

Dedicated to Full Member of the Russian Academy of Sciences
O.N. Chupakhin on his 75th anniversary

Perfluoroepoxyoxolanes in the Synthesis of Fluorine-Containing Heterocycles

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Abstract—Perfluoro-3,4-epoxyoxolane and 3,4-epoxy-2-trifluoromethylpentafluoroepoxyoxolane readily reacted with difunctional nucleophiles via opening of the oxirane ring and subsequent heterocyclization. Their reactions with thiourea and *o*-phenylenediamine gave new fluorine-containing fused heterocyclic compounds, 2-amino-3a-hydroxy-4,4,6,6,6a-pentafluoro-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole and 1,1,3,3-tetrafluoro- and 1-trifluoromethyl-1,3,3-trifluoro-1,3-dihydrofuro[3,4-*b*]quinoxalines, respectively. The molecular and crystalline structures of the products were determined by X-ray analysis.

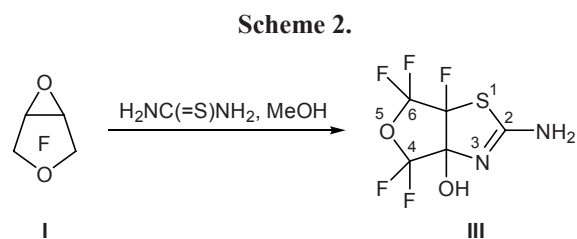
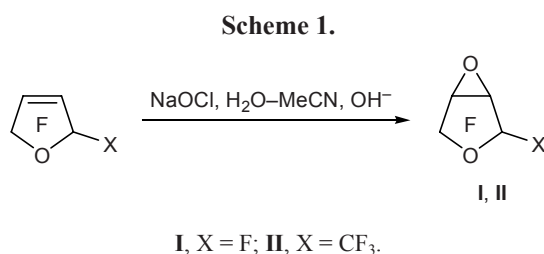
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Perfluoroolefin oxides are important and versatile synthons. They are capable of reacting with both mono- and difunctional nucleophiles and electrophiles to give various polyfunctional organofluorine compounds, as well as heterocyclic systems containing fluorine atoms and perfluoroalkyl groups [1–10]. Reactions of terminal and internal perfluoroolefin oxides have been studied in sufficient detail, whereas heterocyclizations of epoxy compounds derived from perfluorinated cyclic alkenes have not been reported.

We previously synthesized perfluoroepoxyoxolanes **I** and **II** [11] containing oxirane and oxolane rings in a single molecule via epoxidation of the corresponding fluorinated 2,5-dihydrofurans with sodium hypochlorite (Scheme 1). The reactivity of perfluoroepoxyoxolanes **I** and **II** almost was not studied. We only showed that treatment of perfluoro-3,4-epoxyoxolane (**I**) with a strong electrophilic reagent (SbF_5) results in

opening of both oxygen-containing rings with formation of a mixture of products, the major of which was pentafluoroacetoacetyl fluoride [12].

In continuation of our studies on the relations between the structure and properties of perfluoroepoxyoxolanes in the present work we examined reactions of perfluoro(3,4-epoxyoxolane) (**I**) and perfluoro(3,4-epoxy-2-methyloxolane) (**II**) with difunctional nucleophiles with a view to obtain new fluorinated heterocyclic compounds. Compounds **I** and **II** were found to readily react with binucleophiles via opening of the epoxide ring. By reaction of epoxyoxolane **I** with thiourea in methanol under mild conditions we obtained in high yield 2-amino-3a-hydroxy-4,4,6,6,6a-pentafluoro-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**) (Scheme 2).



Apart from IR and NMR (¹H, ¹³C, ¹⁹F) spectroscopy, the structure of compound **III** was studied by

X-ray analysis. Single crystals of **III** were obtained by crystallization from benzene. Furothiazole **III** crystallizes in triclinic crystal system, space group *P*-1. Its unit cell includes three crystallographically independent molecules **A–C** together with two crystallographically independent benzene molecules ($C_{54}H_{42}F_{30}N_{12}O_{12}S_6$ or $6C_5H_3F_5N_2O_2S \cdot 4C_6H_6$) (Table 1). The principal geometric parameters of molecules **A–C** (bond lengths and bond angles) were similar to each other (Tables 2, 3) and to the corresponding standard values. The structure of heterocycle **III** is shown in Fig. 1 (molecule **A**).

