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Reactions of 4-substituted-1-[(difluoromethyl)sulfinyl]polyfluorobenzenes with phenolate anion

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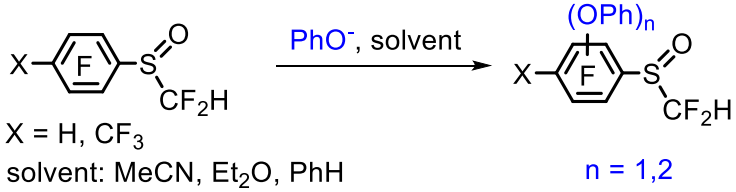
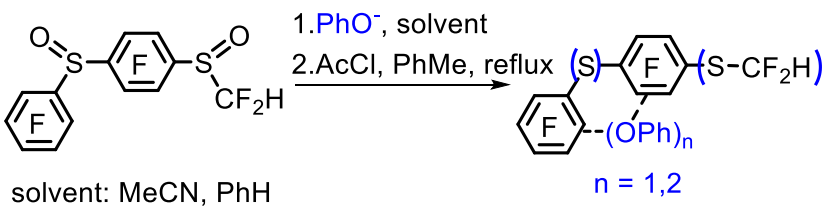
Abstract

The reactions of 4-substituted-polyfluorinated-[(difluoromethyl)sulfinyl]benzenes ([4-X-$C_6F_4S(O)CHF_2$ [X = H, CF_3 and $C_6F_5S(O)$]) with phenolate anion in benzene, Et_2O and CH_3CN have been investigated. The reactions of the substrate (X = H, CF_3) and sodium phenolate in equal amounts resulted in the formation of mixtures of the starting compound, 2-phenoxyderivative and disubstituted products. The two-fold amount of the phenolate afforded the 2,6-disubstituted products for X = H in MeCN and for X = CF_3 in Et_2O. At the same time, 4-CF_3-$C_6F_4S(O)CHF_2$ in CH_3CN gave a mixture of the 2,6- and 2,5-bis(phenoxy) derivatives. Quantum chemical calculations have been performed to explain this phenomenon. For X = $C_6F_5S(O)$ in MeCN, the reaction was accompanied by sulfinyl moiety ipso-substitution.





Keywords: Polyfluoroaromatic compounds, sulfoxides, sodium phenolate, aromatic nucleophilic substitution.

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Introduction

Polyfluorinated organic compounds have found wide practical application.[1] Recently, research into functional derivatives and, in particular, sulfur-containing compounds, has been developing in the area of polyfluorinated organic compounds.[1] The reactions of sulfur-containing polyfluoroarenes with nucleophiles are being studied.[2,3,4] The sulfur atom oxidation state in such compounds can significantly affect the rate and direction of the reaction.[5]

For polyfluoroaromatic compounds, nucleophilic substitution reactions are most typical.[6,7] The presence of an acceptor in the polyfluorinated ring, for example, the difluorosulfinyl group, should facilitate the substitution of fluorine atom, which opens up wide possibilities for various transformations.

Methods for the preparation of low-fluorinated sulfoxides are presented in the literature.[8,9.10] Sulfoxides containing four or more fluorine atoms, however, are practically unknown. Meanwhile, difluoromethyl derivatives of sulfoxides can be obtained on the basis of available polyfluorinated arene thiols[11,12] by their reaction with chlorodifluoromethane, followed by oxidation of the resulting sulfanes.

In connection with the foregoing, we have focused our attention on polyfluoroaromatic sulfoxides bearing a difluoromethyl group since compounds of such structure have not been reported. For this reason, it was reasonable to study the properties and transformations of such compounds.

In general, [(difluoromethyl)sulfinyl]polyfluoroarenes have two centers sensitive to nucleophilic attack – the polyfluoroaromatic core, activated by the electron-withdrawing $S(O)CHF_2$ group ($\sigma_I = 0.51$, $\sigma_R = 0.07$)[13] - and the sulfur atom.

Recently we have shown that [(difluoromethyl)sulfinyl]pentafluorobenzene, $C_6F_5S(O)CHF_2$, readily undergoes attack on the polyfluoroaromatic core, with substitution of the *para*-fluorine atom for OMe, OPh, NHMe and SH groups under the action of the charged (NaOMe, NaOPh, KSH) or uncharged (NH_2Me) nucleophiles. The direction of substitution is consistent with the expected one.[6] Surprisingly, the action of alkali (NaOH) on $C_6F_5S(O)CHF_2$ led to its decomposition, with formation of pentafluorobenzene. This result might be attributed to the attack on the sulfur atom.[14]

The task of the current research was to study the transformations of *para*-substituted [(difluoromethyl)sulfinyl]tetrafluorobenzenes, $4\text{-}XC_6F_4S(O)CHF_2$ [where X = H (**1**), CF_3 (**2**) and $S(O)C_6F_5$ (**3**)] in reactions with nucleophiles, e.g., the phenolate ion. Such substrates do not have a *para*-fluorine atom, are sensitive to nucleophilic attack and, thus, new routes of reaction may be revealed. Phenolate ion is widely used in test experiments and kinetic measurements.[15] Since it was necessary for this study to avoid the presence of water in the reaction mixture, sodium phenolate was obtained by the action of sodium hydride on phenol. The reaction process was monitored by means of ^{19}F NMR spectroscopy. Further confirmation of the structures of the reaction products, if necessary, were proven by counter (alternative) syntheses.

We have shown that reactions of [(difluoromethyl)sulfinyl] benzenes (**1**-**3**) with sodium phenolate led to the nucleophilic substitution of fluorine in the neighboring position of the [(difluoromethyl)sulfinyl] group for phenoxide (**1**). The subsequent substitution reaction also occurred, however, its selectivity depended on the electronic properties of the substituent in the polylfluoroaryl core and solvent polarity. The obtained experimental results are also discussed using quantum-chemical calculations.

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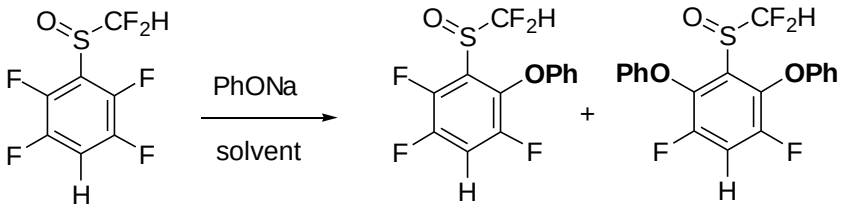
Results and Discussion

Reactions of 3-[(difluoromethyl)sulfinyl]-1,2,4,5-tetrafluorobenzene with sodium phenolate

The sulfinylbenzene (**1**) reacted with sodium phenolate in benzene at 65 °C for 8 h and gave a mixture of the starting compound, 3-[(difluoromethyl)sulfinyl]-1,2,5-trifluoro-4-phenoxybenzene (**4**) and [{2-[(difluoromethyl)sulfinyl]-4,6-difluoro-1,3-phenylene}bis(oxy)]dibenzene (**5**) (Scheme 1 and Table 1, entry 1). The analogous mixture was obtained in Et_2O solution after refluxing for 4 h (entry 2). The same result was observed when the process was carried out in a polar solvent such as MeCN (entry 3). On the contrary, by adding two equivalents of sodium phenolate, only the disubstituted derivative (**5**) was observed in the reaction products (entry 4).



1 **4** **5**

Scheme 1

Table 1. Reactions of sulfinylbenzene (**1**) with sodium phenolate in solvents of differing polarities

Entry	PhONa equiv.	Solvent	T, °C	Time, h	NMR ^{19}F ratio
1	1	PhH	65	8	**1** : **4** : **5** = 19 : 58 : 23
2	1	Et_2O	35 (reflux)	4	**1** : **4** : **5** = 19 : 66 : 16
3	1	MeCN	65	2	**1** : **4** : **5** = 15 : 66 : 19
4	2	MeCN	65	2.5	**1** : **4** : **5** = - : - : 100

Reactions of 1-[(difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene with sodium phenolate

The same set of experiments was carried out with 1-[(difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene with sodium phenolate (**2**) (Scheme 2 and Table 2). The strong electron-withdrawing influence of the trifluoromethyl group ($\sigma_I = 0.38$, $\sigma_R = 0.16$)[13] afforded the opportunity to decrease the temperature of the reaction for compound (**2**) with respect to compound (**1**). When compound (**2**) reacted with sodium phenolate in benzene, a mixture of the starting compound, 1-[(difluoromethyl)sulfinyl]-2,3,5-trifluoro-6-phenoxy-4-(trifluoromethyl)benzene (**6**) and [{2-[(difluoromethyl)sulfinyl]-4,6-difluoro-5-(trifluoromethyl)-1,3-phenylene}bis(oxy)]dibenzene (**7**) was formed (entry 1). The action of sodium phenolate on compound **2** in Et_2O led to the analogous distribution of the products, both at room temperature (entry 2) or at -25°C (entry 3). So, in all cases, the formation of the monosubstituted sulfoxide (**6**) was accompanied with formation of the diphenoxy-substituted product (**7**). When 2 moles of sodium phenolate per mole of substrate were employed, compound (**7**) was the only reaction product (entry 4).

The same reaction between compound **2** and sodium phenolate in polar MeCN, however, surprisingly revealed the formation of the isomeric [{2-[(difluoromethyl)sulfinyl]-3,6-difluoro-5-(trifluoromethyl)-1,4-

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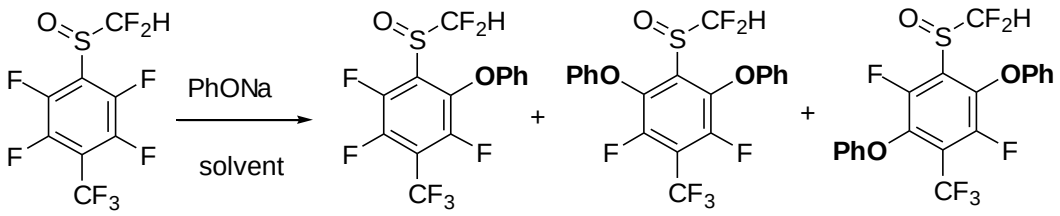
phenylene}bis(oxy)]dibenzene (**8**) alongside compounds **2**, **6** and **7** (entry 5). When 2 equivalents of sodium phenolate were used, the full conversion of the sulfoxide (**2**) was observed with formation of compounds (**7**) and (**8**) in the ratio 64:36 (entry 6). Thus, a polar solvent is the likely reason for the new reaction direction, which was not observed in the case of sulfoxide (**1**).



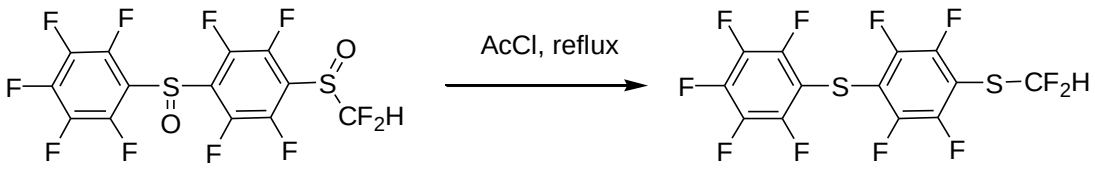
Scheme 2

Table 2. Reactions of sulfinylbenzene (**2**) with sodium phenolate in solvents of differing polarities

Entry	PhONa equiv.	Solvent	T, °C	Time, h	NMR ^{19}F ratio
1	1	PhH	25	8	**2 : 6 : 7 : 8** = 18 : 56 : 25 : -
2	1	Et_2O	25	1	**2** : **6** : **7 : 8** = 12 : 67 : 20 : -
3	1	Et_2O	- 25	4	**2** : **6** : **7 : 8** = 18 : 67 : 16 : -
4	2	Et_2O	30	3	**2** : **6** : **7 : 8** = - : - : 100 : -
5	1	MeCN	25	0.5	**2** : **6** : **7 : 8** = 18 : 58 : 14 : 9
6	2	MeCN	30	0.5	**2** : **6** : **7 : 8** = - : - : 64 : 36

Reactions of 1-[(difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-[(perfluorophenyl)sulfinyl]benzene with sodium phenolate

We have also investigated the reaction of 1-[(difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-[(perfluorophenyl)sulfinyl]benzene (**3**) with sodium phenolate in PhH and MeCN solutions. Complex mixtures of multiple components were formed in both cases. The resulting products, however, were not stable under GC-MS analysis conditions. For these reasons, we tried to reduce S-O fragments of the obtained sulfinylbenzenes. This would have simplified the reaction-mixture composition, since sulfane moieties were not able to form optical isomers. A control experiment consisting of the reduction of compound **3**, using AcCl[16] under reflux conditions, resulted in the formation of (difluoromethyl)[2,3,5,6-tetrafluoro-4-(perfluorophenylthio)phenyl]sulfane (**9**) (92% isolated yield), and demonstrated the feasibility of this approach (Scheme 3).



