization of oxirane **II** according to pathway *b* (Scheme 8) as the main reaction direction. Haloform cleavage of perfluorohexan-3-one (**VIIIb**) by the action of aminophenol (**V**) followed both possible pathways to afford 2-hydroxy-*N*-pentafluoropropanoylaniline (**XIIIb**) and 2-hydroxy-*N*-heptafluorobutanoylaniline (**XIIIc**) together with 1*H*-heptafluoropropane and pentafluoroethane.

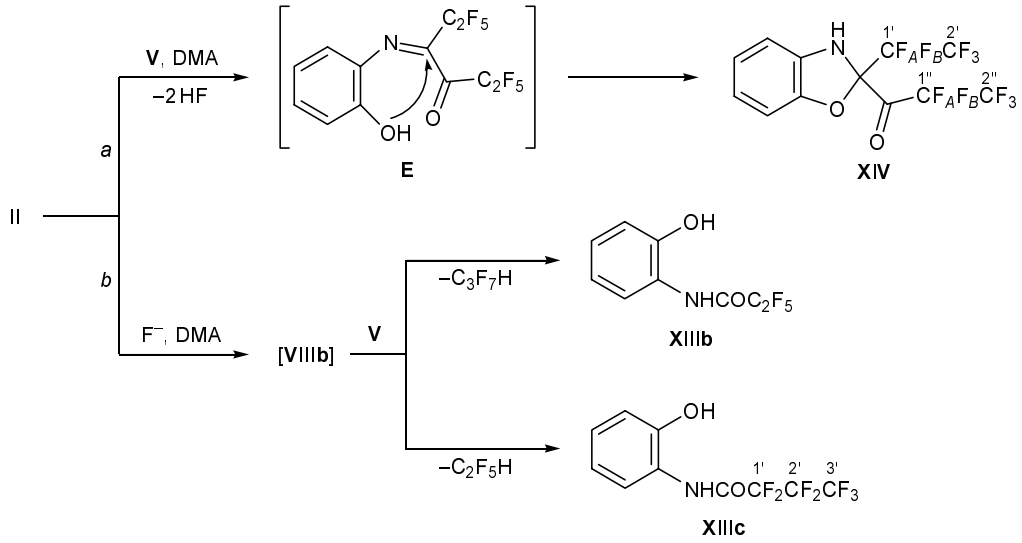
Scheme 7.



Compounds **XIIIb** and **XIV** were isolated as individual substances, and their structure was confirmed by the IR, ^{1}H and ^{19}F NMR, and mass spectra and elemental analyses. Amide **XIIIb** was reported previously [5]. Compounds **XIIIa** and **XIIIc** were identified by ^{19}F NMR spectroscopy and gas chromatography–mass spectrometry [12, 13].

We can conclude that epoxides **I**–**III** derived from internal perfluoroolefins react with difunctional aromatic nucleophiles **IV** and **V** in dioxane to give the corresponding 2,3-bis(perfluoroalkyl)quinoxalines and 2,3-bis(perfluoroalkyl)-2*H*-1,4-benzoxazin-2-ols, respectively, in high yield. Replacement of dioxane by more polar *N*,*N*-dimethylacetamide which possesses a greater solvating power decreases the contribution of the cyclization process (pathway *a*), and quinoxalines and benzoxazinols become minor products. Under these conditions, the main reaction direction is anionic isomerization of the initial oxiranes to ketones which are then converted into 2-perfluoroalkylbenzimidazoles or 2-hydroxy-*N*-perfluoroalkanoylanilines (pathway *b*).

Scheme 8.



EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DRX-400 spectrometer (400, 100, and 376 MHz, respectively) using tetramethylsilane and hexafluorobenzene as internal references. The mass spectra were obtained on a Varian MAT-311 mass spectrometer and on a Fisions GC–MS system (MD 800 detector; HP-5 quartz capillary column, 25 m × 0.25 mm, film thickness 0.25 μm; carrier gas helium; electron impact, 70 eV). The IR spectra were measured in the frequency range from 400 to 4000 cm^{-1} on a Perkin–Elmer Spectrum One FT-IR spectrometer from samples dispersed in mineral oil. Perfluorinated oxiranes **I**–**III** were synthesized by the procedures described in [4]. The product ratios were determined from the intensities of the corresponding signals in the ^{19}F NMR spectra. The product compositions and ratios are given in table.