Furanthiazole **III** is formed as a single stereoisomer with *cis* orientation of the hydroxy group and fluorine atom at the bridgehead carbon atoms. The dihydrothiazole ring adopts pseudo-*envelope* conformation (the C^3 , N^2 , C^5 , and S^1 atoms in molecules **A–C** lie in one plane within 0.025 Å, while the C^4 , C^{4A} , and C^{4B} atoms deviate from the above plane by 0.379(2), 0.339(2), and 0.321(2) Å, respectively. The tetrahydrofuran ring has *twist* conformation, where the maximal deviations from the mean-square plane were observed for the bridgehead carbon atoms [$\sim 0.150(10)$ Å].

Packing of molecules **III** in crystal is determined by a complex hydrogen bond system. All molecules **III** are linked to dimers through intermolecular hydrogen bonds between hydrogen atoms in the hydroxy groups and nitrogen atoms in the heterorings. Another intermolecular hydrogen bond system involving hydrogen atoms in the amino groups and oxygen atoms in the hydroxy groups gives rise to chains with alternating orthogonal arrangement of the dimers. Finally, the chains constitute two-dimensional latticework via shortened polar contacts between the hydroxy groups and heterocyclic sulfur atoms (Tables 4, 5). Shortened polar contacts are also formed between some fluorine atoms and hydrogen atoms in the hydroxy groups (Table 5), and the other fluorine atoms are involved in hydrophobic interactions with solvate benzene molecules located between the layers composed of molecules **III** (Fig. 2).

According to the ^{19}F NMR data, nucleophilic opening of the oxirane ring in unsymmetrical epoxyoxolane **II** by the action of thiourea follows both possible pathways with formation of regioisomeric furothiazoles, each being a couple of diastereoisomers (the ^{19}F NMR spectrum of the product mixture contained four sets of signals); however, we failed to isolate individual isomers.

Perfluoroepoxyoxolanes **I** and **II** reacted with *o*-phenylenediamine to produce fluorinated fused het-

erocyclic compounds, 1,1,3,3-tetrafluoro- and 1,3,3-trifluoro-1-trifluoromethyl-1,3-dihydrofuro[3,4-*b*]quinoxalines **IV** and **V**, respectively (Scheme 3). The structure of compounds **IV** and **V** was confirmed by the IR and 1H , ^{19}F , and ^{13}C NMR spectra and elemental analyses. The molecular structure of furoquinoxaline **IV** was also studied by X-ray analysis. According to the X-ray diffraction data, molecule **IV** is essentially planar (Fig. 3). The maximal deviation from the mean-square plane is observed for the C^1 atom (0.075 Å), while deviations of the other atoms do not exceed 0.035 Å. The average C–F bond length is 1.320(5) Å, and the C–O bond lengths are 1.372(5) Å. The average

Table 1. Crystallographic data for compounds **III** and **IV** and parameters of X-ray diffraction experiments

Parameter	III	IV
Formula	$C_{27}H_{21}F_{15}N_6O_6S_3$	$C_{10}H_4F_4N_2O$
Molecular weight	906.68	244.15
Temperature, K	295(2)	295(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> ₂ / <i>c</i>
<i>a</i> , Å	11.0069(12)	10.267(3)
<i>b</i> , Å	11.9454(14)	12.429(5)
<i>c</i> , Å	14.8010(10)	7.572(2)
α , deg	96.905(7)	90.00(0)
β , deg	104.049(8)	93.99(2)
γ , deg	101.874(10)	90.00(0)
<i>V</i> , Å ³	1817.5(3)	963.9(5)
<i>Z</i>	2	4
<i>d</i> _{calc} , g/cm ³	1.657	1.682
μ , mm ⁻¹	0.331	0.164
Scan range	$2.83 \leq \theta \leq 31.71$	$3.16 = \theta \leq 26.39$
Total number of reflections	25 608	7153
Number of independent reflections	10 877 ($R_{int} = 0.0252$)	1961 ($R_{int} = 0.0356$)
Number of reflections with $I > 2\sigma(I)$	5469	787
Number of refined parameters	551	154
Goodness of fit	0.999	1.001
$R_1 [I > 2\sigma(I)]$	0.0390	0.0399
$wR_2 [I > 2\sigma(I)]$	0.0869	0.0739
R_1 (all reflections)	0.0889	0.1127
wR_2 (all reflections)	0.0944	0.0800
e_{max}/e_{min}	0.291/–0.227	0.154/–0.124