3
1:1
mixture of diastereomers

9, 92%

Scheme 3. Reduction of sulfoxide (**3**) with AcCl forming sulfane (**9**).

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Such a reduction procedure for non-fluorinated sulfoxides is known to demand not such severe conditions, but the reactivity of the polyfluorinated substrates turned out to be remarkably less.[16] The electron-withdrawing character of polyfluoroaryl moiety seems to prevent the effective coordination of the acetyl chloride and sulfinyl group.

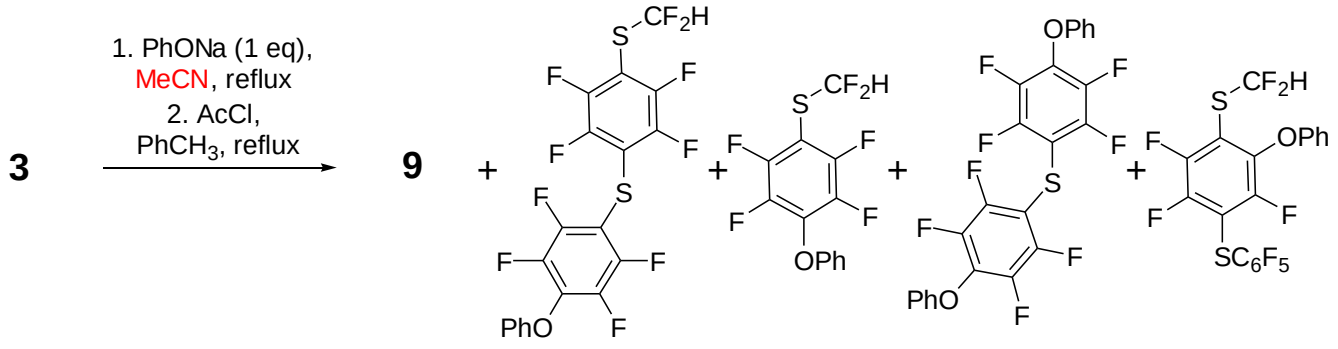
In connection with the foregoing, the reaction mixtures were also subjected to the action of acetyl chloride at reflux temperature. To prevent the chlorination of phenoxy groups, toluene was added to the reaction mixture; the resulting formation of benzyl chloride was recorded using GC-MS spectrometry. Nevertheless, even after the action of acetyl chloride, the obtained mixtures were rather complex and it was not possible to separate them into individual compounds. For this reason, the individual compounds have been synthesized by counter synthesis to provide us with reliable data about the products' structures.

Therefore, the resulting mixtures were analyzed by means of GC-MS spectrometry and ^{19}F NMR spectroscopy for comparison with these specially prepared compounds' spectra. The yields of the products were calculated using ^{19}F NMR spectroscopy with an internal quantitative standard.

Elucidation of the structures of the products obtained are supported by NMR spectra included in the Supplementary Materials.

It was shown that solvent polarity had a remarkable effect on the predominant route of the reaction between substrate (**3**) and NaOPh. Usage of the polar MeCN allowed us to substitute the para-fluorine atom, which is a typical direction of aromatic nucleophilic substitution in polyfluoroarenes (Scheme 4).[6] The reduced product of this transformation was (difluoromethyl){2,3,5,6-tetrafluoro-4-[(2,3,5,6-tetrafluoro-4-phenoxyphenyl)thio]phenyl}sulfane (**10**). (Difluoromethyl)(2,3,5,6-tetrafluoro-4-phenoxyphenyl)sulfane (**11**) and bis(2,3,5,6-tetrafluoro-4-phenoxyphenyl)sulfane (**12**) were found in the reaction mixture in significant amounts.

Formation of such structures obviously is a result of the ipso-attack of the nucleophile on the carbon atom bonded with the sulfinyl group and, in fact, provides a unique reaction pattern which was not observed for sulfoxides (**1**) and (**2**).



		10	**11**	**12**	**13**	
NMR ^{19}F ratio	29	31	16	18	6	
Yield, %	24	26	13	15	5	Total: 83 %

Scheme 4. Composition and distribution of the products obtained in reactions of sulfoxide (**3**) with sodium phenolate in polar MeCN.

On the contrary, the action of sodium phenolate on compound (**3**) in non-polar benzene afforded, after reduction, no noticeable quantities of compound (**10**) (Scheme 5). The main component of the product

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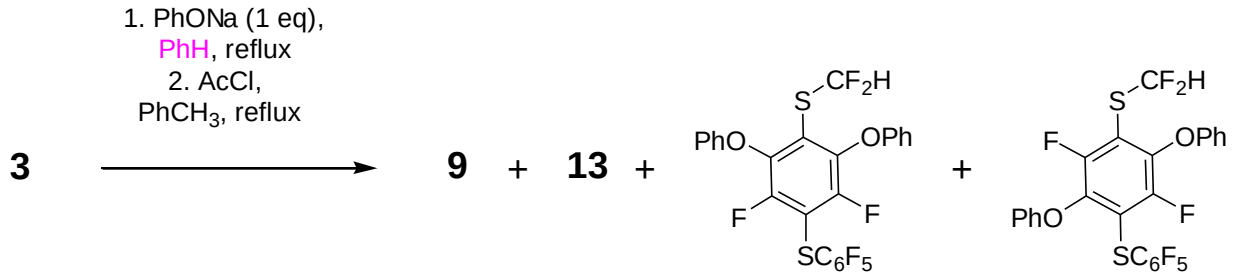
mixture was (difluoromethyl){2,3,5-trifluoro-4-[(perfluorophenyl)thio]-6-phenoxyphenyl}sulfane (**13**) while bis(phenoxy)-substituted compounds {3,5-difluoro-4-[(perfluorophenyl)thio]-2,6-diphenoxyphenyl}(difluoromethyl)sulfane (**14**), and {2,5-difluoro-4-[(perfluorophenyl)thio]-3,6-diphenoxyphenyl}(difluoromethyl)sulfane (**15**), were also formed. Thus, the predominant direction of the process, in a non-polar solvent, is nucleophilic attack on the polyfluoroaromatic ring bearing two sulfinyl groups.



	9	**13**	**14**	**15**	
NMR ^{19}F ratio	23	50	15	11	
Yield, %	19	40	12	9	Total: 80 %

Scheme 5. Composition and distribution of the products obtained in reactions of sulfoxide (**3**) with sodium phenolate in non-polar solvent benzene.

Mechanistic rationale

The results obtained might be explained in terms of an aromatic nucleophilic substitution mechanism. Aromatic nucleophilic substitution in polyfluoroarenes is known to proceed in a step-wise addition-elimination process; addition of the nucleophile is usually a rate-determine stage.[17,18] The regioselectivity of substitution of fluorine in monosubstituted pentafluorobenzenes (C_6F_5X) is governed mainly by the other fluorine atoms rather that the group X, with the exception of powerful electron-donating groups.[6]

Probably for similar reasons, the starting sulfoxide (**1** or **2**) and phenoxyderivative (**4** or **6**, respectively) demonstrated very similar reaction capabilities. Fluorine atoms in position 2 of the starting sulfoxides are activated by the difluoromethylsulfinyl group toward nucleophilic aromatic substitution. The fluorine atoms in position 6 of the substituted products (**4**) and (**6**) undergo the same degree of activation, while the influence of the phenoxy group situated in the meta position is low.

At the same time, the reaction abilities of the fluorine atoms in position 5 of products (**4**) and (**6**) vary depending on the character of the group X. Compound (**4**) reacts with sodium phenolate selectively at position 6, while the fluorine atom in position 5 remains unreactive. On the contrary, sulfoxide (**6**) undergoes nucleophilic substitution at positions 5 and 6 with formation of compounds (**8**) and (**7**), respectively. This effect is obviously a result of a strong electron-withdrawing influence of the trifluoromethyl group, such that it can stabilize the carbanion formed by addition of the phenolate-anion at position 5 of sulfoxide (**6**).

Investigation of reversibility formation of bisphenoxy compounds (7) and (8)

For a better comprehension of the formation process of compounds **7** and **8**, it was necessary to find out if these compounds could transform into each other under the reaction conditions. A mixture of bisphenoxy derivatives (**7**) and (**8**) (ratio 66 : 34 by ^{19}F NMR) and NaF was obtained from the interaction of sulfoxide (**2**) with PhONa (2 eq) after 0.5 h in MeCN. A pure sample of individual compound (**7**) (0.22 eq) was added to the

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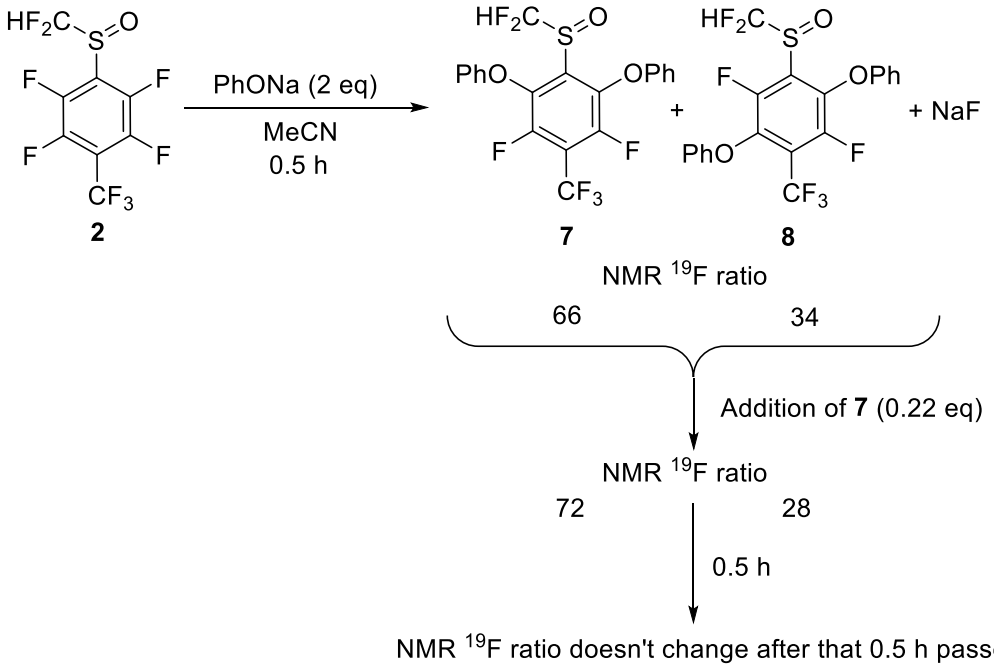
specified mixture, so that the ratio of compounds (**7**) and (**8**) became 72 : 28 (^{19}F NMR). The resulting mixture was kept at the reaction conditions for an additional 0.5 h and then analyzed by means of ^{19}F NMR. The ratio of **7** and **8** was not effectively changed indicating no significant reversibility of aromatic nucleophilic substitution; the fluoride anion could not split the carbon-oxygen bond formed, and no equilibrium between isomers (**7**) and (**8**), under the reaction conditions employed (Scheme 6).

