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Reactions of *N*-Aryl(methyl, trifluoromethyl)sulfonyl-1,4-benzoquinone Monoimines with Sodium Sulfinates

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Abstract—In reactions with sodium sulfinates of N-substituted 1,4-benzoquinone monoimines with the quinoid ring having free positions 2 and/or 6 the fraction of products of 1,4-addition of the sulfinate ion grows in the series $ArSO_2 \rightarrow MeSO_2 \rightarrow CF_3SO_2$. In the case of 2,6-dimethyl derivatives the 1,6-addition is preferable, and the amount of products of 6,1-addition decreases.

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The introduction of superstrong electron-acceptor substituents by replacement of an oxygen atom with the group $=NSO_2CF_3$ [1] made it possible to perform rearrangments previously unknown in organic chemistry: aza-reactions of Curtius, Hofmann, and Lossen [2]. By replacing the carbonyl group of the *p*-benzoquinone with the $=NSO_2CF_3$ group *N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimines were synthesized [3] that are structural analogs of *N*-methyl(aryl)sulfonyl-1,4-benzoquinone monoimines. The van der Waals radii of the methyl and trifluoromethyl groups have close values (0.21 and 0.18 nm [4]), therefore the reactivity difference of these compounds should be governed mainly by different electronic effects of these substituents.

The reactivity of *N*-arylsulfonyl-1,4-benzoquinone monoimines towards sodium arylsulfinates is sufficiently well investigated [5–9]. The alkyl substituents in the quinoid ring notably affect the reaction course [5–9]. Quinone monoimines with the quinoid ring having free positions 2 and/or 6 react with sodium arylsulfinates as a rule regiospecifically providing products of 1,4-addition [6–8]. In reactions of *N*-4-(methylphenyl)sulfonyl-1,4-benzoquinone monoimine [6] and its 2,5-dimethyl- [7] and 3,5-dimethyl derivatives [8] formed up to 15% of the products of 1,6- and 6,1-addition. In the case of *N*-arylsulfonyl-2,6-dialkyl-1,4-benzoquinone monoimines the reaction course is mainly governed by the steric factor: the volume of the substituents in the positions *2* and *6* of the quinoid ring [8].

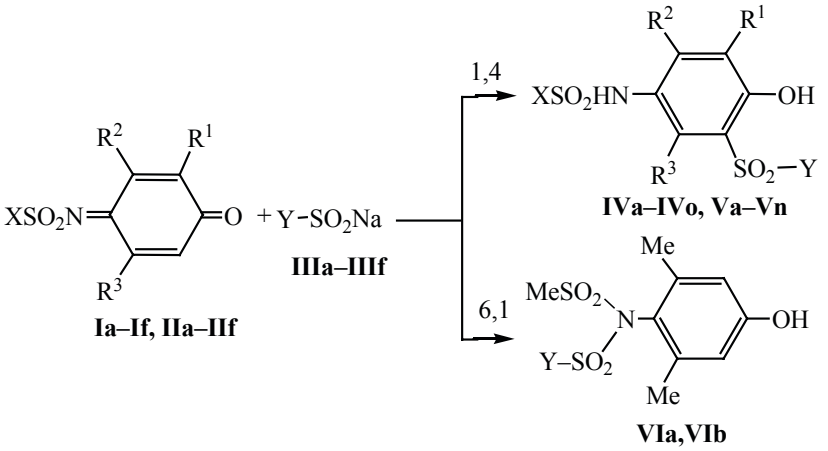
No published information exists on the effect of the steric and donor-acceptor properties of the substituents at the sulfo group on the reactivity of the *N*-substituted 1,4-benzoquinone monoimines with respect to sodium sulfinates.

The aim of this research was to determine the features of reactions of *N*-alkyl(trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines with sodium arylsulfinates containing in the aromatic ring donor (*p*-MeO, *p*-Me) and acceptor (*p*-Cl, *p*-F) substituents, and with sodium trifluoromethylsulfinate CF_3SO_2Na.

N-Methyl(trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines **Ia–Ii, IIa–IIi** were synthesized by procedures described in [3, 10]. The results of reactions between benzoquinone monoimines **Ia–If, IIa–IIf** and sodium sulfinates **IIIa–IIIf** are presented in Scheme 1.

Reactions of quinone imines **Ia–If, IIa–IIf** with sodium sulfinates were carried out in acetic acid at boiling and at room temperature, and also in a mixture of acetic acid and chloroform at cooling to –10°C, therewith the ratio quinone imine–sodium sulfinate was 1 : 2. This choice of conditions is due to the higher reactivity towards

Scheme 1.



X = Me (**I, IV**), CF_3 (**II, V**); **I, II**, $R^1 = R^2 = R^3 = H$ (**a**); $R^2 = R^3 = H$, R^1 = Me (**b**); $R^1 = R^3 = H$, R^2 = Me (**c**); $R^3 = H$, $R^1 = R^2$ = Me (**d**); $R^2 = H$, $R^1 = R^3$ = Me (**e**); $R^1 = H$, $R^2 = R^3$ = Me (**f**); **III**, Y = 4-$MeOC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Ph (**c**), 4-ClC_6H_4 (**d**), 4-FC_6H_4 (**e**), CF_3 (**f**); **IV**, Y = 4-$MeOC_6H_4$ (**a**, **g**, **o**), 4-MeC_6H_4 (**b**, **i**, **k**, **m**), Ph (**c**), 4-ClC_6H_4 (**d**, **j**, **l**, **n**), 4-FC_6H_4 (**e**, **h**, **p**), CF_3 (**f**); $R^1 = R^2 = R^3 = H$ (**a–f**); $R^2 = R^3 = H$, R^1 = Me (**g**, **h**); $R^1 = R^3 = H$, R^2 = Me (**i**, **j**); $R^3 = H$, $R^1 = R^2$ = Me (**k**, **l**); $R^2 = H$, $R^1 = R^3$ = Me (**m**, **n**); $R^1 = H$, $R^2 = R^3$ = Me (**o**, **p**); **V**, Y = 4-$MeOC_6H_4$ (**a**, **k**, **m**), 4-MeC_6H_4 (**b**, **i**, **l**, **n**), Ph (**c**), 4-ClC_6H_4 (**d**, **g**, **h**, **j**), 4-FC_6H_4 (**e**), CF_3 (f); $R^1 = R^2 = R^3 = H$ (**a–f**); $R^2 = R^3 = H$, R^1 = Me (**g**); $R^1 = R^3 = H$, R^2 = Me (**h**); $R^3 = H$, $R^1 = R^2$ = Me (**i**, **j**); $R^2 = H$, $R^1 = R^3$ = Me (**k**, **l**); $R^1 = H$, $R^2 = R^3$ = Me (**m**, **n**); **VI**, Y = 4-$MeOC_6H_4$ (**a**), 4-FC_6H_4 (**b**).

nucleophiles of *N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimines **IIa–IIf**: they react at room temperature and even at cooling [3], in contrast to formerly studied *N*-arylsulfonyl-1,4-benzoquinone monoimines whose reactions with arylsodium sulfinates proceed only in boiling acetic acid [5–9].

The reaction products of *N*-mesyl and *N*-(trifluoromethylsulfonyl) derivatives **Ia–If, IIa–IIf** with sodium sulfinates **IIIa–IIIf** we succeeded to isolate in all events, only at boiling reagents **IIa–IIf** formed unidentified oily substances.

The structure of all possible reaction products was established with the help of ^1H and ^{19}F NMR spectra. The spectra were recorded both from the uncrystallized and recrystallized reaction products, and from the products isolated from the filtrate.

The reactions of quinone monoimines **Ia–Ie, IIa–IIe** with salts **IIIa–IIIf** proceeded regiospecifically along the scheme of 1,4-addition affording methanesulfonamides **IVa–IVn, Va–Vl**. In contrast to the *N*-arylsulfonyl-1,4-benzoquinone monoimines [6, 7] the presence of the products of 6,1-addition was detected only in the case of 3,5-dimethyl-substituted compound **If**, and their amount reached 15% (**VIa**) and 14% (**VIb**). Yet 3,5-dimethyl-*N*-trifluoromethyl-sulfonyl-1,4-benzoquinone monoimine (**IIf**) reacted with arylsodium sulfinates **IIIa, IIIb** exclusively along the scheme of 1,4-addition giving compounds **Vm, Vn**.