Reaction of 2,3-difluoro-2,3-bis(trifluoromethyl)-oxirane (I) with *o*-phenylenediamine (IV). *a*. A glass ampule was charged with 3.0 g (0.014 mol) of compound **I**, 3.0 g (0.028 mol) of diamine **IV**, and 20 ml of dioxane. The ampule was sealed and heated on a boiling water bath with occasional shaking. When the reaction was complete, the ampule was cooled to –70°C and opened, and ^{19}F NMR spectrum of the reaction mixture was recorded (see table). The mixture was poured into 200 ml of ice water, the aqueous (upper) layer was separated, and the organic layer was washed with water once more. The precipitate was filtered off and dried at room temperature, and compound **VIa** thus isolated was purified by column chromatography on silica gel using chloroform as eluent, followed by recrystallization from aqueous ethanol. Yield 1.9 g (51%), mp 121–121.5°C; published data [6]: mp 118°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 8.23–8.27 m (2H, 2CH), 8.36–8.40 m (2H, 2CH). ^{19}F NMR spectrum (acetone-d_6): δ_F 99.4 ppm, s ($2CF_3$). Found, %: C 45.21; H 1.21; F 42.84; N 10.63. $C_{10}H_4F_6N_2$. Calculated, %: C 45.11; H 1.50; F 42.86; N 10.53.

1,1,1,3,3,4,4,4-Octafluorobutane-2,2-diol (IXa). ^{19}F NMR spectrum of the reaction mixture (DMSO-d_6), δ_F, ppm: 38.2 q (2F, 1'-F, $^{4}J_{FF}$ = 10.6 Hz), 82.6 t.q (3F, 1-F, $^{4}J_{FF}$ = 10.6, $^{5}J_{FF}$ = 3.6 Hz), 83.9 q (3F, 2'-F, $^{5}J_{FF}$ = 3.6 Hz).

b. The reaction was performed as described above in *a* using 5.8 g (0.027 mol) of compound **I**, 5.8 g (0.054 mol) of diamine **IV**, and 20 ml of DMA. When the reaction was complete, ^{19}F NMR spectrum of the reaction mixture was recorded, volatile substances were recondensed into a trap cooled to –70°C, and the residue was poured into 200 ml of ice water. The precipitate, 0.9 g, was filtered off and dried at room temperature. According to the ^{19}F NMR data, it was a mixture of 2,3-bis(trifluoromethyl)quinoxaline (**VIa**) and 2-trifluoromethylbenzimidazole (**Xa**) at a ratio of ~2:1. Quinoxaline **VIa** was isolated from the mixture by sublimation at 90–95°C (760 mm), and the residue containing mainly benzimidazole **Xa** was subjected to column chromatography on silica gel using chloroform–methanol (10:0.5, by volume) as eluent; R_f(**VIa**) = 0.91, R_f(**Xa**) = 0.39. An additional amount of compound **Xa** was isolated by extraction of the aqueous phase with chloroform. The extract contain-

ing compounds **Xa** and **IV** (according to the ^{19}F NMR data) was dried over magnesium sulfate, the solvent was removed under reduced pressure, and compound **Xa** was isolated by column chromatography. Recrystallization from aqueous ethanol gave colorless crystals of quinoxaline **VIa** with mp 120–121°C (published data [6]: mp 118°C), yield 0.5 g (7%), and benzimidazole **Xa** with mp 208–210°C (published data [10]; mp 210°C), yield 0.6 g (12%). ^1H NMR spectrum of compound **Xa** (DMSO-d_6), δ, ppm: 7.38–7.41 m (2H, CH), 7.74 m (2H, CH), 13.93 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6): δ_F 99.9 ppm, s (CF_3).