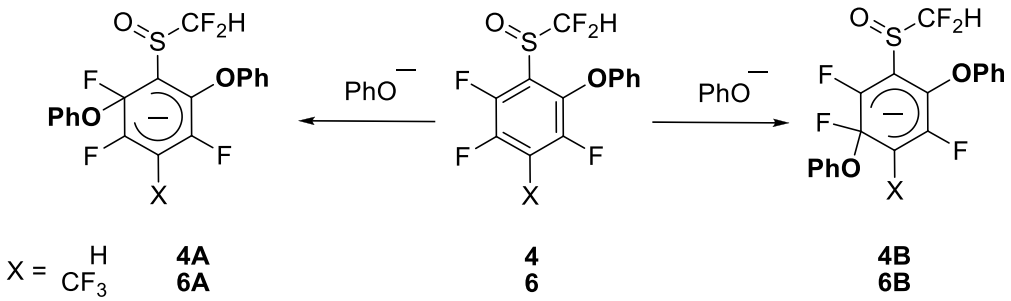


Scheme 6. Reversibility experiment results showing no reversibility or equilibrium for arenes (**7**) and (**8**).

Quantum chemical calculations

The ratio of diphenoxy derivatives in the interaction of compounds (**4**) and (**6**) with the one equivalent of sodium phenolate was determined by means of the quantum chemical calculations of the relative stabilities of sigma-complexes (type **A** and **B**), which are generally considered to be on the path of the nucleophilic substitution reaction (Scheme 7).

The results of quantum-chemistry calculations provided evidence that the probability of the reaction of the nucleophile with the carbon atom in position 5 of sulfoxide (**4**) is ca. 5 kcal per mole more likely than that in position 6, while positions 5 and 6 of the sulfoxide (**6**) revealed nearly the same reactivities.



Scheme 7. Formation of sigma-complexes from compounds **4** or **6** and the phenolate anion.

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As shown below in Table 3, the difference in the total energies of the resulting sigma-complexes is greater in the case of compound **4** (X = H) than for compound **6** (X = CF_3). Independent of the solvent, in the case of X = H, 2,6-bisphenoxy derivative (**5**) will form predominantly. In the case of X = CF_3, however, sigma-complexes of types **A** and **B** turn out to be close in terms of total energy values, so we should expect the formation of both products **7** and **8**. The calculations even predict the approximately equal reaction ability of positions 5 and 6 of compound **6**.

Table 3. Difference between the calculated B3LYP//6-31G(d) total energies of the corresponding sigma complexes depending on the solvent (in the case of PCM SMD)

X	ΔE, kcal/mol			
	gas phase	PhH	Et_2O	MeCN
H	5.32	5.53	5.10	5.09
CF_3	0.11	-0.05	-0.20	-0.34

Where ΔE = E (**B**) - E (**A**).

Reactions of compounds (4) and (6) with ammonium phenolates

We tried to check this assumption by implementation of the same set of chemical transformations of sulfinylbenzenes (**4**) and (**6**) with ammonium phenolate. Tetraalkylammonium salts are considered to display almost pure ionic character between cation and anion species; therefore, such salts are used extensively as phase transfer catalysts.[19] We supposed that the change in the nature of the cation could affect the ratio of the products of the reaction of compound **6** and the phenolate ion. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is known to be a weakly nucleophilic base and is widely used in organic synthesis.[20] Reaction of 3-[(difluoromethyl)sulfinyl]-1,2,5-trifluoro-4-phenoxybenzene (**4**) with phenol in the presence of DBU expectedly led, exclusively, to the formation of product (**5**) (Scheme 8)**.** No differences in the direction of the process were observed (Table 4: entries 1, 2).

On the contrary, the combination of DBU and phenol in the reaction with substrate (**6**) led to formation of various mixtures of products (**7**) and (**8**), depending on the polarity of the solvent employed. The ratio of **7** : **8** turned out to be 72 : 28 in non-polar PhH, 64 : 36 in ether and 50 : 50 in polar MeCN (Table 4, entries 3-5). This result provides evidence that the observed reaction of aromatic fluorine substitution with sodium phenolate probably involves ion pairs, but not the pure phenolate anion. For this reason, the looser ion pair formed by means of DBU displays higher reactivity.

To further verify our assumption, we synthesized benzyltriethylammonium phenolate by an exchange reaction of sodium phenolate with excess of benzyltriethylammonium chloride (TEBAC). The excess of TEBAC was sufficient to prevent introduction of sodium cation to the desired ammonium phenolate. When compound (**6**) was subjected to the action of [$NBnEt_3$][OPh] (1 eq.), either at room or at cold temperatures, a complex mixture of unidentified byproducts, together with **7** and **8**, was formed. For this reason, and due to the high reactivity of this ammonium salt, further experiments were performed with a less-than-equivalent quantity of reagent at low temperature. It was demonstrated that the reaction of compound (**6**) with 0.45 eq. of [$NBnEt_3$][OPh] in Et_2O gave compounds (**7**) and (**8**) in a ratio of 28 : 13 (Table 4, entry 6), while reaction with 0.3 mole of [$NBnEt_3$][OPh] in MeCN resulted in the formation of equal amounts of products (**7**) and (**8**) (Table 4, entry 7). This result, in comparison with the reaction with sodium phenolate, shows that cation has some sort of influence on the reaction ability of the phenolate anion.

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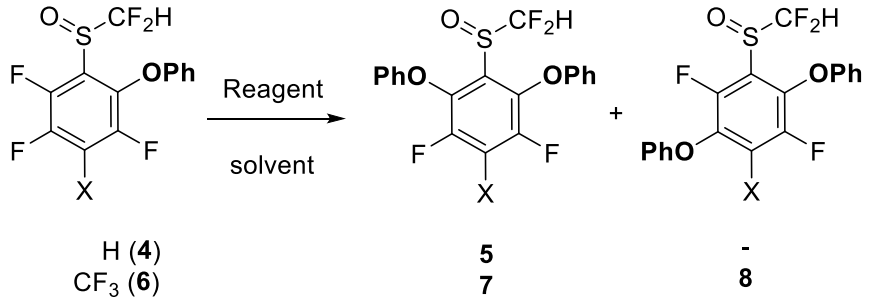


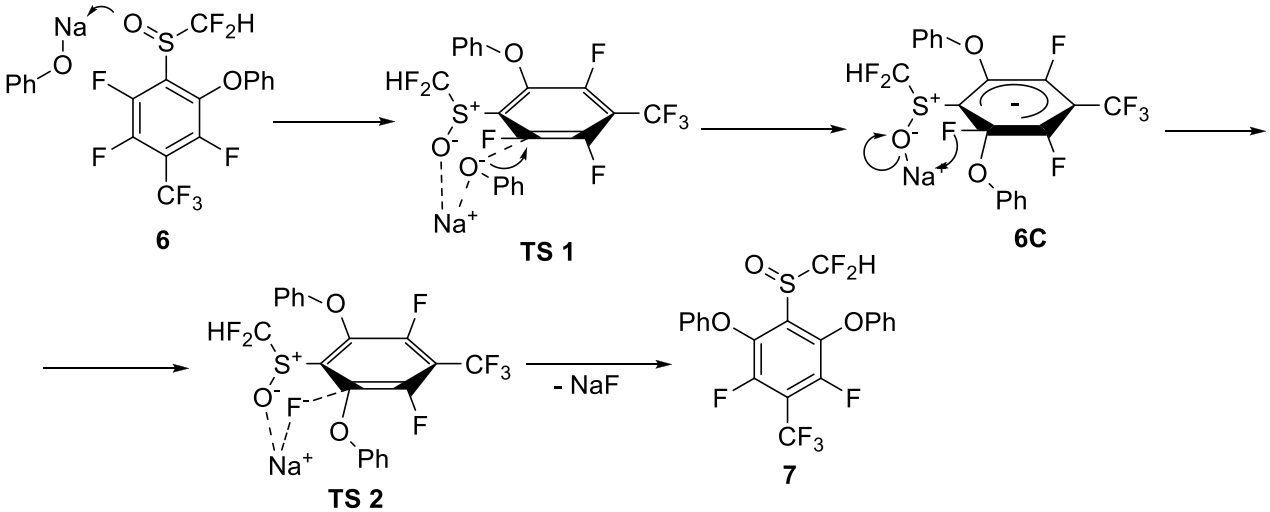
Scheme 8

Table 4. Reaction of sulfinyl benzenes (**4**) and (**6**) with ammonium phenolates

Entry	Substrate	Reagent (equiv.)	Solvent	T, °C	Time, h	NMR ^{19}F ratio
1	**4**	PhOH/DBU (1)	PhH	60	10	**4** : **5** = - : 100
2	**4**	PhOH/DBU (1)	MeCN	60	2.5	**4** : **5** = - : 100
3	**6**	PhOH/DBU (1)	PhH	25	4	**6 : 7 : 8** = - : 72 : 28
4	**6**	PhOH/DBU (1)	Et_2O	25	1	**6 : 7 : 8** = - : 64 : 36
5	**6**	PhOH/DBU (1)	MeCN	30	0.5	**6** : **7 : 8** = - : 50 : 50
6	**6**	$BnEt_3N^+PhO^-$ (0.45)	Et_2O	-25	1	**6 : 7 : 8** = 58 : 28 : 13
7	**6**	$BnEt_3N^+PhO^-$ (0.3)	MeCN	-30	0.5	**6** : **7 : 8** = 72 : 14 : 14

Possible mechanism for the reaction of polyfluorinated sulfinylbenzenes and sodium phenolate

We supposed that the selective formation of compound (**7**) in the reaction of **2** with sodium phenolate in ether (Table 2, entry 4) might be explained by a specific interaction between the reagents in non-polar solvents through coordination of the sodium atom with the oxygen atom of the difluoromethylsulfinyl group, according to Scheme 9 below. Such an association would promote the attack of the carbon atom in position 6 of compound (**6**) by the phenolate ion, with the formation of the sigma-complex (**6C**). The carbon-fluorine bond is then cleaved to give compound (**7**)**,** and sodium fluoride is formed and precipitates out. The analogous schemes as possible explanations were suggested by various researchers to describe the reactivity of pentafluoropyridine and pentafluoronitrobenzene.[21,22]



Scheme 9. Possible mechanism for the reaction of polyfluorinated sulfinylbenzene (**6**) and sodium phenolate.

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Compared to sulfinylbenzenes (**1**) and (**2**), the behavior of compound (**3**) in reactions with sodium phenolate is obviously more complicated, if only because there are two polyfluoroaromatic rings and two sulfinyl groups capable of reactions. At the same time, the solvent polarity also determines the direction of the transformations of compound **3**.

As the polarity of benzene is low, the dissociation of sodium phenolate is hardly possible. It is more likely that sodium phenolate coordinates with the oxygen atoms of the sulfinyl groups of **3** which is analogous to the way it is presented in Scheme 9. The difluoromethylsulfinyl group seems to be less hindered and, therefore, preferable for coordination than the diarylsulfinyl group. For this reason, the *para*-position of structure **3** likely becomes inaccessible for the phenolate ion to attack, and nucleophilic attack on the adjacent carbon atom would, therefore, seem to be the most natural way. The substituted products thus formed are reduced by acetyl chloride to give compounds **13**, **14** and **15**, respectively.

On the other hand, a polar solvent such as MeCN likely promotes the dissociation of sodium phenolate so that the phenolate ion displaces the fluorine atom from the para-position of compound **3**.

