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Synthesis of aryl perfluoroalkyl sulfides from aromatic disulfides

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Thermolysis of xenon(II) bis(perfluoroalkanecarboxylates) in the presence of diaryl disulfides occurs through the S—S bond cleavage to form dihalo-, halonitro-, and halodinitrophenyl perfluoroalkyl sulfides. The latter type of compounds was obtained for the first time. The main side process is the perfluoroalkylation of the aromatic ring.

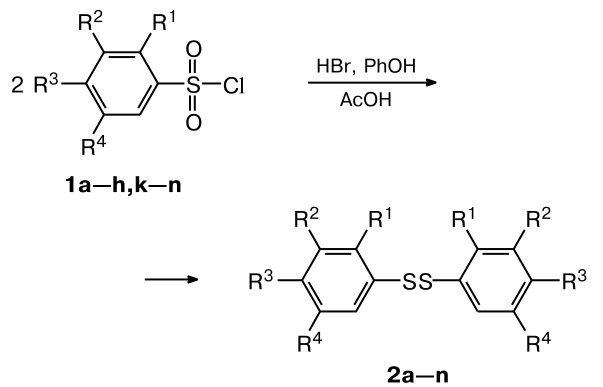
Key words: diaryl disulfides, perfluoroalkylation, aryl perfluoroalkyl sulfides.

It is known[1] that the substitution of the hydrogen atom in aromatic and heterocyclic systems by perfluoroalkyl groups can substantially change the physical and biological properties of molecules. The introduction of "superlipophilic" perfluoroalkylthio groups SR^F ($R^F = CF_3$, C_2F_5, *etc.*) with the highest lipophilicity indices[2] can significantly change the biological effect of the resulting compounds.[3] According to our current scientific interest, we develop the synthesis of new building blocks containing both "superlipophilic" groups and substituents capable of reacting with different nucleophilic agents. These can be, *e.g.*, halogen atoms or nitro groups in the aromatic and heterocyclic compounds activated by other electron-withdrawing substituents.[4] In our opinion, this approach can provide the synthesis of new biologically active compounds.

We developed[5,6] a method for the perfluoroalkylation of thio derivatives of polyhalopyridines based on the thermolysis of xenon(II) bis(perfluoroalkanecarboxylates). This method makes it possible to involve accessible starting compounds such as thiols and disulfides, to introduce the SC_nF_{2n+1} groups (n = 1—3) in high yields, to perform synthesis under mild conditions and isolate easily target products, and to synthesize compounds containing groups sensitive to the nucleophilic attack.

In the present work, we successfully used the method for a series of aromatic compounds. The starting compounds were diaryl disulfides **2a—n** (Tables 1 and 2), the most part of which (except **2i,j**) were synthesized[7—9] by the reduction of the respective sulfonyl chlorides **1** with a solution of HBr in acetic acid in the presence of phenol as an acceptor of liberated Br_2 (Scheme 1).

Scheme 1



1, 2	R¹	R²	R³	R⁴	1, 2	R¹	R²	R³	R⁴
a	F	H	H	NO_2	**h**	H	H	Br	H
b	Cl	H	H	NO_2	**i**	H	NO_2	H	H
c	Br	H	H	NO_2	**j**	H	H	NO_2	H
d	H	NO_2	H	NO_2	**k**	F	H	H	Br
e	H	NO_2	Cl	NO_2	**l**	Cl	H	H	CF_3
f	H	NO_2	Cl	H	**m**	H	Cl	H	Cl
g	Cl	H	H	Cl	**n**	H	Cl	Cl	H

As a rule, xenon(II) bis(perfluoroalkanecarboxylates) were generated in a preliminary step by mixing equimolar amounts of XeF_2 and perfluoroalkanecarboxylic acid in CH_2Cl_2 on cooling (method *A*). Alternatively, method *B* involved the *in situ* addition of XeF_2 to a solution or suspension of a disulfide in perfluoroalkanecarboxylic acid. The mode of conducting the subsequent reaction was determined by both the solubility of the starting disulfides **2a—n** and temperatures of decomposition of xenon bis(perfluoroalkanecarboxylates) upon the generation of

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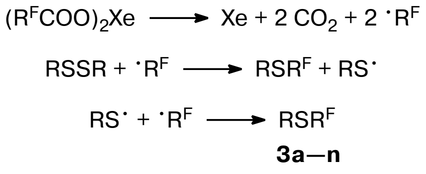
Table 1. Yields and melting points of diaryl disulfides **2a—h,k—n**

Compound	Yield	M.p./°C (Refs.)	Compound	Yield	M.p./°C (Refs.)
2a	82.0	124—126	**2g**	73.5	77—79 (81—82)[14]
2b	85.0	142—144 (143—144)[9]	**2h**	89.0	92—94 (89—90)[14]
2c	90.0	160—162 (159—161)[12]	**2k**	84.0	40—41
2d	83.0	185—187 (186—187)[13]	**2l**	80.0	55—57
2e	90.0	190—192	**2m**	77.5	78—79
2f	88.0	117—119 (116—117)[9]	**2n**	90.0	87—89 (89—90)[15]

perfluoroalkyl radicals. For example, xenon bis(trifluoroacetate) is noticeably decomposed in a CH_2Cl_2 solution even at temperatures about 0 °C, whereas heptafluorobutyrate needs heating to 40—50 °C. Therefore, the C_3F_7S derivatives were usually synthesized in the corresponding perfluoroalkanecarboxylic acid.

The thermolysis of the xenon compounds in the presence of diaryl disulfides **2a—n** produces aryl perfluoroalkyl sulfides. This process is presented in Scheme 2. Free-radical substitution of the RS moieties in aromatic disulfides RSSR under the action of perfluoroalkyl radicals formed upon the thermolysis of xenon bis(perfluoroalkanecarboxylates) results in aryl perfluoroalkyl sulfides **3a—n** and the arylthiyl radicals. The recombination of the RS$^\bullet$ and $^\bullet$R^F radicals also affords the expected derivatives **3a—n**.[5]

Scheme 2



$$(R^FCOO)_2Xe \longrightarrow Xe + 2\,CO_2 + 2\,{}^\bullet R^F$$
$$RSSR + {}^\bullet R^F \longrightarrow RSR^F + RS^\bullet$$
$$RS^\bullet + {}^\bullet R^F \longrightarrow \underset{\mathbf{3a—n}}{RSR^F}$$

R = Aryl, $R^F = C_nF_{2n+1}$ (n = 1—3)

In several cases, we succeeded in isolating individual components of the reaction mixtures obtained upon the reactions of disulfides **2** with xenon bis(perfluoroalkanecarboxylates). If the preparative separation of the reaction products was inefficient, the GC-MS method was used for the analysis. The main components of the reaction mixtures are the respective dihalo-, halonitro-, and halodinitrophenyl perfluoroalkyl sulfides **3—5** (Scheme 3). Their yields can achieve 70% when molecules of the starting disulfides contained several electron-withdrawing substituents (for example, compound **3e**).

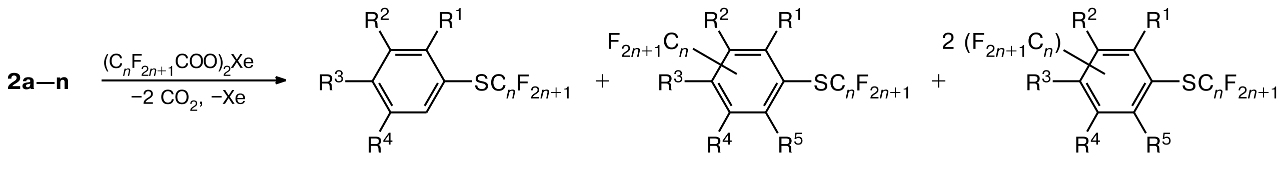
Insertion of one or two perfluoroalkyl radicals into the benzene ring with the simultaneous formation of aryl perfluoroalkyl sulfides represent side processes. The reac-

Table 2. Data on the ^{1}H and ^{13}C NMR spectra, mass spectra, and high-resolution mass spectra of disulfides **2a,k—m**

Compound	NMR (δ, J/Hz)		MS, m/z (I_{rel} (%))	High-resolution mass spectrum		
	δ_H	δ_C		Found, m/z [M]$^+$	Molecular formula	Calculated, M
2a	7.27 (m, H(6)), 8.19 (m, H(4)), 8.53 (m, H(3))	117.0 (d, J = 24.3), 125.3 (d, J = 19.7), 125.8 (d, J = 9.4), 126.5, 144.7 (br.s), 163.7 (d, J = 257.8)	344 [M]$^+$ (92), 173 [M/2 + 1]$^+$ (100), 356 [M/2]$^+$ (32), 126 [M/2 – NO_2]$^+$ (95)	343.974	$C_{12}H_6F_2O_4S_2$	343.974
2k	6.96 (t, H(3), J = 8.8), 7.38 (m, H(4)), 7.69 (dd, H(6), J = 2.4)	117.2 (d, J = 3.5), 117.5 (d, J = 23.2), 125.4 (d, J = 18.8), 132.8 (d, J = 7.7), 133.4, 159.6 (d, J = 248.0)	414 (41), 412 (75) and 410 [M]$^+$ (40), 207 (27), 205 [M/2]$^+$ (26), 126 (100)	413.821 409.825	$C_{12}H_6{}^{81}Br_2F_2S_2$ $C_{12}H_6{}^{79}Br_2F_2S_2$	413.822 409.826
2l	7.48 (dd, (H(3), H(4), $^4J_{H,H}$ = 3.0, $^3J_{H,H}$ = 8.5), 7.86 (s, H(6))	—	422 [M]$^+$ (100), 403 [M – F]$^+$ (11), 352 [M – 2 Cl]$^+$ (6), 211 [M/2]$^+$ (73), 176 [M/2 – Cl]$^+$ (35), 157 [M/2 – Cl – F]$^+$ (14), 142 [M/2 – CF_3]$^+$ (14), 69 [CF_3]$^+$ (7)	421.919	$C_{14}H_6Cl_2F_6S_2$	421.919
2m	7.23 (t, H(4), $^4J_{H,H}$ = 1.7), 7.34 (d, H(2), H(6), $^4J_{H,H}$ = 1.7)	—	356 [M]$^+$ (100), 321 [M – Cl]$^+$ (5), 286 [M – 2 Cl]$^+$ (41), 251 [M – 3 Cl]$^+$ (2), 178 [M/2]$^+$ (40), 142 [M/2 – HCl]$^+$ (58), 107 [M/2 – HCl – Cl]$^+$ (9)	353.865	$C_{12}H_6Cl_4S_2$	353.867

Scheme 3

$$2\ C_nF_{2n+1}COOH + XeF_2 \longrightarrow (C_nF_{2n+1}COO)_2Xe + 2\ HF$$



3a—n, 4a—n, 5a—f **6a—d, 7a,b, 8** **9a,b, 10**

n = 1 (**3**, **6**, **9**), 2 (**4**, **7**, **10**), 3 (**5**, **8**)

Compound	R^1	R^2	R^3	R^4	Compound	R^1	R^2	R^3	R^4	Compound	R^1	R^2	R^3	R^4	R^5
3a	F	H	H	NO$_2$	**4a**	F	H	H	NO$_2$	**5a**	F	H	H	NO$_2$	—
3b	Cl	H	H	NO$_2$	**4b**	Cl	H	H	NO$_2$	**5b**	Cl	H	H	NO$_2$	—
3c	Br	H	H	NO$_2$	**4c**	Br	H	H	NO$_2$	**5c**	Br	H	H	NO$_2$	—
3d	H	NO$_2$	H	NO$_2$	**4d**	H	NO$_2$	H	NO$_2$	**5d**	H	NO$_2$	H	NO$_2$	—
3e	H	NO$_2$	Cl	NO$_2$	**4e**	H	NO$_2$	Cl	NO$_2$	**5e**	F	H	H	Br	—
3f	H	NO$_2$	Cl	H	**4f**	H	NO$_2$	Cl	H	**5f**	H	Cl	Cl	H	—
3g	Cl	H	H	Cl	**4g**	Cl	H	H	Cl	**6a**	F	H	CF$_3$	Br	H
3h	H	H	Br	H	**4h**	H	H	Br	H	**6b**	Cl	*	*	CF$_3$	*
3i	H	NO$_2$	H	H	**4i**	H	NO$_2$	H	H	**6c**	*	Cl	*	Cl	*
3j	H	H	NO$_2$	H	**4j**	H	H	NO$_2$	H	**6d**	*	Cl	Cl	*	*
3k	F	H	H	Br	**4k**	F	H	H	Br	**7a**	Cl	**	**	**	CF$_3$
3l	Cl	H	H	CF$_3$	**4l**	Cl	H	H	CF$_3$	**7b**	**	Cl	**	Cl	**
3m	H	Cl	H	Cl	**4m**	H	Cl	H	Cl	**7c**	**	Cl	Cl	**	**
3n	H	Cl	Cl	H	**4n**	H	Cl	Cl	H						

