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New 4-pentafluorosulfanyl and 4-perfluoroalkylthio derivatives of 1-chloro-2-nitro- and 1-chloro-2,6-dinitrobenzenes

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Abstract

New 4-pentafluorosulfanyl and 4-perfluoroalkylthio derivatives of 1-chloro-2-nitrobenzene and 1-chloro-2,6-dinitrobenzene were prepared from the corresponding bis(4-chloro-3-nitrophenyl)disulfide and bis(4-chloro-3,5-dinitrophenyl)disulfide, respectively. The SF_5 derivatives were obtained by fluorination of the disulfides with AgF_2 according to Sheppard's method, while perfluoroalkylation was carried out by means of thermolytic reactions with xenon(II) bis(perfluoroalkylcarboxylates). The introduction of fluorine-containing, electron-withdrawing substituents into the aromatic ring (in the presence of other deactivating groups) reinforces the activation of the halogen substituent towards nucleophilic attack. Several nucleophilic substitution reactions have been carried out with these compounds, and as a result, some *N*- and *S*-containing groups were introduced in the benzene ring. For example, the previously unknown SF_5, CF_3S, and C_2F_5S analogues of trifluralin (Treflan®) were prepared and characterized. Additional synthetic possibilities for heterocyclic chemistry are presented on the basis of reactions of the new 1-chloro-2,6-dinitrobenzene derivatives with ethyl thioglycolate wherein fluorine-containing derivatives of benzothiazole *N*-oxide were obtained as the main products.

Keywords: Pentafluorosulfanyl benzenes; Perfluoroalkylthio benzenes; Fluorination; Perfluoroalkylation; Heterocycles; Herbicides; Pesticides

1. Introduction

It is well known that the replacement of a hydrogen atom in an aromatic or heterocyclic system by a fluorine atom or a perfluoroalkyl group may have a significant beneficial effect on the physical and biological properties of such a molecule [1,2]. Introduction of groups such as R_FS ($R_F = CF_3$, C_2F_5, etc.) and SF_5, which possess some of the highest lipophilic indices known [3], can be expected to offer an even more enhanced biological effect [4].

One of the primary areas of application for such compounds is in the field of agricultural chemistry. For example, trifluralin (Treflan®) or 2,6-dinitro-4-trifluoromethyl-*N*,*N*-di-*n*-propylaniline has been in agricultural use since the 1960s primarily as a pre-emergence herbicide [5,6]. Based on usage, trifluralin generally ranks in the top 10 agricultural pesticides in terms of annual sales. For example, in 1998 worldwide sales of trifluralin were estimated at US$ 300 million with 24,000 metric tons being produced [7,8]. Surprisingly, even with the recent increased interest in superlipophilic groups [9–13], the corresponding SF_5, CF_3S, and C_2F_5S analogues of trifluralin have not been reported yet.

Thus far, all agriculturally useful SF_5-benzenes have been prepared from *meta*-nitro or the *para*-nitro SF_5-benzenes [11,14,15]. The variety of derivatives possible is thus limited by the ability to synthesize different compounds from these two precursors, something that is made more difficult by having such a strong deactivating group on the aromatic ring [16–18]. A better method to prepare more highly substituted SF_5-benzenes is to utilize aromatic disulfides that contain the desired degree of substitution and then take them through the fluorination steps [19]. Another approach would be to synthesize a disulfide that, once fluorinated, contains a halogen that is activated towards nucleophilic aromatic substitution (i.e., *ortho* or *para* to the SF_5 group) [20]. *Ortho*-substituted SF_5-benzene derivatives [13] are examples of this approach as are the derivatives described herein.

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Accordingly, we have been developing synthetic routes to new aromatic and heterocyclic compounds containing both superlipophilic groups as well as active halogens. The latter are suitable for replacement by different nucleophilic reagents in order to provide numerous new and potentially biologically active molecules. We wish to report herein the SF_5, CF_3S, and C_2F_5S analogues of trifluralin as well as a wide variety of 2,6-dinitroanilines and other derivatives containing these superlipophilic groups. A preliminary report of this work has appeared [20].

2. Results and discussion

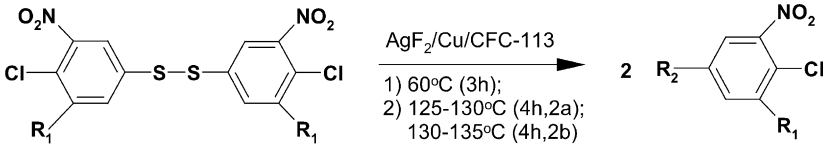
The preparation of the 4-pentafluorosulfanyl and 4-perfluoroalkylthio derivatives of 1-chloro-2-nitro- and 1-chloro-2,6-dinitrobenzene originates from bis(4-chloro-3-nitrophenyl) and bis(4-chloro-3,5-dinitrophenyl)disulfides (**1a**,**b**), which were obtained from the corresponding sulfonyl chloride by reduction with HBr/PhOH in acetic acid [21]. The successful fluorination of disulfide (**1a**) was carried out as shown in Scheme 1, and 1-chloro-2-nitro-4-pentafluorosulfanylbenzene (**2a**) was isolated in 29% yield. Two byproducts were present in the reaction mixture; the first, 1-chloro-3-nitro-6-fluoro-4-pentafluorosulfanylbenzene (**3**) results from aromatic ring fluorination of compound **2a**, while the second, 4-chloro-3-nitrobenzenesulfonyl fluoride (**4**) [22] is believed to result from the presence of metal oxides in the AgF_2 or on the reactor surface. Raising the reaction temperature from 120 to 130 °C increases the yield of target compound **2a** (29%) but at expense of increasing the amount of ring fluorination product **3** (4%). The one-step synthesis of **2** from disulfide **1** represents a marked improvement over its previous four-step synthesis from bis-4-nitrophenyl disulfide in at best 5% overall yield [15]. Compound **2b** was isolated as a lightly yellow colored solid in a 43% yield. The yield from the fluorination process is unusually high (cf. [14]) as most of the aromatic ring is protected with electron-withdrawing groups.

All structures were confirmed by spectroscopic methods and some also by elemental analyses (see Section 3). For example, the ^{19}F NMR spectrum of compound **2a** reveals two multiplets that belong to the resonances of the SF_5 group at 80.40 ppm (axial fluorine, asymmetrical nonet) and 63.19 ppm (equatorial fluorines, d of m, $^2J = 152.0$ Hz). The ^{13}C NMR spectrum of **2a** contains six separate signals; three of which are quintets: the first at δ 151.9 ppm ($^2J_{C-SF_4} = 21.0$ Hz, attributable to the carbon directly attached to the SF_5 group C-4), the second at δ 130.3 ppm ($^3J_{C-SF_4} = 4.0$ Hz, attributable to the carbon atom *ortho* to the SF_5 group and the nitro group, C-3), and the third at δ 123.9 ppm ($^3J_{C-SF_4} = 4.0$ Hz, attributable to the other *ortho* carbon atom, C-5). The broad signal at δ 147.3 ppm can be assigned to the C-2 carbon atom connected to the NO_2 group. The other two resonances, at δ 132.5 and 131.0 ppm, can be assigned to C-6 and C-1, respectively. Compound **2b** gave the typical ^{19}F NMR signals of an AB_4 pattern: a multiplet (asymmetrical nonet) for the axial fluorine atom at 77.43 ppm ($J_{SF-SF_4} = 150.8$ Hz) and a doublet of multiplets for the four equatorial fluorine atoms at 62.22 ppm ($J_{SF_4-SF} = 151.6$ Hz). The ^{13}C NMR spectrum contains four signals; two of which are quintets: the first at 151.5 ppm ($^2J_{C-SF_4} = 23.2$ Hz, attributable to the carbon atom directly bonded to the SF_5 group) and the second at 125.8 ppm ($^3J_{C-SF_4} = 4.6$ Hz, attributable to the carbon atoms *ortho* to the SF_5 group).

Recently, we have also developed a method for perfluoroalkylation of heterocyclic thiols and disulfides by means of thermolytic reactions with xenon (II) bis(perfluoroalkylcarboxylates) [23]. By using disulfides **1a**,**b**, the method was successfully extended to this class of aromatic compounds. A plausible mechanism for the general perfluoroalkylation of compound **1** is shown in Scheme 2.

The pathway of the conversion may be represented as follows. Perfluoroalkyl radicals formed by thermolysis of xenon bis(perfluorocarboxylates) react by free radical displacement of the RS fragment on one of the sulfur atom of the aromatic disulfides **1a**,**b** with the generation of perfluoroalkylsulfides and $RS^{\bullet}$ moiety, which then recombines with R_F radical to form the desired derivatives **2c–f**.

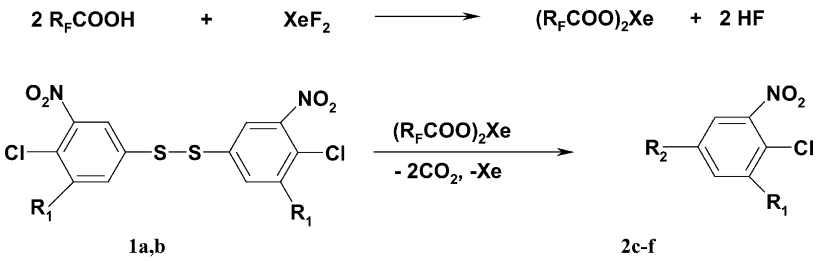
The yield of compounds **2e**,**f** can reach as high as 70% when the molar ratio of reagents is: disulfide:perfluorocarbonic acid:XeF_2 1:5:4. When lower stoichiometries of the perfluorocarbonic acids and XeF_2 were used, some of the starting disulfide remains unreacted. The influence of the solvent (e.g., trifluoroacetic acid, perfluoropropionic acid, dichloromethane, and acetonitrile) on the yield of the products **2e**,**f** was also studied. The best results were obtained when the reaction was carried out in dichloromethane, probably due to the high solubility of the disulfide in this solvent.



