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Synthesis of Symmetrical Disulfides by Reaction of Fluorine-Containing Thiiranes with Cyclic Amines

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Abstract—Regioselective opening of the thiirane ring in fluorine-containing thioglycidyl ethers and [(perfluorobutyl)methyl]thiirane by the action of cyclic amines afforded 1,2-aminothiols which were oxidized *in situ* to symmetrical disulfides. The rate of formation of the latter depended on the amine basicity. According to the NMR data, the resulting disulfides were mixtures of *erythro* and *threo* diastereoisomers.

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Organic disulfides are used in many branches of industry, as well as in fundamental research. They play an important role in biochemical processes [1] and are used as vulcanizing agents [2, 3], extinguisher components [4], and convenient precursors of more complex molecules in organic synthesis [5–8]. Sulfur-containing organic compounds are often used as lubricant additives to improve tribological characteristics [9]. However, all known data refer to hydrocarbyl disulfides, whereas only a few published data are available on fluorinated disulfides.

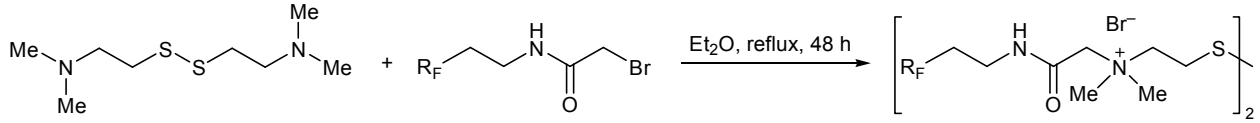
There are two synthetic approaches to symmetrical fluorine-containing disulfides. The first approach involves formation of a disulfide bond between fluorinated molecules, including those containing sulfur atoms, under basic conditions [10, 11]. For example, thiouronium salts of the general formula $[R_F(CH_2)_4SC(NH_2)NH_2]^+X^-$ (X = OTs, Br) reacted with 10 equiv of sodium hydroxide at 70°C (10 h) to give symmetrical disulfides $R_F(CH_2)_4SS(CH_2)_4R_F$ [11]. The second approach is based on the introduction of a polyfluoroalkyl substituent into the molecule of already synthesized symmetrical disulfide. Thebault et al. [12, 13] reported on the reaction of non-fluorinated disulfide, *N*,*N*,*N*′,*N*′-tetramethylcystamine, with *N*-(perfluoroethyl)bromoacetamide to form quaternary ammonium salt (Scheme 1).

The potential of the synthesis of fluorinated symmetrical disulfides via opening of the heterocyclic fragment of fluorine-containing thiiranes by the action of various nucleophiles, including amines, has not been exhausted so far. This reaction was used previously to obtain non-fluorinated analogs [14, 15]. Electron-withdrawing polyfluoroalkyl substituents enhance polarization of the thiirane ring and considerably affect its reactivity, which could lead to the formation of different products.

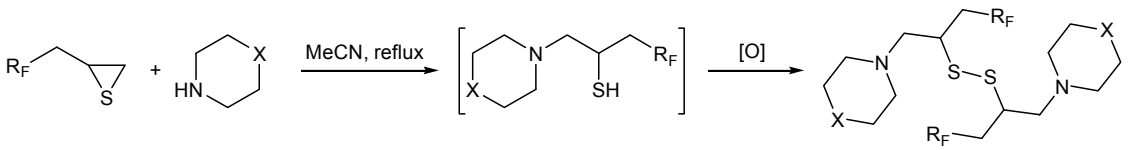
The goal of the present work was to develop a procedure for selective synthesis of fluorine-containing symmetrical disulfides by reaction of polyfluorinated thiiranes with cyclic amines.

It is known that opening of the thiirane ring by the action of nucleophiles yields thiols [16]. These reactions are often accompanied by polymerization or sulfur extrusion [17, 18]. Examples are reactions of thiirane with alkali metal alkoxides or sodium phenoxide in aprotic solvents, which produced high-molec-

Scheme 1.



Scheme 2.