* **6:** R^m = H, H, CF$_3$; m = 2, 3, 5 (**b**), 1, 3, 5 (**c**), 1, 4, 5 (**d**). ** **7:** R^m = H, H, C$_2$F$_5$; m = 2, 3, 5 (**a**), 1, 3, 5 (**b**), 1, 4, 5 (**c**)

8: R^1, R^4, R^5 = H, H, C$_3$F$_7$; R^2 = R^3 = Cl; **9:** R^1 = F; R^2, R^3, R^5 = H, H, CF$_3$; R^4 = Br (**a**); R^1, R^4, R^5 = H, H, CF$_3$; R^2 = R^3 = Cl (**b**)

10: R^1, R^4, R^5 = H, H, C$_2$F$_5$; R^2 = R^3 = Cl

tion mixtures can contain two or three isomers of monosubstituted derivatives (**11—17**). We failed to separate preparatively monosubstitution products **6b—d**, **7a,b**, and **8** into individual isomers and to isolate disubstituted derivatives **9a,b** and **10**. Therefore, in the case of disulfides **2k—n**, the reaction mixtures were studied by GC-MS (Table 3).

It was found that if the *para*-position of the benzene ring is occupied by a substituent (halogen atom or nitro group), the insertion of perfluoroalkyl radicals is not selective and results in a set of products of monosubstitution at all free positions. For example, in the case of disulfide **2n**, all three possible isomers **15—17** were found in the reaction mixture by GC-MS. The degree of perfluoroalkylation of the aromatic fragment decreases when several electron-withdrawing substituents are present. Thus, no by-products were found in the reaction mixture in the case of dinitrochloro derivative **3e**. In the case of disulfides **2a—d,g,i,k** containing no *para*-substituents with respect to the —S—S— group, we observed the predominant perfluoroalkylation of the aromatic ring at position 4 with respect to the perfluoroalkylthio group with the formation of isomers **11—13**. For several reaction mixtures, these derivatives were preparatively isolated and characterized by a complex of physicochemical methods (Tables 4—6). At the same time, in these cases too, the presence of isomer **14** was confirmed by both GC-MS and isolation in the individual state. The mechanism of perfluoroalkylation at position 4 can be presented as follows (Scheme 4): the interaction of diaryl disulfide **2** with the perfluoroalkyl radical generates arylthiyl radical **18**, which is further isomerized to carbon-centered radical **19** with the localization of the radical center in position 4 of the benzene ring. Its subsequent recombination with the perfluoroalkyl radical affords 4-perfluoroalkyl-substituted benzenethiol (**20**), which is further transformed, in the presence of xenon bis(perfluoroalkanecarboxylate), into the respective disulfide **21** and then into derivatives **11—13** (see Scheme 4).

Note that the degree of perfluoroalkylation of the benzene ring decreases in the case of heptafluoropropyl radicals, which can evidently be related to both differences in energy characteristics of intermediates and the influence of steric factors on their insertion into the aromatic ring.

Ab initio quantum-chemical calculations in the STO-3G basis set were carried out for some intermediates

Table 3. Data on GC-MS analysis of the composition of reaction mixtures obtained from disulfides **2k—n**

Disulfide	Composition of reaction mixture** (%)	Molecular formula	τ* /min	MS, m/z ($I_{\rm rel}$(%))***
2k	*1* (1) **3k** (56.4)	$C_7H_3BrF_4S$	4.66	274 $[M]^+$ (100), 255 $[M - F]^+$ (3), 205 $[M - CF_3]^+$ (39), 176 $[M - F - Br]^+$ (8), 126 $[M - CF_3 - Br]^+$ (100), 69 $[CF_3]^+$ (47)
	(2) **6a** (39.7)	$C_8H_2BrF_7S$	3.99	342 $[M]^+$ (87), 273 $[M - CF_3]^+$ (19), 254 $[M - CF_3 - F]^+$ (5), 194 $[M - CF_3 - Br]^+$ (100), 175 $[M - CF_3 - F - Br]^+$ (19), 93 $[M - SCF_3 - CF_3 - Br]^+$ (9), 69 $[CF_3]^+$ (67)
	(3) **9a** (3.9)	$C_9HBrF_{10}S$	4.32	410 $[M]^+$ (57), 391 $[M - F]^+$ (13), 322 $[M - F - CF_3]^+$ (26), 262 $[M - CF_3 - Br]^+$ (89), 193 $[M - 2\,CF_3 - Br]^+$ (21), 161 $[M - CF_3 - SCF_3 - Br]^+$ (14), 99 $[M - 2\,CF_3 - SCF_3 - Br]^+$ (13), 69 $[CF_3]^+$ (100)
2l	*2* (1) **3l** (63.2)	$C_8H_3ClF_6S$	2.83	280 $[M]^+$ (100), 261 $[M - F]^+$ (23), 211 $[M - CF_3]^+$ (66), 176 $[M - CF_3 - Cl]^+$ (31), 157 $[M - CF_3 - Cl - F]^+$ (13), 142 $[M - 2\,CF_3]^+$ (12), 107 $[M - 2\,CF_3 - Cl]^+$ (3), 69 $[CF_3]^+$ (24)
	(2) **6b** (13.7)	$C_9H_2ClF_9S$	2.53	348 $[M]^+$ (100), 329 $[M - F]^+$ (23), 293 $[M - F - Cl]^+$ (1), 279 $[M - CF_3]^+$ (29), 225 $[M - CF_3 - Cl - F]^+$ (29), 210 $[M - 2\,CF_3]^+$ (15), 175 $[M - 2\,CF_3 - Cl]^+$ (4), 106 $[M - 3\,CF_3 - Cl]^+$ (3), 69 $[CF_3]^+$ (17)
	(2) **6b** (23.1)		2.78	348 $[M]^+$ (100), 329 $[M - F]^+$ (23), 313 $[M - Cl]^+$ (1), 279 $[M - CF_3]^+$ (29), 244 $[M - CF_3 - Cl]^+$ (10), 225 $[M - CF_3 - Cl - F]^+$ (16), 175 $[M - 2\,CF_3 - Cl]^+$ (4), 106 $[M - 3\,CF_3 - Cl]^+$ (3), 69 $[CF_3]^+$ (17)
	3 (1) **4l** (44.1)	$C_9H_3ClF_8S$	2.90	330 $[M]^+$ (100), 261 $[M - CF_3]^+$ (46), 211 $[M - C_2F_5]^+$ (65), 176 $[M - C_2F_5 - Cl]^+$ (33), 142 $[M - C_2F_5 - CF_3]^+$ (12), 119 $[C_2F_5]^+$ (8), 69 $[CF_3]^+$ (18)
	(2) **7a** (19.1)	$C_{11}H_2ClF_{13}S$	2.55	448 $[M]^+$ (93), 379 $[M - CF_3]^+$ (100), 329 $[M - C_2F_5]^+$ (26), 310 $[M - 2\,CF_3]^+$ (7), 225 $[M - C_2F_5 - CF_3 - Cl]^+$ (45), 119 $[C_2F_5]^+$ (7), 69 $[CF_3]^+$ (17)
	(2) **7a** (25.9)		2.83	448 $[M]^+$ (55), 379 $[M - CF_3]^+$ (100), 329 $[M - C_2F_5]^+$ (9), 260 $[M - C_2F_5 - CF_3]^+$ (44), 119 $[C_2F_5]^+$ (6), 106 $[M - 2\,C_2F_5 - CF_3 - Cl]^+$ (2), 69 $[CF_3]^+$ (15)
2m	*4* (1) **3m** (52.4)	$C_7H_3Cl_2F_3S$	3.68	246 $[M]^+$ (100), 227 $[M - F]^+$ (6), 211 $[M - Cl]^+$ (2), 177 $[M - CF_3]^+$ (44), 142 $[M - CF_3 - Cl]^+$ (41), 107 $[M - CF_3 - 2\,Cl]^+$ (9), 69 $[CF_3]^+$ (16)
	(2) **6c** (47.6)	$C_8H_2Cl_2F_6S$	3.85	314 $[M]^+$ (100), 279 $[M - Cl]^+$ (2), 245 $[M - CF_3]^+$ (27), 226 $[M - CF_3 - F]^+$ (12), 210 $[M - CF_3 - Cl]^+$ (30), 175 $[M - CF_3 - 2\,Cl]^+$ (9), 143 $[M - SCF_3 - 2\,Cl]^+$ (4), 106 $[M - 2\,CF_3 - 2\,Cl]^+$ (4), 69 $[CF_3]^+$ (14)
	5 (1) **4m** (58.1)	$C_8H_3Cl_2F_5S$	3.40	296 $[M]^+$ (100), 227 $[M - CF_3]^+$ (36), 207 $[M - F - 2\,Cl]^+$ (1), 192 $[M - CF_3 - Cl]^+$ (3), 177 $[M - C_2F_5]^+$ (43), 142 $[M - C_2F_5 - Cl]^+$ (53), 119 $[C_2F_5]^+$ (9), 107 $[M - C_2F_5 - 2\,Cl]^+$ (13), 69 $[CF_3]^+$ (20)
	(2) **7b** (41.9)	$C_{10}H_2Cl_2F_{10}S$	3.80	414 $[M]^+$ (46), 395 $[M - F]^+$ (5), 345 $[M - CF_3]^+$ (100), 295 $[M - C_2F_5]^+$ (4), 276 $[M - 2\,CF_3]^+$ (5), 226 $[M - C_2F_5 - CF_3]^+$ (38), 191 $[M - C_2F_5 - CF_3 - Cl]^+$ (22), 176 $[M - 2\,C_2F_5]^+$ (8), 159 $[M - SC_2F_5 - CF_3 - Cl]^+$ (4), 119 $[C_2F_5]^+$ (6), 69 $[CF_3]^+$ (14)
2n	*6* (1) **3n** (43.2)	$C_7H_3Cl_2F_3S$	5.50	246 $[M]^+$ (100), 227 $[M - F]^+$ (6), 211 $[M - Cl]^+$ (0.5), 192 $[M - Cl - F]^+$ (1), 177 $[M - CF_3]^+$ (84), 142 $[M - CF_3 - Cl]^+$ (71), 107 $[M - CF_3, - 2\,Cl]^+$ (16), 69 $[CF_3]^+$ (36)
	(2) **6d** (14.9)	$C_8H_2Cl_2F_6S$	4.87	314 $[M]^+$ (100), 295 $[M - F]^+$ (15), 245 $[M - CF_3]^+$ (56), 210 $[M - CF_3 - Cl]^+$ (44), 175 $[M - CF_3 - 2\,Cl]^+$ (38), 143 $[M - SCF_3 - 2\,Cl]^+$ (5) 106 $[M - 2\,CF_3 - 2\,Cl]^+$ (12), 69 $[CF_3]^+$ (53)

(*to be continued*)

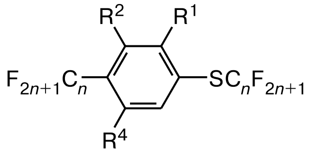
Table 3 (*continued*)