Reaction of 2,3-difluoro-2,3-bis(pentafluoroethyl)oxirane (II) with *o*-phenylenediamine (IV). *a*. The reaction was performed with 4.7 g (0.015 mol) of compound **II** and 3.2 g (0.03 mol) of *o*-phenylenediamine (**IV**) in 20 ml of dioxane as described above for compound **I** (method *a*). After treatment of the reaction mixture with water, crystals separated and were filtered off, dried at room temperature, and subjected to column chromatography on silica gel using chloroform as eluent [R_f(**VIb**) 0.9]. The product was additionally purified by recrystallization from aqueous ethanol. Yield of **VIb** 1.7 g (31%), colorless crystals, mp 53–53.5°C (sublimes). IR spectrum, ν, cm^{-1}: 1564, 1612 (C=C, C=N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.24–8.28 m (2H, CH), 8.35–8.39 m (2H, CH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 54.4 s (4F, CF_2), 83.2 s (6F, CF_3). Found, %: C 39.23; H 1.04; F 51.68; N 7.39. $C_{12}H_4F_{10}N_2$. Calculated, %: C 39.34; H 1.09; F 51.91; N 7.65.

1,1,1,2,2,4,4,5,5,6,6,6-Dodecafluorohexan-3,3-diol (IXb). ^{19}F NMR spectrum of the reaction mixture (DMSO-d_6), δ_F, ppm: 39.2 m (2F, 2'-F), 39.6 t.t (2F, 1-F, $^4J_{FF}$ = 13.5, $^5J_{FF}$ = 7.4 Hz), 42.5 m (2F, 1'-F), 82.7 t (3F, 3'-F, $^4J_{FF}$ = 10.2 Hz), 84.4 t (3F, 2-F, $^5J_{FF}$ = 5.4 Hz).

b. Likewise, the reaction was performed with 3.9 g (0.012 mol) of compound **II** and 2.7 g (0.025 mol) of diamine **IV** in 16 ml of DMA. When the reaction was complete, the ampule was cooled to –70°C and opened, volatile products (C_2F_5H and C_3F_7H) were removed, and the residue was poured into 200 ml of ice water. The precipitate was filtered off. According to the ^{19}F NMR data, it was a mixture of compounds **VIb**, **Xb**, **Xc**, and **XI** at a ratio of ~14:69:14:3; it also contained a small amount of benzodiazine **VIIb** (GC–MS). The product was dried first at room temperature and then at 50–60°C; sublimation of quinoxaline **VIb** started at that temperature; yield 0.2 g (4.4%). When compound **VIb** no longer sublimed, the residue was subjected to column chromatography on silica gel using chloroform–methanol (10:0.5, by volume) as eluent, followed by double recrystallization from aqueous ethanol. Yield of **Xb** 1.5 g (52%), colorless crystals, mp 210–212°C; published data [9]: mp 212–214°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.40–7.42 m (2H, CH), 7.67–7.90 m (2H, CH), 14.0 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 49.9 q (2F, CF_2, $^3J_{FF}$ = 3.0 Hz), 79.9 t (3F, CF_3, $^3J_{FF}$ = 3.0 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 237 (5.4) $[M + 1]^+$, 236 (70.9) $[M]^+$, 217 (10.0) $[M - F]^+$, 168 (7.4), 167 (100) $[M - CF_3]^+$, 147 (28.7) $[M - CF_3 - HF]^+$, 140 (18.4), 116 (5.7) $[M - C_2F_5H]^+$, 102 (14.6) $[C_6H_4NC]^+$, 95 (16.4), 90 (16.5) $[C_6H_4N]^+$, 69 (11.8) $[CF_3]^+$. Found, %: C 45.49; H 2.01; F 40.56, N 11.59. $C_9H_5F_5N_2$. Calculated, %: C 45.76; H 2.12; F 40.25; N 11.86.