1a–1c **2a–2c**, **3a**, **3b** **4a–4c**, **5a**, **5b**

R_F = $H(CF_2)_2CH_2O$ (**a**), $H(CF_2)_4CH_2O$ (**b**), *n*-C_4F_9 (**c**); **2**, **4**, X = O; **3**, **5**, X = NMe.

ular-weight compounds due to weak nucleophilicity of alkoxide ion compared to thiolate ion generated *in situ* as a result of thiirane ring opening [19]. Non-fluorinated thiiranes reacted with amines to give the corresponding 1,2-aminothiols which can be isolated and characterized, whereas prolonged reaction time promoted their dimerization to disulfides [14, 15]. Dimerization of 1,2-aminothiols was accounted for by their oxidation *in situ* in the presence of nitrogen bases [20, 21].

In this work we used as starting compounds fluorine-containing thiiranes **1a**–**1c** prepared as described in [18, 22–25] and various moderately basic cyclic amines, namely aniline (pK_a 4.58), morpholine (pK_a 8.70), and *N*-methylpiperazine (pK_a 9.62) [26] (Scheme 2). The reactions of **1a**–**1c** with cyclic amines were carried out in acetonitrile which enhanced the nucleophilicity of amines. The conversion of the initial reactants was monitored by GC/MS.

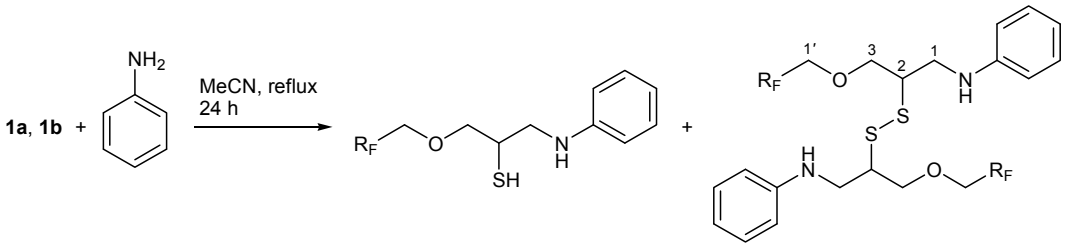
More basic aliphatic amines, such as methylamine (pK_a 10.62 [26]), dimethylamine (pK_a 10.77 [26]), ethylamine (pK_a 10.63 [26]), and diethylamine (pK_a 10.93 [26]) reacted with thiiranes **1a**–**1c** to give mixtures of resinous unidentifiable products. Successful syntheses of disulfides from non-fluorinated thiiranes and cyclic amines were reported in [14, 15].

According to the GC/MS data, the reactions of **1a**–**1c** with *N*-methylpiperazine and morpholine initially give mixtures of thiols **2a**–**2c**, **3a**, and **3b** with disulfides **4a**–**4c**, **5a**, and **5b** (Scheme 2); after 1.5–12 h, thiols **2a**–**2c**, **3a**, and **3b** are completely oxidized to the corresponding disulfides **4a**–**4c**, **5a**, and **5b**, the conversion of **1a**–**1c** being 100%. All our attempts to isolate pure thiols **2a**–**2c**, **3a**, and **3b** were unsuccessful, and their formation in the reaction mixtures was confirmed by GC/MS. We failed to isolate the corresponding disulfide in the reaction of **1c** with *N*-methylpiperazine; in this case, resinous unidentifiable products were formed.

Aniline as the weakest base among the examined amines showed a different reactivity toward thiiranes **1a**–**1c**. The reactions of aniline with thiiranes **1a** and **1b** gave thiols **6a** and **6b** which were converted to disulfides **7a** and **7b** at a much lower rate (Scheme 3). When a mixture of **1a** or **1b** and aniline in acetonitrile was refluxed for 12 h, only thiols **6a** and **6b** were formed, whereas after 24 h the product ratio **6**:**7** was 3:7 according to the ^{1}H NMR data. No complete oxidation of **6a** and **6b** to **7a** and **7b** was achieved under the above conditions after heating for 50 h while bubbling air through the reaction mixture.