Disulfide	Composition of reaction mixture** (%)	Molecular formula	τ* /min	MS, *m/z* (I_{rel}(%))***
	(2) **6d** (19.0)		5.62	314 $[M]^+$ (100), 295 $[M - F]^+$ (15), 260 $[M - F - Cl]^+$ (1), 245 $[M - CF_3]^+$ (62), 210 $[M - CF_3 - Cl]^+$ (15), 143 $[M - SCF_3 - 2\ Cl]^+$ (2), 106 $[M - 2\ CF_3 - 2\ Cl]^+$ (15), 69 $[CF_3]^+$ (41)
	(2) **6d** (10.9)		6.94	314 $[M]^+$ (100), 295 $[M - F]^+$ (12), 279 $[M - Cl]^+$ (1), 245 $[M - Cl]^+$ (50), 175 $[M - CF_3 - 2\ Cl]^+$ (16), 143 $[M - SCF_3 - 2\ Cl]^+$ (6), 106 $[M - 2\ CF_3 - 2\ Cl]^+$ (44), 69 $[CF_3]^+$ (78)
	(3) **9b** (4.5)	$C_9HCl_2F_9S$	4.68	382 $[M]^+$ (100), 363 $[M - F]^+$ (61), 313 $[M - CF_3]^+$ (61), 278 $[M - CF_3 - Cl]^+$ (47), 244 $[M - 2\ CF_3]^+$ (23), 209 $[M - Cl - 2\ CF_3]^+$ (9), 174 $[M - 2\ CF_3 - 2\ Cl]^+$ (6), 105 $[M - 3\ CF_3 - 2\ Cl]^+$ (7), 69 $[CF_3]^+$ (68)
7	(1) **4n** (59.0)	$C_8H_3Cl_2F_5S$	5.73	296 $[M]^+$ (100), 277 $[M - F]^+$ (8), 227 $[M - CF_3]^+$ (8), 177 $[M - C_2F_5]^+$ (95), 142 $[M - C_2F_5, - Cl]^+$ (62), 119 $[C_2F_5]^+$ (18), 69 $[CF_3]^+$ (36)
	(2) **7c** (16.1)	$C_{10}H_2Cl_2F_{10}S$	4.34	414 $[M]^+$ (100), 395 $[M - F]^+$ (8), 345 $[M - CF_3]^+$ (55), 295 $[M - C_2F_5]^+$ (58), 226 $[M - C_2F_5 - CF_3]^+$ (37), 191 $[M - C_2F_5 - CF_3 - Cl]^+$ (44), 159 $[M - SC_2F_5 - CF_3 - Cl]^+$ (8), 119 $[C_2F_5]^+$ (25), 69 $[CF_3]^+$ (56)
	(2) **7c** (14.8)		5.04	414 $[M]^+$ (100), 395 $[M - F]^+$ (7), 345 $[M - CF_3]^+$ (59), 295 $[M - C_2F_5]^+$ (53), 260 $[M - C_2F_5 - Cl]^+$ (15), 226 $[M - C_2F_5 - CF_3]^+$ (15), 159 $[M - SC_2F_5 - CF_3 - Cl]^+$ (5), 119 $[C_2F_5]^+$ (19), 69 $[CF_3]^+$ (41)
	(2) **7c** (7.4)		6.16	414 $[M]^+$ (100), 395 $[M - F]^+$ (8), 345 $[M - CF_3]^+$ (40), 310 $[M - CF_3 - Cl]^+$ (15), 295 $[M - C_2F_5]^+$ (65), 260 $[M - C_2F_5 - Cl]^+$ (45), 226 $[M - C_2F_5 - CF_3]^+$ (38), 191 $[M - C_2F_5 - CF_3 - Cl]^+$ (44), 119 $[C_2F_5]^+$ (31), 69 $[CF_3]^+$ (78)
	(3) **10** (3.9)	$C_{12}HCl_2F_{15}S$	3.33	532 $[M]^+$ (55), 413 $[M - C_2F_5]^+$ (80), 294 $[M - 2\ C_2F_5]^+$ (75), 262 $[M - C_2F_5 - SC_2F_5]^+$ (89), 225 $[M - 2\ C_2F_5 - CF_3]^+$ (59), 193 $[M - SC_2F_5 - C_2F_5 - CF_3]^+$ (94), 119 $[C_2F_5]^+$ (78), 69 $[CF_3]^+$ (100)
8	(1) **5f** (58.7)	$C_7H_3Cl_2F_3S$	6.25	346 $[M]^+$ (100), 327 $[M - F]^+$ (7), 292 $[M - F - Cl]^+$ (2), 258 $[M - F - CF_3]^+$ (1), 227 $[M - C_2F_5]^+$ (27), 192 $[M - Cl - C_2F_5]^+$ (2), 177 $[M - C_3F_7]^+$ (93), 142 $[M - C_3F_7, - Cl]^+$ (68), 107 $[M - C_3F_7 - 2\ Cl]^+$ (16), 69 $[CF_3]^+$ (51)
	(2) **8** (14.3)	$C_{12}H_2Cl_2F_{14}S$	5.68	514 $[M]^+$ (56), 495 $[M - F]^+$ (13), 460 $[M - F - Cl]^+$ (1), 395 $[M - C_2F_5]^+$ (85), 345 $[M - C_3F_7]^+$ (29), 326 $[M - C_2F_5 - CF_3]^+$ (10), 226 $[M - C_3F_7 - C_2F_5]^+$ (93), 191 $[M - C_3F_7 - C_2F_5 - Cl]^+$ (53), 159 $[M - SC_3F_7, - C_2F_5 - Cl]^+$ (15), 106 $[M - 2\ C_3F_7 - 2\ Cl]^+$ (15), 69 $[CF_3]^+$ (100)
	(2) **8** (14.3)		5.89	514 $[M]^+$ (56), 395 $[M - C_2F_5]^+$ (91), 345 $[M - C_3F_7]^+$ (40), 326 $[M - C_3F_7 - F]^+$ (10), 226 $[M - C_2F_5 - C_3F_7]^+$ (43), 159 $[M - SC_3F_7 - C_2F_5 - Cl]^+$ (10), 119 $[C_2F_5]^+$ (13), 69 $[CF_3]^+$ (100)
	(2) **8** (12.8)		6.83	514 $[M]^+$ (100), 495 $[M - F]^+$ (15), 395 $[M - C_2F_5]^+$ (62), 345 $[M - C_3F_7]^+$ (32), 326 $[M - C_2F_5 - CF_3]^+$ (23), 226 $[M - C_2F_5 - C_3F_7]^+$ (40), 191 $[M - C_3F_7 - C_2F_5 - Cl]^+$ (17), 159 $[M - SC_3F_7 - C_2F_5 - CF_3 - Cl]^+$ (4), 119 $[C_2F_5]^+$ (3), 69 $[CF_3]^+$ (23)

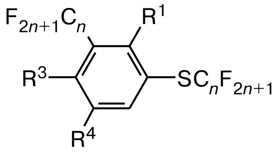
* τ is the retention time.

** (1) $ArSR^F$, (2) monosubstitution product, (3) disubstitution product.

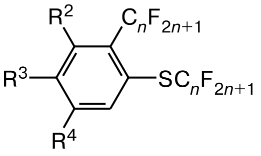
*** Hereinafter the *m/z* values are presented for ions with ^{35}Cl and ^{79}Br.



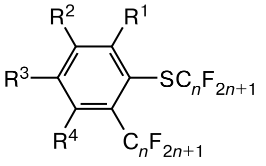
11—13



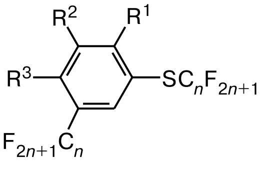
14a,b



15a—c



16a—c



17a—c

n = 1 (**11**, **14**, **15a**, **16a**, **17a**), 2 (**12**, **15b**, **16b**, **17b**), 3 (**13**, **15c**, **16c**, **17c**))

Compound	R^1	R^2	R^4	Compound	R^1	R^2	R^4
11a	F	H	NO_2	**12a**	Cl	H	Cl
11b	Cl	H	NO_2	**12b**	H	NO_2	H
11c	Br	H	NO_2	**12c**	F	H	Br
11d	H	NO_2	NO_2	**13**	F	H	Br
11e	Cl	H	Cl				

14: R^1 = Cl (**a**), Br (**b**); R^3 = H, R^4 = NO_2

15, 16: R^2 = R^3 = Cl, R^4 = H; **17:** R^1 = H, R^2 = R^3 = Cl

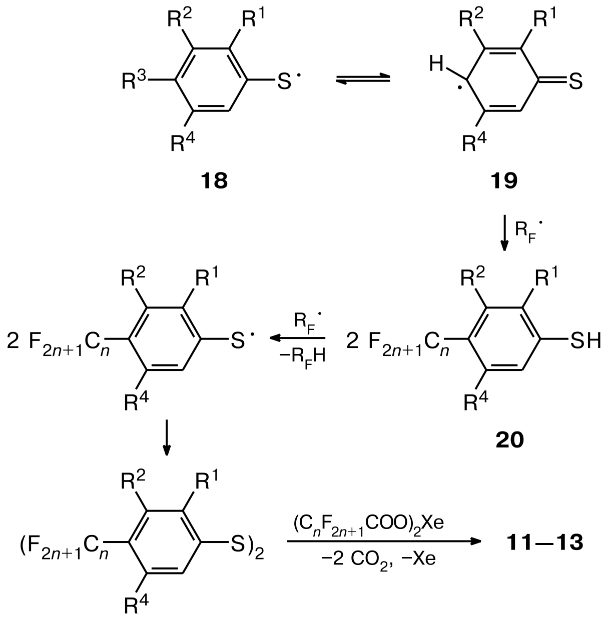
that can be involved in perfluoroalkylation. In the case of radicals **18e,f,h,j** with the substituent $R^3 \neq H$, we found a dependence of the yield of the target product on the wavefunction coefficient (C_S) of the sulfur atom for the highest occupied α-orbital at spin multiplicity 2. This coefficient characterizes the density of probability of the localization of unpaired electron, which ensures the addition of the electrophilic perfluoroalkyl radical[10] to the sulfur atom (Table 7). The general equation relating the yield of the $ArSR^F$ products and C_S coefficient has the form

$$Y(ArSR^F) = 68.4 - 63.2C_S, \qquad (1)$$

Y is the yield of $ArSR^F$.

It is seen from Eq. (1) that a decrease in C_S, which can appear when the benzene ring of reacting species **18** contains electron-withdrawing substituents, increases the yield of the target product, which is the case. It should be noted that the yield of the target product depends slightly on the nature of the perfluoroalkyl radical but is mainly determined by the C_S wavefunction coefficient of the radical $ArS^\bullet$.

Scheme 4



18	R^1	R^2	R^3	R^4	**18**	R^1	R^2	R^3	R^4
a	F	H	H	NO_2	**h**	H	H	Br	H
b	Cl	H	H	NO_2	**i**	H	H	H	NO_2
c	Br	H	H	NO_2	**j**	H	H	NO_2	H
d	H	NO_2	H	NO_2	**k**	F	H	H	Br
e	H	NO_2	Cl	NO_2	**l**	Cl	H	H	CF_3
f	H	NO_2	Cl	H	**m**	H	Cl	H	Cl
g	Cl	H	H	Cl	**n**	H	Cl	Cl	H

Different regularities were revealed from the analysis of the results of calculation of reactive species **18a—d,g,i,k** for R^3 = H. It is found that trifluoromethylation is determined by a set of energy and charge characteristics and, to a great extent, by the energy of the higher occupied β-orbital of the sulfur atom[10] (Table 8). The general equation relating the yield of $ArSR^F$ and the calculated quantum characteristics was established to take the form

$$Y(ArSR^F) = -389 - 68E_\beta^{HOMO} - 169E_\beta^{LUMO} - 640Q_{CS} - 710Q_{H(4)}, \qquad (2)$$

where E_β^{HOMO} and E_β^{LUMO} are the energies of the HOMO and LUMO β-orbitals, Q_{CS} is the charge on the carbon atom of the benzene ring linked with the thio group, and $Q_{H(4)}$ is the charge on the hydrogen atom that is in the *para*-position to the thio group and has multiplicity 4.