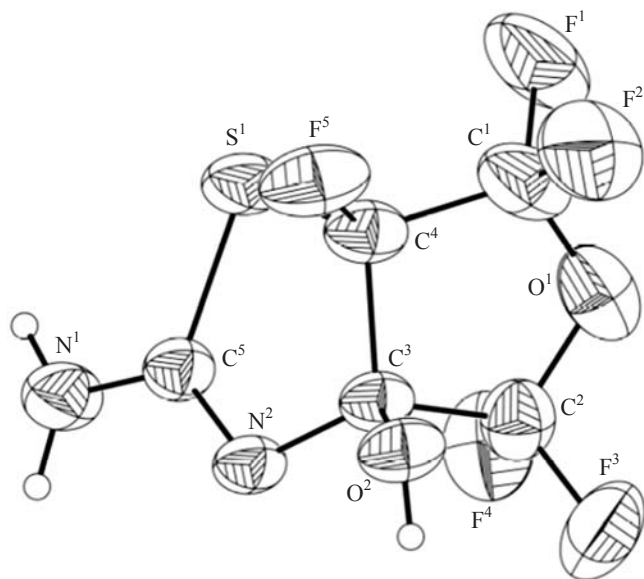


Fig. 1. Structure of molecule **A** of 2-amino-4,4,6,6,6-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%.

C–C bond length in the dihydrofuran ring is 1.479(5) Å, i.e., it is shorter than standard single C–C bond. The bond length and bond angle distribution in the quinoxaline fragment of molecule **IV** is similar to that found previously for quinoxaline [13], except for the C–C bond at which the tetrahydrofuran ring is fused. Its length is 1.366(2) Å against ~1.41 Å for the corre-

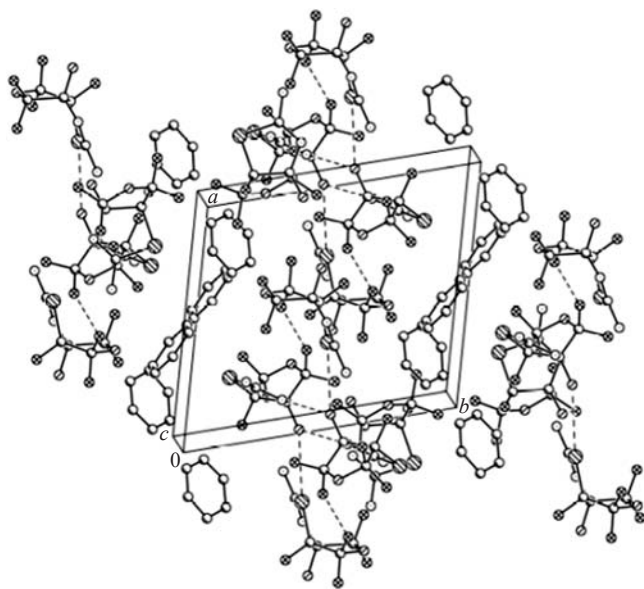
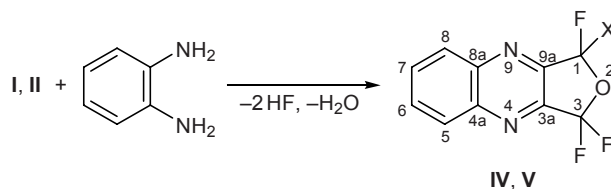


Fig. 2. A fragment of crystal packing of 2-amino-4,4,6,6,6-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**). Hydrogen atoms are not shown.

Scheme 3.



IV, X = F; **V**, X = CF₃.

sponding C–C bond in quinoxaline. Molecules **IV** in crystal are packed in the tail-to-head mode to form parallel zigzag bands oriented along the *b* crystallographic axis, the zigzag angle being 28.9°. The distance between the planes of the bands in the neighboring layers is 3.725 Å, indicating the absence of strong π – π interaction; i.e., only weak van der Waals interactions exist between bands within a layer.