2-Heptafluoropropyl-1*H*-benzimidazole (Xc). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 36.3 m (2F, 2'-F), 51.3 m (2F, 1'-F), 82.8 t (3F, 3'-F, $^4J_{FF}$ = 8.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 286 (49.6) $[M]^+$, 267 (9.5) $[M - F]^+$, 186 (15.0), 168 (7.6), 167 (100) $[M - C_2F_5]^+$, 166 (11.3) $[M - C_2F_5H]^+$, 147 (23.7), 140 (15.0), 116 (9.1) $[M - C_3F_7H]^+$, 102 (12.6) $[C_6H_4NC]^+$, 95 (15.2), 90 (16.8) $[C_6H_4N]^+$, 69 (14.4) $[CF_3]^+$, 64 (9.9), 63 (13.3).

3-Pentafluoroethylquinoxalin-2(1*H*)-one (XI). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 47.0 q (2F, CF_2, $^3J_{FF}$ = 1.4 Hz), 82.2 t (3F, CF_3, $^3J_{FF}$ = 1.4 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (36.4) $[M]^+$, 195 (20) $[M - CF_3]^+$, 167 (100) $[M - CF_3 - CO]^+$, 147 (33.6), 145 (14.5) $[M - C_2F_5]^+$, 140 (15.4), 119 (13.6) $[C_2F_5]^+$, 102 (20.0) $[C_6H_4NC]^+$, 95 (20.0), 90 (55.5) $[C_6H_4N]^+$, 76 (13.6) $[C_6H_4]^+$, 75 (9.1), 69 (35.5) $[CF_3]^+$.

Pentafluoroethane. ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 23.4 d.q (2F, HCF_2, $^2J_{HF}$ = 51.1, $^3J_{FF}$ = 3.0 Hz), 77.8 d.t (3F, CF_3, $^3J_{HF}$ = $^3J_{FF}$ = 3.0 Hz).

1*H*-Heptafluoropropane. ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 23.9 d.t.q (2F, 1-F, $^2J_{HF}$ = 50.2, $^3J_{FF}$ = 4.9, $^4J_{FF}$ = 7.0 Hz), 30.7 d.t (2F, 2-F, $^3J_{HF}$ = $^3J_{FF}$ = 4.9 Hz), 81.2 t (3F, CF_3, $^4J_{FF}$ = 7.0 Hz).

2,3-Bis(pentafluoroethyl)-1,2-dihydroquinoxalin-2-ol (VIIb). Mass spectrum, *m*/*z* (I_{rel}, %): 384 (9.1) $[M]^+$, 265 (100) $[M - C_2F_5]^+$, 245 (18.2) $[M - C_2F_5 - HF]^+$, 217 (45.5) $[M - C_2F_5 - CO - HF]^+$, 197 (10.0), 196 (16.4) $[M - CF_3 - C_2F_5]^+$, 195 (10.0) $[M - C_2F_5 - CF_3H]^+$, 167 (33.6) $[M - C_2F_5 - CO - CF_3H]^+$, 147 (6.4), 129 (6.4), 120 (16.4), 119 (16.4) $[C_2F_5]^+$, 90 (27.3) $[C_6H_4N]^+$, 69 (30.0) $[CF_3]^+$.

Reaction of 2,3-difluoro-2-heptafluoropropyl-3-trifluoromethyloxirane (III) with *o*-phenylenediamine (IV). The reaction was carried out with 4.7 g (0.015 mol) of compound **III** and 3.2 g (0.03 mol) of compound **IV** in 20 ml of dioxane, following the procedure described above for compound **II** (method *a*). After treatment of the reaction mixture with water, the precipitate was filtered off, dried at room temperature, and subjected to column chromatography on silica gel using chloroform–hexane (10:1, by volume) as eluent, R_f(**VIc**) 0.9. The product was additionally recrystallized from aqueous ethanol. Yield of quinoxaline **VIc** 2.0 g (38%), colorless crystals, mp 40–40.5°C (sublimes). IR spectrum, ν, cm^{-1}: 1550, 1600, 1650 (C=C, C=N). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 8.25–8.29 m (2H, CH), 8.36–8.41 m (2H, CH). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 40.8 m (2F, 2"-F), 56.3 m (2F, 1"-F), 84.4 t (3F, 3"-F, $^4J_{FF}$ = 10.0 Hz), 100.3 t.t (3F, 1'-F, $^5J_{FF}$ = 18.7, $^6J_{FF}$ = 6.2 Hz). Found, %: C 39.28; H 1.20; F 52.16; N 7.57. $C_{12}H_4F_{10}N_2$. Calculated, %: C 39.34; H 1.09; F 51.91; N 7.65.