In this case, the formation of the by-product should directly be related to the probability of radical center localization in the *para*-position to the thio group (intermediate **18**). The contribution of this structure is deter-

Table 4. Method of synthesis, yields, and physicochemical characteristics of compounds **3a—j**, **4a—k**, **5a—e**, **11a—e**, **12a—c**, **13**, and **14a,b**

Compound	Method of synthesis	Yield (%)	B.p./°C (p/Torr), [M.p./°C]
1-Fluoro-4-nitro-2-(trifluoromethylthio)benzene (**3a**)	*B*	33.6	Oil, 140 (8)[16]
1-Chloro-4-nitro-2-(trifluoromethylthio)benzene (**3b**)	*A*	24.5	Oil, 126—129 (16 mTorr)[17]
1-Bromo-4-nitro-2-(trifluoromethylthio)benzene (**3c**)	*A*	34.7	Oil
1,3-Dinitro-5-(trifluoromethylthio)benzene (**3d**)	*A*	30.0	Oil (oil[18])
2-Chloro-1,3-dinitro-5-(trifluoromethylthio)benzene(**3e**)	*A*	73.0	[36—38]
1-Chloro-2-nitro-4-(trifluoromethylthio)benzene (**3f**)	*A*	16.1	Oil
1,4-Dichloro-2-(trifluoromethylthio)benzene (**3g**)	*A*	22.5	Oil
1-Bromo-4-(trifluoromethylthio)benzene (**3h**)	*A*	24.6	Oil, 192 [19]
1-Nitro-3-(trifluoromethylthio)benzene (**3i**)	*A*	7.8	Oil
1-Nitro-4-(trifluoromethylthio)benzene (**3j**)	*A*	15.2	Oil, 120 (20)[20]
1-Fluoro-4-nitro-2-(pentafluoroethylthio)benzene (**4a**)	*B*	55.3	Oil
1-Chloro-4-nitro-2-(pentafluoroethylthio)benzene (**4b**)	*A*	37.7	Oil
1-Bromo-4-nitro-2-(pentafluoroethylthio)benzene (**4c**)	*A*	40.2	Oil
1,3-Dinitro-5-(pentafluoroethylthio)benzene (**4d**)	*A*	14.7	[66—67]
2-Chloro-1,3-dinitro-5-(pentafluoroethylthio)benzene (**4e**)	*A*	66.4	Oil
1-Chloro-2-nitro-4-(pentafluoroethylthio)benzene (**4f**)	*A*	16.9	Oil
1,4-Dichloro-2-(pentafluoroethylthio)benzene (**4g**)	*A*	13.3	Oil
1-Bromo-4-(pentafluoroethylthio)benzene (**4h**)	*A*	34.1	Oil
1-Nitro-3-(pentafluoroethylthio)benzene (**4i**)	*A*	8.1	Oil
1-Nitro-4-(pentafluoroethylthio)benzene (**4j**)	*A*	30.3	[37—38]
4-Bromo-4-fluoro-3-(pentafluoroethylthio)benzene (**4k**)	*B*	23.0	Oil
1-Fluoro-2-(heptafluoropropylthio)-4-nitrobenzene (**5a**)	*A*	33.0	Oil
1-Chloro-2-(heptafluoropropylthio)-4-nitrobenzene (**5b**)	*A*	26.7	[28—29]
1-Bromo-2-(heptafluoropropylthio)-4-nitrobenzene (**5c**)	*A*	27.3	Oil
5-(Heptafluoropropylthio)-1,3-dinitrobenzene (**5d**)	*A*	19.0	Oil
1-Bromo-4-fluoro-2-(heptafluoropropylthio)benzene (**5e**)	*B*	16.7	Oil
1-Fluoro-4-nitro-5-trifluoromethyl-2-(trifluoromethylthio)benzene (**11a**)	*B*	6.7	Oil
1-Chloro-4-nitro-5-trifluoromethyl-2-(trifluoromethylthio)benzene (**11b**)	*A*	7.8	Oil
5-Bromo-2-nitro-1-trifluoromethyl-4-(trifluoromethylthio)benzene (**11c**)	*A*	8.8	Oil
1,3-Dinitro-2-trifluoromethyl-5-(trifluoromethylthio)benzene (**11d**)	*A*	1.7	Oil
1,4-Dichloro-5-trifluoromethyl-2-(trifluoromethylthio)benzene (**11e**)	*A*	3.4	Oil
1,4-Dichloro-2-pentafluoroethyl-5-(pentafluoroethylthio)benzene (**12a**)	*A*	5.2	Oil
1-Nitro-2-pentafluoroethyl-5-(pentafluoroethylthio)benzene (**12b**)	*A*	4.4	Oil
1-Bromo-4-fluoro-2-pentafluoroethyl-5-(pentafluoroethylthio)benzene (**12c**)	*B*	9.1	Oil
1-Bromo-4-fluoro-2-heptafluoropropyl-5-(heptafluoropropylthio)benzene (**13**)	*B*	5.4	Oil
1-Chloro-5-nitro-2-trifluoromethyl-3-(trifluoromethylthio)benzene (**14a**)	*A*	3.3	Oil
1-Bromo-5-nitro-2-trifluoromethyl-3-(trifluoromethylthio)benzene (**14b**)	*A*	1.5	Oil

mined by both the charges on atoms linked with the radical center and energy characteristics of E_β^{HOMO} and E_β^{LUMO}. The introduction of electron-withdrawing substituents should favor a decrease in both the HOMO and LUMO energies[10] and the Q_{CS} and $Q_{\mathrm{H(4)}}$ charges and, correspondingly, should decrease the probability of side processes related to the perfluoroalkylation of the benzene ring. As a consequence, the yield of the $\mathrm{ArSR^F}$ compounds should be enhanced.

Unlike the yields in trifluoromethylation reactions, the yield of compounds **4** and **5** with the general formula $\mathrm{ArSR^F}$ ($\mathrm{R^F} = \mathrm{C_2F_5}$ and $\mathrm{C_3F_7}$) was found to depend on the charge characteristics (charges on sulfur, carbon of the benzene ring linked with the thio group, and hydrogen atom in the *para*-position to the thio group) and to be independent of the energy characteristics (Table 9). The general equation has the form

$$\mathrm{Y(ArSR^F)} = -373 + 1040Q_{\mathrm{S}} - 1300Q_{\mathrm{CS}} + 970Q_{\mathrm{H}}, \qquad (3)$$

where Q_{S} is the charge on the sulfur atom, and Q_{H} is the charge on the H(4) atom in the *para*-position to the thio group in the state with multiplicity 2.

Table 5. Data on the ^{1}H and ^{19}F NMR spectra and mass spectra of compounds **3a—j**, **4a—k**, **5a—e**, **11a—e**, **12a—c**, **13**, and **14a,b**

Compound	NMR (δ, J/Hz)		MS, m/z (I_{rel} (%))
	^{1}H	^{19}F	
3a	7.40 (dd, 1 H, H(6), $^3J_{H,H}$ = 9.1, $^3J_{H,F}$ = 7.3); 8.43 (m, 1 H, H(5)); 8.61 (dd, 1 H, H(3), $^4J_{H,F}$ = 5.9, $^4J_{H,H}$ = 2.8)	−93.90 (m, 1 F, F—Ar); −42.12 (d, 3 F, CF_3, $^5J_{CF_3,F}$ = 5.1)	241 $[M]^+$ (100), 222 $[M - F]^+$ (6), 195 $[M - NO_2]^+$ (9), 172 $[M - CF_3]^+$ (5), 126 $[M - NO_2, - CF_3]^+$ (44), 69 $[CF_3]^+$ (17)
3b	7.75 (d, 1 H, H(6), $^3J_{H,H}$ = 8.9); 8.28 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.7); 8.62 (d, 1 H, H(3), $^4J_{H,H}$ = 2.7)	−41.75 (s, CF_3)	257 $[M]^+$ (100), 238 $[M - F]^+$ (4), 211 $[M - NO_2]^+$ (8), 176 $[M - NO_2 - Cl]^+$ (7), 142 $[M - NO_2 - CF_3]^+$ (23), 107 $[M - NO_2 - CF_3 - Cl]^+$ (16), 75 $[C_6H_3]^+$ (3), 69 $[CF_3]^+$ (15)
3c	7.94 (d, 1 H, H(6), $^3J_{H,H}$ = 8.9); 8.18 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.7); 8.61 (d, 1 H, H(3), $^4J_{H,H}$ = 2.4)	−41.78 (s, CF_3)	301 $[M]^+$ (70), 282 $[M - F]^+$ (3), 176 $[M - Br - NO_2]^+$ (61), 153 $[M - CF_3 - Br]^+$ (4), 107 $[M - Br - NO_2 - CF_3]^+$ (59), 69 $[CF_3]^+$ (100)
3d	8.83 (d, 2 H, H(4), H(6), $^4J_{H,H}$ = 1.9); 9.15 (t, 1 H, H(2), $^4J_{H,H}$ = 1.9)	−41.65 (s, CF_3)	268 $[M]^+$ (100), 249 $[M - F]^+$ (5), 222 $[M - NO_2]^+$ (5), 203 $[M - F - NO_2]^+$ (1), 175 $[M - NO_2 - HNO_2]^+$ (15), 106 $[M - NO_2 - HNO_2 - CF_3]^+$ (20)
3e	8.27 (s, H(4), H(6))	−41.62 (s, CF_3)	302 $[M]^+$ (100), 283 $[M - F]^+$ (5), 268 $[M - Cl]^+$ (1), 256 $[M - NO_2]^+$ (2), 233 $[M - CF_3]^+$ (2), 210 $[M - 2\ NO_2]^+$ (9), 141 $[M - 2\ NO_2 - CF_3]^+$ (16), 69 $[CF_3]^+$ (19)
3f	7.64 (d, 1 H, H(6), $^3J_{H,H}$ = 8.4); 7.80 (dd, 1 H, H(5), $^4J_{H,H}$ = 2.1, $^3J_{H,H}$ = 8.4); 8.16 (d, 1 H, H(3), $^4J_{H,H}$ = 2.1)	−42.52 (s, CF_3)	257 $[M]^+$ (100), 238 $[M - F]^+$ (4), 211 $[M - NO_2]^+$ (10), 188 $[M - CF_3]^+$ (7), 142 $[M - NO_2 - CF_3]^+$ (53), 107 $[M - CF_3 - NO_2 - Cl]^+$ (23), 69 $[CF_3]^+$ (32)
3g	7.40 (d, 1 H, H(5), $^3J_{H,H}$ = 7.5); 7.48 (d, 1 H, H(6), $^3J_{H,H}$ = 8.5); 7.75 (s, 1 H, H(3))	−42.09 (s, CF_3)	246 $[M]^+$ (100), 227 $[M - F]^+$ (12), 177 $[M - CF_3]^+$ (84), 142 $[M - CF_3 - Cl]^+$ (93), 107 $[M - CF_3 - 2\ Cl]^+$ (23), 69 $[CF_3]^+$ (48)
3h	7.64 (m, H(2), H(3), H(5), H(6))	−42.43 (s, CF_3)	256 $[M]^+$ (57), 187 $[M - CF_3]^+$ (52), 108 $[M - CF_3 - Br]^+$ (100), 69 $[CF_3]^+$ (90)
3i	7.66 (t, 1 H, H(5), $^3J_{H,H}$ = 7.9); 8.00 (d, 1 H, H(4), $^3J_{H,H}$ = 7.2); 8.37 (dt, 1 H, H(6), $^4J_{H,H}$ = 1.0, $^3J_{H,H}$ = 8.2); 8.53 (t, 1 H, H(2), $^4J_{H,H}$ = 1.7)	−42.54 (s, CF_3)	223 $[M]^+$ (100), 204 $[M - F]^+$ (6), 177 $[M - NO_2]^+$ (26), 108 $[M - NO_2 - CF_3]^+$ (74), 69 $[CF_3]^+$ (73)
3j	7.72 (d, 2 H, H(3), H(5), $^3J_{H,H}$ = 8.0); 8.19 (d, 2 H, H(2), H(6), $^3J_{H,H}$ = 8.0)	−41.00 (s, CF_3)	223 $[M]^+$ (92), 204 $[M - F]^+$ (10), 193 $[M - NO]^+$ (39), 177 $[M - NO_2]^+$ (9), 108 $[M - NO_2 - CF_3]^+$ (69), 69 $[CF_3]^+$ (100)
4a	7.42 (dd, 1 H, H(6), $^3J_{H,F}$ = 7.5, $^3J_{H,H}$ = 9.0); 8.44 (m, 1 H, H(5)); 8.58 (dd, 1 H, H(3), $^4J_{H,F}$ = 9.0, $^4J_{H,H}$ = 7.5)	−93.21 (m, 1 F, F—Ar); −91.54 (dq, 2 F, SCF_2, $^3J_{CF_2,CF_3}$ = 3.0, $^5J_{CF_2,F}$ = 1.6); −83.30 (dt, 3 F, CF_3, $^3J_{CF_2,CF_3}$ = 3.0, $^6J_{CF_3,F}$ = 1.6)	291 $[M]^+$ (100), 272 $[M - F]^+$ (2), 245 $[M - NO_2]^+$ (5), 222 $[M - CF_3]^+$ (21), 172 $[M - C_2F_5]^+$ (14), 126 $[M - NO_2 - C_2F_5]^+$ (42), 69 $[CF_3]^+$ (26)
4b	7.78 (d, 1 H, H(6), $^3J_{H,H}$ = 8.0); 8.35 (d, 1 H, H(5), $^3J_{H,H}$ = 8.0); 8.60 (s, 1 H, H(3))	−91.73 (s, 2 F, SCF_2); −82.14 (s, 3 F, CF_3)	307 $[M]^+$ (100), 291 $[M - O]^+$ (2), 238 $[M - CF_3]^+$ (18), 226 $[M - Cl - NO_2]^+$ (7), 188 $[M - C_2F_5]^+$ (21), 142 $[M - C_2F_5 - NO_2]^+$ (53), 119 $[C_2F_5]^+$ (31), 107 $[M - C_2F_5 - NO_2 - Cl]^+$ (45), 69 $[CF_3]^+$ (65)
4c	7.96 (d, 1 H, H(6), $^3J_{H,H}$ = 8.9); 8.20 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.7); 8.62 (d, 1 H, H(3), $^4J_{H,H}$ 2.4)	−91.29 (s, 2 F, SCF_2); −83.17 (t, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 3.4)	351 $[M]^+$ (100), 282 $[M - CF_3]^+$ (10), 226 $[M - NO_2 - Br]^+$ (22), 186 $[M - NO_2 - C_2F_5]^+$ (16), 157 $[M - NO_2 - CF_3 - Br]^+$ (16), 119 $[C_2F_5]^+$ (16), 107 $[M - C_2F_5 - NO_2 - Br]^+$ (36)