EXPERIMENTAL

The ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker DRX-400 spectrometer at 400, 100, and 376 MHz, respectively, using tetramethylsilane (¹H, ¹³C) and C₆F₆ (¹⁹F) as internal references; the ¹⁹F chemical shifts are given relative to CFCl₃ (positive values correspond to signals located upfield). The IR spectra were measured on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from samples dispersed in mineral oil. The elemental compositions were determined on a Perkin–Elmer 2400 analyzer.

Initial epoxyoxolanes **I** and **II** were synthesized according to the procedure described in [11]. The solvents used in this work were purified and dehydrated by standard methods.

The X-ray diffraction data for compounds **III** and **IV** were acquired at 295(2) K on an Xcalibur-3 automatic four-circle diffractometer equipped with a CCD detector (λ MoK _{α} irradiation, graphite monochromator, ω scanning, scan step 1°) following a standard procedure from a 0.5 × 0.4 × 0.3-mm fragment of a single crystal of **III** and a 0.48 × 0.36 × 0.11-mm fragment of a single crystal (plate) of **IV**. CrysAlis software package [14] was used for data acquisition and processing. No correction for absorption was introduced. The structures were solved by the direct method and were refined by the least-squares procedure in full-matrix anisotropic approximation (isotropic for hydrogen atoms). Some hydrogen atoms were localized directly; their positions were refined independently, while positions of the other hydrogen atoms were calculated on

Table 2. Selected bond lengths (*d*) in the molecule of 2-amino-4,4,6,6,6a-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**)

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
S ¹ –C ⁵	1.7823(15)	S ^{1A} –C ^{5A}	1.7870(16)	S ^{1B} –C ^{5B}	1.7746(18)
S ¹ –C ⁴	1.7841(16)	S ^{1A} –C ^{4A}	1.7831(16)	S ^{1B} –C ^{4B}	1.7858(17)
C ² –O ¹	1.370(2)	C ^{2A} –O ^{1A}	1.375(2)	C ^{2B} –O ^{1B}	1.377(3)
O ¹ –C ¹	1.364(2)	O ^{1A} –C ^{1A}	1.368(2)	O ^{1B} –C ^{1B}	1.354(3)
O ² –C ³	1.3817(17)	O ^{2A} –C ^{3A}	1.3798(18)	O ^{2B} –C ^{3B}	1.3742(18)
C ⁵ –N ¹	1.322(2)	C ^{5A} –N ^{1A}	1.319(2)	C ^{5B} –N ^{1B}	1.332(2)
N ² –C ³	1.4316(19)	N ^{2A} –C ^{3A}	1.4355(19)	N ^{2B} –C ^{3B}	1.4382(19)
N ² –C ⁵	1.2848(18)	N ^{2A} –C ^{5A}	1.2824(19)	N ^{2B} –C ^{5B}	1.281(2)
F ¹ –C ¹	1.338(2)	F ^{1A} –C ^{1A}	1.325(2)	F ^{1B} –C ^{1B}	1.323(2)
F ² –C ¹	1.323(2)	F ^{2A} –C ^{1A}	1.337(2)	F ^{2B} –C ^{1B}	1.348(2)
F ⁵ –C ⁴	1.3638(19)	F ^{5A} –C ^{4A}	1.3705(18)	F ^{5B} –C ^{4B}	1.372(2)

Table 3. Selected bond angles (ω) in the molecule of 2-amino-4,4,6,6,6a-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**)

Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
C ⁵ S ¹ C ⁴	89.16(7)	C ^{4A} S ^{1A} C ^{5A}	89.71(7)	C ^{5B} S ^{1B} C ^{4B}	89.51(8)
C ⁵ N ² C ³	111.48(12)	C ^{5A} N ^{2A} C ^{3A}	111.79(12)	C ^{5B} N ^{2B} C ^{3B}	111.77(13)
N ¹ C ⁵ S ¹	116.52(12)	N ^{1A} C ^{5A} S ^{1A}	117.28(13)	N ^{1B} C ^{5B} S ^{1B}	117.32(15)
N ² C ⁵ N ¹	125.73(15)	N ^{2A} C ^{5A} N ^{1A}	125.09(16)	N ^{2B} C ^{5B} N ^{1B}	124.69(18)
N ² C ⁵ S ¹	117.75(12)	N ^{2A} C ^{5A} S ^{1A}	117.62(12)	N ^{2B} C ^{5B} S ^{1B}	117.98(12)
O ² C ³ N ²	113.88(12)	O ^{2A} C ^{3A} N ^{2A}	113.40(12)	O ^{2B} C ^{3B} N ^{2B}	113.42(13)
C ¹ O ¹ C ²	112.20(15)	C ^{1A} O ^{1A} C ^{2A}	112.58(13)	C ^{1B} O ^{1B} C ^{2B}	113.28(16)
F ⁵ C ⁴ C ¹	110.24(15)	F ^{5A} C ^{4A} C ^{1A}	109.92(13)	F ^{5B} C ^{4B} C ^{1B}	109.31(16)
F ⁵ C ⁴ S ¹	110.63(11)	F ^{5A} C ^{4A} S ^{1A}	110.49(10)	F ^{5B} C ^{4B} S ^{1B}	110.74(12)
F ² C ¹ F ¹	106.24(16)	F ^{1A} C ^{1A} F ^{2A}	105.60(14)	F ^{1B} C ^{1B} F ^{2B}	106.16(18)
F ¹ C ¹ C ⁴	113.91(16)	F ^{1A} C ^{1A} C ^{4A}	111.73(15)	F ^{1B} C ^{1B} C ^{4B}	115.19(18)
F ² C ¹ C ⁴	111.53(18)	F ^{2A} C ^{1A} C ^{4A}	114.07(14)	F ^{2B} C ^{1B} C ^{4B}	110.2(2)

Table 4. Hydrogen bond parameters [$H \cdots A < r(A) + 2.000 \text{ \AA}$, $\angle DHA > 110^\circ$] in the crystalline structure of compound **III**

D–H	<i>d</i> (D–H), Å	<i>d</i> (H \cdots A), Å	$\angle DHA$, deg	<i>d</i> (D \cdots A), Å	A
N ¹ –H ^{1A}	0.86(2)	2.11(2)	169.9(2)	2.962(2)	O ^{2A}
N ¹ –H ^{1B}	0.86(2)	2.45(2)	146.3(2)	3.202(3)	O ^{2B} [$-x + 2, -y + 1, -z + 1$]
O ² –H ²	0.79(2)	1.94(2)	166.6(2)	2.719(2)	N ² [$-x + 1, -y + 1, -z$]
O ^{2B} –H ^{2B}	0.78(2)	1.96(2)	174.4(2)	2.733(2)	N ^{2B} [$-x + 2, -y + 1, -z + 1$]
N ^{1A} –H ^{1AA}	0.94(2)	1.97(2)	172.2(2)	2.905(2)	O ² [$x + 1, y, z$]
O ^{2A} –H ^{2A}	0.80(2)	1.98(2)	156.3(2)	2.726(3)	N ^{2A} [$-x + 2, -y + 1, -z$]

Table 5. Some shortened contacts D \cdots A, D–H \cdots A in the crystalline structure of 2-amino-4,4,6,6,6a-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**)

D–H	<i>d</i> (D–H), Å	<i>d</i> (H \cdots A), Å	$\angle DHA$, deg	<i>d</i> (D \cdots A), Å	A
O ^{2B}	–	–	–	3.111(2)	S ¹ [$2 - x, 1 - y, 1 - z$]
N ^{1A} –H ^{1AA}	0.937	2.605	119.90	3.178(2)	F ⁵ [$x + 1, y, z$]
N ^{1B} –H ^{1BA}	0.803	2.523	145.86	3.220(2)	F ^{3A} [$-x + 2, -y + 1, -z$]