The temperature does not significantly affect the direction of the reactions of quinone imines **Ia–If, IIa–IIf**. The reactions of *N*-mesyl derivatives **Ia–If** at cooling proceeded slower than at boiling, the decolorization of the solution occurred not immediately, but in the course of 12 h. The reactions of *N*-trifluoromethyl derivatives **IIa–IIf** took several seconds both at room temperature and at cooling. In all events the nucleophilicity of the sulfinate did not considerably affect the direction of the reaction.

The results of the reactions of *N*-trifluoromethylsulfonyl derivatives **IIa–IIf** with salts **IIIa–IIIf** proved to be quite unexpected compared with results published in [7–9], which showed that for *N*-aroyl-1,4-benzoquinone monoimines having at the nitrogen atom more acceptor substituent than the arylsulfonyl group and with free positions *2* and/or *6* of the quinoid ring the amount of products of arylsodium sulfinate addition to nitrogen and oxygen atoms increased. In our case irrespective the increased acceptor character of the substituent the opposite trend was observed: For all *N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimines lacking substituents in the positions *2* and *6* of the quinoid ring only the products of 1,4-addition were isolated.

It was suggested in [9] that two mechanisms exist of

the addition of the sulfinate anion: 1) a nucleophilic addition of the sulfinate anion under the conditions of the charge or orbital control (schemes of 1,4- and 6,3-addition); and 2) the addition of an arylsulfinate radical arising due to the oxidation of the arylsulfinate anion with quinone imine (schemes of 1,6- and 6,1-addition). The latter direction prevails at introducing more acceptor substituent to the nitrogen atom of the quinone monoimine, i.e., in the case of *N*-aroyl-1,4-benzoquinone monoimines.

For clear understanding of our results we performed ab initio quantum-chemical calculations of unsubstituted and 3,5(2,6)-dimethyl-substituted *N*-phenyl(methyl, trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines, and also of *N*-benzoyl-1,4-benzoquinone monoimines which like *N*-trifluoromethylsulfonyl derivatives had a stronger acceptor substituent at the nitrogen atom than *N*-arylsulfonyl derivatives, but showed different from *N*-trifluoromethylsulfonyl derivatives reactivity with respect to sulfinates. The optimization of the ground states with respect to all geometrical parameters was carried out by the standard procedure.

The influence of the substituent at the nitrogen atom on the quinoid ring of the quinone monoimine may be estimated by the energy of the donor-acceptor interactions along the system of double bonds N=C–C=C–C=O, namely, $\pi(C^1{=}O) \rightarrow \pi^*(C^2{=}C^3) + \pi(C^2{=}C^3) \rightarrow \pi^*(C^4{=}N) = E_1$ and also $\pi(C^1{=}O) \rightarrow \pi^*(C^5{=}C^6) + \pi(C^5{=}C^6) \rightarrow \pi^*(C^4{=}N) = E_2$, which are sufficiently strong in these compounds. The analysis of calculation results showed that in the series of substituents PhCO → $PhSO_2$ → $MeSO_2$ → CF_3SO_2 the energies of the interactions E_1, E_2, E_3 [$\pi(C^2{=}C^3) \rightarrow \pi^*(C^4{=}N)$] and E_4 [$\pi(C^5{=}C^6) \rightarrow \pi^*(C^4{=}N)$] grew (Table 1) leading to the decrease in the electron density and consequently to the negative charge on the C^2 and C^6 atoms of the quinoid ring (Table 2). In this series the LUMO energy of quinone imine also decreased (Table 1) resulting in diminishing the energy gap between the LUMO of the quinone monoimine and the HOMO of the phenylsulfinate (–684.02 kJ mol^{-1}) and in increasing the possibility of the reaction to occur along the scheme of the nucleophilic addition under the orbital control. In the molecules of quinone monoimines under consideration the distribution of the electron density on the LUMO has the maximum value on the atom C^2 of the quinoid ring and also increases in the series of *N*-substituents $PhSO_2$ → $MeSO_2$ → CF_3SO_2 (Table 3). We believe that these factors favor the growth of the activity of the atoms $C^{2,6}$ with respect to the sulfinate anions resulting in higher yields of the product of 1,4-addition and in the higher reactivity of the quinone monoimines: *N*-Trifluoromethyl derivatives react with sodium sulfinates even in the cold and furnish only the products of 1,4-addition.

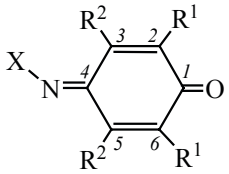
The results of the interaction of 2,6-dialkyl-*N*-methyl-(trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines **Ig–Ii, IIg–IIi** with sodium sulfinates are presented in Scheme 2.

In the reactions of 2,6-dimethyl-*N*-mesyl-1,4-benzoquinone monoimine (**Ig**) with salts **IIIa, IIId** products of 1,6-, 6,1-, and 6,3-addition were obtained. Their content was 72 (**IXa**), 23 (**VIIa**), 5 (**XIa**), and 66 (**IXb**), 29 (**VIIb**), 5% (**XIb**). In comparison with the corresponding *N*-arylsulfonyl derivatives [8, 9] the content of the product of 1,6-addition increased, of 6,3-addition decreased, and the content in the mixture of the product of the 6,1-addition remained the same. The reaction in the cold gave the products in the same ratio, but its duration increased to several days.

For *N*-trifluoromethylsulfonyl analog **IIg** the main products also resulted from the 1,6-addition: 65 (**Xa**), 56% (**Xb**). The content of the products of 6,1- and 6,3-addition was 5 (**VIIIa**), 5 (**VIIIb**), and 30 (**XIIa**), 39% (**XIIb**). Note that compared to *N*-methyl(aryl)-sulfonyl-1,4-benzoquinone monoimines a significant decrease in the amount of the product of the 6,1-addition was observed probably due to the growth in the acceptor characteristic of the substituent at the nitrogen atom [8, 9].

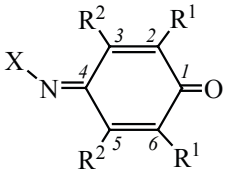
Thus in all cases of the reaction of 2,6-dimethyl-*N*-methyl(trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines (**Ig, IIg**) with salts **IIIa–IIIe** the product of 1,6-addition prevailed. According to calculations 2,6-dimethyl-substituted quinone monoimines possess the largest value of the LUMO energy as compared with analogous 3,5-dimethyl-substituted and unsubstituted in the quinoid ring quinone monoimines (Table 1) that leads to the increase in the energy gap between the quinone imine and the sulfinate and to lower probability of the nucleophilic addition of sulfinate to the quinoid ring of quinone monoimine at the orbital control. In the series of the substituents $PhSO_2$ → $MeSO_2$ → CF_3SO_2 the localization of LUMO on the free atoms $C^{3,5}$ of the quinoid ring in 2,6-dimethylquinone monoimines also decreases (Table 3). As a result for the 2,6-dimethyl-substituted quinone monoimines the process of one-electron transfer leading to the conversion of the arylsulfinate anion into arylsulfinate radical becomes more feasible, and the qui-

Table 1. Energies of donor-acceptor interactions and LUMO in the molecules of *N*-phenyl(methyl, trifluoromethyl)sulfonyl- and *N*-benzoyl-1,4-benzoquinone monoimines