Another observed direction of the process was the attack of the phenolate ion at the carbon atom bonded to the sulfinyl group (ipso attack). In this case, the sulfinyl group acts as a good leaving group. As a result of this process, the C-S bond is cleaved and a C-OPh bond is formed. The products derived from compound **3** by this method are reduced by acetyl chloride to give compounds **11** and **12**, respectively. Substitution of the sulfinyl group by the action of hydroxy anion in reactions of aromatic compounds containing strong electron withdrawing NO_2-group in the para-position, has also been previously described.[23]

Conclusions

Phenolate ion reacts with 4-substituted-[(difluoromethyl)sulfinyl]tetrafluorobenzenes mainly by the mechanism of nucleophilic aromatic substitution. In the examples considered in this paper, mixtures of the starting sulfoxide, as well as mono- and disubstituted products, were obtained. The direction of the process depended on the structure of the substrate, the phenolate-salt cation, and the polarity of the solvent. In nonpolar solvents such as benzene and diethyl ether, the main route of the reaction of difluoromethyl aryl sulfoxides and sodium phenolate is substitution of the fluorine atom adjacent to the difluoromethylsulfinyl group. This process is likely facilitated by the coordination of the sodium cation of the reagent with the oxygen atom of the (difluoromethyl)sulfinyl group.

For compound **3** in polar MeCN, an unexpected direction of the process associated with the replacement of the sulfoxide function with the phenoxy group was also found, apparently the result of an ipso-attack.

Experimental Section

General. The NMR spectra of reaction mixtures or individual compounds were recorded on Bruker AV-300 [300.13 (^{1}H) MHz, 282.40 (^{19}F) MHz, 75.47 (^{13}C)], Bruker AV-400 [400.13 (^{1}H) MHz, 100.61 (^{13}C) MHz], Bruker AV-600 [600.30 (^{1}H) MHz, 564.84 (^{19}F) MHz, 150.95 (^{13}C) MHz] or Bruker DRX-500 [500.13 (^{1}H) MHz, 125.76 (^{13}C) MHz] spectrometers for solutions of samples in CCl_4 : $CDCl_3$ 4:1 v/v [for ^{19}F], $CDCl_3$ [for ^{1}H and ^{13}C] or CD_3CN [for ^{1}H]. NMR coupling constants (*J*) were measured in Hertz (Hz). IR spectra were recorded on a Bruker Vector 22 spectrophotometer from pellets with KBr for solids and from films for liquid samples. UV spectra were obtained on a Hewlett Packard 8453 spectrophotometer from solutions in ethanol. The molecular mass

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and elemental composition were determined from high resolution mass spectra taken on a Thermo Electron Corporation DFS instrument (ionizing electrons energy 70 eV). GC-MS spectra were measured on a Hewlett-Packard G1081A instrument equipped with a gas chromatograph HP 5890 Series II and a mass-selective detector HP 5971 (EI, 70 eV), capillary column HP-5 (5% of diphenyl-, 95% dimethylsiloxane) 30 m × 0.25 mm × 0.25 μm, carrier gas helium, flow rate 1 mL/min. Injector temperature 280 °C, ion source temperature 173 °C. Scanning rate 1.2 scan/s in mass region 30–650 a.u.m. Analytic GLC was carried out on a Hewlett Packard 5980 chromatograph, equipped with a quartz capillary column HP-5 (stationary phase dimethyl diphenyl polysiloxane block copolymer), 30 m × 0.52 mm × 2.6 μm, and a thermal conductivity detector.

Materials. Starting compounds were widely used commercially available products of reagent grade and were purified in the usual manner whenever necessary prior to use. Sodium hydride was used as the commercially available product (CAS 7646-69-7) and wasn't purified. Solvents were purified as usual. 3-[(difluoromethyl)sulfinyl]-1,2,4,5-tetrafluorobenzene (**1**), (difluoromethyl)[2,3,5,6-tetrafluoro-4-(trifluoro-methyl)phenyl]sulfane (**16**), (difluoromethyl)[2,3,5,6-tetrafluoro-4-(perfluorophenylthio)phenyl]sulfane (**9**), were obtained according to our previous work.[24]

The studied (difluoromethylsulfinyl)tetrafluorobenzenes compounds (**1**-**3**) were synthesized from the corresponding sulfanes by the action of 100% nitric acid according to our previous work.[24] Compound (**3**) was used as a 1 : 1 mixture of diastereomers. Characteristic features of the ^{19}F NMR spectra of **1**-**3** are the presence of diastereotopic fluorine atoms in the CF_2H moiety, which showed bonding to an asymmetrical center represented by the sulfoxide function.

Quantum chemical calculations. Calculations of the electron structures for polyfluoroaryl sulfoxides were performed within restricted DFT theory with the B3LYP functional and 6-31G(d) basis set. All calculations were done with the GAMESS[25] package. Stationary potential energy surface points were located and their types and interrelationships were determined by the normal vibrations analysis. The influence of polar media was taken into account within the polarizable continuum model (PCM[26,27], SMD[28]), using built-in parameters for benzene, acetonitrile and diethyl ether. Molecular-orbital and molecular-structure images were constructed by MOLDEN.[29]

Preparation of 4-substituted-[(difluoromethyl)sulfinyl]tetrafluorobenzenes

General procedure. Fuming nitric acid was added to the sulfane with stirring at room temperature. The reaction mixture was stirred at 50 ^{o}C for 3 days. The resulting solution was dissolved in 300 mL of solvent [$CHCl_3$ in case of sulfane (**16**); CH_2Cl_2 in case of sulfane (**9**)], then 300 mL H_2O were added. To the resulting mixture, Na_2CO_3 was added until pH 8 was obtained. The organic layer was separated, dried using $MgSO_4$, and the solvent was evaporated to afford the desired [(difluoromethyl)sulfinyl]tetrafluorobenzene.

1-[(Difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (2). From the reaction of (difluoromethyl)[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]sulfane (**16**) (39.59 g, 131.90 mmol) and fuming nitric acid (138.53 g, 2.20 mol), compound (**2**) (39.43 g, purity by GLC 94 %) was obtained. The product was distilled (1 mm Hg) and two fractions, 1) 2.08 g (bp before 113 ^{o}C, purity by GLC 93 %), and 2) 34.01 g (bp 113-115 ^{o}C, purity by GLC 99 %), were obtained as colorless liquids with a combined yield of 85 %. When cooled to room temperature, the second fraction crystallized to a colorless solid. Mp 29-30 ^{o}C. IR (film, ν_{max}, cm^{-1}): 2991(vw) (CH), 2926(vw) (CH) 1651(w) (Ar_F), 1605(vw), 1487(vs) (Ar_F), 1421(w), 1396(vw), 1327(vs) (CF_3), 1281(w), 1259(w), 1188(m), 1157(s) (CF_3), 1126(s) (CF_3), 1082(s) (S=O), 987(vs) (CF), 935(m), 812 (vw), 787 (w), 771 (vw), 750 (vw), 715(m), 688(w), 658(w), 571(vw), 548(w), 509(w), 482(w), 457 (vw), 419(vw). UV, λ_{max}, nm (log ε): 288 (3.62). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ_H 6.85 (t, $^2J_{HF}$ 55, 1H, $CF_2\underline{H}$) ppm. ^{13}C NMR (100.61 MHz,

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$CDCl_3$): δ_C 114.8 (qt, $^2J_{CF}$ 35, $^2J_{CF}$ 12, C-(4)), 120.0 (ddt, $^1J_{CF}$ 295, $^1J_{CF}$ 287, $^4J_{CF}$ ~3.5, $\underline{C}F_2H$), 120.2 (qm, $^1J_{CF}$ 276, $\underline{C}F_3$), 121.4 (td, $^2J_{CF}$ 15, $^3J_{CF}$ 3.5, C-(1)), 144.5 (dm, $^1J_{CF}$ 266, C-(3,5) or (2,6)), 145.8 (dm, $^1J_{CF}$ 258, C-(3,5) or (2,6)) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -137.2 (m, 2F, F-(3,5)), -136.6 (m, 2F, F-(2,6)), -118.9 (ddt, $^2J_{FF}$ 268, $^2J_{FH}$ 55, $^5J_{FF}$ 3.4, 1F, $C\underline{F}_2H$), -116.1 (ddt, $^2J_{FF}$ 268, $^2J_{FH}$ 55, $^5J_{FF}$ 5.6, 1F, $C\underline{F}_2H$), -58.0 (t, $^4J_{FF}$ 22, 3F, $C\underline{F}_3$) ppm. Anal. calcd for C_8HF_9OS, %: C 30.39; H 0.32; F 54.09; S 10.14; m/z 315.9599. Found, %: C 30.49; H 0.30; F 54.05; S 10.10; m/z 315.9608.

1-[(Difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-[(perfluorophenyl)sulfinyl]benzene (3). From fuming nitric acid (107.60 g, 1.71 mol) and (difluoromethyl){2,3,5,6-tetrafluoro-4-[(perfluorophenyl)thio]phenyl}sulfane **9** (24.30 g, 56.48 mmol) compound **3** (24.97 g) was obtained as mixture of diastereomeres in ratio 1:1. Yield 96 %. Colorless solid, mp 86.3 (decomp.). IR (KBr, ν_{max}, cm^{-1}): 2926(w) (CH), 2854(w) (CH), 1641(m) (Ar_F), 1498(vs) (Ar_F), 1475(vs) (Ar_F), 1396(w), 1331(vw), 1292(m), 1275(m), 1250(s), 1109(vs) (S=O), 1022(w), 984(s) (CF), 775(w), 725(vw), 634(w), 608(w), 494(m), 447(w). UV, λ_{max}, nm (log ε): 237 (4.52), 274 (4.26). ^{1}H NMR (CD_3CN, 600.30 MHz): δ_H 7.03 (t, $^2J_{HF}$ 54.1, 1H, $CF_2\underline{H}$ – one of diast.). 7.04 (t, $^2J_{HF}$ 54.1, 1H, $CF_2\underline{H}$ – one of diast.) ppm; $^{13}C\{^{19}F\}$ NMR (CD_3CN, 150.95 MHz): δ_C (117.9, 118.0, C-(1')), 118.5 ($\underline{C}HF_2$), (121.2, 121.3, C-(1)), (127.8, 127.8, C-(4)), 139.2 (C-(3',5')), (145.3, 145.3, C-(3,5)), (145.6, 145.6, C-(4')), (146.1, 146.1, C-(2',6')), (146.5, 146.5, C-(2,6)) ppm; ^{19}F NMR [CD_3CN, 564.84 MHz]: δ_F (-159.3, m, 4F, F-(3',5')), (-146.3 (tt, $^3J_{CF}$ 20.0, $^4J_{CF}$ 5.7, 1F, F-(4') – one of diast.), (-146.2 (tt, $^3J_{CF}$ 20.0, $^4J_{CF}$ 5.5, 1F, F-(4') – one of diast.), (-139.4 (m, 2F, F-(2',6' or 3,5) – one of diast.), (-139.2 (m, 4F, F-(2',6') or F-(3,5)), -138.9 (m, 2F, F-(2',6' or 3,5) – one of diast), (-136.5 (m, 4F, F-(2,6)), -119.2 (ddt, $^2J_{FF}$ 262.7, $^2J_{FH}$ 54.3, $^5J_{FF}$ 6.3, 1F, $C\underline{F}_2H$ - one of the diast.), -119.1 (ddt, $^2J_{FF}$ 262.5, $^2J_{FH}$ 54.3, $^5J_{FF}$ 6.6, 1F, $C\underline{F}_2H$ - one of the diast.), -117.7 (ddt, $^2J_{FF}$ 262.7, $^2J_{FH}$ 54.1, $^5J_{FF}$ 6.1, 1F, $C\underline{F}_2H$ - one of the diast.), -117.6 (ddt, $^2J_{FF}$ 262.5, $^2J_{FH}$ 54.1, $^5J_{FF}$ 6.1, 1F, $C\underline{F}_2H$ - one of the diast.) ppm. Anal. calcd for $C_{13}HF_{11}O_2S_2$, %: C 33.78; H 0.22; F 45.21; S 13.87; m/z 461.9237. Found, %: C 33.99; H 0.25; F 45.15; S 13.96; m/z 461.9234.