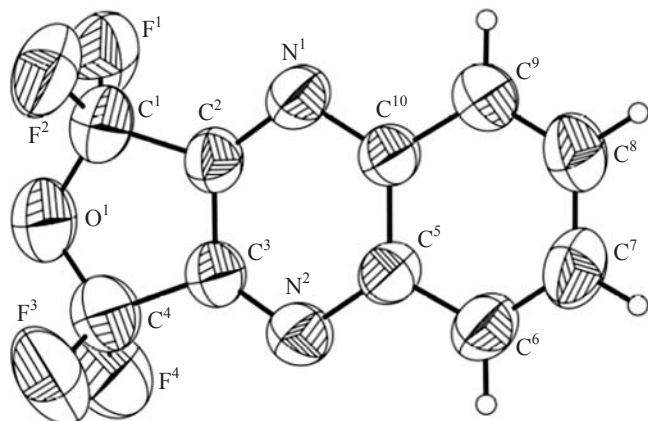


Fig. 3. Structure of the molecule of 1,1,3,3-tetrafluoro-1,3-dihydrofuro[3,4-*b*]quinoxaline (**IV**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%.

the basis of geometry considerations and were included into the refinement procedure according to riding model with dependent thermal parameters. All calculations were performed using SHELX software package [15]. The complete sets of crystallographic data were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 732370 and CCDC 732371 for compounds **III** and **IV**, respectively). These data are available from www.ccdc.cam.ac.uk/data_request/cif upon request.

2-Amino-4,4,6,6,6a-pentafluoro-3a-hydroxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*][1,3]thiazole (**III**).

A glass ampule was charged with 4.0 g (52.6 mmol) of thiourea and 45 ml of methanol, the ampule was cooled with solid carbon dioxide, 4.8 g (24.7 mmol) of epoxyoxolane **I** was added, and the ampule was sealed and heated for 1 h on a water bath at $\sim 50^\circ\text{C}$ with occasional shaking. The ampule was cooled and opened, the mixture was poured into ~ 200 ml of ice water, and the precipitate was filtered off. The filtrate was extracted with diethyl ether, the extract was dried over MgSO_4 and evaporated, and the light yellow residue, 5.8 g, was recrystallized from benzene. Yield 4.2 g (68%), colorless crystals, mp $151\text{--}152^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1578, 1593 (δNH); 1646, 1661 ($\text{C}=\text{N}$); 3353, 3415, 3505, 3526 (OH, NH). ^1H NMR spectrum (acetone- d_6), δ : 7.19 ppm, br.s (NH_2). ^{13}C NMR spectrum, δ_{C} , ppm: 108.37 d.d.d. (C^{3a} , $^2J_{\text{CF}} = 27.4$, 21.4, 16.5 Hz), 113.12 d.d.d.d. (C^{6a} , $^1J_{\text{CF}} = 260.8$, $^2J_{\text{CF}} = 26.9$, 21.6, $^3J_{\text{CF}} = 1.6$ Hz), 123.80 d.d.d. (C^6 , $^1J_{\text{CF}} = 268.9$, 264.0, $^2J_{\text{CF}} = 31.3$ Hz), 124.99 d.d.d.d. (C^4 , $^1J_{\text{CF}} = 280.4$, 269.5, $^3J_{\text{CF}} = 6.6$, 2.8 Hz), 158.20 s (C^2). ^{19}F NMR spectrum, δ_{F} , ppm: 62.25 d.m. (1F, 6- F_A ,

$^2J = 135.2$ Hz), 63.48 d.d.d. (1F, 6- F_B , $^2J = 135.2$, $^4J = 14.2$, 12.4 Hz), 64.02 d.t. (1F, 4- F_A , $^2J = 130.2$, $^4J = 11.5$ Hz), 73.25 d.m. (1F, 4- F_B , $^2J = 130.2$ Hz), 133.35 m (1F, 6a-F). Found, %: C 24.28; H 1.32; F 37.56; N 10.94; S 12.65. $\text{C}_5\text{H}_3\text{F}_5\text{N}_2\text{SO}_2$. Calculated, %: C 24.01; H 1.21; F 37.98; N 11.19; S 12.82.

1,1,3,3-Tetrafluoro-1,3-dihydrofuro[3,4-*b*]quinoxaline (**IV**).