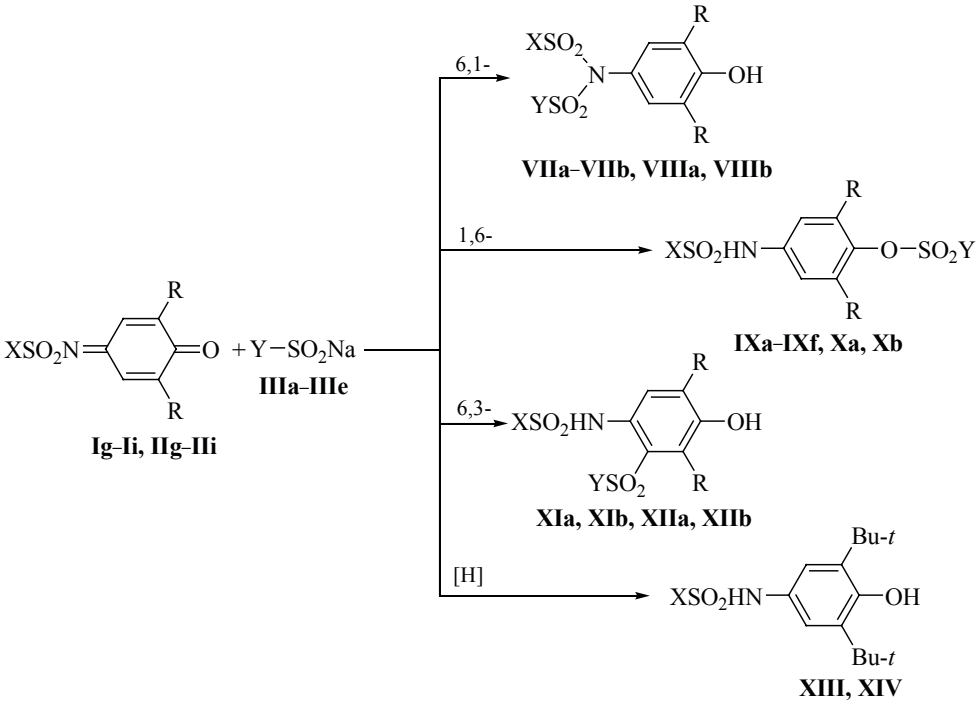
Type of interaction	R^1, R^2	Energy, kJ mol^{-1}			
		X = PhCO	X = $PhSO_2$	X = $MeSO_2$	X = CF_3SO_2
$\pi(C^1{=}O) \rightarrow \pi^*(C^2{=}C^3)$ + $\pi(C^2{=}C^3) \rightarrow \pi^*(C^4{=}N)$ (E_1)	$R^1 = R^2 = H$	102.91	112.40	113.95	118.88
	R^1 = Me, R^2 = H	107.59	118.59	120.13	125.57
	R^1 = H, R^2 = Me	100.19	111.69	111.82	118.46
$\pi(C^1{=}O) \rightarrow \pi^*(C^5{=}C^6)$ + $\pi(C^5{=}C^6) \rightarrow \pi^*(C^4{=}N)$ (E_2)	$R^1 = R^2 = H$	96.56	101.32	103.08	108.18
	R^1 = Me, R^2 = H	100.65	105.80	107.68	113.40
	R^1 = H, R^2 = Me	93.72	97.64	98.06	105.00
$\pi(C^2{=}C^3) \rightarrow \pi^*(C^4{=}N)$ (E_3)	$R^1 = R^2 = H$	75.49	84.52	85.94	90.20
	R^1 = Me, R^2 = H	81.64	92.25	93.72	98.56
	R^1 = H, R^2 = Me	73.02	83.77	83.81	89.79
$\pi(C^5{=}C^6) \rightarrow \pi^*(C^4{=}N)$ (E_4)	$R^1 = R^2 = H$	69.39	73.74	75.32	80.05
	R^1 = Me, R^2 = H	74.82	79.80	81.38	86.82
	R^1 = H, R^2 = Me	67.21	70.47	70.68	77.29
E (LUMO)	$R^1 = R^2 = H$	–364.97	–383.93	–393.96	–437.30
	R^1 = Me, R^2 = H	–341.74	–360.43	–368.67	–410.10
	R^1 = H, R^2 = Me	–340.45	–366.53	–375.00	–417.09

Table 2. Charges on carbon atoms of quinoid ring in *N*-phenyl(methyl, trifluoromethyl)sulfonyl- and *N*-benzoyl-1,4-benzoquinone monoimines



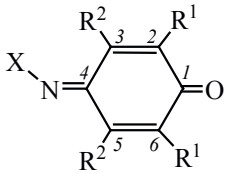
Atom	R^1, R^2	Charge, au of charge			
		X = PhCO	X = $PhSO_2$	X = $MeSO_2$	X = CF_3SO_2
C^2	$R^1 = R^2 = H$	–0.244	–0.232	–0.229	–0.216
	R^1 = H, R^2 = Me	–0.249	–0.239	–0.238	–0.225
C^6	$R^1 = R^2 = H$	–0.255	–0.252	–0.249	–0.239
	R^1 = H, R^2 = Me	–0.262	–0.257	–0.254	–0.246

Scheme 2.



X = Me (**I, VII, IX, XI, XIII**), CF_3 (**II, VIII, X, XII, XIV**); **I, II**, R = Me (**g**), *i*-Pr (**h**), *t*-Bu (**i**); **III**, Y = 4-$MeOC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Ph (**c**), 4-ClC_6H_4 (**d**), 4-FC_6H_4 (**e**); **VII, IX, XI**, R = Me, Y = 4-$MeOC_6H_4$ (**a**), 4-ClC_6H_4 (**b**); R = *i*-Pr, Y = 4-$MeOC_6H_4$ (**c**), 4-ClC_6H_4 (**d**); R = *t*-Bu, Y = 4-$MeOC_6H_4$ (**e**), 4-ClC_6H_4 (**f**); **VIII, X, XII**, R = Me, Y = 4-$MeOC_6H_4$ (**a**), 4-MeC_6H_4 (**b**).

Table 3. LUMO density on carbon atoms of quinoid ring in *N*-phenyl(methyl, trifluoromethyl)sulfonyl- and *N*-benzoyl-1,4-benzoquinone monoimines



Atom of quinoid ring	R^1, R^2	LUMO density		
		X = $PhSO_2$	X = $MeSO_2$	X = CF_3SO_2
C^2	$R^1 = R^2 = H$	0.084	0.085	0.089
	R^1 = Me, R^2 = H	0.128	0.128	0.124
	R^1 = H, R^2 = Me	0.086	0.086	0.092
C^6	$R^1 = R^2 = H$	0.070	0.071	0.071
	R^1 = Me, R^2 = H	0.098	0.100	0.094
	R^1 = H, R^2 = Me	0.068	0.068	0.010
C^3	$R^1 = R^2 = H$	0.068	0.066	0.061
	R^1 = Me, R^2 = H	0.076	0.073	0.065
	R^1 = H, R^2 = Me	0.076	0.070	0.070
C^5	$R^1 = R^2 = H$	0.064	0.062	0.055
	R^1 = Me, R^2 = H	0.065	0.064	0.055
	R^1 = H, R^2 = Me	0.069	0.065	0.059

none monoimine transforms into a quinone monoimine radical. Further the quinone monoimine radical reacts with the sulfinate radical along the schemes of 1,6- and 6,1-addition.

The predominant formation of the products of sulfinate 1,6-addition to the 2,6-dimethyl-substituted quinone imines may be ascribed to a supplementary stabilization by the methyl groups of the radical center on the oxygen atom owing to the hyperconjugation effect. The decrease in the amount of products obtained by the addition to nitrogen atom of 2,6-dimethyl-1,4-benzoquinone monoimines in the series of the nitrogen substituents $PhSO_2 \rightarrow MeSO_2 \rightarrow CF_3SO_2$ is due to the increase in the acceptor qualities of the substituent at this atom and consequently to the diminishing negative charge of the nitrogen atom of the quinone monoimine radical.

The reactions of 2,6-diisopropyl derivative **Ih** with salts **IIIa, IIId** required more severe conditions (boiling in glacial acetic acid over 7 h). In this case the content of the products of the 1,6- and 6,1-addition reached 44 (**IXc**), 59 (**IXd**) and 56 (**VIIc**), 41% (**VIId**). The same products ratios were previously observed for *N*-arylsulfonyl analogs [49–52 (1,6-) and 48–51% (6,1-)] [10, 11]. With *N*-trifluoromethylsulfonyl derivative **IIh** complex mixtures of compounds were obtained whose composition we failed to determine.

In the reaction of *N*-mesylimine **Ii** with salts **IIIa, IIId** at boiling in the glacial acetic acid for 10 h up to 5% of amide **XIII** formed, the reduction product of quinone imine **Ii**. The mixture also contained the hydrolysis product of the initial imine, 2,6-di-*tert*-butyl-1,4-benzoquinone. The content of products of 6,1- and 1,6-addition (not accounting for compound **XIII** and the hydrolysis product) was 86 (**VIIe**), 85 (**VIIf**) and 14 (**IXe**), 15% (**IXf**). The content in the mixture of the product of 6,1-addition was somewhat higher than in the case of *N*-arylsulfonyl-1,4-benzoquinone monoimines [55–65 (6,1-) and 35–45% (1,6-)] [8, 9].