We succeeded in accomplishing complete oxidation of mixtures **6a**/**7a** and **6b**/**7b** only after isolating them from the reaction mixtures by HPLC and subsequently heating in boiling acetonitrile in the presence of *N*-methylpiperazine. After 5 h, the reaction mixtures contained only disulfides **7a** and **7b**. Guseinova et al. [27] previously synthesized compound **6a** by heating in a sealed ampule without a solvent at 95–100°C for 10 h, but the formation of disulfide **7a** was not noted. Presumably, thiol **6a** cannot be oxidized to disulfide **7a** in the absence of air. The conversion of thiirane **1c** in

Scheme 3.



1a, **1b** **6a**, **6b** **7a**, **7b**

R_F = $H(CF_2)_2$ (**a**), $H(CF_2)_4$ (**b**).

the reaction with aniline in boiling acetonitrile did not exceed 2% after 20 h. Further studies are necessary to rationalize this result.

Our data suggest that opening of the thiirane ring in **1a**–**1c** by the action of amines and subsequent oxidation of thiols **2a**–**2c**, **3a**, **3b**, **6a**, and **6b** to symmetrical disulfides **4a**–**4c**, **5a**, **5b**, **7a**, and **7b** with atmospheric oxygen are sensitive to the amine nature. Increased basicity of the amine favors formation of thiolate ion which then reacts with atmospheric oxygen according to single-electron transfer mechanism, and dimerization of the sulfanyl radicals thus formed yields the corresponding disulfides [28].

The molecular ion peaks of 1,2-aminothiols **2a**–**2c**, **3a**, and **3b** had a relative intensity of lower than 0.1%, and the intensity of the molecular ion peaks of **6a** and **6b** did not exceed 10%. The characteristic peaks were those belonging to the $[M - HS]^+$ ions with relative intensities of 0.1–10%, and the $[CH_2R]^+$ ions (R = morpholin-4-yl, 4-methylpiperazin-1-yl, anilino) had the maximum intensity. Compounds **4a**–**4c**, **5a**, **5b**, **7a**, and **7b** displayed no molecular ion peak in the mass spectra, while the heaviest ion was $[R_FCH_2CH(SS)CH_2R]^+$ with a relative intensity of up to 2%. This ion decomposed via successive elimination of two sulfur atoms, and the $[CH_2R]^+$ ion was the most abundant.

As shown in [29], bis(3-chloro-1,1,1-trifluoropropan-2-yl) disulfide obtained by reaction of 3,3,3-trifluoroprop-1-ene with sulfur monochloride at 115–120°C exists as a mixture of *erythro* and *threo* diastereoisomers; however, the isomer ratio was not given. Molecules of disulfides **4a**–**4c**, **5a**, **5b**, **7a**, and **7b** possess two asymmetric carbon atoms, so that they also can exist as mixtures of *threo* and *erythro* isomers. The diastereoisomers showed insignificant differences in the ^{1}H NMR chemical shifts, and signal doubling was observed only for a few protons of compounds **4a** and **5a** with a relatively short fluoroalkyl radical. For example, the terminal HCF_2 proton of **4a** resonated in the ^{1}H NMR spectrum as two triplets of triplets ($^2J_{HF}$ = 53.2, $^2J_{HF}$ = 4.8 Hz) with as small displacement as 1.9 Hz. In the ^{1}H–{^{19}F} double resonance spectrum recorded with broad-band decoupling from fluorine nuclei, the spectral pattern is considerably simpler, and two singlets corresponding to two diastereoisomers are observed.

Friction coefficients for 2% emulsions of compounds **4a**, **4b**, and **5b** in I-20A commercial oil

Load, N	I-20A	I-20A/**4a**	I-20A/**4b**	I-20A/**5b**
10	0.099	0.046	0.016	0.055
20	0.101	0.061	0.051	0.054
30	0.107	0.071	0.066	0.072
60	0.116	0.091	0.096	0.093

On the other hand, the ^{13}C NMR spectra of all disulfides **4a**–**4c**, **5a**, **5b**, **7a**, and **7b** displayed different signals from almost all carbon atoms in the vicinity of the chiral centers. The diastereoisomer ratio for disulfides **4a**, **4b**, **5a**, **5b**, **7a**, and **7b** was about 1 : 1, while the isomer ratio for compound **4c** was 2.3 : 1.