1,1,1,3,3,4,4,5,5,6,6,6-Dodecafluorohexane-2,2-diol (IXc). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 37.4 m (2F, 3'-F), 41.9 m (2F, 2'-F), 42.05 m (2F, 1'-F), 82.4 t.t (3F, 4'-F, $^4J_{FF}$ = 9.9, $^3J_{FF}$ = 2.9 Hz), 82.8 t.t (3F, 1-F, $^4J_{FF}$ = 10.7, $^5J_{FF}$ = 5.4 Hz).

The ^{19}F NMR spectrum of dihydroxy derivative **IXb** was identical to that of a sample obtained as described above in the reaction of compound **II** with diamine **IV** (method *a*).

Reaction of 2,3-difluoro-2,3-bis(trifluoromethyl)-oxirane (I) with 2-aminophenol (V). *a*. A glass ampule was charged with 4.6 g (0.021 mol) of compound **I**, 4.7 g (0.043 mol) of 2-aminophenol (**V**), and 60 ml of dioxane. The ampule was sealed and heated on a boiling water bath with occasional shaking. When the reaction was complete, the ampule was cooled to –70°C and opened, ^{19}F NMR spectrum of the mixture was recorded (see table), and the mixture was poured into 200 ml of ice water. The aqueous (upper) layer was separated, the organic layer was washed with an additional portion of water, and the precipitate was filtered off, dried at ~40°C, and subjected to column chromatography on silica gel using chloroform as eluent. The product was recrystallized from hexane–benzene (3:1). Yield of compound **XIIa** 4.1 g (67%), colorless crystals, mp 126–127°C. IR spectrum, ν, cm^{-1}: 1585, 1600, 1635 (C=C, C=N); 2770, 3120 br (OH). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.19–7.21 m (1H, CH), 7.26–7.30 m (1H, CH), 7.53–7.57 m (1H, CH), 7.64–7.66 m (1H, CH), 8.73 br.s (1H, OH). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 82.2 q (3F, 1"-F, $^5J_{FF}$ = 8.5 Hz), 97.4 q (3F, 1'-F, $^5J_{FF}$ = 8.5 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 91.24 q (C^2, $^2J_{CF}$ = 36.2 Hz), 117.25 s (C^8), 120.06 q ($C^{1"}$, $^1J_{CF}$ = 276.2 Hz), 122.14 q ($C^{1'}$, $^1J_{CF}$ = 288.0 Hz), 124.87 s (C^5), 129.43 s (C^{4a}), 130.45 s (C^6), 134.36 s (C^7), 143.76 q (C^3, $^2J_{CF}$ = 35.9 Hz), 144.16 s (C^{8a}). Mass spectrum, *m*/*z* (I_{rel}, %): 285 (39.2) $[M]^+$, 268 (12.5) $[M - OH]^+$, 256 (19.6) $[M - H - CO]^+$, 246 (27.5), 218 (7.5), 217 (8.1), 216 (94.8) $[M - CF_3]^+$, 196 (90.0) $[M - CF_3 - HF]^+$, 188 (78.5) $[M - CO - CF_3]^+$, 168 (100), 140 (24.5), 132 (10.0), 103 (7.5), 102 (93.5) $[C_6H_4NC]^+$, 90 (20.0) $[C_6H_4N]^+$, 76 (26.5) $[C_6H_4]^+$, 69 (50.2) $[CF_3]^+$. Found, %: C 42.32; H 1.82; F 39.87; N 4.88. $C_{10}H_5F_6NO_2$. Calculated, %: C 42.11; H 1.75; F 40.00; N 4.91.

b. The reaction was carried out in a similar way with 4.6 g (0.021 mol) of compound **I** and 4.7 g (0.043 mol) of aminophenol **V** in 20 ml of DMA. When the reaction was complete, volatile products were recondensed into a trap cooled to –70°C, and the residue was treated with water. The precipitate was filtered off, dried at 50–60°C, and recrystallized from hexane–benzene (3:1). We thus isolated 0.7 g (12%) of compound **XIIIa**.