The reaction of *N*-trifluoromethylsulfonyl analog **IIi** with salts **IIIa, IIId** was carried out in a mixture of glacial acetic acid and chloroform at heating to 50°C for several days for at the room temperature the reaction proceeded very slow. According to the ^{1}H NMR data the main reaction product was amide **XIV**, the product of reduction of quinone imine **IIi**. The ^{1}H NMR spectrum contained also signals of 2,6-di-*tert*-butyl-1,4-benzoquinone (singlets in the region 1.24 and 6.51 ppm), and in the ^{19}F NMR spectrum, the signal of the trifluoromethanesulfonic acid (–79.6 × –80.2 ppm), hydrolysis product of quinone imine **IIi** [1].

On recrystallization from aqueous acetic acid of the mixtures of reaction products obtained from imines **Ig, Ih** and salt **IIId** we succeeded to isolate two individual products of 1,6-addition, amides **IXb, IXd**.

In the case of *N*-mesyl-1,4-benzoquinone monoimines **Ig–Ii** owing to the more bulky substituents in the *ortho*-position with respect to the carbonyl group the amount of the products of 1,6-addition decreases, and that of the products of 6,1-addition increases which may be attributed to the effect of the steric factors and also to the diminished or lacking conjugation effect in the event of the isopropyl and *tert*-butyl groups in the positions *2* and *6*. Besides the introduction into the *ortho*-position with respect to the carbonyl group in 2,6-dialkyl-substituted quinone imines **Ig–Ii**, **IIg–IIi** of substituents more bulky than the methyl group impedes the reaction to proceed along the scheme of 6,3-addition; the corresponding products were found only for compounds **Ig, IIg**. The reduction of *N*-trifluoromethylsulfonyl-2,6-di-*tert*-butyl-1,4-benzoquinone monoimine **IIi** in the reaction with sodium sulfinates **IIIa, IIId** apparently originates from the infeasibility of the 1,6-addition because of the bulk of the substituent in the quinoid ring and also due to the lack of the hyperconjugation effect, and the 6,1-addition becomes unfavorable due to the increased acceptor properties of the substituent at the nitrogen atom.

The structure and composition of obtained compounds **IV–XIV** were proved by IR and ^{1}H, ^{19}F NMR spectroscopy and by elemental analysis.

The analysis of the mixtures of products of the reactions between quinone imines **If–Ii** with sodium arylsulfinates was performed based on the data of [6–8, 11]. According to [11], the singlet signal of the protons of the $MeSO_2$ group of *N*-phenylmethanesulfonamide appeared in the ^{1}H NMR spectrum in the region δ 3.00 ppm, and in the spectrum of *N*-mesyl-*N*-phenylmethanesulfonamide, at δ 3.40 ppm, namely, the substitution of a hydrogen atom attached to nitrogen resulted in the downfield shift of the protons of $MeSO_2$ group. In the spectra of products of 1,4- and 1,6-addition **IVa–IVp, IXa–IXf** the proton signals of the mesyl group are observed in the region δ 2.94–3.04 and 3.01–3.03 ppm respectively, whereas in the products of 6,1-addition **VIa, VIb, VIIa–VIIf** they are located more downfield, 3.54–3.66 ppm. According to [8], the chemical shifts of the aromatic protons of the aminophenol fragment in the *N*-arylsulfonyl derivatives

had the characteristic values 6.56–6.69 (6,1-addition) and 6.94–7.17 ppm (1,6-addition). In the spectra of the corresponding reaction products obtained from *N*-mesyl-1,4-benzoquinone monoimines and sodium arylsulfinates (compounds **VIa, VIb, VIIa–VIIf, IXa–IXf**) the signals of the aromatic protons appear in the region δ 6.48–6.79 and 6.92–7.24 ppm respectively.

The fluorine signals in the ^{19}F NMR spectra of the products of 1,4-addition of sodium sulfinates to quinine imines **IIa–IIf** were attributed based on the published data on the chemical shifts of the $=NSO_2CF_3$ group in various compounds [3, 12]. The singlet of the trifluoromethylsulfonyl group of compounds **Va–Vn** appeared in the ^{19}F NMR spectra in the region δ –74.8 to –76.4 ppm. It is known that in the spectrum of *N*-(4-hydroxyphenyl)-1,1,1-trifluoromethanesulfonamides it is observed in the region δ –75.1 to –76.4 ppm [3], and in the spectrum of *N*-phenyl-*N*-(trifluoromethylsulfonyl)-1,1,1-trifluoromethanesulfonamide, at –78.9 ppm [12]. In the spectra of the products of the addition at the oxygen atom and of products of the 6,3-addition the singlets of the trifluoromethylsulfonyl group are observed in the region δ –75.6 to –75.7 and –75.3 to –75.4 ppm respectively, and of the products of the addition at the nitrogen atom **VIIIa**, **VIIIb**, at –75.8 to –75.9 ppm. The signals of the aromatic protons of the aminophenol fragment in the *N*-trifluoromethylsulfonyl derivatives are observed at δ 6.71–6.75 (6,1-addition) (**VIIIa**, **VIIIb**), 7.01–7.05 (1,6-addition) (**Xa, Xb**), and 7.04–7.09 ppm (6,3-addition) (**XIIa, XIIb**).

In the IR spectra of compounds **IXb, IXd** absorption bands in the region 3310–3350 cm^{-1} are present belonging to NH group. The characteristic absorption bands of the products of the 1,4-addition **IVa–IVp, Va–Vn** are observed in the interval 3160–3270 (NH) and 3270–3400 cm^{-1} (OH).

Therefore as a result of the performed research it was established that in the series of 1,4-benzoquinone monoimines with the *N*-substituents $PhSO_2 \rightarrow MeSO_2 \rightarrow CF_3SO_2$ having the free positions *2* and/or *6* of the quinoid ring with growing acceptor property of the substituent at the nitrogen atom the LUMO energy of the quinine monoimine decreased and the influence of the substituent on the C=C bonds of the quinoid ring grew accordingly raising the activity of the positions *2* and *6* of the quinoid ring with respect to the sulfinate ion and leading to the prevalence of the 1,4-addition to the ring of the quinone monoimine at the orbital control. As a result the reactions of the *N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimines with sodium sulfinates proceed strictly regiospecifically along the scheme of 1,4-addition.

The direction of the sulfinates reaction along 1,6- and 6,1-addition occurs by the mechanism of one electron transfer. In event of 2,6-dimethyl-*N*-aryl(methyl, trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines the products of 1,6-addition prevail apparently due to the supplementary stabilization of the radical center on the oxygen atom by the hyperconjugation with the methyl groups.

Consequently, the reactivity of *N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimines on the one hand is characteristic of *N*-sulfonyl derivatives and on the other hand, the presence of a strong trifluoromethyl group leads to the appearance of the properties characteristic of *N*-aroyl-1,4-benzoquinone monoimines.

EXPERIMENTAL

All calculations were carried out using the program GAUSSIAN 03 [13]. The molecular structure of compounds under study was calculated in the framework of the density functional theory using B3LYP functional [14–19]. In the calculations the standard basic set 6-31+G(d) was used [20, 21]. The conjugation and hyperconjugation interactions in the molecules were investigated in the framework of the theory of natural binding orbitals (NBO) [22] applying the program NBO 5.0 [23].

IR spectra of compounds synthesized were recorded on a spectrophotometer Bruker Vertex-70 from pellets with KBr (compounds **IV–XIV**) and in $CHCl_3$ (compounds **I, II**). ^1H NMR spectra were registered on a spectrometer Varian VXR-300 (300 MHz) from solution in DMSO-d_6 of compounds **IV, Va–Ve, Vg–Vn**, **VI–XIV** and in $CDCl_3$ of compounds **I, II, Vf**. The chemical shifts are reported with respect to TMS. ^{13}C NMR spectra were obtained on a spectrometer Varian VXR-300 (75.4 MHz) from solutions in $CDCl_3$. ^{19}F NMR spectra were taken on an instrument Varian Gemini-200 (188.14 MHz), the chemical shifts are reported with respect to fluorotrichloromethane. The purity of quinone imines and the products of their reactions was checked by TLC on Silufol UV-254 plates, eluents ethanol–chloroform, 1 : 10, benzene–hexane, 10 : 1, hexane–ethyl acetate, 1 : 2, development under UV irradiation.