(*to be continued*)

Table 5 (*continued*)

Compound	NMR (δ, *J*/Hz)		MS, *m*/*z* (I_{rel} (%))
	^{1}H	^{19}F	
4d	8.83 (t, H(4), H(6), $^4J_{H,H}$ = 2.0); 9.16 (t, H(2), $^4J_{H,H}$ = 2.0)	−90.94 (q, 2 F, SCF_2, $^3J_{CF_2,CF_3}$ = 3.3), −82.53 (t, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 3.4)	318 $[M]^+$ (100), 299 $[M - F]^+$ (1), 272 $[M - NO_2]^+$ (2), 249 $[M - CF_3]^+$ (19), 225 $[M - NO_2 - HNO_2]^+$ (17), 203 $[M - NO_2 - CF_3]^+$ (2), 157 $[M - 2\ NO_2 - CF_3]^+$ (1), 153 $[M - NO_2 - C_2F_5]^+$ (1), 119 $[C_2F_5]^+$ (8), 106 $[M - NO_2 - HNO_2 - C_2F_5]^+$ (21), 75 $[M - 2\ NO_2 - SC_2F_5]^+$ (23)
4e	8.27 (s, H(4), H(6))	−90.88 (q, 2 F, SCF_2, $^3J_{CF_2,CF_3}$ = 3.3); −82.74 (t, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 3.4)	352 $[M]^+$ (100), 316 $[M - Cl]^+$ (1), 283 $[M - CF_3]^+$ (6), 237 $[M - CF_3 - NO_2]^+$ (2), 233 $[M - C_2F_5]^+$ (4), 191 $[M - CF_3 - 2\ NO_2]^+$ (2), 187 $[M - C_2F_5 - NO_2]^+$ (1), 106 $[M - 2\ NO_2 - C_2F_5 - Cl]^+$ (20)
4f	7.66 (d, 1 H, H(6), $^3J_{H,H}$ = 8.4); 7.81 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.1); 8.17 (d, 1 H, H(3), $^4J_{H,H}$ = 2.1)	−91.70 (s, 2 F, SCF_2); −82.88 (s, 3 F, CF_3)	307 $[M]^+$ (100), 271 $[M - Cl]^+$ (1), 188 $[M - C_2F_5]^+$ (18), 142 $[M - C_2F_5 - NO_2]^+$ (60), 119 $[C_2F_5]^+$ (8), 107 $[M - C_2F_5 - NO_2 - Cl]^+$ (26), 75 $[M - SC_2F_5 - NO_2 - Cl]^+$ (11), 69 $[CF_3]^+$ (27)
4g	7.46 (d, 2 H, H(5), H(6), $^3J_{H,H}$ = 8.2); 7.75 (s, 1 H, H(3))	−91.58 (s, 2 F, SCF_2); −83.32 (s, 3 F, CF_3)	296 $[M]^+$ (75), 177 $[M - C_2F_5]^+$ (75), 142 $[M - C_2F_5 - Cl]^+$ (100), 107 $[M - C_2F_5 - 2\ Cl]^+$ (30), 69 $[CF_3]^+$ (76)
4h	7.42 (m, H(2), H(3), H(5), H(6))	−90.45 (s, 2 F, SCF_2); −82.10 (s, 3 F, CF_3)	306 $[M]^+$ (91), 287 $[M - F]^+$ (1), 237 $[M - CF_3]^+$ (2), 208 $[M - Br - F]^+$ (17), 189 $[M - C_2F_5]^+$ (68), 158 $[M - CF_3 - Br]^+$ (6), 119 $[C_2F_5]^+$ (21), 108 $[M - C_2F_5 - Br]^+$ (100), 69 $[CF_3]^+$ (47)
4i	7.58 (t, 1 H, H(5), $^3J_{H,H}$ = 8.0); 7.91 (d, 1 H, H(4), $^3J_{H,H}$ = 8.0); 8.27 (d, 1 H, H(6), $^3J_{H,H}$ = 8.0); 8.45 (s, 1 H, H(2))	−90.53 (s, 2 F, SCF_2); −82.44 (s, 3 F, CF_3)	273 $[M]^+$ (100), 254 $[M - F]^+$ (1), 227 $[M - NO_2]^+$ (16), 157 $[M - HNO_2 - CF_3]^+$ (6), 154 $[M - C_2F_5]^+$ (9), 108 $[M - NO_2 - C_2F_5]^+$ (83), 69 $[CF_3]^+$ (58)
4j	7.27 (d, 2 H, H(3), H(5), $^3J_{H,H}$ = 8.0); 8.18 (d, 2 H, H(2), H(6), $^3J_{H,H}$ = 8.0)	−91.58 (s, 2 F, SCF_2); −82.19 (s, 3 F, CF_3)	273 $[M]^+$ (100), 254 $[M - F]^+$ (2), 243 $[M - NO]^+$ (35), 227 $[M - NO_2]^+$ (5), 207 $[M - HNO_2 - F]^+$ (14), 157 $[M - CF_3 - HNO_2]^+$ (9), 124 $[M - NO - C_2F_5]^+$ (19), 108 $[M - C_2F_5 - NO_2]^+$ (84), 69 $[CF_3]^+$ (80)
4k	7.10 (dd, 1 H, H(6), $^3J_{H,H}$ = 8.8, $^3J_{H,F}$ = 8.0); 7.63 (m, 1 H, H(5)); 7.79 (dd, 1 H, H(3), $^4J_{H,F}$ = 6.1, $^4J_{H,H}$ = 2.5)	−106.35 (m, 1 F, F—Ar); −91.88 (m, 2 F, SCF_2); −83.33 (dt, CF_3, $^3J_{CF_3,CF_2}$ = 3.3, $^6J_{CF_3,F}$ = 1.4)	323 $[M]^+$ (92), 305 $[M - F]^+$ (1), 255 $[M - CF_3]^+$ (12), 226 $[M - F - Br]^+$ (17), 205 $[M - C_2F_5]^+$ (33), 176 $[M - CF_3 - Br]^+$ (14), 126 $[M - C_2F_5 - Br]^+$ (100), 69 $[CF_3]^+$ (35)
5a	7.42 (dd, 1 H, H(6), $^3J_{H,H}$ = 9.2, $^3J_{H,F}$ = 7.5); 8.45 (m, 1 H, H(5)); 8.60 (dd, 1 H, H(3), $^4J_{H,F}$ = 5.8, $^4J_{H,H}$ = 2.7)	−124.16 (br.s, 2 F, CF_2); −92.95 (m, 1 F, F—Ar); −87.29 (m, 2 F, SCF_2); −80.52 (t, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 9.3)	341 $[M]^+$ (100), 322 $[M - F]^+$ (5), 295 $[M - NO_2]^+$ (2), 276 $[M - F - NO_2]^+$ (3), 222 $[M - C_2F_5]^+$ (43), 172 $[M - C_3F_7]^+$ (18), 126 $[M - C_3F_7 - NO_2]^+$ (46), 94 $[M - SC_3F_7 - NO_2]^+$ (10), 69 $[CF_3]^+$ (33)
5b	7.78 (d, 1 H, H(6), $^3J_{H,H}$ = 8.0); 8.30 (d, 1 H, H(5), $^3J_{H,H}$ = 8.0); 8.63 (s, 1 H, H(3))	−123.48 (s, 2 F, $SCF_2C\underline{F}_2CF_3$); −86.32 (s, 2 F, SCF_2); −79.70 (s, 3 F, CF_3)	357 $[M]^+$ (100), 311 $[M - NO_2]^+$ (2), 292 $[M - NO_2 - F]^+$ (2), 276 $[M - NO_2 - Cl]^+$ (3), 238 $[M - C_2F_5]^+$ (39), 182 $[M - C_3F_7]^+$ (19), 142 $[M - C_3F_7 - NO_2]^+$ (31), 107 $[M - C_3F_7 - NO_2 - Cl]^+$ (25), 69 $[CF_3]^+$ (40)
5c	7.96 (d, 1 H, H(6), $^3J_{H,H}$ = 8.9); 8.21 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.7); 8.62 (d, 1 H, H(3), $^4J_{H,H}$ = 2.7)	−124.21 (s, 2 F, $SCF_2C\underline{F}_2CF_3$); −87.06 (m, 2 F, SCF_2); −80.65 (s, 3 F, CF_3)	401 $[M]^+$ (84), 385 $[M - O]^+$ (2), 282 $[M - C_2F_5]^+$ (30), 232 $[M - C_3F_7]^+$ (16), 203 $[M - C_2F_5 - Br]^+$ (12), 186 $[M - C_3F_7 - NO_2]^+$ (26), 157 $[M - C_2F_5 - NO_2 - Br]^+$ (33), 107 $[M - C_3F_7 - NO_2 - Br]^+$ (74), 69 $[CF_3]^+$ (100)

(*to be continued*)

Table 5 (*continued*)