1, R_1=H (a), NO_2 (b)

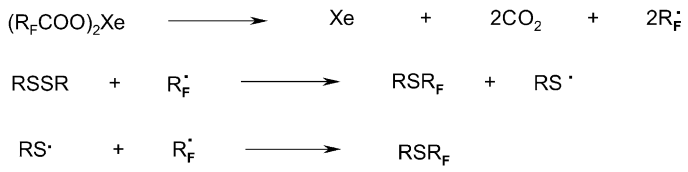
2, R_1=H, R_2=SF_5 (a), R_1=NO_2, R_2=SF_5 (b)

Scheme 1.



1a,b 2c-f

	R_1	R_2
2c	H	SCF_3
2d	H	SC_2F_5
2e	NO_2	SCF_3
2f	NO_2	SC_2F_5



Where: R = 4-chloro-3-nitrophenyl or 4-chloro-3,5-dinitrophenyl, $R_F = CF_3$, C_2F_5

Scheme 2.

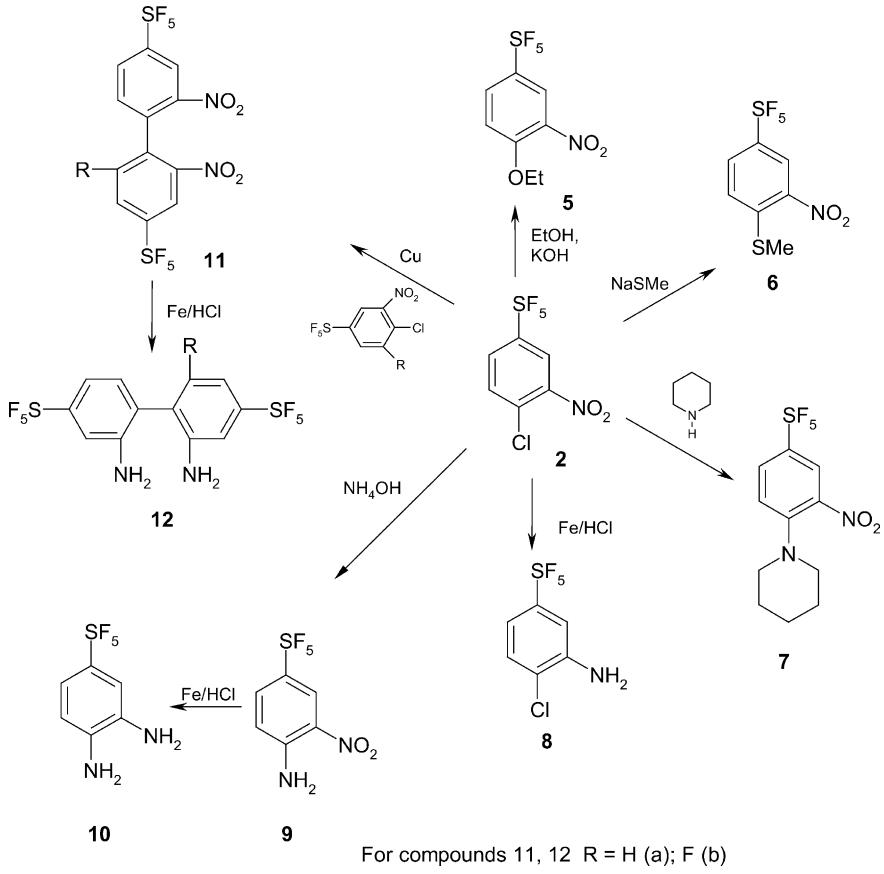
Compounds **2c**,**d** were obtained as yellowish oils in yields of about 16–17%, while **2e**,**f** were isolated as brownish or yellow crystals in the range of 66–70% yield. ^{19}F NMR spectra of compounds **2c**,**e** displays singlets at −42.52 and −41.62 ppm that can be attributed to the fluorine atoms of CF_3S group. Likewise, two signals at −91.70 and −82.88 ppm (for **2d**) or −90.88 and −82.88 ppm (for **2f**) (confirm the presence of the C_2F_5S moiety). As expected, five resonances appear in the ^{13}C NMR spectra of compounds **2c**,**e** for the five different types of carbon atoms. Quartets with a large $^1J_{C-F}$ coupling constant of about 310 Hz are due to the CF_3 groups, while the other two quartets: at 128.0 ($^3J_{C-SCF_3} = 2.5$ Hz), 132.6 ($^4J_{C-SCF_3} = 1.0$ Hz) (for **2c**) and at 126.6 ppm ($^3J_{C-SCF_3} = 2.7$ Hz), 134.2 ppm ($^4J_{C-SCF_3} = 1.1$ Hz) (for **2e**) are due to the *ipso* carbon atom (connected directly to CF_3S group) and the carbon atoms *ortho* to that carbon atom, respectively.

The reactivity of compound **2a** with a variety of different nucleophiles revealed the susceptibility of the chlorine atom to nucleophilic aromatic substitution. The coupling reaction of **2a** in the presence of copper–bronze was also carried out. As a result, the biphenyl derivative **11a** was obtained as shown in Scheme 3. This coupling reaction was carried out in the presence of the ring fluorinated derivative **3**, and the asymmetric biphenyl **11b** was found to be in the reaction mixture. A small amount of 1-nitro-3-pentafluorosulfanylbenzene was also detected, which is a product of dechlorination of starting material **2a**. Dinitrobiphenyls **11a**,**b** were reduced into the corresponding diamino derivatives **12a**,**b** in the presence of Fe powder. The general reaction conditions can be found in Section 3 and in Scheme 3.

Compounds **2b**,**d**,**f** readily react with secondary amines at room temperature to give excellent yields of analogs of the famous trifluoromethyl-substituted 2,6-dinitroaniline herbicides, e.g. trifluralin (Treflan®) (Scheme 4).

Both the chlorine and at least one of the nitro substituents in 1-chloro-2,6-dinitro-4-trifluoromethyl benzene can act as good leaving groups and reactions of this substituted benzene with sulfur-containing nucleophiles (e.g., potassium ethylxanthate) proceed by a two-step process with the formation of thianthrene derivatives [24]. By analogy to the results shown in [24], one would expect the formation of thianthrenes **16a**,**b** from **2b**,**e** according to Route **A** in Scheme 5. But instead, Route **B** was observed under the same reaction conditions. First, the chlorine atom was substituted with an ethyl xanthate group to give the intermediates **15a**,**b**, which after loss of a molecule of COS (similar to decarboxylation) resulted in the formation of the *S*-ethyl-derivatives **17a**,**b**.

The possibility to explore the heterocyclic chemistry of compounds **2b**,**e**,**f** became available through their reactions with ethyl thioglycolate [25]. These reactions proceeded through the intermediate formation of the thioglycolate derivatives **18a–c** (not isolated), followed by an intramolecular ring closure involving one of the nitro groups in presence of base (NEt_3), thereby giving the benzothia-



Scheme 3.

zole-*N*-oxides **19a–c**. The transformation of benzothiazole-*N*-oxide **19b** into the hydroxamic acid **20** in the presence of hydroxylamine displays the reactivity of these heterocyclic compounds (Scheme 6).

3. Experimental

Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel 60, 230–400 mesh (Merck), with the solvents indicated. TLC was run on silica gel 60 F_{254} plates (Merck). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on either a Bruker AM 360 or 500 spectrometer, using Me_4Si and $CFCl_3$ as internal standards, respectively, and $CDCl_3$ or Me_2SO-d_6 as solvent unless otherwise stated. Chemical shifts are reported in ppm; second-order spectra, especially the typical AB_4 spin-patterns observed for SF_5 groups, were simulated with the aid of our PC version of LAOCN3 [26]. Infrared spectra were recorded on a BioRad FTS-40 FT-IR spectrometer; frequencies are reported in cm^{-1}. GC–MS analyses were carried out on a Hewlett-Packard (HP) 5890 gas chromatograph-spectrometer (70 eV) using a 30 m capillary column. The assignment of the mass-spectral fragments for compounds **13a–h** and **14a–d** was aided by the previous work of Mallen and co-workers on benefin and trifluralin [27]. High-resolution mass spectra (HRMS) were recorded on a VG Instruments Autospec mass spectrometer, where the uncertainty in the mass measurements was ±0.002 Da. Proof-of-purity was indicated by a single peak in the GC chromatogram, the absence of extra signals in the multinuclear NMR spectra, and an exact mass determination.

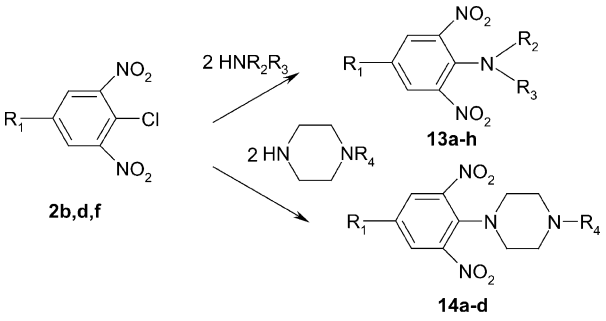
3.1. Preparation of disulfides *1a,b*

3.1.1. Bis(4-chloro-3-nitrophenyl)disulfide (*1a*)

The starting disulfide was obtained by reduction of the commercially available 4-chloro-3-nitrobenzenesulfonyl chloride (Aldrich) with an HBr solution in glacial acetic acid in presence of phenol [21]. The disulfide **1a** was obtained in 85% yield overall as yellow crystals, mp 115 °C (lit. 116–117 °C [21]).