The ^{1}H NMR spectral data given in [27] for compound **6a** included only the range δ 2.85–3.45 ppm for the $CH_2CH(SH)CH_2NH$ protons, whereas no $H(CF_2)_2CH_2$ signals were given. The ^{1}H NMR spectrum of mixture **6a**/**7a** recorded by us under analogous conditions contained a doublet at δ ~1.7 ppm with a coupling constant of ~9 Hz due to the SH proton. Thus, we have refined chemical shifts of protons in some functional groups of fluorine-containing thiols and disulfides.

It is known that non-fluorinated disulfides are used as lubricant additives [9]. There are no data on similar application of fluorine-containing analogs, though fluorine atoms, as well as sulfur atoms, are active species capable of forming monomolecular layers on the surface of metal friction pair, which improves tribological characteristics of lubricant oils. Compounds **4a**, **4b**, and **5b** are sparingly soluble in I-20A industrial oil; however, ultrasonic dispersion method made it possible to obtain 2% emulsions of **4a**, **4b**, and **5b** in I-20A, which were stable over 1–1.5 h. The friction coefficients of the obtained compositions were compared with that of the unmodified oil (see table). In all cases, the friction coefficients of I-20A modified with disulfides **4a**, **4b**, and **5b** were lower than that of the initial oil. The best effect was attained at small loads (10 and 20 N), whereas raising the load to 30 and 60 N reduced the effect.

In summary, we have proposed a convenient synthetic approach to symmetrical fluorine-containing disulfides, which is based on the reaction of thiiranes containing polyfluorinated substituents with cyclic amines in a polar aprotic solvent. The rate of formation of the target disulfides depends on the amine basicity: more basic amines ensure higher reaction rate. The resulting fluorine-containing disulfides attract interest as lubricant additives.

EXPERIMENTAL

The NMR spectra were recorded on Bruker DRX-400 and Avance 500 spectrometers (400 and 500 MHz, respectively, for ^{1}H; 376 and 470 MHz for ^{19}F; 126 MHz for ^{13}C); the chemical shifts were measured relative to tetramethylsilane (^{1}H), hexafluorobenzene (^{19}F), or solvent signal (^{13}C). Signals in the NMR spectra of **4a** were assigned using 2D ^{1}H–^{13}C HSQC technique. The IR spectra (400–4000 cm^{-1}) were recorded on a Perkin Elmer Spectrum One spectrometer equipped with an ATR accessory. The elemental analyses were obtained with a Perkin Elmer 2400 automated CHN analyzer. Gas chromatographic/mass spectrometric analysis was performed with a Trace GC Ultra DSQ II chromatograph coupled with a mass-selective detector [Thermo TR-5ms capillary column, 30 m × 0.25 mm, film thickness 0.25 μm (polydimethylsiloxane containing 5% of phenyl groups); oven temperature programming from 40°C (3 min) to 280°C at a rate of 10 deg/min; injector temperature 250°C, detector temperature 200°C, interface temperature 250°C; carrier gas helium, split ratio 1:50, flow rate 1.0 mL/min; total ion current monitoring, a.m.u. range 20–1000; electron impact, 70 eV]. Preparative HPLC was done with an Agilent 1200 semipreparative liquid chromatograph equipped with an autosampler (900 μL), diode array detector (λ 200 nm), and fraction collector; ZORBAX Eclipse XDB-C18 semipreparative column, 9.4 mm × 250 mm, grain size 5 μm; room temperature; eluent acetonitrile–water (75:25 by volume), flow rate 4 mL/min, isocratic elution. The friction coefficients were measured with a CSM Instruments tribometer using a ball/disk friction pair (6-mm ball and 35-mm disk made of steel 3 with a Rockwell hardness of 60–63 (C scale); loads 10, 20, 30, and 60 N, number of cycles 10000; lubricant dose 100 μL; all tests were carried out in quadruplicate; the measurement error did not exceed 0.002.