Compound	NMR (δ, *J*/Hz)		MS, *m/z* (I_{rel} (%))
	^{1}H	^{19}F	
5d	8.83 (s, 2 H, H(4), H(6), $^4J_{\text{H,H}}$ = 2.0); 9.19 (t, 1 H, H(2), $^4J_{\text{H,H}}$ = 2.0)	−123.68 (br.s, 2 F, $SCF_2C\underline{F}_2CF_3$); −86.87 (t, 2 F, SCF_2, $^3J_{S,CF_2,CF_2}$ = 9.0); −80.45 (t, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 9.0)	368 $[M]^+$ (100), 349 $[M - F]^+$ (19), 333 $[M - F - O]^+$ (15), 299 $[M - CF_3]^+$ (11), 275 $[M - NO_2 - HNO_2]^+$ (43), 249 $[M - C_2F_5]^+$ (96), 233 $[M - C_2F_5 - O]^+$ (9), 199 $[M - C_3F_7]^+$ (28), 183 $[M - C_3F_7 - O]^+$ (9), 169 $[C_3F_7]^+$ (45), 153 $[M - C_3F_7 - NO_2]^+$ (15), 119 $[C_2F_5]^+$ (18)
5e	7.10 (dd, 1 H, H(6), $^3J_{\text{H,H}}$ = 8.7, $^3J_{\text{H,F}}$ = 8.1); 7.63 (m, 1 H, H(5)); 7.80 (dd, 1 H, H(3), $^4J_{\text{H,F}}$ = 6.1, $^4J_{\text{H,H}}$ = 2.5)	−124.25 (br.s, 2 F, $SCF_2C\underline{F}_2CF_3$); −106.07 (m, 1 F, F—Ar); −87.53 (m, 2 F, SCF_2); −80.60 (dt, 3 F, CF_3, $^3J_{CF_3,CF_2}$ = 9.0, $^4J_{CF_3,CF_2}$ = 0.8)	374 $[M]^+$ (100), 355 $[M - F]^+$ (2), 295 $[M - Br]^+$ (1), 276 $[M - F - Br]^+$ (24), 255 $[M - C_2F_5]^+$ (32), 205 $[M - C_3F_7]^+$ (36), 176 $[M - C_2F_5 - Br]^+$ (34), 126 $[M - C_3F_7 - Br]^+$ (92), 94 $[M - SC_3F_7 - Br]^+$ (12), 69 $[CF_3]^+$ (31)
11a	7.70 (d, H(6), $^3J_{\text{H,F}}$ = 7.9); 8.31 (d, H(3), $^4J_{\text{H,F}}$ = 5.9)	−93.60 (m, 1 F, F—Ar); −61.04 (s, 3 F, CF_3); −41.04 (d, 3 F, SCF_3, $^5J_{S,CF_3,F}$ = 5.2)	309 $[M]^+$ (100), 290 $[M - F]^+$ (15), 263 $[M - NO_2]^+$ (10), 194 $[M - NO_2 - CF_3]^+$ (93), 175 $[M - F - NO_2 - CF_3]^+$ (10), 106 $[M - NO_2 - F - 2CF_3]^+$ (3), 69 $[CF_3]^+$ (33)
11b	7.90 (s, H(6)); 8.20 (s, H(3))	−60.86 (s, $ArCF_3$); −40.78 (s, SCF_3)	325 $[M]^+$ (100), 306 $[M - F]^+$ (14), 279 $[M - NO_2]^+$ (11), 244 $[M - Cl - NO_2]^+$ (7), 210 $[M - NO_2 - CF_3]^+$ (32), 175 $[M - CF_3 - NO_2 - Cl]^+$ (44), 143 $[M - Cl - NO_2 - SCF_3]^+$ (5), 106 $[M - 2\ CF_3 - NO_2 - Cl]^+$ (14), 69 $[CF_3]^+$ (27)
11c	8.16 (s, H(6)); 8.24 (s, H(3))	−60.73 (s, $ArCF_3$); −40.86 (s, SCF_3)	369 $[M]^+$ (89), 350 $[M - F]^+$ (11), 323 $[M - NO_2]^+$ (8), 254 $[M - NO_2 - CF_3]^+$ (58), 244 $[M - NO_2 - Br]^+$ (14), 175 $[M - NO_2 - CF_3 - Br]^+$ (100), 143 $[M - NO_2 - SCF_3 - Br]^+$ (12), 106 $[M - NO_2 - 2\ CF_3 - Br]^+$ (49), 69 $[CF_3]^+$ (91)
11d	8.16 (s, H(4), H(6))	−56.96 (s, $ArCF_3$); −39.94 (s, SCF_3)	336 $[M]^+$ (100), 317 $[M - F]^+$ (18), 290 $[M - NO_2]^+$ (1), 271 $[M - F - NO_2]^+$ (2), 244 $[M - 2\ NO_2]^+$ (4), 143 $[M - 2\ NO_2 - SCF_3]^+$ (25), 106 $[M - 2\ CF_3 - 2\ NO_2]^+$ (16), 69 $[CF_3]^+$ (45)
11e	7.63 (s, H(6)); 7.84 (s, H(3))	−63.82 (s, $ArCF_3$); −41.20 (s, SCF_3)	314 $[M]^+$ (100), 295 $[M - F]^+$ (18), 279 $[M - Cl]^+$ (1), 245 $[M - CF_3]^+$ (33), 226 $[M - CF_3 - F]^+$ (5), 211 $[M - CF_3 - Cl]^+$ (38), 175 $[M - CF_3 - 2\ Cl]^+$ (11), 106 $[M - 2\ CF_3 - 2\ Cl]^+$ (4), 69 $[CF_3]^+$ (18)
12a	7.64 (s, H(6)); 7.92 (s, H(3))	−112.42 (s, $ArCF_2$); −90.85 (s, SCF_2); −83.77, −83.64 (both s, 3 F each, CF_3)	414 $[M]^+$ (65), 345 $[M - CF_3]^+$ (100), 226 $[M - CF_3 - C_2F_5]^+$ (62), 191 $[M - CF_3 - C_2F_5 - Cl]^+$ (50), 69 $[CF_3]^+$ (45)
12b	7.84 (d, 1 H, H(4), $^3J_{\text{H,H}}$ = 8.0); 8.03 (s, 1 H, H(6)); 8.06 (d, 1 H, H(3), $^3J_{\text{H,H}}$ = 8.0)	−109.47 (s, $ArCF_2$); −89.94 (s, SCF_2); −82.40, −82.06 (both s, 3 F each, CF_3)	391 $[M]^+$ (72), 322 $[M - CF_3]^+$ (42), 226 $[M - C_2F_5 - NO_2]^+$ (17), 157 $[M - C_2F_5 - CF_3 - NO_2]^+$ (38), 119 $[C_2F_5]^+$ (26), 69 $[CF_3]^+$ (66)
12c	7.49 (d, H(6), $^3J_{\text{H,F}}$ = 8.5); 8.07 (d, H(3), $^4J_{\text{H,F}}$ = 6.3)	−112.00 (br.s, 2 F, $ArCF_2$); −103.85 (m, F—Ar); −91.00 (s, 2 F, SCF_2); −83.37, −83.02 (both s, 3 F each, CF_3)	442 $[M]^+$ (91), 423 $[M - F]^+$ (6), 373 $[M - CF_3]^+$ (100), 344 $[M - F - Br]^+$ (22), 275 $[M - F - Br - CF_3]^+$ (4), 254 $[M - C_2F_5 - CF_3]^+$ (51), 175 $[M - C_2F_5 - CF_3 - Br]^+$ (66), 119 $[C_2F_5]^+$ (24), 69 $[CF_3]^+$ (53)

(*to be continued*)

Table 5 (*continued*)

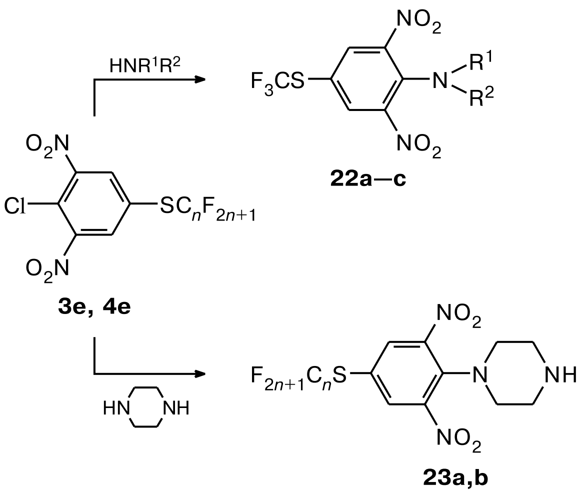
Compound	NMR (δ, *J*/Hz)		MS, *m*/*z* (I_{rel} (%))
	^{1}H	^{19}F	
13	7.47 (d, H(6), $^3J_{H,F}$ = 8.5); 8.05 (d, H(3), $^4J_{H,F}$ = 6.3)	−124.43, −124.14 (both br.s, 2 F each, CF$_2$); −108.77 (m, 2 F, ArCF$_2$); −103.77 (t, 1 F, F—Ar, $^5J_{F,CF_2}$ = 6.4); −86.71 (m, 2 F, SCF$_2$); −80.54 (t, 3 F, CF$_3$, $^3J_{CF_3,CF_2}$ = 10.0); −80.49 (t, 3 F, CF$_3$, $^3J_{CF_3,CF_2}$ = 9.3)	542 [M]$^+$ (61), 523 [M − F]$^+$ (10), 423 [M − C$_2$F$_5$]$^+$ (90), 375 [M − C$_3$F$_7$]$^+$ (16), 344 [M − C$_2$F$_5$ − Br]$^+$ (15), 294 [M − C$_3$F$_7$ − Br]$^+$ (23), 254 [M − C$_3$F$_7$ − C$_2$F$_5$]$^+$ (76), 175 [M − C$_3$F$_7$ − C$_2$F$_5$ − Br]$^+$ (100), 143 [M − SC$_3$F$_7$ − C$_2$F$_5$ − Br]$^+$ (20), 119 [C$_2$F$_5$]$^+$ (19), 69 [CF$_3$]$^+$ (52)
14a	8.60 (d, H(6), $^4J_{H,H}$ = 2.6); 8.80 (d, H(4), $^4J_{H,H}$ = 2.6)	−63.98 (s, ArCF$_3$); −41.29 (s, SCF$_3$)	325 [M]$^+$ (100), 306 [M − F]$^+$ (11), 279 [M − NO$_2$]$^+$ (13), 244 [M − Cl − NO$_2$]$^+$ (7), 210 [M − NO$_2$ − CF$_3$]$^+$ (87), 175 [M − Cl − CF$_3$ − NO$_2$]$^+$ (42), 143 [M − Cl − SCF$_3$ − NO$_2$]$^+$ (9), 106 [M − 2 CF$_3$ − NO$_2$ − Cl]$^+$ (14), 69 [CF$_3$]$^+$ (49)
14b	8.62 (s, H(6)); 8.78 (s, H(4))	−63.91 (s, ArCF$_3$); −41.38 (s, SCF$_3$)	369 [M]$^+$ (78), 254 [M − NO$_2$ − CF$_3$]$^+$ (23), 244 [M − NO$_2$ − Br]$^+$ (49), 175 [M − NO$_2$ − CF$_3$ − Br]$^+$ (79), 106 [M − NO$_2$ − 2 CF$_3$ − Br]$^+$ (4), 69 [CF$_3$]$^+$ (100)

This equation shows that the higher the charge on the sulfur atom and the more positive the charge on the H(4) atom, which is observed when electron-withdrawing substituents are introduced into the benzene ring, the higher the yield of the target product.

These differences in perfluoroalkylation reactions depending on the size of the perfluoroalkyl radical are related, most likely, to steric effects for the addition of relatively bulky pentafluoroethyl and pentafluoropropyl radicals,[10] whereas the reactions involving the trifluoromethyl radical are predominantly determined by the energy of electronic structure rearrangement and are characterized by $E_β^{HOMO}$ and $E_β^{LUMO}$.

Thus, the method proposed for the formation of aryl perfluoroalkyl sulfides from aromatic disulfides can be of preparative value for compounds containing several electron-withdrawing substituents in the aromatic ring. This method was used for the first time to synthesize compounds **3e** and **4e**, which can be used as starting compounds in the synthesis of a series of new amino derivatives. The presence of a fluorine-containing electron-withdrawing substituent along with two nitro groups in the benzene ring increases the chlorine atom mobility in molecules of compounds **3e** and **4e**. These compounds react readily with secondary amines at room temperature, which results in a series of analogs of the known herbicides based on 4-amino-2,6-dinitrobenzotrifluoride[3] in high yields (Scheme 5).