Reactions of sulfinylbenzenes (**1**) **and** (**2**) **with sodium phenolate**

General procedure. The weighed portion of PhOH was dissolved in the appropriate volume of the dried solvent in argon (Ar) atmosphere. Then a ca. 1M phenol solution was added to stirred ca. 1M sodium hydride suspension and, after termination of gas evolution, the obtained suspension was added dropwise to a ca. 0.5 M solution of compound (**1**) or (**2**) with stirring in Ar atmosphere. The obtained reaction mixture was stirred at the indicated temperature for the indicated time. At the end of the reaction the solvent was evaporated under the reduced pressure and the residue was dissolved in $CHCl_3$, washed with water and dried using $MgSO_4$. Then solution was filtered, the solvent was evaporated off under reduced pressure, and the residue was characterized by ^{1}H and ^{19}F NMR spectroscopy and GC-MS.

3-[(Difluoromethyl)sulfinyl]-1,2,5-trifluoro-4-phenoxybenzene (**4**). From sulfoxide (**1**) (3.70 g, 14.91 mmol) and PhOH (1.60 g, 17.00 mmol) in PhH, a mixture of sulfinylbenzenes (4.44 g, ratio of **1** : **4** : **5** = 19 : 58 : 23) was obtained. Recrystallization from a mixture of hexane-PhH (v/v = 3:1) at -20 °C gave 3.62 g of the solid. Sublimation at 51-65 °C (1 Torr) afforded 0.30 g of compound (**1**) and at 91-94 °C (1 Torr) 2.05 g (43%) of compound (**4**). White solid. Mp 70-71 °C. IR (KBr, ν_{max}, cm^{-1}): 3061(w) (CH), 3010(w) (CH), 1605(w), 1593(w), 1491(vs) (Ar_F), 1427(m), 1362(w), 1329(vw), 1288(m), 1271(m), 1236(m), 1198(s) (CF), 1119(s) (CF), 1072(s) (S=O), 1022(w), 935(s), 876(w), 808(w), 748(m), 710(w), 688(m), 673(w), 544(w), 486(w), 465(w), 442(w). UV, λ_{max}, nm (log ε): 291 (3.72). ^{1}H NMR (CD_3CN, 400.13 MHz): δ_H 6.97 (m, 2H, H-(2',6')), 7.06 (ddd, $^2J_{HF}$ 55.3, $^2J_{HF}$ 54.1, $^5J_{HF}$ 0.8, 1H, $CF_2\underline{H}$), 7.15 (tt, $^3J_{HH}$ ~7, $^4J_{HH}$ ~1, 1H, H-(4')), 7.36 (m, 2H, H-(3',5')), 7.64 (td, $^3J_{HF}$ 10, $^4J_{HF}$ 7.4, 1H, H-(1)) ppm; ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ_C 111.9 (t, $^2J_{CF}$ 22.9, C-(6)), 115.6 (C-(2',6')), 120.3 (ddd, $^1J_{CF}$ 291, $^1J_{CF}$ 284, $^4J_{CF}$ 5, $\underline{C}F_2H$), 123.4 (dd, $^2J_{CF}$ 14, $^3J_{CF}$ 7.5, C-(3)), 124.2 (C-(4')), 130.0 (C-(3',5')), 138.5 (ddd, $^2J_{CF}$ 14.3, $^3J_{CF}$ ~3.5, $^4J_{CF}$ ~3.5, C-(4)), 146.1 (ddd, $^1J_{CF}$ 257, $^2J_{CF}$ 14.9, $^4J_{CF}$ ~4, C-(2)), 147.1 (ddd, $^1J_{CF}$ 255, $^2J_{CF}$ 14, $^3J_{CF}$ 10,

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C-(1)), 150.7 (ddd, $^{1}J_{CF}$ 257, $^{3}J_{CF}$ 8.4, $^{4}J_{CF}$ ~3.5, C-(5)), 157.4 (C-(1')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.4 MHz]: δ_F -139.0 (m, 1F, F-(2)), -134.9 (ddd, $^{3}J_{FF}$ 22, $^{3}J_{HF}$ 10, $^{4}J_{FF}$ 1.5, 1F, F-(1)), -125.6 (dd, $^{5}J_{FF}$ 14.4, $^{3}J_{HF}$ 10, 1F, F-(5)), -119.9 (ddd, $^{2}J_{FF}$ 271, $^{2}J_{FH}$ 56, $^{5}J_{FF}$ 3.5, 1F, C$\underline{F}_2$H), -114.4 (ddd, $^{2}J_{FF}$ 270, $^{2}J_{FH}$ 54, $^{5}J_{FF}$ 3.8, 1F, C$\underline{F}_2$H) ppm. Anal. calcd for $C_{13}H_7F_5O_2S$, %: C 48.45; H 2.19; F 29.48; S 9.95; m/z 322.0081. Found, %: C 48.42; H 2.22; F 29.30; S 10.03; m/z 322.0079.

Sulfoxide (**5**) (0.40 g, yield – 7 %) was obtained from the residue after sublimation by crystallization from hexane-PhH (v/v 3:1).

[{2-[(Difluoromethyl)sulfinyl]-4,6-difluoro-1,3-phenylene}bis(oxy)]dibenzene (**5**). Sulfoxide (**1**) (0.344 g, 1.386 mmol) and PhOH (0.266 g, 2.826 mmol) in MeCN gave 0.485 g of the solid. Following recrystallization, compound **5** (0.330 g, 60 %) was obtained as a white solid. Mp 113-114 °C (hexane : PhH 3:1 v/v). IR (KBr, ν_{max}, cm^{-1}): 3074(w) (CH), 3045(vw) (CH), 3018(vw) (CH), 1605(w), 1587(w), 1489(m) (Ar_F), 1468(vs) (Ar_F), 1416(w), 1348(w), 1327(vw), 1261(w), 1225(m), 1203(s), 1174(m), 1161(w), 1153(w), 1136(w), 1113(s) (S=O), 1093(m), 1068(m), 1024(w), 989(vw), 937(s), 899(w), 862(w), 804(w), 781(m), 750(m), 742(m), 729(w), 687(m), 565(vw), 546(w), 500(vw), 476(w), 463(vw). UV, λ_{max}, nm (log ε): 267 (3.56), 273 (3.60), 302 (3.86). ^{1}H NMR (CD_3CN, 400.13 MHz): δ_H 7.03 (m, 4H, H-(2',2'',6',6'')), 7.15 (tt, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 0.9, 2H, H-(4',4'')), 7.20 (dd, $^{2}J_{HF}$ 57, $^{2}J_{HF}$ 54.4, 1H, C$\underline{F}_2$H), 7.38 (m, 4H, H-(3',3'',5',5'')), 7.60 (t, $^{3}J_{HF}$ 10, 1H, H-(5)) ppm; ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ_C 111.8 (t, $^{2}J_{CF}$ 23.4, C-(5)), 115.9 (C-(2',2'',6',6'')), 120.3 (dd, $^{1}J_{CF}$ 290, $^{1}J_{CF}$ 282, C$\underline{F}_2$H), 124.5 (C-(4',4'')), 129.3 (d, $^{3}J_{CF}$ 7.2, C-(2)), 130.2 (C-(3',3'',5',5'')), 139.5 (dd, $^{2}J_{CF}$ 13, $^{4}J_{CF}$ 4, C-(1,3)), 151.7 (dd, $^{1}J_{CF}$ 257.3, $^{3}J_{CF}$ 9.7, C-(4,6)), 157.5 (C-(1',1'')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.4 MHz]: δ_F -124.7 (d, $^{3}J_{FH}$ 10, 2F, F-(4,6)), -120.0 (dd, $^{2}J_{FF}$ 272, $^{2}J_{FH}$ 57, 1F, C$\underline{F}_2$H), -113.54 (dd, $^{2}J_{FF}$ 272, $^{2}J_{FH}$ 54.4, 1F, C$\underline{F}_2$H) ppm. Anal. calcd for $C_{19}H_{12}F_4O_3S$, %: C 57.58; H 3.05; F 19.17; S 8.09; m/z 396.0438. Found, %: C 57.88; H 3.19; F 19.14; S 8.32; m/z 396.0441.

1-[(Difluoromethyl)sulfinyl]-2,3,5-trifluoro-6-phenoxy-4-(trifluoromethyl)benzene (**6**). From sulfoxide (**2**) (4.61 g, 14.58 mmol) and PhOH (1.55 g, 16.47 mmol) in PhH, a mixture of sulfinylbenzenes (5.57 g, ratio of **2** : **6** : **7** = 18 : 56 : 25) was obtained. Recrystallization from a mixture of hexane-PhH (v/v = 3:1) followed by cooling to -20 °C gave 4.25 g of the solid. Sulfinylbenzene (**2**) was separated by sublimation at 71-75 °C (1.0 Torr) and compound (**6**) (2.49 g, 39 %) was isolated by sublimation at 97-100 °C (1.0 Torr) as a white solid. Mp 69-70°C. IR (KBr, ν_{max}, cm^{-1}): 3068(vw) (CH), 2999(vw) (CH), 1635(w) (Ar_F), 1597(w), 1473(vs) (Ar_F), 1377(w), 1325(s) (CF_3), 1279(w), 1254(w), 1192(s) (CF), 1163(s) (CF), 1153(s) (CF_3), 1124(s) (CF_3), 1111(s) (S=O), 1076(m), 1026(w), 985(s) (CF), 935(m), 887(vw), 822(w), 783(vw), 764(w), 746(m), 725(w), 687(m), 661(w), 498(w), 473(vw). UV, λ_{max}, nm (log ε): 273 (3.53), 300 (3.71).

^{1}H NMR (CD_3CN, 400.13 MHz): δ_H 7.02 (m, 2H, H-(2',6')), 7.05 (t, $^{2}J_{HF}$ 54.1, 1H, $CF_2\underline{H}$), 7.18 (tt, $^{3}J_{HH}$ 7.4, $^{4}J_{H\mathbf{H}}$ 0.9, 1H, H-(4')), 7.38 (m, 2H, H-(3',5')) ppm; ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ_C 114.7 (qt, $^{2}J_{CF}$ 35, $^{2}J_{CF}$ 13, C-(4)), 115.7 (C-(2',6')), 120.3 (ddd, $^{1}J_{CF}$ 292, $^{1}J_{CF}$ 287, $^{4}J_{CF}$ 4, C$\underline{F}_2$H), 120.4 (q, $^{1}J_{CF}$ 276, C$\underline{F}_3$), 124.7 (C-(4')), 126.9 (dd, $^{2}J_{CF}$ 14, $^{3}J_{CF}$ ~6.5, C-(1)), 130.2 (C-(3',5')), 139.2 (ddd, $^{2}J_{CF}$ 14.5, $^{3}J_{CF}$ ~4, $^{4}J_{CF}$ ~4, C-(6)), 145.1 (dd, $^{1}J_{CF}$ 267.4, $^{2}J_{CF}$ 16, C-(2)), 146.7 (ddd, $^{1}J_{CF}$ 259, $^{2}J_{CF}$ 14.7, $^{3}J_{CF}$ ~4.5, C-(3)), 148.7 (d, $^{1}J_{CF}$ 267.8, C-(5)), 157.2 (C-(1')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -137.2 (ddt, $^{3}J_{FF}$ 22, $^{5}J_{FF}$ 15, $^{5}J_{F\text{-}C\underline{F}2H}$ ~4, 1F, F-(2)), -136.5 (dqd, $^{3}J_{FF}$ 22, $^{4}J_{F\text{-}C\underline{F}3}$ 22, $^{4}J_{FF}$ 3.8, 1F, F-(3)), -127.1 (qdd, $^{4}J_{F\text{-}C\underline{F}3}$ 22, $^{5}J_{FF}$ ~15, $^{4}J_{FF}$ 3.8, F-(5)), -119.4 (ddd, $^{2}J_{FF}$ 269.7, $^{2}J_{FH}$ 55.9, $^{5}J_{FF}$ 3.0, 1F, C$\underline{F}_2$H), -114.4 (ddd, $^{2}J_{FF}$ 269.7, $^{2}J_{FH}$ 54.4, $^{5}J_{FF}$ 4.5, 1F, C$\underline{F}_2$H), -58.0 (t, $^{4}J_{FF}$ 22, 3F, C$\underline{F}_3$) ppm. Anal. calcd for $C_{14}H_6F_8O_2S$, %: C 43.09; H 1.55; F 38.95; S 8.22; m/z 389.9955. Found, %: C 43.27; H 1.62; F 39.07; S 8.42; m/z 389.9952.