General procedure for the reaction of thiiranes 1a–1c with amines. A round-bottom flask equipped with a reflux condenser and a magnetic stirrer was charged with 20 mL of acetonitrile, 10 mmol of thiirane **1a**–**1c**, and 20 mmol of the corresponding amine. The mixture was heated to the boiling point and kept for 12–24 h under reflux. It was then cooled and washed with 30 mL of water, the organic layer was separated, and the aqueous layer was extracted with chloroform (2 × 5 mL). The combined extracts were dried over $MgSO_4$, the solvent was distilled off, and the product was purified by preparative HPLC or flash chromatography using methylene chloride as eluent.

Intermediate 1,2-aminothiols **2a**–**2c**, **3a**, **3b**, **6a**, and **6b** were characterized only by mass spectral data.

1-(Morpholin-4-yl)-3-(2,2,3,3-tetrafluoropropyloxy)propane-2-thiol (2a). Mass spectrum, *m/z* (I_{rel}, %): 291 (0.2) $[M]^+$, 258 (0.3) $[M - HS]^+$, 171 (1.0), 145 (2.7), 100 (100), 70 (8.5), 56 (16.1), 42 (12.2).

1-(Morpholin-4-yl)-3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propane-2-thiol (2b). Mass spectrum, *m/z* (I_{rel}, %): 391 (0.01) $[M]^+$, 358 (0.05) $[M - HS]^+$, 271 (0.2), 245 (0.7), 145 (0.9), 100 (100), 70 (14.1), 56 (28.2), 42 (20.3).

1-(Morpholin-4-yl)-4,4,5,5,6,6,7,7,7-nonafluoroheptane-2-thiol (2c). Mass spectrum, *m/z* (I_{rel}, %): 379 (0.05) $[M]^+$, 360 (0.1) $[M - F]^+$, 346 (0.6) $[M - HS]^+$, 292 (0.4), 146 (0.8), 126 (2.2), 100 (100), 70 (5.1), 56 (8.3), 42 (5.0).

1-(1-Methylpiperazin-4-yl)-3-(2,2,3,3-tetrafluoropropyloxy)propane-2-thiol (3a). Mass spectrum, *m/z* (I_{rel}, %): 304 (0.05) $[M]^+$, 302 (1.0) $[M - 2]^+$, 271 (9.2) $[M - HS]^+$, 113 (100), 70 (60.2), 42 (40.7).

1-(1-Methylpiperazin-4-yl)-3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)propane-2-thiol (3b). Mass spectrum, *m/z* (I_{rel}, %): 404 (0.02) $[M]^+$, 402 (1.0) $[M - 2]^+$, 371 (8.4) $[M - HS]^+$, 113 (100), 70 (71.8), 42 (39.7).

1-Anilino-3-(2,2,3,3-tetrafluoropropyloxy)]-propane-2-thiol (6a). Mass spectrum, *m/z* (I_{rel}, %): 297 (9.7) $[M]^+$, 264 (1.1) $[M - HS]^+$, 106 (100), 77 (28.8), 51 (24.9).

1-Anilino-3-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-propane-2-thiol (6b). Mass spectrum, *m/z* (I_{rel}, %): 397 (1.2) $[M]^+$, 364 (0.3) $[M - HS]^+$, 106 (100), 77 (27.9), 51 (27.1).