Quinone imines Ia–Ii, IIa–IIi were prepared by

procedure [3] by the oxidation of the corresponding aminophenols with silver oxide or with 4-(diacetoxyiodo) toluene in chloroform or dichloromethane. The characteristics of compounds **Ia–Ig, IIa–IIg** are in agreement with those published in [3], of compound **Ih**, in [10].

Sodium sulfinates IIIa–IIIe were obtained by procedure [24], reagent **IIIf**, by method [25].

2,6-Diisopropyl-*N*-mesyl-1,4-benzoquinone monoimine (Ih). Yield 92%, mp 67–68°C (mp 67–68°C [10]). ^{1}H NMR spectrum, δ, ppm: 1.13 d (6H, 6-CH$\underline{Me}_2$, *J* 6.9 Hz), 1.16 d (6H, 2-CH$\underline{Me}_2$, *J* 7.2 Hz), 3.00–3.15 m (2H, 2,6-C$\underline{H}Me_2$), 3.25 s (3H, $MeSO_2$), 6.67 d (1H, H^5, $J_{5,3}$ 2.4 Hz), 7.63 d (1H, H^3). Found, %: N 5.11, 5.13. $C_{13}H_{19}NO_3S$. Calculated, %: N 5.20.

2,6-Di-*tert*-butyl-*N*-mesyl-1,4-benzoquinone monoimine (Ii). Yield 91%, mp 88–90°C. ^{1}H NMR spectrum, δ, ppm: 1.29 br.s (18H, *t*-Bu), 3.24 br.s (3H, $MeSO_2$), 6.70 br.s (1H, H^5), 7.69 br.s (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 29.40 (2,6-C$\underline{Me}_3$), 35.89 (2-$\underline{C}Me_3$), 36.37 (6-$\underline{C}Me_3$), 43.11 ($MeSO_2$), 124.05 (C^3), 132.92 (C^5), 157.24 (C^2), 157.53 (C^6), 166.23 (C=N), 186.15 (C=O). Found, %: N 4.75, 4.77. $C_{15}H_{23}NO_3S$. Calculated, %: N 4.71.

2,6-Diisopropyl-*N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimine (IIh). Yield 91%, mp 51– 52°C. ^{1}H NMR spectrum, δ, ppm: 1.05 d (12H, 2,6-CH$\underline{Me}_2$, *J* 6.6 Hz), 2.97–3.10 m (2H, 2,6-C$\underline{H}Me_2$), 6.85 br.s (2H, H^{3,5}). ^{19}F NMR spectrum, δ, ppm: –79.03 s (CF_3). ^{13}C NMR spectrum, δ, ppm: 20.44 (2,6-CH$\underline{Me}_2$), 26.80 (2,6-$\underline{C}HMe_2$), 118.70 q (CF_3, *J* 319.5 Hz), 128.47 (C^{3,5}), 156.06 (C^{2,6}), 169.11 (C=N), 183.44 (C=O). Found, %: N 4.35, 4.38. $C_{13}H_{16}F_3NO_3S$. Calculated, %: N 4.33.

2,6-Di-*tert*-butyl-*N*-trifluoromethylsulfonyl-1,4-benzoquinone monoimine (IIi). Yield 90%, mp 68–70°C. ^{1}H NMR spectrum, δ, ppm: 1.24 br.s (18H, *t*-Bu), 6.99 br.s (2H, H^{3,5}). ^{19}F NMR spectrum, δ, ppm: –79.07 c (CF_3). Found, %: N 4.03, 4.06. $C_{15}H_{20}F_3NO_3S$. Calculated, %: N 3.99.

Reaction of quinone imines Ia–Ii, IIa–IIi with sodium sulfinates IIIa–IIIf. *a.* To a stirred solution of 2 mmol of quinone imine **Ia–Ii** in 20 ml of glacial acetic acid at room temperature or at boiling was added in one portion 4 mmol of dry salt **IIIa–IIIf**. After the solution decolorized it was cooled and poured on ice. The colorless precipitate was filtered off and washed in succession with cold and warm water. At the recrystallization of the target compound from glacial acetic acid it was precipitated by adding a double volume of water. The precipitate was filtered off and dried.

b. To a solution of 2 mmol of quinone imine **Ia–Ii, IIa–IIi** in 10 ml of chloroform or dichloromethane was added dropwise a solution of 4 mmol of salt **IIIa–IIIf** in 10 ml of glacial acetic acid at room temperature or at cooling to –10°C while passing argon flow. Reactions of quinone imines **IIa–IIi** were monitored by ^{19}F NMR spectra. Quinone imines **Ig–Ii, IIg–IIi** reacted within 10–12 h at 50°C, quinone imines **Ia–If**, within 12 h without heating. On the completion of the reaction the solution was evaporated in a vacuum, the residue was poured on ice at stirring, the colorless precipitate was worked up as in procedure *a*.

***N*-[4-Hydroxy-3-(4-methoxyphenylsulfonyl) phenyl]methanesulfonamide (IVa).** Yield 87%, mp 80–82°C. ^{1}H NMR spectrum, δ, ppm: 2.94 s (3H, $MeSO_2$), 3.83 s (3H, MeO), 6.87 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.11 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz), 7.32 d.d (1H, H^6, $J_{6,5}$ 9.0 Hz, $J_{6,2}$ 2.4 Hz), 7.79 d (1H, H^2, $J_{2,6}$ 2.4 Hz), 7.84 d (2H, H$^{2'6'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz), 9.58 br.s (1H, NH), 10.73 s (1H, OH). Found, %: N 3.89, 3.93. $C_{14}H_{15}NO_6S_2$. Calculated, %: N 3.92.

***N*-(4-Hydroxy-3-tosylphenyl)methanesulfonamide (IVb).** Yield 88%, mp 153–154°C. ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, Ts), 2.95 s (3H, $MeSO_2$), 6.88 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.35 d.d (1H, H^6, $J_{6,5}$ 9.0, $J_{6,2}$ 2.4 Hz), 7.39 d (2H, H$^{3',5'}$, Ts, *J* 8.1 Hz), 7.78 d (2H, H$^{2',6'}$, Ts, *J* 8.1 Hz), 7.80 d (1H, H^2, $J_{2,6}$ 2.4 Hz), 9.61 s (1H, NH), 10.73 s (1H, OH). Found, %: N 3.99, 4.03. $C_{14}H_{15}NO_5S_2$. Calculated, %: N 4.10.

***N*-[4-Hydroxy-3-(phenylsulfonyl)phenyl]methanesulfonamide (IVc).** Yield 78%, mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 2.96 s (3H, $MeSO_2$), 6.91 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.37 d.d (1H, H^6, $J_{6,5}$ 9.0, $J_{6,2}$ 2.4 Hz), 7.58–7.92 m (5H, Ph), 7.83 d (1H, H^2, $J_{2,6}$ 2.4 Hz), 9.62 s (1H, NH), 10.78 s (1H, OH). Found, %: N 4.18, 4.23. $C_{13}H_{13}NO_5S_2$. Calculated, %: N 4.28.

***N*-[4-Hydroxy-3-(4-chlorophenylsulfonyl)phenyl]-methanesulfonamide (IVd).** Yield 76%, mp 179–180°C. ^{1}H NMR spectrum, δ, ppm: 2.97 s (3H, $MeSO_2$), 6.93 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.38 d.d (1H, H^6, $J_{6,5}$ 9.0, $J_{6,2}$ 2.7 Hz), 7.69 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.4 Hz), 7.82 d (1H, H^2, $J_{2,6}$ 2.7 Hz), 7.92 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.4 Hz), 9.64 s (1H, NH), 10.87 s (1H, OH). Found, %: N 3.89, 3.91. $C_{13}H_{12}ClNO_5S_2$. Calculated, %: N 3.87.