A glass ampule was charged with 5.0 g (46.3 mmol) of *o*-phenylenediamine and 20 ml of diethylene glycol dimethyl ether, the ampule was cooled with solid carbon dioxide, 4.5 g (23.2 mmol) of epoxyoxolane **I** was added, and the ampule was sealed and heated for 2 h at $\sim 70^\circ\text{C}$ on a water bath. The ampule was cooled and opened, the mixture was poured into ice water, and the precipitate was filtered off, dried in air, and subjected to column chromatography on silica gel using chloroform–hexane (8:1) as eluent. The product was additionally purified by recrystallization from hexane. Yield 3.24 g (57%), colorless crystals, mp $107\text{--}108^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1436, 1470, 1506 ($\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm: 8.26 m (2H, 5-H, 8-H), 8.44 m (2H, 6-H, 7-H). ^{13}C NMR spectrum, δ_{C} , ppm: 123.31 t.t. (C^1 , C^3 , $^1J_{\text{CF}} = 263.6$, $^3J_{\text{CF}} = 1.8$ Hz), 131.32 s (C^6 , C^7), 135.00 s (C^5 , C^8), 143.68 d.d.d. (C^{3a} , C^{9a} , $^2J_{\text{CF}} = 31.6$, 30.1, $^3J_{\text{CF}} = 1.6$ Hz), 145.49 s (C^{4a} , C^{8a}). ^{19}F NMR spectrum: δ_{F} 73.61 ppm, s (1-F, 3-F). Found, %: C 49.24; H 1.58; F 31.30; N 11.48. $\text{C}_{10}\text{H}_4\text{F}_4\text{N}_2\text{O}$. Calculated, %: C 49.18; H 1.64; F 31.15; N 11.48.

1,3,3-Trifluoro-1-trifluoromethyl-1,3-dihydrofuro[3,4-*b*]quinoxaline (**V**).

Following an analogous procedure, from 2.0 g (8.2 mmol) of epoxyoxolane **II** and 1.78 g (16.4 mmol) of *o*-phenylenediamine in 15 ml of diethylene glycol dimethyl ether we obtained 1.8 g of a light brown residue which was purified by column chromatography on silica gel using chloroform–hexane (4:1) as eluent, followed by recrystallization from hexane. Yield 1.16 g (48%), colorless crystals, mp $47\text{--}48^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1431, 1471, 1508 ($\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm: 8.28 m (2H, 6-H, 7-H), 8.47 m (2H, 5-H, 8-H). ^{13}C NMR spectrum, δ_{C} , ppm: 108.09 d.q.d.d. (C^1 , $^1J_{\text{CF}} = 246.5$, $^2J_{\text{CF}} = 39.6$, $^3J_{\text{CF}} = 4.1$, 2.1 Hz); 120.30 q.d.d. (CF_3 , $^1J_{\text{CF}} = 284.0$, $^2J_{\text{CF}} = 42.4$, $^4J_{\text{CF}} = 5.3$ Hz); 125.07 d.d.d. (C^3 , $^1J_{\text{CF}} = 266.0$, 261.8, $^3J_{\text{CF}} = 1.6$ Hz); 131.41 s, 131.45 s, 135.24 s, 135.33 s (C^5 , C^6 , C^7 , C^8); 143.54 br.s, 143.84 br.s (C^{4a} , C^{8a}); 144.04 d.t. (C^{9a} , $^2J_{\text{CF}} = 19.9$, $^3J_{\text{CF}} = 2.5$ Hz); 145.61 d.d. (C^{3a} , $J_{\text{CF}} = 13.6$, 1.2 Hz). ^{19}F NMR spectrum, δ_{F} , ppm: 67.53 d.d.q. (1F, 3 F_A , $^2J_{\text{AB}} = 153.2$, $^4J_{3A,1} = 5.2$, $^5J_{3A,1'} = 1.3$ Hz), 74.98 d.d. (1F, 3- F_B , $^2J_{BA} = 153.2$, $^4J_{3B,1} = 9.0$ Hz),

81.38 d.d (3F, 1'-F, $^3J_{1',1} = 4.7$, $^5J_{1',3,4} = 1.3$ Hz), 119.28 d.d.q (1F, 1-F, $^4J_{1,3B} = 9.0$, $^4J_{1,3A} = 5.2$, $^3J_{1,1'} = 4.7$ Hz). Found, %: C 45.09; H 1.16; F 38.75; N 9.66. $C_{11}H_4F_6N_2O$. Calculated, %: C 44.90; H 1.36; F 38.78; N 9.52.

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