3.1.2. Bis(4-chloro-3,5-dinitrophenyl)disulfide (*1b*)

This starting aromatic disulfide was obtained in a three-step synthesis. First, the potassium salt of 4-chloro-3,5-dinitrobenzene sulfonic acid was obtained from chlorobenzene [28]. Second, this salt was transformed into the corresponding sulfonyl chloride according to Ullmann's procedure [29]. Third, 20 g (0.066 mol) of the sulfonyl chloride was gradually dissolved in 340 mL of glacial acetic



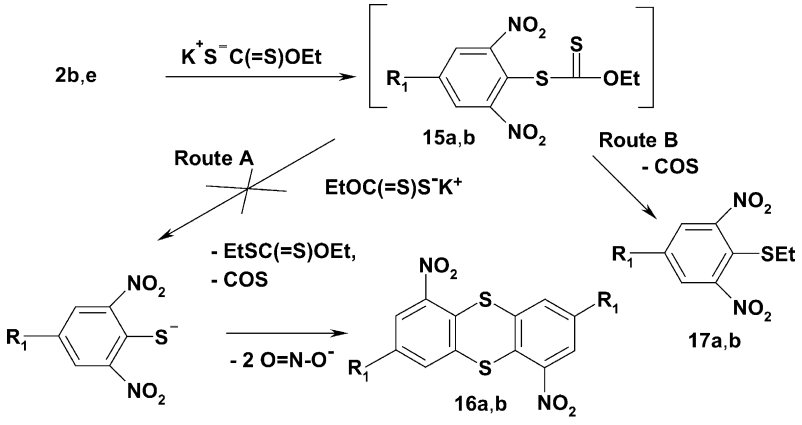
R_1= SF_5	R_2	R_3
13a	C_3H_7	C_3H_7
13b	C_3H_7	$CH_2C_3H_5$ (methylcyclopropane)
13c	C_2H_5	*n*-C_4H_9
13d	C_2H_5	$CH_2C(CH_3)$=CH_2
13e	C_3H_7	C_4H_7O (tetrahydrofurfuryl)
R_1 = SCF_3		
13f	C_2H_5	*n*-C_4H_9
13g	C_3H_7	$CH_2C_3H_5$ (methylcyclopropane)
13h	C_2H_5	$CH_2C(CH_3)$=CH_2
R_1 = SF_5	R_4	
14a	H	
14b	CH_3	
R_1 = SCF_3		
14c	H	
R_1 = SC_2F_5		
14d	H	

Scheme 4.

acid saturated with 35 g of gaseous HBr. Phenol (6.9 g) was added to the reaction mixture, which was first heated carefully under stirring to 55–60 °C (exothermic reaction), and then to 65–70 °C. The reaction mixture was kept at 60 °C with stirring for ca. 26 h. The solid that precipitated was collected by filtration after cooling the reaction mixture; washed with glacial acetic acid, ethanol, and hexane; and then dried. Yield is 14 g (90%). The precipitate was recrystallized from glacial acetic acid to give a yellow solid (13.3 g, mp 188–189 °C). ^{1}H NMR ($CDCl_3$): δ 8.09 (s); IR (Nujol): 3063 (C–H), 1536, 1351, 1278, 1129, 1054, 914, 883, 722 cm^{-1}; MS *m/z* (rel. int.): 466 $[M]^+$ (73), 234 $[M/2+H]^+$ (100), 233 $[M/2]^+$ (23), 218 $[(M/2+H)-O]^+$ (8), 188 $[M/2+H-NO_2]^+$ (31); HRMS calcd. for $C_{12}H_4Cl_2N_4O_8S_2$, 465.885, found 465.883.

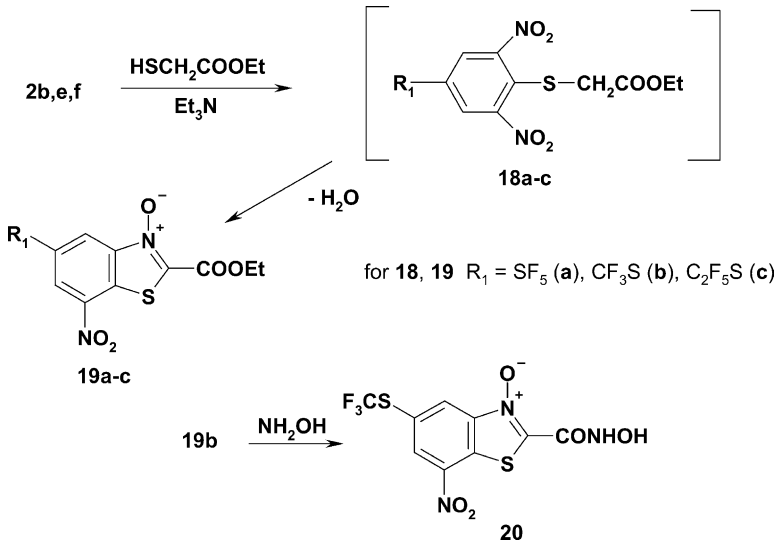
3.2. Fluorination of disulfides (general method)

The reaction with AgF_2 was performed in a stainless steel reactor that had previously been passivated with elemental fluorine. While being passivated, the reactor contained six copper sheets (10 mm × 100 mm × 0.2 mm) that would later be used in the reactions. The reactor was charged with 0.033 mol of disulfide **1a**,**b**, 195 g of AgF_2, and the copper strips, with all manipulations being carried out within a dry box. The vessel was then closed, evacuated on a vacuum line, cooled to 0 °C, and 125 mL of CFC 113 was transferred in. After warming to room temperature, the vessel was held at 60 °C for 2 h and then at 125–130 °C for 3 h (for **2a**) or at 130–135 °C for 4 h (for **2b**), under intermittent shaking. The reactor was then cooled to room temperature, and the reaction mixture was extracted three times with chloroform. The extract was filtered, washed with a 10% aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. After removal of the chloroform, the resulting oil was separated by column chromatography (silica, hexane:benzene 4:1 (for **2a**) or hexane:benzene 3:1 (for **2b**)).



for **15**,**16**,**17** R_1 = SF_5 (**a**), CF_3S (**b**)

Scheme 5.



Scheme 6.

*3.2.1. 1-Chloro-2-nitro-4-pentafluorosulfanylbenzene (**2a**)*

Yield 29%, yellow oil, $n_D^{25} = 1.4834$. ^{1}H NMR ($CDCl_3$) [15]: δ 7.71 (1H, d, $J = 8.8$ Hz, Ar), 7.92 (1H, dd, $J = 8.8$, 2.5 Hz, Ar), 8.30 (1H, d, $J = 2.5$ Hz, Ar). ^{19}F NMR: δ 63.19 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 80.40 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF). ^{13}C NMR: δ 123.9 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-3), 130.3 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5), 131.0 (s, C-1), 132.5 (s, C-6), 147.3 (broad s, C-2), 151.9 (qu, $^2J_{C-SF_4} = 21.0$ Hz, C-4). IR (neat): 3110 (aromatic C–H stretch), 1596, 1551, 1499 (asymmetric N–O stretch), 1359 (symmetric N–O stretch), 909, 853, 832 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 283 $[M]^+$ (91), 264 $[M - F]^+$ (28), 129 $[M - NO_2–SF_4]^+$ (100). HRMS calcd. for $C_6H_3ClF_5NO_2S$ 282.949 (for ^{35}Cl) and 284.946 (for ^{37}Cl), found 282.949 and 284.945, respectively.

*3.2.2. 1-Chloro-2-fluoro-6-nitro-4-pentafluorosulfanylbenzene (**3**)*

Yield 4%, yellow oil, $n_D^{25} = 1.4682$. ^{1}H NMR ($CDCl_3$): δ 7.83 (1H, dd, $J = 8.1$, 2.5 Hz, Ar), 8.14 (1H, m, Ar). ^{19}F NMR: δ −106.93 (s, 1F, F–Ar), 60.78 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 76.76 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF). ^{13}C NMR: δ 118.4 (m, $^2J_{C-F} = 26.6$, $^3J_{C-SF_4} = 4.0$ Hz, C-3), 119.1 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5), 120.5 (d, $^2J_{C-F} = 21.4$ Hz, C-1), 148.2 (broad s, C-6), 151.5 (m, C-4), 158.2 (d, $J_{C-F} = 257.5$ Hz, C-2). IR (neat): 3113 (aromatic C–H stretch), 1556, 1467, 1431 (asymmetric N–O stretch), 1364 (symmetric N–O stretch), 907, 862, 813 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 301 $[M]^+$ (100), 282 $[M - F]^+$ (23). HRMS calcd. for $C_6H_2ClF_6NO_2S$ 300.940, found 300.939.

*3.2.3. 4-Chloro-3-nitrobenzenesulfonyl fluoride (**4**)*

mp 56–58 °C (lit. 58–60 °C [22]). ^{1}H NMR ($CDCl_3$): δ 7.90 (1H, d, $J = 8.5$ Hz), 8.16 (1H, dd, $J = 8.5$, 2.0 Hz), 8.52 (1H, d, $J = 2.0$ Hz). ^{19}F NMR: δ 64.61 (s). MS *m/z* (rel. int.): 239 $[M]^+$ (100), 209 $[M - NO]^+$ (35), 126 $[209 - SO_2F]^+$ (66). HRMS calcd. for $C_6H_3ClFNO_4S$ 238.946, found 238.944.

*3.2.4. 1-Chloro-2,6-dinitro-4-pentafluorosulfanylbenzene (**2b**)*

Yield 9.35 g (43%) as slightly yellow solid, mp 85–87 °C. ^{1}H NMR ($CDCl_3$): δ 8.40 (s, Ar); ^{19}F NMR: δ 63.18 (d of m, 4F, $J_{SF_4-SF} = 152.8$ Hz, SF_4), 77.42 (m, 1F, $J_{SF-SF_4} = 152.8$ Hz, SF); ^{13}C NMR: δ 124.6 (s, C-1), 125.8 (qu, $^3J_{C-SF_4} = 4.6$ Hz, C-3, C-5), 149.3 (s, C-2, C-6), 151.5 (qu, $^2J_{C-SF_4} = 23.4$ Hz, C-4). MS *m/z* (rel. int.): 328 $[M]^+$ (47), 309 $[M - F]^+$ (11), 247 $[M - NO_2–Cl]^+$ (11), 236 $[M - 2NO_2]^+$ (10), 217 $[309-2NO_2]^+$ (11), 201 $[247-NO_2]^+$, $[M - SF_5]^+$ (7), 109 $[M - SF_5–2NO_2]^+$ (100). HRMS calcd. for $C_6H_2ClF_5N_2O_4S$ 327.934, found 327.934.