***N*-[4-Hydroxy-3-(4-fluorophenylsulfonyl)phenyl] methanesulfonamide (IVe).** Yield 81%, mp 179–180°C. ^{1}H NMR spectrum, δ, ppm: 2.96 s (3H, $MeSO_2$), 6.92 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.36 d.d (1H, H^6, $J_{6,5}$ 8.7, $J_{6,2}$ 2.4 Hz), 7.41–8.00 m (4H, 4-FC_6H_4), 7.81 d (1H, H^2, $J_{2,6}$ 2.4 Hz), 9.58 s (1H, NH), 10.78 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –105.36 s (4-FC_6H_4). Found, %: N 4.00, 4.02. $C_{13}H_{12}FNO_5S_2$. Calculated, %: N 4.06.

***N*-[4-Hydroxy-3-(trifluoromethylsulfonyl)phenyl] methanesulfonamide (IVf).** Yield 91%, mp 75–78°C. ^{1}H NMR spectrum, δ, ppm: 2.95 s (3H, $MeSO_2$), 7.15 d (1H, H^5, $J_{5.6}$ 8.7 Hz), 7.60 d.d (1H, H^6, $J_{6,5}$ 8.7, $J_{6,2}$ 2.4 Hz), 7.67 d (1H, H^2, $J_{2,6}$ 2.4 Hz), 9.75 s (1H, NH), 11.71 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –76.70 c (CF_3). Found, %: N 4.34, 4.37. $C_8H_8F_3NO_5S_2$. Calculated, %: N 4.39.

***N*-[4-Hydroxy-3-methyl-5-(4-methoxyphenylsulfonyl)phenyl]methanesulfonamide (IVg).** Yield 92%, mp 134–135°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, 3-Me), 2.95 s (3H, $MeSO_2$), 3.83 s (3H, MeO), 7.12 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 7.25 d (1H, H^2, $J_{2,6}$ 2.1 Hz), 7.66 d (1H, H^6, $J_{6,2}$ 2.1 Hz), 7.84 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 9.58 br.s (1H, NH). Found, %: N 3.79, 3.83. $C_{15}H_{17}NO_6S_2$. Calculated, %: N 3.77.

***N*-[4-Hydroxy-3-methyl-5-(4-fluorophenylsulfonyl) phenyl]methanesulfonamide (IVh).** Yield 91%, mp 176–178°C. ^{1}H NMR spectrum, δ, ppm: 2.09 s (3H, 3-Me), 2.95 s (3H, $MeSO_2$), 7.23 d (1H, H^2, $J_{2,6}$ 2.1 Hz), 7.37–7.99 m (4H, 4-FC_6H_4), 7.65 d (1H, H^6, $J_{6,2}$ 2.1 Hz), 9.50 br.s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –105.49 s (4-FC_6H_4). Found, %: N 3.83, 3.87. $C_{14}H_{14}FNO_5S_2$. Calculated, %: N 3.90.

***N*-[4-Hydroxy-2-methyl-5-tosylphenyl]methanesulfonamide (IVi).** Yield 70%, mp 187–189°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (3H, 2-Me), 2.36 s (3H, Ts), 2.97 s (3H, $MeSO_2$), 6.76 s (1H, H^3), 7.38 d (2H, H$^{3',5'}$, Ts, *J* 7.8 Hz), 7.76 s (1H, H^6), 7.77 d (2H, H$^{2',6'}$, Ts, *J* 7.8 Hz), 9.09 s (1H, NH), 10.79 s (1H, OH). Found, %: N 3.85, 3.89. $C_{15}H_{17}NO_5S_2$. Calculated, %: N 3.94.

***N*-[4-Hydroxy-2-methyl-5-(4-chlorophenylsulfonyl)phenyl]methanesulfonamide (IVi).** Yield 90%, mp 210–212°C. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, 2-Me), 2.99 s (3H, $MeSO_2$), 6.78 s (1H, H^3), 7.68 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.4 Hz), 7.77 s (1H, H^6), 7.90 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.4 Hz), 9.11 s (1H, NH), 10.94 s (1H, OH). Found, %: N 3.75, 3.77. $C_{14}H_{14}ClNO_5S_2$. Calculated, %: N 3.73.

***N*-(4-Hydroxy-2,3-dimethyl-5-tosylphenyl)-methanesulfonamide (IVk).** Yield 91%, mp 189–191°C. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, 3-Me), 2.23 s (3H, 2-Me), 2.37 s (3H, Me in Ts), 2.95 s (3H, $MeSO_2$), 7.40 d (2H, H$^{3',5'}$, Ts, *J* 8.4 Hz), 7.68 s (1H, H^6), 7.79 d (2H, H$^{2',6'}$, Ts, *J* 8.4 Hz), 9.15 br.s (1H, NH), 9.65 br.s (1H, OH). Found, %: N 3.71, 3.77. $C_{16}H_{19}NO_5S_2$. Calculated, %: N 3.79.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-chlorophenylsulfonyl)phenyl]methanesulfonamide (IVl).** Yield 75%, mp 196–198°C. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, 3-Me), 2.24 s (3H, 2-Me), 2.97 s (3H, $MeSO_2$), 7.69 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 9.0 Hz), 7.70 s (1H, H^6), 7.90 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 9.0 Hz), 9.18 br.s (1H, NH), 9.77 br.s (1H, OH). Found, %: N 3.51, 3.55. $C_{15}H_{16}ClNO_5S_2$. Calculated, %: N 3.59.

***N*-[4-Hydroxy-3,6-dimethyl-5-tosylphenylmethanesulfonamide (IVm).** Yield 87%, mp 183–186°C. ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, Me in Ts), 2.33 s (3H, 3-Me), 2.40 s (3H, 6-Me), 2.95 s (3H, $MeSO_2$), 7.41 s (1H, H^2), 7.45 d (2H, H$^{3',5'}$, Ts, *J* 8.1 Hz), 7.78 d (2H, H$^{2',6'}$, Ts, *J* 8.1 Hz), 9.02 s (1H, NH), 10.45 br.s (1H, OH). Found, %: N 3.75, 3.79. $C_{16}H_{19}NO_5S_2$. Calculated, %: N 3.79.

***N*-[4-Hydroxy-3,6-dimethyl-5-(4-chlorophenylsulfonyl)phenyl]methanesulfonamide (IVn).** Yield 90%, mp 155–157°C. ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, 3-Me), 2.55 s (3H, 6-Me), 2.96 s (3H, $MeSO_2$), 7.40 s (1H, H^2), 7.71 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.1 Hz), 7.90 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.1 Hz), 9.06 s (1H, NH), 10.19 br.s (1H, OH). Found, %: N 3.55, 3.57. $C_{15}H_{16}ClNO_5S_2$. Calculated, %: N 3.59.

***N*-[4-Hydroxy-2,6-dimethyl-5-(4-methoxyphenylsulfonyl)phenyl]methanesulfonamide (IVo).** ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, 6-Me), 2.59 s (3H, 2-Me), 3.03 s (3H, $MeSO_2$), 3.83 s (3H, MeO), 6.69 s (1H, H^3), 7.12 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 7.82 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 8.84 s (1H, NH), 10.54 s (1H, OH).

***N*-[4-Hydroxy-2,6-dimethyl-5-(4-fluorophenylsulfonyl)phenyl]methanesulfonamide (IVp).** ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, 6-Me), 2.66 s (3H, 2-Me), 3.04 s (3H, $MeSO_2$), 6.66 s (1H, H^3), 7.38–7.97 m (4H, 4-FC_6H_4), 8.87 s (1H, NH), 10.64 c (1H, OH). ^{19}F, δ, ppm: –102.74 s (4-FC_6H_4).

***N*-[4-Hydroxy-3-(4-methoxyphenylsulfonyl) phenyl]-1,1,1-trifluoromethanesulfonamide (Va).** Yield 60%, mp 166–167°C. ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, MeO), 7.00 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.15 d

(2H, H$^{3',5'}$, 4-MeOC$_6$H$_4$, J 8.7 Hz), 7.40 d.d (1H, H^6, $J_{6,5}$ 8.7 Hz, $J_{6,2}$ 1.8 Hz), 7.81 d (1H, H^2, $J_{2,6}$ 1.8 Hz), 7.86 d (2H, H$^{2',6'}$, 4-MeOC$_6$H$_4$, J 8.7 Hz), 11.11 s (1H, NH), 11.89 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.26 s (CF$_3$). Found, %: N 3.38, 3.39. $C_{14}H_{12}F_3NO_6S_2$. Calculated, %: N 3.40.