Sulfoxide (**7**) (0.48 g, yield = 6 %) was obtained from the residue following sublimation by crystallization from hexane.

[{2-[(difluoromethyl)sulfinyl]-4,6-difluoro-5-(trifluoromethyl)-1,3-phenylene}bis(oxy)]dibenzene (**7**). Sulfoxide (**2**) (1.56 g, 4.93 mmol) and PhOH (0.95 g, 10.09 mmol) in Et_2O gave 2.09 g of crude product. Following recrystallization, sulfinylbenzene (**7**) (1.70 g, 74 %) was obtained as a white solid. Mp 110-111 °C

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(hexane). IR (KBr, ν_{max}, cm^{-1}): 3064 (vw) (CH), 3045 (vw) (CH), 3020 (vw) (CH), 1620 (w), 1605 (w) (Ar_F), 1595 (m), 1491 (s) (Ar_F), 1466 (vs) (Ar_F), 1371 (w), 1317 (vs) (CF_3), 1252 (m), 1198 (s) (CF), 1165 (s) (CF_3), 1142 (s) (CF), 1109 (s) (S=O), 1072 (m), 1024 (w), 989 (s) (CF), 935 (m), 843 (vw), 754 (m), 723 (vw), 688 (m), 565 (w), 490 (w). UV, λ_{max}, nm (log ε): 266 (3.50), 273 (3.51), 312 (3.85). ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 7.08 (m, 4H, H-(2',2'',6',6'')), 7.18 (tt, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.0, 2H, H-(4',4'')), 7.19 (dd, $^2J_{HF}$ 56, $^2J_{HF}$ 54, 1H, $CF_2\underline{H}$), 7.40 (m, 4H, H-(3',3'',5',5'')) ppm; ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ_C 114.8 (qt, $^2J_{CF}$ 34, $^2J_{CF}$ 13, C-(5)), 115.9 (C-(2',2'',6',6'')), 120.6 (q, $^1J_{CF}$ 276, $\underline{C}F_3$), 120.7 (dd, $^1J_{CF}$ 291.4, $^1J_{CF}$ 283.4, $\underline{C}F_2H$), 124.5 (C-(4',4'')), 130.2 (C-(3',3'',5',5'')), 132.9 (d, $^3J_{CF}$ 7.0, C-(2)), 140.1 (dd, $^2J_{CF}$ 13.6, $^4J_{CF}$ 4.6, C-(1,3)), 149.5 (d, $^1J_{CF}$ 268.5, C-(4,6)), 157.5 (C-(1',1'')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -126.2 (q, $^4J_{FF}$ 22.7, 2F, F-(4,6)), -119.7 (dd, $^2J_{FF}$ 272, $^2J_{FH}$ 56, 1F, $C\underline{F}_2H$), -112.9 (dd, $^2J_{FF}$ 272, $^2J_{FH}$ 54, 1F, $C\underline{F}_2H$), -57.9 (t, $^4J_{FF}$ 22.7, 3F, $C\underline{F}_3$) ppm. Anal. calcd for $C_{20}H_{11}F_7O_3S$, %: C 51.73; H 2.39; F 28.61; S 6.90; m/z 464.0312. Found, %: C 51.49; H 2.46; F 28.65; S 6.96; m/z 464.0319.

[{2-[(difluoromethyl)sulfinyl]-3,6-difluoro-5-(trifluoromethyl)-1,4-phenylene}bis(oxy)]dibenzene (8). Sulfoxide **2** (1.79 g, 5.66 mmol) and PhOH (1.22 g, 12.96 mmol) in MeCN gave 2.09 g of solid. A mixture of isomers (**7**) and (**8**) (1.57 g, 60 %) in the ratio 58 : 42 was obtained by recrystallization from hexane. ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 7.02 (ddd, $^2J_{HF}$ 55, $^2J_{HF}$ 54, $^5J_{HF}$ ~1, 1H, $CF_2\underline{H}$), ~7.07 (m, 2H, H_{1Ph}-(2,6), 7.09 (m, 2H, H_{4Ph}-(2,6), ~7.18 (1H, H_{1Ph}-(4)), 7.20 (tt, $^3J_{HH}$ 7.4, $^4J_{HH}$ ~1.0, 1H, H_{4Ph}-(4), ~7.40 (m, 4H, $H_{1Ph\ and\ 4Ph}$-(3,5)) ppm; ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ_C 115.2 ($C_{1Ph\ or\ 4Ph}$-(2,6)), 115.7 ($C_{1Ph\ or\ 4Ph}$-(2,6)), 119.7 (qdd, $^2J_{CF}$ 33, $^2J_{CF}$ 10.5, $^3J_{CF}$ ~2.2, C-(5)), 120.4 (ddd, $^1J_{CF}$ 292, $^1J_{CF}$ 286, $^4J_{CF}$ ~5, $\underline{C}F_2H$), 121.2 (qm, $^1J_{CF}$ 276, $\underline{C}F_3$), 124.0 ($C_{1Ph\ or\ 4Ph}$-(4)), 124.5 ($C_{1Ph\ or\ 4Ph}$-(4)), 126.7 (dd, $^2J_{CF}$ 15.7, $^3J_{CF}$ 6.9, C-(2)), 130.0 ($C_{1Ph\ or\ 4Ph}$-(3,5)), 130.1 ($C_{1Ph\ or\ 4Ph}$-(3,5)), 138.8 (d, $^2J_{CF}$ ~15.5, C-(4)), 139.9 (dd, $^2J_{CF}$ ~19, $^3J_{CF}$ 4, C-(1)), 149.3 (dd, $^1J_{CF}$ 267, $^4J_{CF}$ ~2, C-(6)), 151.3 (dd, $^1J_{CF}$ 260, $^4J_{CF}$ 3.6, C-(3)), 157.3 (d, $^4J_{CF}$ 1.9, C-(1') or (1'')), 157.4 (d, $^4J_{CF}$ 1.7, C-(1') or C-(1'')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -127.6 (qd, $^4J_{FF}$ 27, $^5J_{FF}$ 15.1, 1F, F-(6)), -126.9 (dt, $^5J_{FF}$ 15.1, $^5J_{FF}$ 4.5, 1F, F-(3)), -119.7 (ddd, $^2J_{FF}$ 268.2, $^2J_{FH}$ 55, $^5J_{FF}$ 4.5, 1F, $C\underline{F}_2H$), -114.9 (ddd, $^2J_{FF}$ 268.2, $^2J_{FH}$ 54, $^5J_{FF}$ 4.5, 1F, $C\underline{F}_2H$), -57.9 (d, $^4J_{FF}$ 27, 3F, $C\underline{F}_3$) ppm. Anal. calcd for **7** + **8** ($C_{20}H_{11}F_7O_3S_1$), %: C 51.73; H 2.39; F 28.61; S 6.90; m/z 464.0312. Found, %: C 51.73; H 2.38; F 28.79; S 6.80; m/z 464.0317.

Reduction of 1-[(difluoromethyl)sulfinyl]-2,3,5,6-tetrafluoro-4-[(perfluorophenyl)sulfinyl]benzene (3) to (difluoromethyl)[2,3,5,6-tetrafluoro-4-([perfluorophenylthio)]phenyl)sulfane (9) by acetyl chloride. Acetyl chloride (8.19 g, 104.33 mmol) was added to compound **3** (1.26 g, 2.73 mmol) and the resulted solution was refluxed during 5 h. The excess of acetyl chloride was then evaporated off and the residue was dissolved in water (30 mL) to form a precipitate, which was filtered off to give 1.08 g (92 %) of the desired sulfane (**9**). The analytical characteristics of sulfane **9** correspond to literature data.[Error! Bookmark not defined.]

Reaction of compound (3) with sodium phenolate with subsequent reduction of the resulted mixture by acetyl chloride. General procedure. The weighed portion of PhOH was dissolved in the appropriate volume of the dried solvent in Ar atmosphere. Then phenol solution was added to stirred sodium hydride suspension and, after termination of gas evolution, the obtained suspension was added dropwise to a ca. 0.5 M solution of compound (**3**) with stirring in Ar atmosphere. The obtained reaction mixture was refluxed with stirring for 2 h. The solvent from the resulted mixture was evaporated, then the residue was dissolved in 50 mL $CHCl_3$. The solution was washed with water, and the organic layer was separated and dried using $MgSO_4$. Then the solvent was evaporated, and toluene and acetyl chloride were added to the crude residue. The resulting solution was refluxed for 480 h to achieve, according ^{19}F NMR spectroscopy, full conversion of sulfoxides to the corresponding sulfanes. Then, the excess of acetyl chloride and toluene was evaporated. The residue thus obtained was treated with $CHCl_3$ (50 mL) and water (50 mL). Sodium carbonate was added to the resulting mixture until pH 8. The organic layer was separated, dried using $MgSO_4$, and the solvent was evaporated off

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under reduced pressure, and the product was analyzed by means of GC-MS and quantitative ^{19}F NMR spectroscopy with fluorobenzene (PhF) as internal standard.

In MeCN solution. Phenol (1.48 g, 15.73 mmol) in MeCN (15 mL) was treated with a suspension of NaH (0.61 g, 15.25 mmol) in MeCN (15 mL), and the resulting suspension was added to a solution of compound **3** (6.81 g, 14.73 mmol) in MeCN (30 mL), as described above, to give 7.94 g of the crude product, which was then subjected to the action of acetyl chloride (34.05 g, 0.434 mol) in the presence of toluene (5.44 g, 59.04 mmol) to afford a 7.15 g of mixture of sulfanes **9** : **10** : **11** : **12** : **13** in the ratio 29 : 31 : 16 : 18 : 6 (by ^{19}F NMR), respectively. Thus, yields of the products were 24% (**9**), 26% (**10**), 13% (**11**), 15% (**12**), and 5% (**13**).

In benzene solution. Phenol (1.35 g, 14.34 mmol) in PhH (15 mL) was treated with a suspension of NaH (0.57 g, 14.25 mmol) in PhH (15 mL), and the resulting suspension was added to solution of compound **3** (6.29 g, 13.61 mmol) in PhH (27 mL), as described above, to give 7.23 g of the crude product, which was then subjected to the action of acetyl chloride (52.88 g, 0.674 mol) in the presence of toluene (5.06 g, 54.92 mmol) to afford a 7.01 g sulfanes mixture of **9** : **13** : **14** : **15** in a ratio of 23 : 50 : 15 : 11 (by ^{19}F NMR), respectively. Thus, yields of the products were 19% (**9**), 40% (**13**), 12% (**14**), and 9% (**15**).