*3.3. Perfluoroalkylation of bis(4-chloro-3,5-dinitrobenzene) disulfide (**1**)—general method*

Disulfide **1a**,**b** (8.57 mmol) was added under stirring at −30 °C to a mixture of XeF_2 and the corresponding perfluorocarbonic acid in 30 mL of CH_2Cl_2 (the molecular ratio of disulfide:XeF_2:perfluorocarbonic acid was 1:3–4:5–6). The reaction mixture was stirred while gradually being allowed to warm to room temperature. The end of gas evolution determined the end of the reaction. The reaction mixture was then washed with a saturated solution of $NaHCO_3$ and dried on Na_2SO_4. After removal of solvent, the remaining residue was separated via column chromatography (silica, hexane:benzene 1:2).

*3.3.1. 1-Chloro-2-nitro-4-trifluoromethylthiobenzene (**2c**)*

Yield 16.2%, yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.64 (1H, d, $J = 8.4$ Hz, Ar), 7.80 (1H, dd, $J = 2.1$, 8.1 Hz, Ar), 8.16

(1H, d, $J = 2.1$ Hz, Ar); ^{19}F NMR: δ −42.52 (s, CF_3); ^{13}C NMR: δ 128.0 (q, $^3J_{C-SCF_3} = 2.5$ Hz, C-4), 128.8 (q, $J_{CF_3} = 309.1$ Hz, CF_3), 130.4 (s, C-1), 132.6 (q, $^4J_{C-SCF_3} = 1.0$ Hz, C-5), 133.0 (s, C-6), 140.2 (q, $^4J_{C-SCF_3} = 0.9$ Hz, C-3), 148.1 (broad s, C-2). MS *m/z* (rel. int.): 257 $[M]^+$ (100), 238 $[M - F]^+$ (4), 211 $[M - NO_2]^+$ (10), 188 $[M - CF_3]^+$ (7), 142 $[211-CF_3]^+$ (53), 107 $[142-Cl]^+$ (23), 69 $[CF_3]^+$ (32). HRMS calcd. for $C_7H_3ClF_3NO_2S$, 256.952, found 256.953.

3.3.2. 1-Chloro-2-nitro-4-pentafluoroethylthiobenzene (**2d**)

Yield 16.9%, yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.66 (1H, d, $J = 8.4$ Hz, Ar), 7.81 (1H, dd, $J = 2.1$, 8.1 Hz, Ar), 8.17 (1H, d, $J = 2.1$ Hz, Ar); ^{19}F NMR: δ −91.70 (2F, s, CF_2–CF_3), −82.88 (3F, s, CF_2–CF_3); ^{13}C NMR: δ 118.4 (qt, $J_{CF} = 286.6$ Hz, $^2J_{C-CF_3} = 36.2$ Hz, CF_2–CF_3), 119.7 (tq, $^2J_{C-CF_3} = 41.1$ Hz, $J_{CF} = 290.9$ Hz, CF_2–**CF_3**), 123.3 (t, $^3J_{C-SCF_3} = 3.0$ Hz, C-4), 130.7 (s, C-1), 132.9 (s, C-6), 133.4 (s, C-5), 141.0 (s, C-3), 148.1 (m, C-2). MS *m/z* (rel. int.): 307 $[M]^+$ (100), 271 $[M - Cl]^+$ (1), 188 $[M - C_2F_5]^+$ (18), 142 $[188-NO_2]^+$ (60), 119 $[C_2F_5]^+$ (8), 107 $[142-Cl]^+$ (26), 75 $[M - SC_2F_5–NO_2–Cl]^+$ (11), 69 $[CF_3]^+$ (27). HRMS calcd. for $C_8H_3ClF_5NO_2S$, 306.949, found 306.949.

3.3.3. 1-Chloro-2,6-dinitro-4-trifluoromethylthiobenzene (**2e**)

Yield 70%, brownish crystals, mp 35–37 °C. ^{1}H NMR ($CDCl_3$): δ 8.27 (s, Ar); ^{19}F NMR: δ −41.62 (s, CF_3); ^{13}C NMR: δ 123.6 (C-1), 126.6 (q, $^3J_{C-SCF_3} = 2.7$ Hz, C-4), 128.3 (q, $^1J_{C-F} = 310.1$ Hz, CF_3), 134.2 (q, $^4J_{C-SCF_3} = 1.1$ Hz, C-3, C-5), 149.8 (s, C-2, C-6). MS *m/z* (rel. int.): 302 $[M]^+$ (100), 283 $[M - F]^+$ (5), 256 $[M - NO_2]^+$ (2), 233 $[M - CF_3]^+$ (2), 210 $[M - 2NO_2]^+$ (9), 141 $[210-CF_3]^+$ (16), 69 $[CF_3]^+$ (19). HRMS calcd. for $C_7H_2ClF_3N_2O_4S$, 301.938, found 301.937.

3.3.4. 1-Chloro-2,6-dinitro-4-pentafluoroethylthiobenzene (**2f**)

Yield 66%, yellow crystals, mp 65–67 °C. ^{1}H NMR ($CDCl_3$): δ 8.27 (s, Ar); ^{19}F NMR: δ −90.88 (q, 2F, $J_{F-F} = 3.3$ Hz, CF_2CF_3), −82.74 (t, 3F, $J_{F-F} = 3.3$ Hz, CF_2CF_3). MS *m/z* (rel. int.): 352 $[M]^+$ (100), 283 $[M - CF_3]^+$ (6), 237 $[283-NO_2]^+$ (2), 233 $[M - C_2F_5]^+$ (4), 191 $[237-NO_2]^+$ (2), 187 $[233-NO_2]^+$ (1), 106 $[187-NO_2–Cl]^+$ (20). HRMS calcd. for $C_8H_2ClF_5N_2O_4S$, 351.934, found 351.934.

3.4. Reactions of compound **2a** with nucleophiles

3.4.1. Preparation of 1-ethoxy-2-nitro-4-pentafluorosulfanylbenzene (**5**)

To solution of 0.06 g (1.0 mmol) of KOH in 5 mL of absolute ethanol was added 0.284 g (1.0 mmol) of compound **2a**. The mixture was maintained at room temperature for 3 h and then the ethanol was removed under vacuum. The residue was washed with water and dissolved in benzene. The benzene layer was dried over sodium sulfate and then evaporated in vacuum. The residue was washed with hexane and then recrystallized from hexane to yellow-white solid that weighed 0.20 g, a 68% overall yield, mp 65–66 °C. ^{1}H NMR ($CDCl_3$): 1.51 (3H, t, $J = 7.0$ Hz, CH_3), 4.26 (2H, quartet, $J = 7.0$ Hz, CH_2), 7.12 (1H, d, $J = 9.0$ Hz, Ar), 7.90 (1H, dd, $J = 9.0$, 2.8 Hz, Ar), 8.25 (1H, d, $J = 2.8$ Hz, Ar); ^{19}F NMR: δ 61.74 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 80.54 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF); ^{13}C NMR: δ 14.0 (s, CH_3), 66.3 (s, CH_2), 113.9 (s, C-6), 124.1 (qu, $^3J_{C-SF_4} = 4.9$ Hz, C-3), 131.4 (C-5, qu, $^3J_{C-SF_4} = 4.9$ Hz), 138.6 (s, C-2), 144.9 (qu, $^2J_{C-SF_4} = 20.0$ Hz, C-4), 154.1 (C-1). IR (Nujol): 3126, 3097 (aromatic C–H stretch), 1618, 1587, 1533 (asymmetric N–O stretch), 1361 (symmetric N–O stretch), 913, 878, 865, 840 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 293 $[M]^+$ (35), 274 $[M - F]^+$ (25), 265 $[M - C_2H_4]^+$ (100), 249 $[M - C_2H_4O]^+$ (40), 235 $[265-NO]^+$ (13), 127 $[SF_5]^+$ (33). HRMS calcd. for $C_8H_8F_5NO_3S$ 293.015, found 293.014.

3.4.2. Preparation of 1-methylthio-2-nitro-5-pentafluorosulfanylbenzene (**6**)

Into a solution of 0.284 g (1.0 mmol) of compound **2a** and 5 mL of ethanol was added 0.10 g (1.4 mmol) of sodium thiomethoxide. The solution was maintained at room temperature for 3 h and then the solvent was removed under vacuum. The dried residue was washed with water and solid was extracted with benzene. The benzene extract was dried over sodium sulfate. The resulting residue was washed with hexane and then recrystallized from hexane. The product was obtained as a yellow solid (0.24 g) in an 81% yield, mp 107–108 °C. ^{1}H NMR ($CDCl_3$): δ 2.56 (3H, s, MeS), 7.47 (1H, d, $J = 8.9$ Hz, Ar), 7.93 (1H, dd, $J = 8.9$, 2.3 Hz, Ar), 8.67 (1H, d, $J = 2.3$ Hz, Ar); ^{19}F NMR: δ 63.46 (d of m, 4F, d, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 82.01 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF); ^{13}C NMR: δ 16.0 (s, CH_3), 124.2 (qu, $^3J_{C-SF_4} = 4.6$ Hz, C-3), 125.8 (s, C-6), 130.2 (broad s, C-5), 144.2 (broad s, C-2), 144.4 (s, C-1), 149.0 (qu, $^2J_{C-SF_4} = 20.0$ Hz, C-4). IR (Nujol): 3113 (aromatic C–H stretch), 1600, 1560, 1520 (asymmetric N–O stretch), 1342 (symmetric N–O stretch), 902, 849 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 295 $[M]^+$ (100), 280 $[M - CH_3]^+$ (7), 276 $[M - F]^+$ (24), 265 $[M - NO]^+$ (63), 264 $[M - CH_3S]^+$ (13), 250 $[280-NO]^+$ (14), 234 $[280-NO_2]^+$ (7). HRMS calcd. for $C_7H_6F_5NO_2S_2$ 294.976, found 294.975.