***N*-[4-Hydroxy-3-tosylphenyl]-1,1,1-trifluoromethanesulfonamide (Vb).** Yield 61%, mp 149–151°C. ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, Me in Ts), 6.99 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.42 d.d (1H, H^6, $J_{6,5}$ 8.7, $J_{6,2}$ 1.2 Hz), 7.43 d (2H, H$^{3',5'}$, Ts, J 6.9 Hz), 7.80 d (2H, H$^{2',6'}$, Ts, J 6.9 Hz), 7.82 d (1H, H^2, $J_{2,6}$ 1.2 Hz), 11.14 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –75.01 s (CF$_3$). Found, %: N 3.51, 3.55. $C_{14}H_{12}F_3NO_5S_2$. Calculated, %: N 3.54.

***N*-[4-Hydroxy-3-(phenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vc).** Yield 91%, mp 137–139°C. ^{1}H NMR spectrum, δ, ppm: 7.20 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.63 d.d (1H, H^6, $J_{6,5}$ 8.7, $J_{6,2}$ 1.2 Hz), 7.82–8.15 m (5H, Ph), 8.05 d (1H, H^2, $J_{2,6}$ 1.2 Hz), 11.32 s (1H, NH), 12.08 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.04 s (CF$_3$). Found, %: N 3.63, 3.67. $C_{13}H_{10}F_3NO_5S_2$. Calculated, %: N 3.67.

***N*-[4-Hydroxy-3-(4-chlorophenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vd).** Yield 82%, mp 168–169°C. ^{1}H NMR spectrum, δ, ppm: 6.98 d (1H, H^5, $J_{5,6}$ 7.8 Hz), 7.43 d.d (1H, H^6, $J_{6,5}$ 7.8, $J_{6,2}$ 1.2 Hz), 7.70 d (2H, H$^{3',5'}$, 4-ClC$_6$H$_4$, J 8.7 Hz), 7.81 br.s (1H, H^2, $J_{2,6}$ 1.2 Hz), 7.90 d (2H, H$^{2',6'}$, 4-ClC$_6$H$_4$, J 8.7 Hz), 11.27 s (1H, NH), 12.04 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –74.93 s (CF$_3$). Found, %: N 3.41, 3.44. $C_{13}H_9ClF_3NO_5S_2$. Calculated, %: N 3.37.

***N*-[4-Hydroxy-3-(4-fluorophenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Ve).** Yield 59%, mp 189–191°C. ^{1}H NMR spectrum, δ, ppm: 6.98 d (1H, H^5, $J_{5,6}$ 8.7 Hz), 7.39–7.44 d.d (1H, H^6, $J_{6,5}$ 8.7, $J_{6,2}$ 1.2 Hz), 7.43–7.99 m (4H, 4-FC$_6$H$_4$), 7.79 d (1H, H^2, $J_{2,6}$ 1.2 Hz), 11.24 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –74.84 s (CF$_3$), –104.51 s (4-FC$_6$H$_4$). Found, %: N 3.51, 3.55. $C_{13}H_9F_4NO_5S_2$. Calculated, %: N 3.51.

***N*-[4-Hydroxy-3-(trifluoromethylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vf).** Yield 66%, mp 87–89°C. ^{1}H NMR spectrum, δ, ppm: 7.20 d (1H, H^5, $J_{5,6}$ 9.0 Hz), 7.48 br.s (1H, NH), 7.66 br.s (1H, H^2), 7.67 d (1H, H^6, $J_{6,5}$ 9.0 Hz), 8.60 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.75 s (CF$_3$SO$_2$NH), –79.48 s (CF$_3$SO$_2$). Found, %: N 3.70, 3.73. $C_8H_5F_6NO_5S_2$. Calculated, %: N 3.75.

***N*-[4-Hydroxy-3-methyl-5-(4-chlorophenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vg).** Yield 60%, mp 167–170°C. ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, 3-Me), 7.33 br.s (1H, H^2), 7.68 br.s (1H, H^6), 7.69 d (2H, H$^{3',5'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 7.90 d (2H, H$^{2',6'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 10.14 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –75.03 s (CF$_3$). Found, %: N 3.20, 3.27. $C_{14}H_{11}ClF_3NO_5S_2$. Calculated, %: N 3.26.

***N*-[4-Hydroxy-2-methyl-5-(4-chlorophenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vh).** Yield 63%, mp 163–165°C. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, 2-Me), 6.84 s (1H, H^3), 7.69 d (2H, H$^{3',5'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 7.74 s (1H, H^6), 7.90 d (2H, H$^{2',6'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 11.22 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –75.99 s (CF$_3$). Found, %: N 3.21, 3.29. $C_{14}H_{11}ClF_3NO_5S_2$. Calculated, %: N 3.26.

***N*-[4-Hydroxy-2,3-dimethyl-5-tosylphenyl]-1,1,1-trifluoromethanesulfonamide (Vi).** Yield 90%, mp 170–173°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, 3-Me), 2.27 s (3H, 2-Me), 2.43 s (3H, Me in Ts), 7.45 d (2H, H$^{3',5'}$, Ts, J 8.4 Hz), 7.69 s (1H, H^6), 7.82 d (2H, H$^{2',6'}$, Ts, J 8.4 Hz), 9.91 s (1H, NH), 11.60 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.79 s (CF$_3$). Found, %: N 3.25, 3.29. $C_{16}H_{16}F_3NO_5S_2$. Calculated, %: N 3.31.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-chlorophenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vj).** Yield 92%, mp 198–200°C. ^{1}H NMR spectrum, δ, ppm: 2.09 s (3H, 3-Me), 2.24 s (3H, 2-Me), 7.68 s (1H, H^6), 7.69 d (2H, H$^{3',5'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 7.88 d (2H, H$^{2',6'}$, 4-ClC$_6$H$_4$, J 8.4 Hz), 10.07 s (1H, NH), 11.67 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.89 s (CF$_3$). Found, %: N 3.10, 3.12. $C_{15}H_{13}ClF_3NO_5S_2$. Calculated, %: N 3.16.

***N*-[4-Hydroxy-3,6-dimethyl-5-(4-methoxyphenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vk).** Yield 91%, mp 165–168°C. ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, 3-Me), 2.33 s (3H, 6-Me), 3.89 s (3H, MeO), 7.21 d (2H, H$^{3',5'}$, 4-MeOC$_6$H$_4$, J 8.4 Hz), 7.36 s (1H, H^2), 7.85 d (2H, H$^{2',6'}$, 4-MeOC$_6$H$_4$, J 8.4 Hz), 10.55 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –76.13 s (CF$_3$). Found, %: N 3.13, 3.19. $C_{16}H_{16}F_3NO_6S_2$. Calculated, %: N 3.19.

***N*-[4-Hydroxy-3,6-dimethyl-5-tosylphenyl]-1,1,1-trifluoromethanesulfonamide (Vl).** Yield 78%, mp 175–177°C. ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, 3-Me), 2.35 s (3H, 6-Me), 2.46 s (3H, Me in Ts), 7.39 s (1H, H^2), 7.49 d (2H, H$^{3',5'}$, Ts, J 7.5 Hz), 7.81 d (2H, H$^{2',6'}$, Ts, J 7.5 Hz), 10.60 s (1H, NH), 11.48 br.s (1H,

OH). ^{19}F NMR spectrum, δ, ppm: –76.13 c (CF_3). Found, %: N 3.24, 3.30. $C_{16}H_{16}F_3NO_5S_2$. Calculated, %: N 3.31.

***N*-[4-Hydroxy-2,6-dimethyl-5-(4-methoxyphenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (Vm).** Yield 65%, mp 142–145°C. ^{1}H NMR spectrum, δ, ppm: 2.27 s (3H, 2-Me), 2.59 s (3H, 6-Me), 3.85 s (3H, MeO), 6.74 s (1H, H^{3}), 7.11 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 7.83 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 10.78 s (1H, NH), 11.34 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –76.67 s (CF_3). Found, %: N 3.24, 3.25. $C_{16}H_{16}F_3NO_6S_2$. Calculated, %: N 3.19.