(Difluoromethyl){2,3,5,6-tetrafluoro-4-[(2,3,5,6-tetrafluoro-4-phenoxyphenyl)thio]phenyl}sulfane (10). Mp 68-71 ^{o}C. IR (KBr, ν_{max}, cm^{-1}): 3064(vw) (CH), 3045(vw) (CH), 1635 (w) (Ar_F), 1624 (vw), 1593 (m), 1483 (vs) (Ar_F), 1471 (vs) (Ar_F), 1437 (m), 1408 (w), 1387 (w), 1313 (m), 1296 (w), 1252 (w), 1207 (s) (CF), 1196 (m), 1169 (w), 1149 (vw), 1105 (m), 1090 (m), 1074 (m), 1059 (m), 1047 (m), 1024 (w), 980 (s) (CF), 964 (s) (CF), 868 (m), 812 (m), 781 (w), 744 (m), 723 (w), 687 (m), 631 (w), 619 (w), 588 (vw), 496 (w). UV, λ_{max}, nm (log ε): 205 (4.52), 259 (4.23), 266 (4.23), 273 (4.25). ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 7.05 (m, 2H, H-(2'',6'')), 7.11 (t, $^2J_{HF}$ 55.2, 1H, $CF_2\underline{H}$), 7.17 (br.t, $^3J_{HH}$ 7.5, 1H, H-(4'')), 7.38 (m, 2H, H-(3'',5'')) ppm; ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ_C 105.5 (t, $^2J_{CF}$ 20.3, $\underline{C}$-(1')), 106.8 (tt, $^2J_{CF}$ 21, $^3J_{CF}$ ~3.5, $\underline{C}$-(1)), 115.7 (t, $^2J_{CF}$ 19.0, $\underline{C}$-(4)), 116.0 (C-(2'',6'')), 118.3 (t, $^1J_{CF}$ ~280.5, $\underline{C}F_2H$), 124.4 (C-(4'')), 130.1 (C-(3'',5'')), 136.2 (tt, $^2J_{CF}$ ~13, $^3J_{CF}$ ~3.5, (C-(4')), 142.0 (dm, $^1J_{CF}$ 255, C-(2',6') or (3',5')), 146.8 (dm, $^1J_{CF}$ 252, C-(2',6') or (3',5')), 147.8 (dm, $^1J_{CF}$ ~252, (C-(2,3,5,6)), 157.1 (C-(1'')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -153.2 (m, 2F, F-(3'',5'')), -133.4 (m, 2F, F-(2',6') or (3,5)), -133.2 (m, 2F, F-(2',6') or (3,5)), -130.5 (m, 2F, F-(2,6)), -92.0 (dt, $^2J_{FH}$ 55.9, $^5J_{FF}$ 4.5, 2F, $C\underline{F}_2H$) ppm. Anal. calcd for $C_{19}H_6F_{10}OS_2$, %: C 45.25; H 1.20; F 37.67; S 12.71; m/z 503.9695. Found, %: C 45.39; H 1.21; F 37.60; S 12.66; m/z 503.9691.

(Difluoromethyl)(2,3,5,6-tetrafluoro-4-phenoxyphenyl)sulfane (11). Mp 44-45. IR (KBr, ν_{max}, cm^{-1}): 3066 (vw) (CH), 2974 (vw) (CH), 1637 (w) (Ar_F), 1591 (m), 1491 (vs) (Ar_F), 1456 (m), 1406 (m), 1387 (vw), 1315 (m), 1288 (w), 1209 (s) (CF), 1163 (w), 1136 (vw), 1093 (m), 1078 (s) (CF), 1049 (s) (CF), 1001 (w), 976 (s), 904 (vw), 872 (m), 835 (vw), 816 (w), 771 (w), 750 (s) (CF), 731 (m), 692 (m), 669 (vw), 656 (vw), 604 (vw), 552 (vw), 484 (w), 465 (w). UV, λ_{max}, nm (log ε): 210 (4.32), 248 (3.97). ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 7.08 (m, 2H, H-(2',6')), 7.10 (t, $^1J_{HF}$ 55, 1H, $CF_2\underline{H}$), 7.19 (tt, $^3J_{HH}$ ~7, $^4J_{HH}$ 1, 1H, H-(4')), 7.40 (m, 2H, H-(3',5')) ppm; ^{13}C NMR (125.76 MHz, $CDCl_3$): δ_C 100.4 (tm, $^2J_{CF}$ ~21, C-(1)), 116.1 (C-(2',6')), 118.5 (t, $^1J_{CF}$ 280.0, $\underline{C}F_2H$), 124.4 (C-(4')), 130.1 (C-(3',5')), 137.0 (tt, $^2J_{CF}$ ~13, $^3J_{CF}$ ~4, C-(4)), 142.0 (dm, $^1J_{CF}$ 253, C-(3,5)), 148.8 (ddt, $^1J_{CF}$ 250, $^2J_{CF}$ ~12, $^3J_{CF}$ ~3.7, C-(2,6)), 157.0 (C-(1')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.4 MHz]: δ_F -153.1 (m, 2F, F-(3,5)), -131.7 (m, 2F, F-(2,6)), -92.5 (dt, $^1J_{FH}$ 56, $^4J_{FH}$ ~4, $C\underline{F}_2H$) ppm. Anal. calcd for $C_{13}H_6F_6OS$, %: C 48.16; H 1.87; F 35.16; S 9.89; m/z 324.0038. Found, %: C 47.86; H 1.96; F 35.19; S 9.93; m/z 324.0034.

Bis(2,3,5,6-tetrafluoro-4-phenoxyphenyl)sulfane (**12**). Mp 126-129 ^{o}C. IR (KBr, ν_{max}, cm^{-1}): 3078 (vw) (CH), 3064 (vw) (CH), 3045 (vw) (CH), 1593 (m), 1489 (vs) (Ar_F), 1400 (w), 1281 (vw). 1203 (s) (CF), 1169 (m), 1088 (m), 1074 (w), 1024 (vw), 978 (m), 868 (m), 744 (m), 687 (w), 496 (vw). UV, λ_{max}, nm (log ε): 254 (4.28), 258 (4.28), 265 (4.27), 272 (4.23). ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 7.05 (m, 4H, H-(2',2'',6',6'')), 7.17 (t, $^3J_{HH}$ 7.4, 2H, H-(4',4'')), 7.38 (m, 4H, H-(3',3'',5',5'')) ppm; ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ_C 106.8 (br.t, $^2J_{CF}$ ~20, C-(1)),

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115.9 (C-(2',2'',6',6'')), 124.3 (C-(4',4'')), 130.0 (C-(3',3'',5',5'')), 135.6 (t, $^{2}J_{CF}$ ~13, C-(4)), 141.9 (dd, $^{1}J_{CF}$ 255, $^{2}J_{CF}$ ~15, C-(3,5)), 147.8 (dd, $^{1}J_{CF}$ 250, $^{2}J_{CF}$ ~12, C-(2,6)), 157.0 (C-(1',1'')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.4 MHz]: δ_F -153.3 (m, 4F, F-(3,5)), -134.0 (m, 4F, F-(2,6)) ppm. Anal. calcd for $C_{24}H_{10}F_8O_2S$, %: C 56.04; H 1.96; F 29.55; S 6.23; m/z 514.0268. Found, %: C 55.98; H 1.94; F 29.73; S 6.33; m/z 514.0278.

(Difluoromethyl){2,3,5-trifluoro-4-[(perfluorophenyl)thio]-6-phenoxyphenyl}sulfane (13). Mp 64-67 °C. IR (KBr, ν_{max}, cm^{-1}): 3066 (vw) (CH), 2980 (vw) (CH), 2922 (vw) (CH), 1641 (w) (Ar_F), 1593 (w), 1516 (s) (Ar_F), 1493 (vs) (Ar_F), 1462 (vs) (Ar_F), 1379 (w), 1323 (m), 1294 (vw), 1248 (m), 1207 (s) (CF), 1169 (w), 1155 (vw), 1093 (m), 1066 (m), 1049 (m), 1026 (w), 1014 (w), 970 (s) (CF), 899 (vw), 864 (m), 829 (w), 808 (w), 787 (vw), 754 (s), 733 (w), 692 (w), 646 (w), 494 (w). UV, λ_{max}, nm (log ε): 208 (4.50), 211 (4.49), 215 (4.49), 275 (4.04). ^{1}H NMR (CD_3CN, 400.13 MHz): δ_H 6.86 (m, 2H, H-(2',6')), 7.07 (td, $^{2}J_{HF}$ 56, $^{5}J_{HF}$ ~0.5, 1H, $CF_2\underline{H}$), 7.12 (tt, $^{3}J_{HH}$ ~7.5, $^{4}J_{HH}$ ~1, 1H, H-(4')), 7.34 (m, 2H, H-(3',5')) ppm; ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ_C 105.8 (tm, $^{2}J_{CF}$ ~21, C_{C6F5}-(1)), 114.1 (dt, $^{2}J_{CF}$ ~16.5, $^{3}J_{CF}$ ~4.5, C-(1)), 114.3 (t, $^{2}J_{CF}$ ~20, C-(4)), 115.2 (C-(2',6')), 118.6 (td, $^{1}J_{CF}$ 280, $^{4}J_{CF}$ ~3, $\underline{C}F_2H$), 123.7 (C-(4')), 130.0 (C-(3',5')), 138.0 (dm, $^{1}J_{CF}$ 255, C_{C6F5}-(3,5)), 140.6 (dd, $^{2}J_{CF}$ 14, $^{3}J_{CF}$ 4, C-(6)), 142.7 (dtt, $^{1}J_{CF}$ 258, $^{2}J_{CF}$ ~13, $^{3}J_{CF}$ ~5, C_{C6F5}-(4)), 147.5 (dm, $^{1}J_{CF}$ 250, C_{C6F5}-(2,6)), 147.6 (ddd, $^{1}J_{CF}$ 253, $^{2}J_{CF}$ 16, $^{3}J_{CF}$ 4, C-(3 or 2)), 148.2 (ddd, $^{1}J_{CF}$ 252, $^{2}J_{CF}$ 15, $^{3}J_{CF}$ 4, C-(3 or 2)), 151.5 (ddd, $^{1}J_{CF}$ 254, $^{3}J_{CF}$ ~3, $^{4}J_{CF}$ ~3, C-(5)), 157.2 (C-(1')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -160.8 (m, 2F, F_{C6F5}-(3,5)), -150.9 (tt, $^{3}J_{FF}$ ~21, $^{4}J_{FF}$ ~4, 1F, F_{C6F5}-(4)), -132.9 (m, 2F, F_{C6F5}-(2,6)), -131.6 (ddt, $^{3}J_{FF}$ 24, $^{4}J_{FF}$ 3, $^{6}J_{FF}$ 3, 1F, F-(3)), -129.4 (ddt, $^{3}J_{FF}$ 24, $^{5}J_{FF}$ 12, $^{5}J_{FF}$ 5.3, 1F, F-(2)), -122.5 (dm, $^{5}J_{FF}$ 12, 1F, F-(5)), -92.3 (dd, $^{2}J_{FH}$ 57.4, $^{5}J_{FF}$ 5.3, 2F, $C\underline{F}_2H$) ppm. Anal. calcd for $C_{19}H_6F_{10}OS_2$, %: C 45.25; H 1.20; F 37.67; S 12.71; m/z 503.9695. Found, %: C 45.32; H 1.18; F 37.58; S 12.72; m/z 503.9686.

{3,5-difluoro-4-[(perfluorophenyl)thio]-2,6-diphenoxyphenyl}(difluoromethyl)sulfane (14). Mp 93 °C (decomp.). IR (KBr, ν_{max}, cm^{-1}): 3070 (vw) (CH), 3045 (vw) (CH), 2924 (vw) (CH), 1637 (w) (Ar_F), 1591 (m), 1562 (w), 1516 (s) (Ar_F), 1489 (vs) (Ar_F), 1443 (vs) (Ar_F), 1377 (w), 1363 (vw), 1319 (w), 1292 (w), 1236 (w), 1200 (vs) (CF), 1167 (m), 1092 (m), 1068 (m), 1039 (s) (CF), 1022 (w), 984 (m), 970 (s) (CF), 945 (w), 895 (vw), 862 (m), 850 (w), 829 (vw), 812 (w), 787 (vw), 754 (m), 739 (w), 698 (w), 685 (w), 648 (w), 559 (vw), 485 (w). UV, λ_{max}, nm (log ε): 204 (4.37), 275 (3.96). ^{1}H NMR (CD_3CN, 400.13 MHz): δ_H 6.91 (m, 4H, H-(2',2'',6',6'')), 7.12 (t, $^{3}J_{HH}$ 7.4, 2H, H-(4',4'')), 7.14 (t, $^{2}J_{HF}$ 57, 1H, $CF_2\underline{H}$), 7.35 (m, 4H, H-(3',3'',5',5'')) ppm; ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ_C 106.3 (tm, $^{2}J_{CF}$ ~21, C_{C6F5}-(1)), 113.5 (t, $^{2}J_{CF}$ 20, C-(4)), 115.2 (C-(2',2'',6',6'')), 119.1 (t, $^{1}J_{CF}$ 279, $\underline{C}F_2H$), 121.8 (t, $^{3}J_{CF}$ ~2, C-(1)), 123.6 (C-(4',4'')), 130.0 (C-(3',3'',5',5'')), 137.9 (dm, $^{1}J_{CF}$ 254, C_{C6F5}-(3,5)), 140.8 (dd, $^{2}J_{CF}$ 14, $^{4}J_{CF}$ 4, C-(2,6)), 142.4 (dtt, $^{1}J_{CF}$ 258, $^{2}J_{CF}$ 13.6, $^{3}J_{CF}$ ~5, C_{C6F5}-(4)), 147.2 (dm, $^{1}J_{CF}$ 250, C_{C6F5}-(2,6)), 152.6 (dd, $^{1}J_{CF}$ 254, $^{3}J_{CF}$ ~3.5, C-(3,5)), 157.1 (C-(1')) ppm; ^{19}F NMR [CCl_4, $CDCl_3$, 282.40 MHz]: δ_F -161.1 (m, 2F, F_{C6F5}-(3,5)), -151.5 (tt, $^{3}J_{FF}$ 20, $^{4}J_{FF}$ 3.0, 1F, F_{C6F5}-(4)), -133.4 (m, 2F, F_{C6F5}-(2,6)), -120.7 (t, $^{6}J_{FF}$ 3.0, 2F, F-(3,5)), -92.4 (d, $^{2}J_{FH}$ 58.2, 2F, $C\underline{F}_2H$) ppm. Anal. calcd for $C_{25}H_{11}F_9O_2S_2$, %: C 51.91; H 1.92; F 29.56; S 11.08; m/z 578.0051. Found, %: C 51.64; H 1.97; F 29.39; S 11.18; m/z 578.0048.