3.4.3. Preparation of 2-nitro-4-pentafluorsulfanyl-1-piperidinobenzene (**7**)

To a solution of 0.284 g (1.00 mmol) of compound **2a** and 5 mL of ethanol was added 0.15 mL of piperidine. The reaction was maintained at room temperature for 3 h and then refluxed for 20 min. The solvent was then removed under vacuum and the resulting dry residue was washed with water. The residue was then extracted with benzene and dried with

sodium sulfate. The benzene was evacuated and residue was purified by column chromatography on silica gel, which was eluted with a mixture of hexane:benzene 1.5:1. The residue from the column was crystallized from hexane to yield 0.23 g (69%) of orange-red solid, mp 80–81 °C. ^{1}H NMR ($CDCl_3$): δ 1.68 (2H, m, piperidine), 1.72 (4H, t, $J = 5.4$ Hz, piperidine), 3.14 (4H, t, $J = 5.4$ Hz, piperidine), 7.06 (1H, d, $J = 9.2$ Hz, Ar), 7.73 (1H, dd, $J = 9.2$, 2.3 Hz, Ar), 8.18 (1H, d, $J = 2.3$ Hz, Ar); ^{19}F NMR: δ 61.86 (d of m, 4F, $^2J_{SF_4-SF} = 151.7$ Hz, SF_4), 81.85 (m, 1F, $^2J_{SF-SF_4} = 151.7$ Hz, SF); ^{13}C NMR: δ 23.7 (s), 25.5 (s), 51.9 (s), 119.4 (C-6), 125.3 (qu, $^3J_{C-SF_4} = 4.6$ Hz, C-3), 130.5 (qu, $^3J_{C-SF_4} = 4.7$ Hz, C-5), 138.3 (broad s, C-2), 143.4 (qu, $^2J_{C-SF_4} = 21.8$ Hz, C-4), 148.0 (s, C-1). IR (Nujol): 3122 (aromatic C–H stretch), 1610, 1563, 1522 (asymmetric N–O stretch), 1302 (symmetric N–O stretch), 888, 845 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 332 $[M]^+$ (25), 315 $[M - OH]^+$ (100), 297 $[315 - H_2O]^+$ (20), 285 $[315 - NO]^+$ (61), 270 $[297 - HCN]^+$ (37), 256 $[297 - CH_2CN]^+$ (35), 245 $[315 - C_4H_8N]^+$ (23), 230 $[315 - C_5H_{11}N]^+$ (37). HRMS calcd. for $C_{11}H_{13}F_5N_2O_2S$ 332.062, found 332.062.

3.4.4. Preparation of 2-nitro-4-pentafluorosulfanylaniline (**9**)

A solution containing 5.20 g (0.18 mol) of compound **2a** and 10 mL of 27% ammonia was sealed in an ampoule and heated to 130–135 °C for 4 h. The solid product was filtered, washed with water, and dried in air. The residue was purified by column chromatography on silica gel, which was eluted with benzene. Unreacted starting material (**2a**, 1.30 g) and an orange solid (**9**, 2.60 g, 72%) were collected, mp 137–138 °C. ^{1}H NMR ($CDCl_3$): δ 6.42 (2H, broad s, NH_2), 6.86 (1H, d, $J = 9.2$ Hz, Ar), 7.70 (1H, dd, $J = 9.2$, 2.5 Hz, Ar), 8.57 (1H, d, $J = 2.5$ Hz, Ar); ^{19}F NMR: δ 63.53 (d of m, 4F, $^2J_{SF_4-SF} = 149.0$ Hz, SF_4), 83.81 (m, 1F, $^2J_{SF-SF_4} = 149.0$ Hz, SF); ^{13}C NMR: δ 118.4 (s, C-6), 125.2 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-3), 130.1 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-5), 132.3 (s, C-2), 142.3 (qu, $^2J_{C-SF_4} = 20.0$ Hz, C-4), 145.9 (s, C-1). IR (neat): 3481, 3349 (aromatic N–H stretch asymmetric, symmetric), 1632, 1571, 1515 (asymmetric N–O stretch), 835 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 264 $[M]^+$ (100), 248 $[M - NH_2]^+$ (7), 245 $[M - F]^+$ (9), 218 $[M - NO_2]^+$ (28). HRMS calcd. for $C_6H_5F_5N_2O_2S$ 263.999, found 263.998.

3.5. Coupling reaction of 1-chloro-2-nitro-4-pentafluorosulfanylbenzene (**2a**)

A mixture of 3.60 g (0.0127 mol) of compound **2a** (containing a several percent of fluorinated derivative **4**) and 3 g of sea sand was heated under stirring in a flask to 210 °C and 2 g of Cu–bronze powder was added gradually in a temperature range 220–225 °C. After 0.5 h the reaction mixture had transformed into a solid, and the solid mass kept at this temperature for next 1 h. The reaction mixture was extracted 3–4 times with hot chloroform, and the chloroform solutions were filtered. The solvent was evacuated in vacuum and the remaining residue was separated on a column packed with silica (eluant benzene:hexane 1:2). The first separated compound was 0.4 g of recovered starting material **2**, the second—0.15 g of dechlorination process product 1-nitro-3-pentafluorosulfanylbenzene, the third—asymmetrical biphenyl **11b**, and fourth—0.95 g of biphenyl **11a**. Two last compounds were recrystallized from hexane.

3.5.1. 2,2′-Dinitro-4,4′-bis-pentafluorosulfanylbiphenyl (**11a**)

Yield 34%, mp 199–200 °C. ^{1}H NMR ($CDCl_3$): δ 7.46 (1H, d, $J = 8.4$ Hz, Ar), 8.53 (1H, dd, $J = 8.4$, 2.1 Hz, Ar), 8.70 (1H, d, $J = 2.1$ Hz, Ar); ^{19}F NMR: δ 62.93 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 80.27 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF); ^{13}C NMR: δ 123.4 (qu, $^3J_{C-SF_4} = 4.2$ Hz, C-3, C-3′), 131.0 (qu, $^3J_{C-SF_4} = 4.6$ Hz, C-5, C-5′), 131.1 (s, C-6, C-6′), 136.0 (s, C-1, C-1′), 146.3 (broad s, C-2, C-2′), 154.0 (qu, $^2J_{C-SF_4} = 20.8$ Hz, C-4, C-4′). IR (Nujol): 1539 (asymmetric N–O stretch), 907, 876, 842 cm^{-1} (S–F). MS *m/z* (rel. int.): 496 $[M]^+$ (1), 495 $[M - H]^+$ (1), 477 $[M - F]^+$ (26), 450 $[M - NO_2]^+$ (100), 434 $[450-O]^+$ (18), 420 $[450-NO]^+$ (11).

3.5.2. 2,2′-Dinitro-6-fluoro-4,4′-bis-pentafluorosulfanylbiphenyl (**11b**)

mp 151–152 °C. ^{1}H NMR ($CDCl_3$): δ 6.18 (1H, dd, $J = 8.6$, 1.8 Hz, Ar), 7.46 (1H, d, $J = 8.6$ Hz, Ar), 8.16 (1H, d, $J = 9.3$ Hz, Ar), 8.51 (1H, s, Ar), 8.77 (1H, d, $J = 1.8$ Hz, Ar); ^{19}F NMR: δ −106.93 (1F, s, Ar–F), 60.40 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 60.72 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 76.62 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF), 77.63 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF); ^{13}C NMR: δ 119.1 (s, C-3, C-3′), 119.5 (m, C-5), 123.8 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5′), 125.1 (d, $^2J_{C-F} = 20.8$ Hz, C-1), 129.0 (s, C-1′), 131.3 (s, C-6′), 146.8 (s, C-2′), 147.0 (s, C-2), 154.4 (qu, $^2J_{C-SF_4} = 21.3$ Hz, C-4, C-4′), 158.3 (d, $J_{C-F} = 257.6$ Hz, C-6). IR (Nujol): 1575 (asymmetric N–O stretch), 921, 897, 862, 837 cm^{-1} (S–F). MS *m/z* (rel. int.): 495 $[M - F]^+$ (1), 468 $[M - NO_2]^+$ (100), 452 $[468-O]^+$ (17), 438 $[468-NO]^+$ (15), 360 $[468-SF_4]^+$ (44).

3.6. Reductions of nitrocompounds were carried out with Fe powder by refluxing in ethanol in presence of hydrochloric acid according to general method described in [13]

3.6.1. 2-Chloro-5-pentafluorosulfanylaniline (**8**)

Purified by column chromatography on silica gel, eluted with hexane:benzene 1:1. Yield 83% of yellowish oil, $n_D^{24} = 1.4965$. ^{1}H NMR ($CDCl_3$): δ 4.25 (2H, broad s, NH_2), 7.04 (1H, dd, $J = 8.8$, 2.8 Hz, Ar), 7.13 (1H, d, $J = 2.8$ Hz, Ar), 7.29 (1H, d, $J = 8.8$, Ar); ^{19}F NMR: δ

60.57 (d of m, 4F, $^2J_{SF_4-SF} = 151.0$ Hz, SF_4), 82.11 (m, 1F, $^2J_{SF-SF_4} = 151.0$ Hz, SF); ^{13}C NMR: δ 112.9 (C-6), 116.0 (qu, $^3J_{C-SF_4} = 4.8$ Hz C-4), 121.9 (s, C-2), 129.2 (s, C-3), 143.0 (C-1), 153.0 (qu, $J = 18.0$ Hz, C-5). IR (neat): 3505, 3408 (aromatic N–H stretch asymmetric, symmetric), 1632 (N–H bend), 1313 (symmetric N–O stretch), 846, 813 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 253 $[M]^+$ (100), 145 $[M - SF_4]^+$ (100), 126 $[M - SF_5]^+$ (45). HRMS calcd. for $C_6H_5ClF_5NS$ 252.975, found 252.975.