***N*-(2-Hydroxyphenyl)trifluoroacetamide (XIIIa).** ^{19}F NMR spectrum (DMSO-d_6): δ_F 88.8 ppm, s (CF_3).

Reaction of 2,3-difluoro-2,3-bis(pentafluoroethyl)oxirane (II) with 2-aminophenol (V). *a*. The reaction was performed with 3.0 g (0.009 mol) of compound **II** and 2.0 g (0.018 mol) of aminophenol **V** in 40 ml of dioxane according to the procedure described above for the reaction of **I** with **V** (method *a*). When the reaction was complete, the ampule was opened, and the mixture was poured into 200 ml of ice water and extracted with chloroform. The extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was subjected to vacuum distillation. Yield of compound **XIIb** 1.5 g (42%), oily substance, bp 76–80°C (10 mm). IR spectrum, ν, cm^{-1}: 1589, 1598, 1625 (C=C, C=N), 3182, 3445, 3595, 3687 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.50 br.s (1H, OH), 7.01–7.03 m (1H, CH), 7.15–7.19 m (1H, CH), 7.38–7.40 m (1H, CH), 7.56–7.59 m (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 37.9 d.d.d (1F, 1"-F_B, $^2J_{FF}$ = 282.8, $^5J_{1'\text{-}B,1"\text{-}B}$ = 29.4, $^5J_{1'\text{-}A,1"\text{-}B}$ = 19.8 Hz), 38.7 d.d.d (1F, 1"-F_A, $^2J_{FF}$ = 282.8, $^5J_{1'\text{-}B,1"\text{-}A}$ = 15.2, $^5J_{1'\text{-}A,1"\text{-}A}$ = 10.2 Hz), 48.6 d.d.d (1F, 1'-F_B, $^2J_{FF}$ = 300.5, $^5J_{1'\text{-}B,1"\text{-}B}$ = 29.4,

$^5J_{1'\text{-}B,1''\text{-}A}$ = 15.2 Hz), 51.1 d.d.d (1F, 1'-F_A, $^2J_{FF}$ = 300.5, $^5J_{1'\text{-}A,1''\text{-}B}$ = 19.8, $^5J_{1'\text{-}A,1''\text{-}A}$ = 10.2 Hz), 81.1 s (3F, 2''-F), 82.9 d (3F, 2'-F, J = 1.8 Hz). Mass spectrum, m/z (I_{rel}, %): 385 (9.9) $[M]^+$, 368 (6.9) $[M - OH]^+$, 356 (6.1), 346 (6.7), 267 (7.5), 266 (100) $[M - C_2F_5]^+$, 246 (24.7) $[M - C_2F_5 - HF]^+$, 238 (21.8), 218 (43.0) $[M - C_2F_5 - CO - HF]^+$, 190 (9.1), 169 (6.5), 168 (51.3) $[M - C_2F_5 - CO - CF_3H]^+$, 119 (18.6) $[C_2F_5]^+$, 102 (40.6) $[C_6H_4NC]^+$, 93 (5.5) $[C_6H_5O]^+$, 91 (10.6) $[C_6H_4NH]^+$, 76 (12.2) $[C_6H_4]^+$, 75 (5.4), 69 (13.6) $[CF_3]^+$. Found, %: C 37.82; H 1.73; F 49.55; N 3.94. $C_{12}H_5F_{10}NO_2$. Calculated, %: C 37.40; H 1.30; F 49.35; N 3.64.