Bis[6,6,7,7-tetrafluoro-1-(morpholin-4-yl)-4-oxaheptan-2-yl] disulfide (4a, *erythro–threo* ~1:1**).** Yield 77%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 2858, 2812 (C–H), 1099 (C–F, C–O–C). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 2.46 m [4H, $N(CH_2)_2$], 2.52–2.60 m (2H, 1-H), 3.07 t.t and 3.09 t.t (1H each, 2-H, J = 7.3, 5.4 Hz), 3.69 m [4H, $O(CH_2)_2$], 3.76–3.90 m (4H, 3-H, 1′-H), 5.93 t.t (1H, 3′-H, J = 53.2, 4.8 Hz). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 49.29 and 49.35 (C^2), 53.89 [$N(CH_2)_2$], 59.35 and 59.39 (C^1), 66.86 [$O(CH_2)_2$], 68.14 t and 68.17 t ($C^{1'}$, J = 28.1 Hz), 72.51 (C^3), 109.20 t.t ($C^{3'}$, J = 249.5, 34.8 Hz), 114.95 t.t ($C^{2'}$, J = 250.2, 26.9 Hz). ^{19}F NMR spectrum (470 MHz, $CDCl_3$), δ_F, ppm: 22.33 d.m (2F, 3′-F, J = 53.0 Hz), 36.93 m (2F, 2′-F). Found, %: C 41.13; H 5.54; F 26.80; N 4.74; S 10.87. $C_{20}H_{32}F_8N_2O_4S_2$. Calculated, %: C 41.37; H 5.56; F 26.18; N 4.82; S 11.04.

Bis[6,6,7,7,8,8,9,9-octafluoro-1-(morpholin-4-yl)-4-oxanonan-2-yl] disulfide (4b, *erythro–threo* ~1:1**).** Yield 69%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 2920, 2857 (C–H), 1166 (C–F), 1114 (C–O–C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 2.44 m [4H, $N(CH_2)_2$], 2.51–2.63 m (2H, 1-H), 3.09 m (1H, 2-H), 3.68 m [4H, $O(CH_2)_2$], 3.84 m (2H, 3-H), 3.98 t (2H, 1′-H, J = 13.9 Hz), 6.06 t.t (1H, 3′-H, J = 52.0, 5.5 Hz). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 49.27 and 49.42 (C^2), 53.85 [$N(CH_2)_2$], 59.33 and 59.34 (C^1), 66.86 [$O(CH_2)_2$], 67.95 t ($C^{1'}$, J = 25.5 Hz), 72.93 and 72.94 (C^3), 107.62 t.t ($C^{5'}$, J = 254.1, 30.8 Hz), 110.07 t.t.t ($C^{3'}$ or $C^{4'}$, J = 264.5, 29.7, 26.9 Hz), 110.87 t.t.t ($C^{4'}$ or $C^{3'}$, J = 265.1, 33.6, 31.3 Hz), 115.40 t.t ($C^{2'}$, J = 256.8, 30.7 Hz). ^{19}F NMR spectrum (470 MHz, $CDCl_3$), δ_C, ppm: 24.47 d.m (2F, 5′-F, J = 52.0 Hz), 31.53 m (2F, 4′-F), 36.16 m (2F, 3′-F), 41.97 m (2F, 2′-F). Found, %: C 36.52; H 4.13; F 38.89; N 3.59; S 8.04. $C_{24}H_{32}F_{16}N_2O_4$. Calculated, %: C 36.93; H 4.13; F 38.94; N 3.59; S 8.21.

Bis[3,3,4,4,5,5,6,6,6-nonafluoro-1-(morpholin-4-yl)hexan-2-yl] disulfide (4c, *erythro–threo* ~2.3:1**).** Yield 75%, amorphous solid, mp 54–59°C. IR spectrum, ν, cm^{-1}: 2815 (C–H), 1216 (C–N), 1131 (C–F), 1117 (C–O–C). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.31–2.85 m [8H, $N(CH_2)_2$, 1-H, 3-H], 3.21 m (1H, 2-H), 3.63–3.73 m [4H, $O(CH_2)_2$]. ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 32.42 t and 32.81 t (C^3, J = 21.1 Hz), 40.71 and 40.82 (C^2), 53.57 [$N(CH_2)_2$], 62.58 and 62.71 (C^1), 66.79 and 66.81 [$O(CH_2)_2$], 108.72 t.q.m (C^6, J = 266.7, 38.7 Hz), 110.33 t.t.t (C^5, J = 265.7, 33.6, 32.3 Hz), 117.35 q.t (C^7, J = 288.1, 33.3 Hz), 118.05 t.t (C^4, J = 255.9, 31.3 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 35.80 m (2F, 6-F), 37.36 m (2F, 5-F), 49.92 m (2F, 4-F), 80.68 m (2F, 7-F). Found, %: C 34.69; H 3.36; F 46.21; N 3.64; S 8.62. $C_{22}H_{26}F_{18}N_2O_2S_2$. Calculated, %: C 34.92; H 3.46; F 45.20; N 3.70; S 8.48.