Scheme 5



22	R^1	R^2
a	Et	Bu
b	Pr	cyclopropylmethyl
c	Et	methallyl

23: *n* = 1 (**a**), 2 (**b**)

In compounds **3—5d**, one and two nitro groups were reduced to afford amino (**24**) and diamino derivatives (**25a—c**), respectively. One nitro group was selectively reduced with hydrazine hydrate on refluxing in ethanol. The diamines were prepared by the action of iron in the presence of HCl (Scheme 6).

Compounds **25a—c** can find use as monomers in the synthesis of such an important class of modern materials as fluorine-containing polyimides.[11]

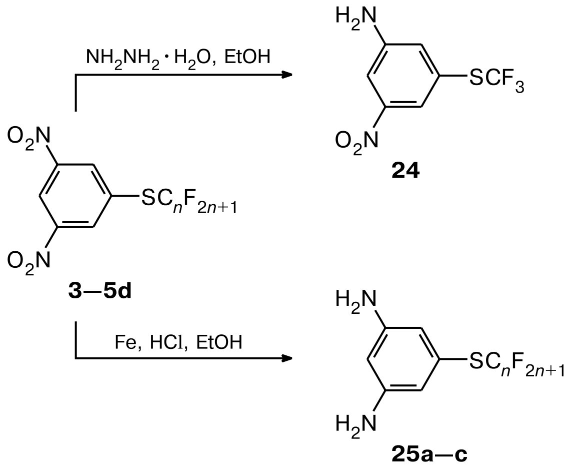
Table 6. Data on the ^{13}C NMR spectra and high-resolution mass spectra of compounds **3a,b,d—g**, **4a,c,d—g,k**, **5a,d,e**, and **6a**

Compound	^{13}C NMR (δ, J/Hz)	High-resolution mass spectrum		
		Found, m/z [M]$^+$	Molecular formula	Calculated, M
3a	114.0 (dq, C(2), $^2J_{CF}$ = 20.8, $^3J_{CCF_3}$ = 2.6); 117.6 (d, C(6), $^2J_{CF}$ = 25.4); 128.5 (qd, CF_3, J_{CF} = 310.0, $^4J_{CF}$ = 1.6); 129.7 (d, C(5), $^3J_{CF}$ = 10.2); 134.1 (s, C(3)); 144.3 (s, C(4)); 166.7 (d, C(1), J_{CF} = 263.3)	240.9827	$C_7H_3F_4NO_2S$	240.9821
3b	126.4 (q, C(2), $^3J_{CCF_3}$ = 2.4); 126.7 (s, C(6)); 128.5 (q, CF_3, J_{CF} = 310.1); 131.4 (s, C(5)); 132.3 (q, C(3), $^4J_{CF}$ = 1.1); 139.8 (s, C(1)); 146.5 (q, C(4), $^5J_{CF}$ = 0.9)	256.9533	$C_7H_3ClF_3NO_2S$	256.9525
3d	120.9 (s, C(2)); 128.5 (q, CF_3, J_{CF} = 309.7); 129.3 (q, C(5), $^3J_{CCF_3}$ = 2.5); 135.3 (q, C(4), C(6), $^4J_{CCF_3}$ = 1.1); 148.7 (br.s, C(1), C(3))	267.9766	$C_7H_3F_3N_2O_4S$	267.9766
3e	123.6 (s, C(2)); 126.6 (q, C(5), $^3J_{CCF_3}$ = 2.7); 128.3 (q, CF_3, J_{CF} = 310.1); 134.2 (q, C(4), C(6), $^4J_{CCF_3}$ = 1.1); 149.8 (s, C(1), C(3))	301.9367	$C_7H_2ClF_3N_2O_4S$	301.9376
3f	124.8 (q, C(4), $^3J_{CCF_3}$ = 2.5); 128.8 (q, CF_3, J_{CF} = 309.1); 130.4 (s, C(1)); 132.6 (q, C(5), $^4J_{CCF_3}$ = 1.0); 133.0 (s, C(6)); 140.2 (q, C(3), $^4J_{CCF_3}$ = 0.9); 148.1 (br.s, C(2))	256.9521	$C_7H_3ClF_3NO_2S$	256.9525
3g	—	245.9258	$C_7H_3Cl_2F_3S$	245.9285
4a	112.5 (dt, C(2), $^2J_{CF}$ = 21.4, $^3J_{CCF_3}$ = 3.4); 117.5 (d, C(6), $^2J_{CF}$ = 25.8); 118.4 (qt, CF_2, J_{CF} = 286.9, $^2J_{CF}$ = 36.2); 119.5 (tqd, CF_3, J_{CF} = 282.9, $^2J_{CF}$ = 41.4, $^5J_{CF}$ = 1.2); 129.6 (d, C(5), $^3J_{CF}$ = 10.2); 134.9 (s, C(3)); 144.3 (d, C(4), $^4J_{CF}$ = 2.9); 167.3 (d, C(1), J_{CF} = 263.3)	290.9792	$C_8H_3F_6NO_2S$	290.9789
4c	—	352.8946	$C_8H_3BrF_5NO_2S$	352.8968
4d	118.3 (qt, CF_2, J_{CF} = 286.6, $^2J_{CF}$ = 35.8); 119.3 (tq, CF_3, J_{CF} = 292.4, $^2J_{CF}$ = 41.6); 121.3 (s, C(2)); 127.8 (t, C(5), $^3J_{CCF_3}$ = 3.2); 136.3 (s, C(4), C(6)); 148.7 (br.s, C(3), C(1))	317.9752	$C_8H_3F_5N_2O_4S$	317.9734
4e	—	351.9336	$C_8H_2ClF_5N_2O_4S$	351.9343
4f	118.4 (qt, CF_2, J_{CF} = 286.6, $^2J_{CCF_3}$ = 36.2); 119.7 (tq, CF_3, J_{CF} = 290.9, $^2J_{CF}$ = 41.1); 123.3 (t, C(4), $^3J_{CCF_3}$ = 3.0); 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))	306.9486	$C_8H_3ClF_5NO_2S$	306.9493
4g	—	295.9222	$C_8H_3Cl_2F_5S$	295.9253
4k	112.2 (dt, C(2), $^3J_{CCF_3}$ = 2.9, $^3J_{CF}$ = 20.0); 116.8 (q, C(4), $^4J_{CF}$ = 4.1); 118.2 (q, C(6), $^2J_{CF}$ = 24.5); 118.4 (qt, CF_2, J_{CF} = 286.5, $^2J_{CF}$ = 36.5); 119.6 (tq, CF_3, J_{CF} = 291.6, $^2J_{CF}$ = 41.0); 137.0 (q, C(5), $^3J_{CF}$ = 8.2); 141.5 (s, C(3)); 163.0 (d, C(1), J_{CF} = 253.6)	323.9038	$C_8H_3BrF_6S$	323.9043
5a	—	340.9728	$C_9H_3F_8NO_2S$	340.9757
5d	—	367.9710	$C_9H_3F_7N_2O_4S$	367.9702
5e	109.3 (tm, CF_2, J_{CF} = 267.1, $^2J_{CF}$ = 38.5); 112.8 (qt, C(2), $^2J_{CF}$ = 19.8, $^3J_{CCF_3}$ = 3.2); 117.4 (d, C(4), $^4J_{CF}$ = 4.1); 118.3 (qm, CF_3, J_{CF} = 290.7, $^2J_{CF}$ = 32.4, $^3J_{CF}$ = 1.6); 118.7 (d, C(6), $^2J_{CF}$ = 24.5); 122.6 (t.t, SCF_2, J_{CF} = 293.4, $^2J_{CF}$ = 34.0); 137.6 (d, C(5), $^3J_{CF}$ = 8.2); 142.4 (s, C(3)); 164.0 (d, C(1), J_{CF} = 253.6)	373.9008	$C_9H_3BrF_8S$	373.9011
6a	117.0 (dq, C(6), $^2J_{CF}$ = 28.4, $^3J_{CCF_3}$ = 5.5); 118.5 (d, C(2), $^2J_{CF}$ = 20.2); 120.7 (q, CF_3, J_{CF} = 274.5); 128.2 (q, SCF_3, J_{CF} = 309.9); 129.1 (dq, C(5), $^2J_{CCF_3}$ = 35.8, $^3J_{CF}$ = 8.7); 134.8 (s, C(3)); 144.1 (s, C(4)); 164.2 (d, C(1), J_{CF} = 262.9)	341.8947	$C_8H_2BrF_7S$	341.8948

Table 7. Wavefunction coefficients of the sulfur atom (C_S) in radicals **18e,f,h,j** and yields of compounds $ArSR^F$ ($R^F = CF_3$ (**3e,f,h,j**), and C_2F_5 (**4e,f,h,j**))

Intermediate **18**	C_S	Yield (%))	
		3	**4**
e	0.032	73.0	66.4
f	0.801	16.1	16.9
h	0.489	24.6	34.1
j	0.799	15.2	30.3

Scheme 6



25: n = 1 (**a**), 2 (**b**), 3 (**c**)

Experimental

Column chromatography was carried out on silica gel 60, 230—400 mesh (Merck), and TLC was performed on plates with silica gel 60 F_{254} (Merck). NMR spectra were recorded on Bruker AM 360 or Bruker AM 500 spectrometers with working frequencies of 360 and 500 MHz, respectively, in $CDCl_3$ using Me_4Si or $CFCl_3$ as internal standards. IR spectra were obtained on BioRad FTS-40 FT-IR and Specord M-80 instruments in Nujol. GC-MS analysis was carried out on a Hewlett—Packard 5890 GC-mass spectrometer (70 eV) using a capillary column (30 m) with HP1 oil. High-resolution mass spectra were recorded on a VG Autospec mass spectrometer.

Synthesis of disulfides 2a—n (general procedure). Arenesulfonyl chloride (0.25 mol) was dissolved in glacial AcOH (1.25 L) saturated with gaseous HBr (125 g). Phenol (25.9 g, 0.275 mol) was added, and the reaction mixture was slowly heated with stirring to 55—60 °C (exothermic reaction). The reaction mixture was stirred at this temperature for 24—36 h, cooled to ≈20 °C, and diluted with water. The precipitate that formed was filtered off, washed with water, dried in air, and recrystallized from EtOH or AcOH. The yields of the resulting compounds, melting points, and data on the ^1H and ^{13}C NMR and mass spectra are presented in Tables 1 and 2.

Reactions of disulfides 2a—n with perfluoroalkyl radicals (general procedure). Method *A*. A disulfide **2** (2.7 mmol) was added with stirring at −20 °C to a mixture of XeF_2 (1.4 g, 8.2 mmol), perfluoroalkanecarboxylic acid (1.2—1.8 mL), and CH_2Cl_2 (30 mL). The mixture spontaneously warmed to +5 °C.

Method *B*. XeF_2 (1.4 g, 8.2 mmol) was added at 30 °C with stirring to a mixture of the starting disulfide (2.74 mmol) in perfluoroalkanecarboxylic acid (4.2—6.0 mL, 54.8 mmol). In both cases, the end of the reaction was determined by the end of gas liberation.

The reaction mixture obtained by methods *A* or *B* was neutralized with a solution of Na_2CO_3, extracted with chloroform, and dried with Na_2SO_4. The solvent was removed *in vacuo*. The residue was chromatographed on silica gel (light petroleum (**3g,h**, **4g,h,k**, **5e**, **6e**, **7a,c**, and **8**) or a benzene—heptane (1 : 2) mixture (**3a—f,i,j**, **4a—f,i,j**, **5a—d**, **6a—d**, **7b**, and **9a,b**) as eluents). The yields of the synthesized compounds, melting points, and data on the ^1H, ^{13}C, and ^{19}F NMR and mass spectra are presented in Tables 3, 7, and 8.