3.6.2. 4-Pentafluorosulfanyl-1,2-phenylenediamine (**10**)

Purified by column chromatography on silica gel, eluted with benzene. Yield 87% of slight-yellow crystals, mp 70–71 °C. ^{1}H NMR ($CDCl_3$): δ 3.47 (4H, broad s, NH_2), 6.64 (1H, d, $J = 8.5$ Hz, Ar), 7.10 (1H, dd, $J = 8.5$, 2.6 Hz, Ar), 7.12 (1H, d, $J = 2.6$ Hz, Ar); ^{19}F NMR: δ 65.33 (d of m, 4F, $^2J_{SF_4-SF} = 148.0$ Hz, SF_4), 88.51 (m, 1F, $^2J_{SF-SF_4} = 148.0$ Hz, SF); ^{13}C NMR: δ 114.3 (s, C-6), 114.4 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-3), 118.5 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-5), 133.2 (s, C-2), 138.1 (s, C-1), 145.6 (qu, $^2J_{C-SF_4} = 17$ Hz, C-4). IR (neat): 3489, 3445, 3400, 3370, 3328 (aromatic N–H stretch asymmetric, symmetric), 1625 (N–H bend), 1080 (C–N stretch), 846 cm^{-1} (aromatic C–N stretch). MS *m/z* (rel. int.): 234 $[M]^+$ (100), 126 $[M - SF_4]^+$ (50), 107 $[M - SF_5]^+$ (50). HRMS calcd. for $C_6H_7F_5N_2S$ 234.025, found 234.023.

3.6.3. 2,2′-Diamino-4,4′-bis-pentafluorosulfanylbiphenyl (**12a**)

Purified by column chromatography on silica gel, eluted with hexane:benzene 1:2. Yield 86% as slight-yellow solid, mp 191–192 °C (methanol). ^{1}H NMR ($CDCl_3$): δ 3.87 (2H, broad s, NH_2), 7.16 (1H, d, $J = 8.4$ Hz, Ar), 7.19 (1H, d, $J = 2.0$ Hz, Ar), 7.22 (1H, dd, $J = 8.4$, 2.0 Hz, Ar); ^{19}F NMR: δ 62.56 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 84.67 (m, 1F, $^2J_{SF-SF_4} = 152.0$ Hz, SF); ^{13}C NMR: δ 113.4 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-3, C-3′), 116.0 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5, C-5′), 125.4 (s, C-1, C-1′), 130.9 (s, C-6, C-6′), 144.2 (s, C-2, C-2′), 154.8 (qu, $^2J_{C-SF_4} = 17.4$ Hz, C-4, C-4′). IR (Nujol): 3433, 3405, 3304, 3205, 1635 (NH), 916, 856, 810 cm^{-1} (S–F). MS *m/z* (rel. int.): 436 $[M]^+$ (100), 419 $[M - NH_3]^+$ (23), 309 $[M - SF_5]^+$ (41). HRMS calcd. for $C_{12}H_{10}F_{10}N_2S_2$ 436.013, found 436.012. Anal. calcd.: C, 33.03; H, 2.31; N, 6.42; S, 14.70. Found: C, 33.47; H, 2.51; N, 6.35; S, 14.97.

3.6.4. 2,2′-Diamino-6-fluoro-4,4′-bis-pentafluorosulfanylbiphenyl (**12b**)

Purified by column chromatography on silica gel, eluted with hexane:benzene 1:2. Yield 88% as slight-yellow solid, mp 139–141 °C (methanol). ^{1}H NMR ($CDCl_3$): δ 3.87 (2H, broad s, NH_2), 6.98 (1H, dd, $J = 9.0$, 2.0 Hz, Ar), 6.99 (1H, s, Ar), 7.17 (1H, d, $J = 8.7$ Hz, Ar), 7.21 (1H, s, Ar), 7.22 (1H, dd, $J = 9.0$, 2.0 Hz, Ar); ^{19}F NMR: δ −110.12 (s, 1F, F–Ar), 62.05 (d of m, 4F, $^2J_{SF_4-SF} = 150.0$ Hz, SF_4), 62.49 (d of m, 4F, $^2J_{SF_4-SF} = 150.0$ Hz, SF_4), 83.17 (m, 1F, $^2J_{SF-SF_4} = 150.0$ Hz, SF), 84.28 (m, 1F, $^2J_{SF-SF_4} = 150.0$ Hz, SF); ^{13}C NMR: δ 103.5 (d, $^3J_{C-SF_4} = 4.0$ Hz, C-3), 108.5 (s, C-3′), 112.5 (d, $^2J_{C-F} = 20.0$ Hz, C-1), 113.3 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5), 116.0 (qu, $^3J_{C-SF_4} = 4.0$ Hz, C-5′), 118.3 (s, C-1′), 131.5 (s, C-6′), 144.8 (s, C-2′), 146.0 (d, $^3J_{C-F} = 5.0$ Hz, C-2), 154.9 (qu, $^2J_{C-SF_4} = 17.8$ Hz, C-4′), 155.3 (qu, $^2J_{C-SF_4} = 17.4$ Hz, C-4), 159.7 (d, $J_{C-F} = 247.1$ Hz, C-6). IR (Nujol): 3482, 3431, 3333, 3223 (NH), 917, 841, 810, 791 cm^{-1} (S–F). MS *m/z* (rel. int.): 454 $[M]^+$ (100), 434 $[M - HF]^+$ (33), 327 $[M - SF_5]^+$ (41). HRMS calcd. for $C_{12}H_9F_{11}N_2S_2$ 454.003, found 436.004. Anal. calcd.: C, 31.72; H, 2.00; N, 6.17; S, 14.12. Found: C, 32.13; H, 1.91; N, 6.09; S, 14.52.

3.7. Reactions of secondary amines with 1-chloro-2,6-dinitrobenzene derivatives (**2b**,**c**)—general method for the preparation of **13a–h** and **14a–d**

To a solution of 1.5 mmol of 1-chloro-2,6-dinitrobenzene derivative **2b**,**c** in 10 mL of methanol (or ethanol) was added under stirring 2.5 equivalents of amine. After 30 min the solvent was removed under vacuum. The resulting residue was washed with water and extracted with benzene or chloroform. After drying over Na_2SO_4, the product was purified by column chromatography [silica, hexane:benzene 4:1 (dialkylamino derivatives)] or recrystallized from aqueous ethanol (or heptane for the piperazine derivatives).

3.7.1. 2,6-Dinitro-4-pentafluorosulfanyl-N,N-di-n-propylaniline (**13a**)

Yield 84% as an orange-red solid, mp 66–67 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (6H, t, $J = 7.3$ Hz, CH_3), 1.62 (4H, m, $J = 7.3$ Hz, CH_2), 2.97 (4H, t, $J = 7.3$ Hz, NCH_2), 8.19 (2H, s, Ar); ^{19}F NMR: δ 63.81 (d of m, 4F, $^2J_{SF_4-SF} = 152.1$ Hz, SF_4), 80.65 (m, 1F, $^2J_{SF-SF_4} = 152.1$ Hz, SF); ^{13}C NMR: δ 11.1, 20.7, 54.0, 127.7 (s, C-3, C-5), 140.9 (C-2, C-6), 142.8 (qu, $^2J_{C-SF_4} = 22.2$ Hz, C-4), 143.9 (C-1). IR (Nujol): 3075, 1615, 1539, 1349, 1175, 1113, 980, 911, 860 (S–F), 824 cm^{-1}. MS *m/z* (rel. int.): 393 $[M]^+$ (12), 376 $[M - OH]^+$ (19), 364 $[M - Et]^+$ (81), 348 $[M - OEt]^+$ (36), 322 $[364 - C_3H_6]^+$ (29), 306 $[348 - C_3H_6]^+$ (29). HRMS calcd. for $C_{12}H_{16}F_5N_3O_4S$, 393.078, found 393.077.

3.7.2. 2,6-Dinitro-4-pentafluorosulfanyl-N-ethyl-N-n-butylaniline (**13b**)

Yield 84% as yellow crystals, mp 82–84 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 7.2$ Hz, CH_3), 1.18 (3H, t, $J = 7.2$ Hz, CH_3), 1.28 (2H, m, CH_2), 1.57 (2H, m, CH_2), 2.99 (2H, t, $J = 7.5$ Hz, CH_2–N), 3.11 (2H, q, $J = 6.8$ Hz, CH_2–N), 8.19 (2H, s, Ar). ^{19}F NMR: δ 63.37 (d of m, 4F, $J_{SF_4-SF} = 152.4$ Hz, SF_4), 80.18 (m, 1F, $J_{SF-SF_4} = 152.4$ Hz, SF). MS *m/z* (rel. int.): 393 $[M]^+$ (8), 376 $[M - OH]^+$ (20), 350 $[M - C_3H_7]^+$ (100), 334 $[M - OC_3H_7]^+$ (28), 322 $[350 - C_2H_4]^+$ (52), 306 $[334 - C_2H_4]^+$ (10). HRMS calcd. for $C_{12}H_{16}F_5N_3O_4S$, 393.078, found 393.077.

*3.7.3. 2,6-Dinitro-4-pentafluorosulfanyl-N-propyl-N-cyclopropanemethylaniline (**13c**)*

Yield 81% as orange crystals, mp 64–65 °C. ^{1}H NMR ($CDCl_3$): δ 0.16 (2H, m, CH_2), 0.58 (2H, m, CH_2), 0.88 (3H, t, $J = 7.5$ Hz, CH_3), 1.59 (3H, m, CH, CH_2), 2.90 (2H, d, $J = 6.8$ Hz, CH_2N), 3.09 (2H, m, CH_2N), 8.21 (2H, s, Ar); ^{19}F NMR: δ 63.39 (d of m, 4F, $J_{SF_4-SF} = 151.7$ Hz, SF_4), 80.18 (m, 1F, $J_{SF-SF_4} = 151.7$ Hz, SF); ^{13}C NMR: 4.0, 9.2, 11.1, 54.1, 57.5, 127.7 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-3, C-5), 141.0 (s, C-2, C-6), 143.1 (qu, $^2J_{C-SF_4} = 22.5$ Hz, C-4), 144.3 (s, C-1). MS *m/z* (rel. int.): 405 $[M]^+$ (15), 388 $[M - OH]^+$ (74), 376 $[M - Et]^+$ (100), 364 $[M - C_3H_5]^+$ (20), 360 $[M - OEt]^+$ (15), 322 $[376-C_4H_6]^+$ (43), 306 $[360-C_4H_6]^+$ (22). HRMS calcd. for $C_{13}H_{16}F_5N_3O_4S$ 405.078, found 405.078.