Bis[6,6,7,7-tetrafluoro-1-(4-methylpiperazin-1-yl)-4-oxaheptan-2-yl] disulfide (5a, *erythro–threo* ~1:1**).** Yield 77%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 2815 (C–H), 1216 (C–F), 1131 (C–N), 1117 (C–O–C). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.28 s (3H, CH_3), 2.32–2.64 m [10H, 1-H, $N(CH_2)_2$], 3.06 m (1H, 2-H), 3.73–3.93 m (4H, 3-H, 1′-H), 5.94 t.t (1H, 3′-H, J = 53.2, 4.9 Hz). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 45.91 and 45.92 (NCH_3), 49.50 and 49.51 (C^2), 53.33 and 55.00 [$N(CH_2)_2$], 58.71 and 58.81 (C^1), 68.18 t and 68.21 t ($C^{1'}$, J = 28.3 Hz), 72.57 (C^3), 109.14 t.t ($C^{3'}$, J = 249.5, 34.4 Hz), 114.95 t.t ($C^{2'}$, J = 250.1, 26.6 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 22.03 d.m (2F, 3′-F, J = 53.0 Hz), 36.72 m (2F, 2′-F). Found, %: C 43.34; H 6.66; F 24.84; N 9.16; S 10.33. $C_{22}H_{38}F_8N_4O_2S_2$. Calculated, %: C 43.56; H 6.31; F 25.05; N 9.24; S 10.57.

Bis[6,6,7,7,8,8,9,9-octafluoro-1-(4-methylpiperazin-1-yl)-4-oxanonan-2-yl] disulfide (5b, *erythro–threo* ~1:1**).** Yield 77%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 2940, 2800 (C–H), 1163 (C–F), 1121 (C–O–C). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.28 s (3H, CH_3), 2.32–2.64 m [10H, 1-H, $N(CH_2)_2$], 3.09 m (1H, 2-H), 3.83 (2H, 3-H), 3.98 t (2H, 1′-H, J = 14.0 Hz), 6.06 t.t (1H, 3′-H, J = 52.0, 5.4 Hz). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 45.94 and 45.96 (NCH_3), 49.49 and 49.58 (C^2), 53.34 and 55.03 [$N(CH_2)_2$], 58.74 and 58.78 (C^1), 67.97 t ($C^{1'}$, J = 25.4 Hz), 73.04 and 73.08 (C^3), 107.61 t.t ($C^{5'}$, J = 253.8, 30.5 Hz), 110.06 t.t.t ($C^{3'}$ or $C^{4'}$, J = 263.8, 31.0, 26.6 Hz), 110.86 t.t.t ($C^{4'}$ or $C^{3'}$, J = 264.6, 32.9, 31.1 Hz), 115.41 t.t ($C^{2'}$, J = 256.6, 30.6 Hz). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ_F, ppm: 24.45 d.m (2F, 5′-F, J = 52.0 Hz), 31.45 m (2F, 4′-F), 36.12 m (2F, 3′-F), 41.97 m (2F, 2′-F). Found, %: C 38.81; H 4.85; F 37.54; N 6.93; S 8.09. $C_{26}H_{38}F_{16}N_4O_2S_2$. Calculated, %: C 38.71; H 4.75; F 37.68; N 6.94; S 7.95.

Disulfides 7a and 7b (*general procedure***).** Mixtures **6a**/**7a** and **6b**/**7b** were obtained according to the general procedure for the reaction of thiiranes **1a** and **1b** with amines. Acetonitrile, 10 mL, and *N*-methylpiperazine, 5 mmol (0.5 g), were added to 1 g of mixture **6a**/**7a** or **6b**/**7b**, and the mixture was refluxed for 5 h. The mixture was washed with 30 mL of water, the organic layer was separated, and the aqueous layer was extracted with chloroform (2×5 mL). The extracts were combined with the organic phase and dried over $MgSO_4$, the solvent was distilled off, and the product was purified by flash chromatography using methylene chloride as eluent.