3-Nitro-5-(trifluoromethylthio)aniline (24). A mixture of 1,3-dinitro-5-(trifluoromethylthio)benzene (0.31 g, 1.16 mmol) and hydrazine hydrate (0.25 g, 5.00 mmol) in EtOH (20 mL) was refluxed for 6 h. The solvent was distilled off, and the residue was washed with water (50 mL) and dissolved in benzene. The solution was dried with Na_2SO_4 and concentrated *in vacuo*. After recrystallization from hexane, compound **24** (0.1 g, 36.2%) was obtained as orange crystals, m.p. 118—120 °C (Ref. 18:

Table 8. Quantum characteristics of radicals **18a—d,g,i,k** and yields of compounds $ArSR^F$ (R^F = CF_3 (**3a—d,g,i**), C_2F_5 (**4a—d,g,i,k**), and C_3F_7 (**5a—c,k**))

Intermediate **18**	Q_S	$-Q_{CS}$	Q_H	Q_{H4}	$-E_β^{HOMO}$	$E_β^{LUMO}$	Yield (%)		
	a.u.				eV		**3**	**4**	**5**
a	0.1464	0.1331	0.0955	0.0773	6.9863	4.8944	33.6	55.3	33.0
b	0.1569	0.1111	0.0993	0.0813	7.1076	4.6753	24.5	37.7	26.7
c	0.1525	0.1189	0.0969	0.0796	7.6223	6.6864	34.7	40.2	27.3
d	0.1352	0.1143	0.1026	0.1038	7.3029	4.5395	30.0	14.7	—
g	0.1507	0.1129	0.0861	0.0804	6.9044	5.8697	22.5	13.3	—
i	0.1307	0.1182	0.0923	0.0773	6.8079	5.0562	7.8	8.1	—
k	0.1352	0.1348	0.0789	—	—	—	—	23.0	16.7

117—121 °C). ^{1}H NMR, δ: 4.21 (s, 2 H, NH_2); 7.21 (s, 1 H, H(4)); 7.58 (t, 1 H, H(2), $^4J_{H,H}$ = 2.0 Hz); 7.83 (s, 1 H, H(6)). ^{13}C NMR, δ: 111.1 (s, C(2)); 119.6 (q, C(6), $^4J_{CCF_3}$ = 0.9 Hz); 126.7 (q, C(4), $^4J_{CCF_3}$ = 0.9 Hz); 126.8 (q, C(5), $^3J_{CCF_3}$ = 2.3 Hz); 129.2 (q, CF_3, J_{CF} = 303.6 Hz); 148.1 (s, C(3)); 149.4 (s, C(1)). ^{19}F NMR, δ: −42.49 (s, CF_3). IR, ν/cm^{-1}: 3420 (NH_2). MS, *m/z* (I_{rel} (%)): 238 $[M]^+$ (100), 222 $[M - F]^+$ (1), 192 $[M - NO_2]^+$ (19), 123 $[M - NO_2 - CF_3]^+$ (41). Found: *m/z* 238.0022 $[M]^+$. $C_7H_5F_3N_2O_2S$. Calculated: M = 238.0024.

Reduction of 1,3-dinitro-4-perfluoroalkylthiobenzenes (3d, 4d, and 5d) (general procedure). An Fe powder (4—5 mmoles per NO_2 group) was added portionwise with stirring to a boiling solution of a nitro compound in ethanol (5 mL) containing concentrated HCl (0.2 mL). The mixture was refluxed for 8 h until the nitro compound disappeared completely (TLC) and then refluxed with active carbon, filtered, cooled to ≈20 °C, and neutralized with aqueous NH_4OH. The solvent was removed *in vacuo* and extracted with benzene. The organic layer was dried with Na_2SO_4. The solvent was removed, and the product was purified by column chromatography and recrystallization from hexane. Vacuum sublimation was carried out for complete purification.

5-Trifluoromethylthio-1,3-phenylenediamine (25a). The yield was 65.1%, yellowish crystals, m.p. 110—112 °C. ^{1}H NMR, δ: 3.67 (s, 4 H, NH_2); 6.06 (d, 1 H, H(2), $^4J_{H,H}$ = 1.9 Hz); 6.36 (d, 2 H, H(4), H(6), $^4J_{H,H}$ = 1.7 Hz). ^{13}C NMR, δ: 103.4 (s, C(2)); 112.8 (q, C(4), C(6), $^4J_{CCF_3}$ = 0.5 Hz); 125.6 (q, C(5), $^3J_{CCF_3}$ = 2.1 Hz); 129.8 (q, CF_3, J_{CF} = 307.8 Hz); 148.1 (s, C(1), C(3)). ^{19}F NMR, δ: −42.85 c (CF_3). IR, ν/cm^{-1}: 3348 (NH_2). MS, *m/z* (I_{rel} (%)): 208 $[M]^+$ (100), 189 $[M - F]^+$ (4), 139 $[M - CF_3]$ (16), 122 $[M - CF_3 - NH_3]^+$ (4), 69 $[CF_3]^+$ (10). Found: *m/z* 208.0260 $[M]^+$. $C_7H_7F_3N_2S$. Calculated: M = 208.0282.

5-Pentafluoroethylthio-1,3-phenylenediamine (25b). The yield was 68.2%, yellowish crystals, m.p. 103—105 °C. ^{1}H NMR, δ: 3.40 (s, 4 H, NH_2); 6.09 (t, 1 H, H(4), $^4J_{H,H}$ = 1.7 Hz); 6.38 (d, 2 H, H(2), H(6), $^4J_{H,H}$ = 1.7 Hz). ^{19}F NMR, δ: −91.96 (s, CF_2); −83.01 (s, CF_3). IR, ν/cm^{-1}: 3350 (NH_2). MS, *m/z* (I_{rel} (%)): 258 $[M]^+$ (100), 139 $[M - C_2F_5]^+$ (9). Found: *m/z* 258.0248 $[M]^+$. $C_8H_7F_5N_2S$. Calculated: M = 258.0250.

5-Heptafluoropropylthio-1,3-phenylenediamine (25c). The yield was 57.2%, yellowish crystals, m.p. 82—84 °C. ^{1}H NMR, δ: 3.52 (s, 4 H, NH_2); 6.07 (t, 1 H, H(4), $^4J_{H,H}$ = 1.7 Hz); 6.37 (d, 2 H, H(2), H(6), $^4J_{H,H}$ = 1.7 Hz). ^{19}F NMR, δ: −124.32 (s, CF_2); −87.46 (s, SCF_2); −80.45 (s, CF_3). IR, ν/cm^{-1}: 3352 (NH_2). MS, *m/z* (I_{rel} (%)): 308 $[M]^+$ (100), 289 $[M - F]^+$ (4), 239 $[M - CF_3]^+$ (16), 69 $[CF_3]^+$ (10). Found: *m/z* 308.0218 $[M]^+$. $C_9H_7F_7N_2S$. Calculated: M = 308.0215.

Reactions of secondary amines with chloro-2,6-dinitro-4-perfluoroalkylthiobenzenes (general procedure). The corresponding amine (2.5 equiv.) was added with stirring to a solution of chloro-2,6-dinitro-4-perfluoroalkylthiobenzene (1.5 mmol) in MeOH or EtOH (10 mL). The mixture was refluxed for 30 min. The solvent was removed *in vacuo*, and the residue was washed with water and dissolved in benzene or chloroform. The organic layer was dried with Na_2SO_4 and purified by chromatography on a column with silica gel (hexane—benzene mixture (4 : 1) as the eluent) (compounds **22a—c**) or by recrystallization from EtOH or heptane (compounds **23a,b**).

***N*-Butyl-*N*-ethyl-2,6-dinitro-4-trifluoromethylthioaniline (22a).** The yield was 84%, orange-red crystals, m.p. 56—58 °C. ^{1}H NMR, δ: 0.88, 1.18 (both t, 3 H each, CH_3, J = 7.2 Hz); 1.28, 1.57 (both m, 2 H each, CH_2); 2.98 (t, 2 H, CH_2, J = 7.2 Hz); 3.10 (q, 2 H, CH_2N, J = 6.1 Hz); 8.07 (s, 2 H, Ar). ^{19}F NMR, δ: −41.90 (s). MS, *m/z* (I_{rel} (%)): 367 $[M]^+$ (2), 350 $[M - OH]^+$ (6), 324 $[M - C_3H_7]^+$ (100), 308 $[M - C_3H_7O]^+$ (11), 296 $[M - C_3H_7 - C_2H_4]^+$ (25). Found: *m/z* 367.082 $[M]^+$. $C_{13}H_{16}F_3N_3O_4S$. Calculated: M = 367.081.

***N*-Cyclopropylmethyl-*N*-propyl-2,6-dinitro-4-trifluoromethylthioaniline (22b).** The yield was 82%, yellowish-orange crystals, m.p. 54—55 °C. ^{1}H NMR, δ: 0.16, 0.58 (both m, 2 H each, CH_2); 0.88 (t, 3 H, CH_3, J = 7.5 Hz); 1.59 (m, 3 H, CH, CH_2); 2.90 (d, 2 H, CH_2, J = 6.8 Hz); 3.09 (m, 2 H, CH_2N); 8.21 (s, 2 H, Ar). ^{19}F NMR, δ_F: −41.87 (s). MS, *m/z* (I_{rel} (%)): 379 $[M]^+$ (7), 362 $[M - OH]^+$ (24), 350 $[M - Et]^+$ (51), 334 $[M - OEt]^+$ (3), 296 $[M - Et - C_4H_6]^+$ (5). Found: *m/z* 379.079 $[M]^+$. $C_{14}H_{16}F_3N_3O_4S$. Calculated: M = 379.081.

***N*-Ethyl-*N*-methallyl-2,6-dinitro-4-trifluoromethylthioaniline (22c).** The yield was 84%, yellow crystals, m.p. 76—77 °C. ^{1}H NMR, δ: 1.17 (t, 3 H, CH_3, J = 7.2 Hz); 1.73 (s, 3 H, CH_3); 3.10 (q, 2 H, CH_2, J = 7.0 Hz); 3.53, 5.00 (both s, 2 H each, CH_2); 8.19 (s, 2 H, Ar). ^{19}F NMR, δ: −41.76 (s). MS, *m/z* (I_{rel} (%)): 365 $[M]^+$ (20), 348 $[M - OH]^+$ (72), 324 $[M - \mathrm{Allyl}]^+$ (28), 308 $[M - \mathrm{AllylO}]^+$ (45), 296 $[M - \mathrm{Allyl} - C_2H_4]^+$ (6).

2,6-Dinitro-4-(trifluoromethylthio)-1-piperazinobenzene (23a). The yield was 84%, yellow-red crystals, m.p. 114—115 °C. ^{1}H NMR, δ: 1.72 (s, 1 H, NH); 2.96, 3.07 (both br.s, 4 H each, CH_2); 8.02 (s, 2 H, Ar). ^{19}F NMR, δ: −42.95 (s). MS, *m/z* (I_{rel} (%)): 352 $[M]^+$ (11), 322 $[M - NO]^+$ (18), 310 $[M - C_3H_6]^+$ (11), 280 $[M - NO - C_3H_6]^+$ (51), 259 $[M - NO - C_4H_8NH]^+$ (17), 246 (7), 218 (10). Found: *m/z* 352.044 $[M]^+$. $C_{11}H_{11}F_3N_4O_4S$. Calculated: M = 352.046.

2,6-Dinitro-1-piperazino-4-(pentafluoroethylthio)benzene (23b). The yield was 83%, yellow crystals, m.p. 55—57 °C. ^{1}H NMR, δ: 2.27 (s, 1 H, NH); 2.98, 3.09 (both q, 4 H each, 2 CH_2, J = 5.17 Hz); 8.03 (s, 2 H, Ar). ^{19}F NMR, δ: −82.81 (s, 3 F, CF_3); −91.99 (s, 2 F, CF_2). MS, *m/z* (I_{rel} (%)): 402 $[M]^+$ (11), 372 $[M - NO]^+$ (26), 360 $[M - C_3H_6]^+$ (10), 330 $[M - NO - C_3H_6]^+$ (46), 309 $[M - NO - C_4H_8NH]^+$ (12), 283 (11). Found: *m/z* 402.043. $C_{12}H_{11}F_5N_4O_4S$. Calculated: M = 402.042.

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