b. Likewise, the reaction was performed with 5.5 g (0.017 mol) of compound **II** and 3.5 g (0.032 mol) of aminophenol **V** in 20 ml of DMA. When the reaction was complete, volatile products (C_2F_5H and C_3F_7H) were removed, the mixture was poured into ice water, and the organic layer (bottom) was separated and washed with water. According to the ^{19}F NMR and GC–MS data, the precipitate was a mixture of compounds **XIV**, **XIIIb**, and **XIIIc** at a ratio of ~26:57:17); it was filtered off, dried at room temperature, and subjected to fractional crystallization from hexane–benzene (1:1) to isolate 1.4 g (31.8%) of amide **XIIIb** with mp 115–116°C (published data [5]: mp 117–118°C) and 0.8 g of a mixture of amides **XIIIb** and **XIIIc** at a ratio of ~7:3 (according to the NMR data). The solvent was removed from the filtrate under reduced pressure, and the residue was recrystallized twice from hexane to isolate 0.2 g (3%) of compound **XIV** as colorless crystals with mp 97–98°C. IR spectrum, ν, cm^{-1}: 1504, 1605, 1632 (C=C), 1763 (C=O), 3315 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.61 br.s (1H, NH), 6.83–6.85 m (1H, CH), 6.92–6.96 m (1H, CH), 7.06–7.13 m (2H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 43.3 d.m (2F, 1'-F_B, 1''-F_B, $^2J_{1'\text{-}A,1'\text{-}B} \approx {}^2J_{1''\text{-}A,\,1''\text{-}B} \approx$ 287.7 Hz), 48.7 d.m (2F, 1'-F_A, 1''-F_A, $^2J_{1'\text{-}A,1'\text{-}B} \approx {}^2J_{1''\text{-}A,1''\text{-}B} \approx$ 287.7 Hz), 83.85 t (3F, CF_3, $^3J_{FF}$ = 2.1 Hz), 83.86 t (3F, CF_3, $^3J_{FF}$ = 2.1 Hz). Mass spectrum, m/z (I_{rel}, %): 385 (27.8) $[M]^+$, 267 (11.3), 266 (100) $[M - C_2F_5]^+$, 238 (12.4) $[M - C_2F_5 - CO]^+$, 218 (9.9) $[M - C_2F_5 - CO - HF]^+$, 169 (6.1) $[M - C_2F_5 - CO - CF_3]^+$, 168 (13.5), 119 (5.8) $[C_2F_5]^+$, 102 (14.2) $[C_6H_4NC]^+$, 93 (7.2) $[C_6H_5O]^+$, 69 (7.0) $[CF_3]^+$. Found, %: C 37.32; H 1.35; F 49.58; N 3.38. $C_{12}H_5F_{10}NO_2$. Calculated, %: C 37.40; H 1.30; F 49.35; N 3.64.

***N*-(2-Hydroxyphenyl)pentafluoropropanamide (XIIIb).** ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.14 br.s (1H, OH), 6.91–7.00 m (2H, CH), 7.10–7.14 m (1H, CH), 7.98–8.00 m (1H, CH), 8.58 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 41.3 q (2F, CF_2, $^3J_{FF}$ = 1.6 Hz), 80.5 t (3F, CF_3, $^3J_{FF}$ = 1.6 Hz). Mass spectrum, m/z (I_{rel}, %): 255 (39.5) $[M]^+$, 168 (10.0) $[M - CF_3 - H_2O]^+$, 137 (6.8), 136 (100) $[M - C_2F_5]^+$, 119 (11.8) $[C_2F_5]^+$, 108 (35.1) $[M - C_2F_5CO]^+$, 90 (6.3) $[C_6H_4N]^+$, 80 (48.1) $[C_5H_5NH]^+$, 79 (7.4), 69 (10.4) $[CF_3]^+$.