Bis(1-anilino-6,6,7,7-tetrafluoro-4-oxaheptan-2-yl) disulfide (7a, *erythro–threo* ~1:1**).** Yield 80%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 3411 (N–H), 2923 (C–H), 1602, 1505 (C–N), 1199 (C–F, C–O–C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 3.11 m (1H, 2-H), 3.27 m (1H, 1-H), 3.47 m (1H, 1-H), 3.55–4.07 m (5H, 3-H, 1′-H, NH), 5.86 t (1H, 3′-H, J = 53.2 Hz), 6.59 m (2H, *m*-H), 6.73 m (1H, *p*-H), 7.16 m (2H, *o*-H). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 44.17 and 44.28 (C^1), 51.00 and 51.49 (C^2), 67.91 t and 67.94 t ($C^{1'}$, J = 28.1 Hz), 72.56 and 72.58 (C^3), 109.18 t.t ($C^{3'}$, J =

249.7, 35.1 Hz), 112.91 and 112.94 (C^o), 114.81 t.t and 114.82 t.t ($C^{2'}$, J = 250.0, 26.7 Hz), 118.04 and 118.06 (C^p), 129.41 (C^m), 147.12 and 147.13 (C^i). ^{19}F NMR spectrum (470 MHz, $CDCl_3$), δ_F, ppm: 22.81 d.m and 22.86 d.m (2F, 3′-F, J = 53.0 Hz), 37.17 m (2F, 2′-F). Found, %: C 47.46; H 4.82; F 25.60; N 4.41; S 10.77. $C_{24}H_{28}F_8N_2O_2S_2$. Calculated, %: C 48.64; H 4.76; F 25.65; N 4.73; S 10.82.

Bis(1-anilino-6,6,7,7,8,8,9,9-octafluoro-4-oxa-nonan-2-yl) disulfide (7b, *erythro–threo* ~1:1**).** Yield 80%, dark yellow viscous oil. IR spectrum, ν, cm^{-1}: 3410 (N–H), 2917 (C–H), 1602, 1506 (C–N), 1167 (C–F), 1120 (C–O–C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 3.14 m (1H, 2-H), 3.29 m (1H, 1-H), 3.54 m (1H, 1-H), 3.70 m (1H, 3-H), 3.75–3.91 m (3H, 3-H, 1′-H), 3.97 br.s (1H, NH), 6.03 t.t (1H, 5′-H, J = 52.0, 5.3 Hz), 6.61 d (2H, *m*-H, J = 7.1 Hz), 6.73 m (1H, *p*-H), 7.17 m (2H, *o*-H). ^{13}C NMR spectrum (126 MHz, $CDCl_3$), δ_C, ppm: 44.27 and 44.39 (C^1), 51.16 and 51.63 (C^2), 67.89 t ($C^{1'}$, J = 25.6 Hz), 73.11 and 73.13 (C^3), 107.62 t.t ($C^{5'}$, J = 254.3, 30.9 Hz), 110.11 t.t.t ($C^{3'}$ or $C^{4'}$, J = 263.8, 30.1, 27.1 Hz), 110.90 t.t.t ($C^{4'}$ or $C^{3'}$, J = 265.4, 33.2, 31.9 Hz), 113.01 and 113.03 (C^o), 115.32 t.t ($C^{2'}$, J = 257.5, 30.6 Hz), 118.07 and 118.09 (C^p), 129.42 (C^m), 147.19 (C^i). ^{19}F NMR spectrum (470 MHz, $CDCl_3$), δ_F, ppm: 24.51 d.m (2F, 5′-F, J = 52.0 Hz), 31.54 m (2F, 4′-F), 36.37 m (2F, 3′-F), 42.06 m (2F, 2′-F). Found, %: C 42.39; H 3.51; F 37.97; N 3.56; S 8.13. $C_{28}H_{28}F_{16}N_2O_2S_2$. Calculated, %: C 42.43; H 3.56; F 38.35; N 3.53; S 8.09.

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