{2,5-difluoro-4-[(perfluorophenyl)thio]-3,6-diphenoxyphenyl}(difluoromethyl)sulfane (**15**). Mp 82 °C. IR (KBr, ν_{max}, cm^{-1}): 3066 (vw) (CH), 3043 (vw) (CH), 2955 (vw) (CH), 2924 (w) (CH), 2850 (vw) (CH), 1724 (vw), 1641 (w) (Ar_F), 1595 (m), 1518 (s) (Ar_F), 1487 (vs) (Ar_F), 1441 (vs) (Ar_F), 1371 (w), 1321 (m), 1292 (w), 1234 (m), 1209 (s) (CF), 1167 (m), 1153 (w), 1099 (m), 1070 (s) (CF), 1038 (m), 1024 (w), 972 (s) (CF), 943 (w), 891 (w), 862 (w), 839 (w), 800 (w), 752 (s), 721 (vw), 692 (w), 687 (w), 650 (w), 554 (vw), 484 (w), 426 (vw). UV, λ_{max}, nm (log ε): 267 (4.05), 275 (4.06), 285 (4.08). ^{1}H NMR (CD_3CN, 300.13 MHz): δ_H 6.77 (m, 2H, H_{3Ph}-(2,6)), 6.96 (m, 2H, H_{6Ph}-(2,6)), 7.04 (t, $^{2}J_{HF}$ 56, 1H, $CF_2\underline{H}$), 7.06 (t, $^{3}J_{HH}$ 7.4, 1H, H_{3Ph}-(4)), 7.13 (t, $^{3}J_{HH}$ 7.4, 1H, H_{6Ph}-(4)), 7.27 (m, 2H, H_{3Ph}-(3,5)), 7.37 (m, 2H, H_{6Ph}-(3,5)). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ_C 106.5 (tm, $^{2}J_{CF}$ ~20, C_{C6F5}-(1)), 113.1 (dd, $^{2}J_{CF}$ 19.7, $^{3}J_{CF}$ ~2, C-(1)), 114.3 ($C_{3Ph\ or\ 6Ph}$-(2,6)), 115.4 ($C_{3Ph\ or\ 6Ph}$-(2,6)), 118.7 (td, $^{1}J_{CF}$ 280, $^{4}J_{CF}$ ~3.5, $\underline{C}F_2H$), 120.8 (d, $^{4}J_{CF}$ ~18, C-(4)), 123.6 ($C_{3Ph\ or\ 6Ph}$-(4)), 123.7 ($C_{3Ph\ or\ 6Ph}$-(4)), 129.8 ($C_{3Ph\ or\ 6Ph}$-(3,5)), 130.0 ($C_{3Ph\ or\ 6Ph}$-(3,5)), 137.8 (dm, $^{1}J_{CF}$ 254, C_{C6F5}-(3,5)), 139.4 (dd, $^{2}J_{CF}$ 16, $^{3}J_{CF}$ ~2.5, $\underline{C}$(3)), 141.7 (dd, $^{2}J_{CF}$ 14.6, $^{4}J_{CF}$ ~2, $\underline{C}$(6)), 142.1 (dtt, $^{1}J_{CF}$

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258, $^{2}J_{CF}$ 13.5, $^{3}J_{CF}$ ~5, C_{C6F5}-(4)), 147.8 (dm, $^{1}J_{CF}$ 249, C_{C6F5}-(2,6)), 151.8 (dd, $^{1}J_{CF}$ 252.7, $^{4}J_{CF}$ 3.7, C(2) or C(5)), 153.0 (dd, $^{1}J_{CF}$ 253.4, $^{4}J_{CF}$ 3.5, C(2) or C(5)), 156.6 (d, $^{4}J_{CF}$ 1.4, $C_{3Ph\ or\ 6Ph}$-(1)), 157.4 (d, $^{4}J_{CF}$ 1.6, $C_{3Ph\ or\ 6Ph}$-(1)). ^{19}F NMR [CCl_4, $CDCl_3$, 282.4 MHz]: δ_F -161.6 (m, 2F, F(3',5')), -152.6 (tt, $^{3}J_{FF}$ 20.4, $^{4}J_{FF}$ 3.0, 1F, F(4')), -133.3 (m, 2F, F(2',6')), -122.0 (d, $^{5}J_{FF}$ 12.8, 1F, F-(5)), -119.0 (dt, $^{5}J_{FF}$ 12.8, $^{5}J_{FF}$ 5.3, 1F, F-(2)), -92.9 (dd, $^{2}J_{FH}$ 58.2, $^{5}J_{FF}$ 5.3, 2F, CF_2H). Anal. calcd for $C_{25}H_{11}F_9O_2S_2$, %: C 51.91; H 1.92; F 29.56; S 11.09; m/z 578.0051. Found, %: C 52.22; H 2.05; F 29.55; S 10.69; m/z 578.0049.

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Supplementary Material

The Supplementary Material contains ^{1}H, ^{13}C and ^{19}F NMR spectra data for compounds **2**-**8** and **10**-**15** are presented in the online version of the text.

References

1. Kirsch, P. *Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Applications*. 2nd Completely Revised and Enlarged Edn.Wiley-VCH: Weinheim, 2013. http://dx.doi.org/10.1002/352760393X.
2. Das, P., Tokunaga, E., Shibata, N. *Tetrahedron Lett.* **2017**, *58*, 4803-4815 https://doi.org/10.1016/j.tetlet.2017.11.015.
3. Politanskaya, L., Tretyakov, E. *J. Fluor. Chem*. **2020**, *236*, 109592 https://doi.org/10.1016/j.jfluchem.2020.109592.
4. Ranjbar-Karimi, R., Danesteh, R., Beiki-Shoraki, K. *Arab. J. Chem.* **2019**, *12*, 2037-2043 https://doi.org/10.1016/j.arabjc.2014.12.025.
5. Platonov, V.E., Maksimov, A.M., Maslovsky, P.I. *J. Fluor. Chem*. **1995**, *75*, 41-49 https://doi.org/10.1016/0022-1139(95)03294-N.
6. Brooke, G.M. *J. Fluorine Chem*. **1997**, *86*, 1. https://doi.org/10.1016/S0022-1139(97)00006-7.
7. Pažitný, A., Solčán, T., Végh, D. *J. Fluor. Chem*. **2009**, *130*, 267-294, https://doi.org/10.1016/j.jfluchem.2008.12.013.
8. Xu X.H., Matsuzaki K., Shibata N. *Chem. Rev.* **2015,** *115*, 731-764. https://doi.org/10.1021/cr500193b.
9. Kaiser D., Klose I., Oost R., Neuhaus J., Maulide N. *Chem. Rev.* **2019**, *119*, 8701-8780 https://doi.org/10.1021/acs.chemrev.9b00111.
10. Krishnamurti, V., Barrett, C., Surya Prakash, G.K. *Emerging Fluorinated Motifs: Synthesis, Properties, and Applications*, First Edition. Wiley-VCH: Weinheim **2020,** 477-549. https://doi.org/10.1002@9783527824342.ch17.
11. Alsop, D.J., Burdon, J. and Tatlow, J.C. *J. Chem. Soc*. **1962**, 1801-1805.

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https://doi.org/10.1039/JR9620001801.
12. Maksimov, A. M.; Platonov, V. E. *Fluorine Notes* **1999**, *4*, 5-6. http://notes.fluorine1.ru/contents/history/1999/4_1999/letters/index.html.
13. Hansch, C., Leo, A. and Taft, R.W. *Chem. Rev*. **1991**, *91*, 165-195. https://doi.org/10.1021/cr00002a004.
14. Koshcheev B.V., Maksimov, A.M., Platonov, V.E., Shelkovnikov V.V. *Rus. J. Org. Chem*., **2017**, *53*, 1012-1016 https://doi.org/10.1134/S1070428017070089.
15. Ji, P., Atherton, J., Page, M.I. *Org. Biomol. Chem*., **2012**, *10*, 5732-5739. https://doi.org/10.1039/c2ob25064k.
16. Madesclaire, M. *Tetrahedron* **1988**, *44*, 6537-6580 and references therein. https://doi.org/10.1016/S0040-4020(01)90096-1.
17. Beletskaya, I.P., Artamkina, G.A., Mil`chenko, A.Yu., Sazonov, P.K., Shtern, M.M. *J. Phys. Org. Chem.* **1996**, *9*, 319-328. https://doi.org/10.1002/(SICI)1099-1395(199606)9:6<319::AID-POC786>3.0.CO;2-7.
18. Vlasov, V.M., Os`kina, I.A. *Rus. J. Org. Chem*. **2001**, *37*, 260-269. https://doi.org/10.1023/A:1012391231937.
19. Starks, C.M. *J. Am. Chem. Soc*. **1971**, *93*, 195-199. https://doi.org/10.1021/ja00730a033.
20. K. Kaupmees, A. Trummal, and I. Leito. *Croat. Chem. Acta* **2014**, *87*, 385–395. http://dx.doi.org/10.5562/cca2472.
21. Banks, R.E., Jondi, W., Tipping, A.E. *J. Chem. Soc. Chem. Commun*. **1989**, 1268. http://dx.doi.org/10.1039/C39890001268.
22. Vinogradov, A.S., Platonov, V.E. *Russ. J. Org. Chem*. **2015**, *51*, 1388-1394. https://doi.org/10.1134/S107042801510005X.
23. Chisari, A., Waccarone, E., Parisi, G., and Perrini, G *J. Chem. Soc*. PT2, **1982**, No.8, 957-959. https://doi.org/10.1039/P29820000957.
24. Maksimov, A.M., Kireenkov, V.V., Platonov, V.E. *Rus. Chem. Bull*. **1996**, *45*, 153-155. https://doi.org/10.1007/BF01433751.
25. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., et. al. *J. Comput. Chem*. **1993**, *14*, 1347-1363. https://doi.org/10.1002/jcc.540141112.
26. S.Miertus, E.Scrocco, J.Tomasi. *Chem. Phys*. **1981**, *55*, 117-129. https://doi.org/10.1016/0301-0104(81)85090-2.
27. Tomasi, J., Persico M. *Chem.Rev.* **1994**, *94*, 2027-2094. https://doi.org/10.1021/cr00031a013.
28. Marenich, A.V., Cramer, C.J., Truhlar D.G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396. https://doi.org/10.1021/jp810292n.
29. Schaftenaar, G., Noordik, J.H. *J. Comput.-Aided Mol. Des*. **2000**, *14*, 123-134. https://doi.org/10.1023/A:1008193805436.

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