***N*-(2-Hydroxyphenyl)heptafluorobutanamide (XIIIc).** ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 36.2 s (2F, 2'-F), 43.6 q (2F, 1'-F, $^4J_{FF}$ = 8.5 Hz), 82.6 t (3F, 3'-F, $^4J_{FF}$ = 8.5 Hz).

Reaction of 2,3-difluoro-2-heptafluoropropyl-3-trifluoromethyloxirane (III) with 2-aminophenol (V). The reaction was performed in a similar way using 3.5 g (0.011 mol) of compound **III** and 2.4 g (0.022 mol) of compound **V** in 55 ml of dioxane. After treatment with water, the organic (bottom) layer was separated and was left to stand for crystallization. The solid material thus obtained was a mixture of isomeric compounds **XIIc** and **XIId** at a ratio of 51:49; it was subjected to column chromatography on silica gel using chloroform as eluent, followed by triple recrystallization from hexane. Yield of 2-heptafluoropropyl-3-trifluoromethyl-2*H*-1,4-benzoxazin-2-ol (**XIIc**) 1.0 g (23%), colorless crystals, mp 115°C (sublimes). IR spectrum, ν, cm^{-1}: 1580, 1590, 1630 (C=C, C=N), 2660, 2710, 3150 br (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.51 br.s (1H, OH), 7.04–7.07 m (1H, CH), 7.19–7.22 m (1H, CH), 7.40–7.44 m (1H, CH), 7.60–7.62 m (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 36.8 d.d (1F, 2''-F_B, $^2J_{FF}$ = 293.6, $^3J_{1''\text{-}A,2''\text{-}B}$ = 11.2 Hz), 38.1 d.d.d.q (1F, 2''-F_A, $^2J_{FF}$ = 293.6, $^3J_{1''\text{-}B,2''\text{-}A}$ = 11.4, $^3J_{1''\text{-}A,2''\text{-}A}$ = 4.1, $^6J_{1',2''\text{-A}}$ = 2.5 Hz), 40.3 d.q.d.q (1F, 1''-F_B, $^2J_{FF}$ = 289.6, $^5J_{1',1''\text{-}B}$ = 15.4, $^3J_{1''\text{-}B,2''\text{-}A}$ = 11.4, $^4J_{1''\text{-}B,3''}$ = 10.0 Hz), 42.5 d.d.q.q.d (1F, 1''-F_A, $^2J_{FF}$ = 289.6, $^3J_{1''\text{-}A,2''\text{-}B}$ = 11.2, $^5J_{1',1''\text{-}A}$ = $^4J_{1''\text{-}A,3''}$ = 10.0, $^3J_{1''\text{-}A,2''\text{-}A}$ = 4.1 Hz), 80.9 t (3F, 3''-F, $^4J_{1''\text{-}B,3''}$ = 10.0 Hz), 95.7 d.d.d (3F, 1'-F, $^5J_{1',1''\text{-}B}$ = 15.4, $^5J_{1',1''\text{-}A}$ = 10.0, $^6J_{1',2''\text{-}A}$ = 2.5 Hz). Found, %: C 37.44; H 1.37; F 49.53; N 3.62. $C_{12}H_5F_{10}NO_2$. Calculated, %: C 37.40; H 1.30; F 49.35; N 3.64.

3-Heptafluoropropyl-2-trifluoromethyl-2*H*-1,4-benzoxazin-2-ol (XIId). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 38.0 br.s (2F, 2'-F), 50.9 d.q.q (1F, 1'-F_B, $^2J_{FF}$ = 298.1, $^5J_{FF}$ = 13.6, $^4J_{FF}$ = 9.9 Hz), 53.8 d.q.q (1F, 1'-F_A, $^2J_{FF}$ = 298.1, $^5J_{FF}$ = 11.0, $^4J_{FF}$ = 9.9 Hz), 78.7 d.d.t (3F, 1''-F, $^5J_{1'\text{-}B,1''}$ = 13.6, $^5J_{1'\text{-}A,1''}$ = 11.0, $^6J_{FF}$ = 1.2 Hz), 82.1 t (3F, 3'-F, $^4J_{FF}$ = 9.9 Hz).

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