*3.7.4. 2,6-Dinitro-4-pentafluorosulfanyl-N-ethyl-N-2′-methylallylaniline (**13d**)*

Yield 84% as yellow crystals, mp 64–65 °C. ^{1}H NMR ($CDCl_3$): δ 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 1.73 (3H, s, CH_3), 3.10 (2H, q, $J = 7.0$ Hz, CH_2), 3.53 (2, s, CH_2), 5.0 (2H, s, CH_2), 8.19 (2H, s, Ar). ^{19}F NMR: δ 63.36 (d of m, 4F, $J_{SF_4-SF} = 152.2$ Hz, SF_4), 80.01 (m, 1F, $J_{SF-SF_4} = 152.2$ Hz, SF). MS *m/z* (rel. int.): 391 $[M]^+$ (20), 374 $[M - OH]^+$ (100), 350 $[M - Allyl]^+$ (36), 334 $[M - OAllyl]^+$ (52), 322 $[350-C_2H_4]^+$ (25), 306 $[334-C_2H_4]^+$ (17). HRMS calcd. for $C_{12}H_{14}F_5N_3O_4S$ 391.063, found 391.060.

*3.7.5. 2,6-Dinitro-4-pentafluorosulfanyl-N-propyl-N-tetrahydrofurfurylaniline (**13e**)*

Yield 77% as orange crystals, mp 66–68 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (3H, t, $J = 7.4$ Hz, CH_3), 1.44 (1H, m, CH), 1.64 (2H, m, CH_2), 1.83 (2H, m, CH_2), 2.01 (1H, m, CH), 2.95 (1H, dd, $J = 3.9$ Hz, $J = 14.4$ Hz, CH), 3.07 (2H, m, CH_2), 3.18 (1H, dd, $J = 7.2$ Hz, $J = 14.4$ Hz, CH), 3.72 (2H, m, CH_2), 4.15 (1H, m, CH), 8.20 (2H, s, Ar). ^{19}F NMR: δ 64.98 (d of m, 4F, $J_{SF_4-SF} = 152.2$ Hz, SF_4), 81.75 (m, 1F, $J_{SF-SF_4} = 152.2$ Hz, SF). ^{13}C NMR: δ 11.0, 21.1, 25.4, 29.8, 55.9, 56.2, 68.1, 127.4 (s, C-3, C-5), 141.1 (s, C-2, C-6), 143.7 (qu, $^2J_{C-SF_4} = 22.8$ Hz, C-4), 144.8 (s, C-1). MS *m/z* (rel. int.): 435 $[M]^+$ (<1), 434 $[M - H]^+$ (<1), 417 $[434-OH]^+$ (<1), 363 [434−Tetrahydrofurfuryl]$^+$ (100), 347 $[M - OTetrahydrofurfuryl]^+$ (21), 321 $[363-C_3H_6]^+$ (87), 305 $[347-C_3H_6]^+$ (37). HRMS calcd. for $C_{14}H_{18}F_5N_3O_5S$ 435.089, found 435.086.

*3.7.6. 2,6-Dinitro-4-trifluoromethylthio-N-ethyl-N-butylaniline (**13f**)*

Yield 84% as an orange-red solid, mp 56–58 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 7.2$ Hz, CH_3), 1.18 (3H, t, $J = 7.2$ Hz, CH_3), 1.28 (2H, m, CH_2), 1.57 (2H, m, CH_2), 2.98 (2H, t, $J = 7.2$ Hz, CH_2N), 3.10 (2H, q, 6.1 Hz, CH_2N), 8.07 (2H, s, Ar); ^{19}F NMR: δ −41.90 (s, CF_3). MS *m/z* (rel. int.): 367 $[M]^+$ (2), 350 $[M - OH]^+$ (6), 324 $[M - C_3H_7]^+$ (100), 308 $[M - C_3H_7O]^+$ (11), 296 $[324-C_2H_4]^+$ (25). HRMS calcd. for $C_{13}H_{16}F_3N_3O_4S$ 367.081, found 367.082.

*3.7.7. 2,6-Dinitro-4-trifluoromethylthio-N-propyl-N-cyclopropanemethylaniline (**13g**)*

Yield 82% as yellow-orange crystals, mp 54–55 °C. ^{1}H NMR ($CDCl_3$): δ 0.16 (2H, m, CH_2), 0.58 (2H, m, CH_2), 0.88 (3H, t, $J = 7.5$ Hz, CH_3), 1.59 (3H, m, CH, CH_2), 2.90 (2H, d, $J = 6.8$ Hz, CH_2–N), 3.09 (2H, m, CH_2N), 8.21 (2H, s, Ar). ^{19}F NMR: δ −41.87 (s, CF_3). MS *m/z* (rel. int.): 379 $[M]^+$ (7), 362 $[M - OH]^+$ (24), 350 $[M - Et]^+$ (51), 334 $[M - OEt]^+$ (3), 296 $[350-C_4H_6]^+$ (5). HRMS calcd. for $C_{14}H_{16}F_3N_3O_4S$ 379.081, found 379.079.

*3.7.8. 2,6-Dinitro-4-trifluoromethylthio-N-ethyl-N-2′-methylallylaniline (**13h**)*

Yield 84% as yellow crystals, mp 76–77 °C. ^{1}H NMR ($CDCl_3$): δ 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 1.73 (3H, s, CH_3), 3.10 (2H, q, $J = 7.0$ Hz, CH_2N), 3.53 (2H, s, CH_2), 5.0 (2H, s CH_2), 8.19 (2H, s, Ar); ^{19}F NMR: δ −41.76 (s, CF_3). MS *m/z* (rel. int.): 365 $[M]^+$ (20), 348 $[M - OH]^+$ (72), 324 $[M - Allyl]^+$ (28), 308 $[M - OAllyl]^+$ (45), 296 $[324-C_2H_4]^+$ (6). HRMS calcd. for $C_{13}H_{14}F_3N_3O_4S$ 365.063, found 365.060.

*3.7.9. 2,6-Dinitro-1-piperazino-4-pentafluorosulfanylbenzene (**14a**)*

Yield 91% as orange-yellow crystals, mp 164–165 °C. ^{1}H NMR ($CDCl_3$): δ 2.50 (4H, m, CH_2), 3.13 (4H, m, CH_2), 8.14 (2H, s, Ar). ^{19}F NMR: δ 63.22 (d of m, 4F, $J_{SF_4-SF} = 152.5$ Hz, SF_4), 79.62 (m, 1F, $J_{SF-SF_4} = 152.5$ Hz, SF). MS *m/z* (rel. int.): 378 $[M]^+$ (11), 361 $[M - OH]^+$ (10), 348 $[M - NO]^+$ (22), 336 $[M - C_2H_4N]^+$ (34), 306 $[336 - NO]^+$ (100), 290 $[336 - NO_2]^+$ (37), 285 $[M - H–2NO_2]^+$ (65), 272 $[361 - C_2H_4N–HNO_2]^+$ (36), 260 $[306 - NO_2]^+$ (36), 244 $[290 - NO_2]^+$ (42). HRMS calcd. for $C_{10}H_{11}F_5N_4O_4S$ 378.042, found 378.041.

*3.7.10. 2,6-Dinitro-1-N-methylpiperazino-4-pentafluorosulfanylbenzene (**14b**)*

Yield 91% as yellow crystals, mp 129–131 °C. ^{1}H NMR ($CDCl_3$): δ 2.34 (3H, s, CH_3), 2.50 (4H, m, CH_2), 3.14 (4H, m, CH_2), 8.14 (2H, s, Ar). ^{19}F NMR: δ 63.25 (d of m, 4F, $J_{SF_4-SF} = 152.5$ Hz, SF_4), 79.62 (m, 1F, $J_{SF-SF_4} = 152.5$ Hz, SF). MS *m/z* (rel. int.): 392 $[M]^+$ (96), 349 $[M - C_2H_5N]^+$ (96), 348 $[M - H–C_2H_5N]^+$ (65), 304 $[M - C_2H_4N–NO_2]^+$ (51), 289 $[M - C_3H_7N–NO_2]^+$ (100), 273 $[M - H–C_4H_9N–NO_2]^+$ (49), 258 $[304 - NO_2]^+$ (79), 244 $[M - C_3H_6N–2NO_2]^+$ (78). HRMS calcd. for $C_{11}H_{13}F_5N_4O_4S$, 392.058, found 392.057.

*3.7.11. 2,6-Dinitro-1-piperazino-4-trifluoromethylthiobenzene (**14c**)*

Yield 84% as orange-yellow crystals, mp 114–115 °C. ^{1}H NMR ($CDCl_3$): δ 1.72 (1H, s, NH), 2.96 (4H, bs, CH_2), 3.07 (4H, bs, CH_2N), 8.02 (2H, s, Ar). ^{19}F NMR: δ −42.95 (s, CF_3). MS *m/z* (rel. int.): 352 $[M]^+$ (11), 322 $[M - NO]^+$ (18), 310 $[M - C_2H_4N]^+$ (11), 280 $[310 - NO]^+$ (51), 259

$[M - H–2NO_2]^+$ (17), 246 $[310 - OH–HNO_2]^+$ (7), 218 $[310 - 2NO_2]^+$ (10). HRMS calcd. for $C_{11}H_{11}F_3N_4O_4S$ 352.046, found 352.044.

3.7.12. 2,6-Dinitro-1-piperazino-4-pentafluoroethylthiobenzene (**14d**)

Yield 83% as yellow crystals, mp 55–57 °C. ^{1}H NMR ($CDCl_3$): δ 2.27 (1H, s, NH), 2.98 (4H, q, $J = 5.13$ Hz, CH_2), 3.09 (4H, q, $J = 5.17$ Hz, CH_2N), 8.03 (2H, s, Ar). ^{19}F NMR: δ −82.81 (3F, s, CF_2CF_3), −91.99 (2F, s, CF_2CF_3). MS *m/z* (rel. int.): 402 $[M]^+$ (11), 372 $[M - NO]^+$ (26), 360 $[M - C_2H_4N]^+$ (10), 330 $[360 - NO]^+$ (46), 309 $[M - H–2NO_2]^+$ (12), 283 $[330 - HNO_2]^+$ (11). HRMS calcd. for $C_{12}H_{11}F_5N_4O_4S$ 402.042, found 402.043.

3.8. Reactions of 1-chloro-2,6-dinitrobenzene derivatives **2b** and **2e** with potassium ethyl xanthate—general method for the preparation of **17a** and **17b**

To a solution containing 0.44 g (2.75 mmol) of potassium ethyl xanthate in 3 mL of DMF, 2.5 mmol of 1-chloro-2,6-dinitrobenzene derivative (**2b**,**e**) was added in one portion. The reaction mixture was heated to 80 °C and stirred at that temperature for 10 h, after which time it was stirred for 5 h at room temperature. The solvent Me_2NCOH was then removed under vacuum. The remaining residue was washed with a 10% solution of hydrochloric acid and extracted with chloroform. The solvent layer was dried over Na_2SO_4 and then evaporated. The resulting residue was purified by column chromatography (silica, benzene:-hexane 1:2).

3.8.1. 1-Ethylthio-2,6-dinitro-4-pentafluorosulfanylbenzene (**17a**)

Yield 9% as orange red crystals, mp 97–99 °C. ^{1}H NMR ($CDCl_3$): δ 1.27 (3H, t, $J = 7.4$ Hz, CH_3), 2.94 (2H, q, $J = 7.4$ Hz, CH_2), 8.25 (2H, s, Ar). ^{19}F NMR: δ 62.98 (d of m, 4F, $^2J_{SF_4-SF} = 152.0$ Hz, SF_4), 78.12 (1F, m, $^2J_{SF-SF_4} = 152.0$ Hz, SF). ^{13}C NMR: δ 14.3, 30.9, 124.5 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-3, C-5), 130.9 (s, C-2, C-6), 151.8 (qu, $^2J_{C-SF_4} = 20.0$ Hz, C-4), 153.4 (s, C-1). MS *m/z* (rel. int.): 354 $[M]^+$ (21), 326 $[M - C_2H_4]^+$ (18), 309 $[326 - OH]^+$ (38), 296 $[326 - NO]^+$ (31), 232 $[326 - 2HNO_2]^+$ (100). HRMS calcd. for $C_8H_7F_5N_2O_4S_2$ 353.977, found 353.976.

3.8.2. 1-Ethylthio-2,6-dinitro-4-trifluoromethylthiobenzene (**17b**)

Yield 28% as orange crystals, mp 50–52 °C. ^{1}H NMR ($CDCl_3$): 1.26 (3H, t, $J = 7.5$ Hz, CH_3), 2.94 (2H, q, $J = 7.5$ Hz, CH_2), 8.12 (2H, s, Ar). ^{19}F NMR: δ −41.63 (s, CF_3). MS *m/z* (rel. int.): 328 $[M]^+$ (54), 300 $[M - C_2H_4]^+$ (32), 283 $[300 - OH]^+$ (67), 270 $[300 - NO]^+$ (73), 223 $[300 - HNO_2]^+$ (26), 206 $[300 - 2HNO_2]^+$ (100), 176 $[M - C_2H_4S–2HNO_2]^+$ (82). HRMS calcd. for $C_9H_7F_3N_2O_4S_2$ 327.980, found 327.978.

3.9. Reactions of 1-chloro-2,6-dinitrobenzene derivatives with ethyl thioglycolate—general method for the preparation of **19a–c**

Triethylamine (1.2 mL, 8.4 mmol) was added to a ice-cooled mixture of 7.6 mmol of 1-chloro-2,6-dinitrobenzene derivative (**2b**,**e**,**f**) and 0.91 g (7.6 mmol) of ethyl thioglycolate (in ethanol). The reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was separated by filtration, washed with water and ethanol, and dried.

3.9.1. 2-Ethoxycarbonyl-7-nitro-5-pentafluorosulfanylbenzothiazole-N-oxide (**19a**)

Yield 24% as orange crystals, mp 174–176 °C. ^{1}H NMR ($CDCl_3$): δ 1.48 (3H, t, $J = 7.0$ Hz, CH_3), 4.55 (2H, q, $J = 7.0$ Hz, CH_2), 8.97 (1H, s, Ar), 8.99 (1H, s, Ar). ^{19}F NMR: δ 64.04 (d of m, 4F, $J_{SF_4-SF} = 152.2$ Hz, SF_4), 78.58 (m, 1F, $J_{SF-SF_4} = 152.2$ Hz, SF); ^{13}C NMR: δ 14.1 (s, CH_3), 63.5 (s, CH_2), 123.4 (qu, $^3J_{C-SF_4} = 4.9$ Hz, C-4), 124.1 (qu, $^3J_{C-SF_4} = 4.8$ Hz, C-6), 126.5 (s, C-2), 138.0 (s, C-8), 141.9 (C-7), 146.3 (C-9), 152.3 (qu, $^2J_{C-SF_4} = 22.4$ Hz, C-5), 156.4 (C=O). IR (Nujol) 1740 cm^{-1} (C=O). MS *m/z* (rel. int.): 394 $[M]^+$ (10), 378 $[M - O]^+$ (8), 333 $[378 - OEt]^+$ (56), 306 $[333 - HCN]^+$ (100), 260 $[306 - NO_2]^+$ (24), 248 $[C_6H_3F_5NO_2S]^+$ (12), 201 $[248 - NO_2]^+$ (17). HRMS calcd. for $C_{10}H_7F_5N_2O_5S_2$ 393.972, found 393.971.

3.9.2. 2-Ethoxycarbonyl-7-nitro-5-trifluoromethylthiobenzothiazole-N-oxide (**19b**)

Yield 75% as orange crystals, mp 134–136 °C. ^{1}H NMR ($CDCl_3$): δ 1.46 (3H, t, $J = 7.2$ Hz, CH_3), 4.53 (2H, q, $J = 7.2$ Hz, CH_2), 8.84 (2H, s, Ar); ^{19}F NMR: δ −42.03 (s, CF_3); ^{13}C NMR: 14.1 (s, CH_3), 63.3 (s, CH_2), 125.7 (s, C-5), 126.1 (s, C-2), 128.6 (q, $J_{C-F} = 310.0$ Hz, CF_3), 132.4 (s, C-4), 132.7 (s, C-6), 137.4 (s, C-8), 142.4 (s, C-7), 147.0 (C-9), 159.5 (C=O). IR (Nujol) 1740 cm^{-1} (C=O). MS *m/z* (rel. int.): 368 $[M]^+$ (6), 352 $[M - O]^+$ (39), 333 $[352 - F]^+$ (14), 322 $[M - NO_2]^+$ (30), 307 $[352 - OEt]^+$ (39), 280 $[307–HCN]^+$ (100), 250 $[280 - HCN]^+$ (20), 234 $[280–NO_2]^+$ (27), 222 $[250 - CO]^+$ (13). HRMS calcd. for $C_{11}H_7F_3N_2O_5S_2$ 367.975, found 367.976.

3.9.3. 2-Ethoxycarbonyl-7-nitro-5-pentafluoroethylthiobenzothiazole-N-oxide (**19c**)

Yield 67% as orange crystals, mp 145–147 °C. ^{1}H NMR ($CDCl_3$): δ 1.48 (3H, t, $J = 7.2$ Hz, CH_3), 4.56 (2H, q, $J = 7.2$ Hz, CH_2), 8.85 (1H, s, Ar), 8.88 (1H, d, $J = 1.7$ Hz, Ar). ^{19}F NMR: δ −91.15 (s, 2F, CF_2CF_3), −82.62 (s, 3F, CF_2CF_3). IR (Nujol) 1740 cm^{-1} (C=O). MS *m/z* (rel. int.): 418 $[M]^+$ (20), 402 $[M - O]^+$ (55), 386 (15), 372 $[M - NO_2]^+$ (17), 357 $[402 - OEt]^+$ (48), 346 $[M - OEt–HCN]^+$ (28), 330 $[357 - HCN]^+$ (100), 311 $[357 - NO_2]^+$ (14), 284 $[330 - NO_2]^+$ (25). HRMS calcd. for $C_{12}H_7F_5N_2O_5S_2$ 417.972, found 417.973.

*3.10. 7-Nitro-5-trifluoromethylthiobenzothiazol-N-oxide-2-ylhydroxamic acid (**20**)*

A solution of $NH_2OH{\cdot}HCl$ (0.11 g, 1.6 mmol) and NaOH (0.13 g, 3.3 mmol) in methanol was added to a mixture of 0.50 g (1.4 mmol) of 1-ethoxycarbonyl-7-nitro-5-trifluoromethylthiobenzothiazole-*N*-oxide (**9b**) in methanol. Stirring was maintained for 5 h, after which the solvent was removed under vacuum and the remaining residue was dissolved in water. This aqueous solution was acidified with hydrochloric acid, and a precipitate formed. The precipitate was collected, washed with water and methanol, and dried. Yield 52% as orange crystals, mp 229–231 °C. ^{1}H NMR (Me_2SO-d_6): δ 8.54 (1H, s, Ar), 8.53 (1H, s, Ar), 11.83 (1H, bs, NH); ^{19}F NMR: δ −42.45 (s, CF_3). IR (Nujol): 3450, 3150, 1650 cm^{-1}. MS *m/z* (rel. int.): 355 $[M]^+$ (2), 339 $[M-O]^+$ (3), 323 $[M-NHOH]^+$ (12), 305 $[323-H_2O]^+$ (14), 295 $[M-CONHOH]^+$ (15), 280 $[323-O\text{–}HCN]^+$ (53), 275 $[295-HF]^+$ (27), 250 $[280-NO]^+$ (35), 234 $[280-NO_2]^+$ (29). HRMS calcd. for $C_9H_4F_3N_3O_5S_2$ 354.954, found 354.955.

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