***N*-[4-Hydroxy-2,6-dimethyl-5-tosylphenyl]-1,1,1-trifluoromethanesulfonamide (Vn).** Yield 91%, mp 153–155°C. ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, 2-Me), 2.43 s (3H, Me in Ts), 2.63 s (3H, 6-Me), 6.77 s (1H, H^{3}), 7.43 d (2H, H$^{3',5'}$, Ts, *J* 8.1 Hz), 7.80 d (2H, H$^{2',6'}$, Ts, *J* 8.1 Hz), 10.81 s (1H, NH), 11.23 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –76.41 s (CF_3). Found, %: N 3.34, 3.35. $C_{16}H_{16}F_3NO_5S_2$. Calculated, %: N 3.31.

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)methanesulfonamide (VIa).** ^{1}H NMR spectrum, δ, ppm: 1.88 s (6H, 2,6-Me), 3.65 s (3H, $MeSO_2$), 3.87 s (3H, MeO), 6.48 s (1H, H^{3,5}), 7.16 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 7.71 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 9.73 s (1H, OH).

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-fluorophenylsulfonyl)methanesulfonamide (VIb).** ^{1}H NMR spectrum, δ, ppm: 1.90 s (6H, 2,6-Me), 3.66 s (3H, $MeSO_2$), 6.50 s (1H, H^{3,5}), 7.44 d (2H, H$^{3',5'}$, 4-FC_6H_4, *J* 8.4 Hz), 7.93 d (2H, H$^{2',6'}$, 4-FC_6H_4, *J* 8.4 Hz), 9.74 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –102.60 s (4-FC_6H_4).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)methanesulfonamide (VIIa).** ^{1}H NMR spectrum, δ, ppm: 2.12 s (6H, 3,5-Me), 3.54 s (3H, $MeSO_2$), 3.88 s (3H, MeO), 6.73 s (1H, H^{2,6}), 7.17 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 9.3 Hz), 7.74 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 9.3 Hz), 8.81 s (1H, OH).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-(4-chlorophenylsulfonyl)methanesulfonamide (VIIb).** ^{1}H NMR spectrum, δ, ppm: 2.14 s (6H, 3,5-Me), 3.58 s (3H, $MeSO_2$), 6.79 s (1H, H^{2,6}), 7.75 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.4 Hz), 7.84 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.4 Hz), 8.86 s (1H, OH).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N*-(4-methoxyphenylsulfonyl)methanesulfonamide (VIIc).** ^{1}H NMR spectrum, δ, ppm: 1.05 d (12H, 3,5-CH$\underline{Me}_2$, *J* 6.9 Hz), 3.18–3.27 m (2H, 3,5-C$\underline{H}Me_2$), 3.62 s (3H, $MeSO_2$), 3.86 s (3H, MeO), 6.61 s (1H, H^{2,6}), 7.16 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 9.2 Hz), 7.70 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 9.2 Hz), 8.63 s (1H, OH).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N*-(4-chlorophenylsulfonyl)methanesulfonamide (VIId).** ^{1}H NMR spectrum, δ, ppm: 1.05 d (12H, 3,5-CH$\underline{Me}_2$, *J* 6.9 Hz), 3.18–3.25 m (2H, 3,5-C$\underline{H}Me_2$), 3.66 s (3H, $MeSO_2$), 6.63 s (1H, H^{2,6}), 7.77 d (4H, 4-ClC_6H_4, *J* 8.4 Hz), 8.70 br.s (1H, OH).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenylsulfonyl)methanesulfonamide (VIIe).** ^{1}H NMR spectrum, δ, ppm: 1.24 br.s (18H, 3,5-CMe_3), 3.60 s (3H, $MeSO_2$), 3.86 s (3H, MeO), 6.70 s (1H, H^{2,6}), 7.16 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz), 7.70 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz), 9.78 s (1H, OH).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-chlorophenylsulfonyl)methanesulfonamide (VIIf).** ^{1}H NMR spectrum, δ, ppm: 1.29 br.s (18H, 3,5-CMe_3), 3.65 s (3H, $MeSO_2$), 6.72 s (1H, H^{2,6}), 7.76 br.s (4H, 4-ClC_6H_4), 9.74 s (1H, OH).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)-1,1,1-trifluoromethanesulfonamide (VIIIa).** ^{1}H NMR spectrum, δ, ppm: 2.16 s (6H, 3,5-Me), 3.77 s (MeO), 6.71 s (1H, H^{2,6}), 7.17 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 7.86 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz). ^{19}F NMR spectrum, δ, ppm: –75.83 s (CF_3).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-tosyl-1,1,1-trifluoromethanesulfonamide (VIIIb).** ^{1}H NMR spectrum, δ, ppm: 2.19 s (6H, 3,5-Me), 2.42 s (3H, Me in Ts), 6.75 s (1H, H^{2,6}), 7.33 d (2H, H$^{3',5'}$, Ts, *J* 8.4 Hz), 7.88 d (2H, H$^{2',6'}$, Ts, *J* 8.4 Hz). ^{19}F NMR spectrum, δ, ppm: –75.93 s (CF_3).

***N*-[3,5-Dimethyl-4-(4-methoxyphenoxy)phenyl]methanesulfonamide (IXa).** ^{1}H NMR spectrum, δ, ppm: 2.03 s (6H, 3,5-Me), 3.02 s (3H, $MeSO_2$), 3.90 s (3H, MeO), 6.92 s (1H, H^{2,6}), 7.24 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 7.90 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 9.0 Hz), 9.79 s (1H, NH).

***N*-[3,5-Dimethyl-4-(4-chlorophenoxy)phenyl]methanesulfonamide (IXb).** Yield 66%, mp 185–187°C. ^{1}H NMR spectrum, δ, ppm: 2.04 s (6H, 3,5-Me), 3.03 s (3H, $MeSO_2$), 6.94 s (1H, H^{2,6}), 7.82 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.4 Hz), 8.02 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.4 Hz), 9.82 s (1H, NH). Found, %: N 3.63, 3.67. $C_{15}H_{16}ClNO_5S_2$. Calculated, %: N 3.59.

***N*-[3,5-Diisopropyl-4-(4-methoxyphenoxy)-phenyl] methanesulfonamide (IXc).** ^{1}H NMR spectrum, δ, ppm: 1.03 d (12H, 3,5-CH$\underline{Me}_2$, *J* 6.9 Hz), 3.02 s (3H, $MeSO_2$), 3.02–3.10 m (2H, 3,5-C$\underline{H}Me_2$), 3.90 s (3H, MeO), 7.03 s (1H, H^{2,6}), 7.24 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.3 Hz), 7.92 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.3 Hz), 9.79 c (1H, NH).

***N*-[3,5-Diisopropyl-4-(4-chlorophenoxy)phenyl] methanesulfonamide (IXd).** Yield 59%, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm: 1.05 d (12H, 3,5-CH$\underline{Me}_2$, *J* 6.9 Hz), 2.94–3.03 m (2H, 3,5-C$\underline{H}Me_2$), 3.03 s (3H, $MeSO_2$), 7.03 s (1H, H^{2,6}), 7.83 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.3 Hz), 8.04 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.3 Hz), 9.98 s (1H, NH). Found, %: N 3.08, 3.12. $C_{19}H_{24}ClNO_5S_2$. Calculated, %: N 3.14.

***N*-[3,5-Di-*tert*-butyl-4-(4-methoxyphenoxy)phenyl] methanesulfonamide (IXe).** ^{1}H NMR spectrum, δ, ppm: 1.25 s (18H, 3,5-CMe_3), 3.03 s (3H, $MeSO_2$), 3.90 s (3H, MeO), 7.22 s (1H, H^{2,6}), 7.24 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.3 Hz), 7.92 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.3 Hz), 9.79 s (1H, NH).

***N*-[3,5-Di-*tert*-butyl-4-(4-chlorophenoxy)phenyl] methanesulfonamide (IXf).** ^{1}H NMR spectrum, δ, ppm: 1.24 s (18H, 3,5-CMe_3), 3.01 s (3H, $MeSO_2$), 7.24 s (1H, H^{2,6}), 7.38 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 8.3 Hz), 7.60 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 8.3 Hz), 9.74 s (1H, NH).

***N*-[3,5-Dimethyl-4-(4-methoxyphenoxy)phenyl]-1,1,1-trifluoromethanesulfonamide (Xa).** ^{1}H NMR spectrum, δ, ppm: 2.06 s (6H, 3,5-Me), 3.83 s (3H, MeO), 7.00 s (1H, H^{2,6}), 7.11 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 7.78 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.4 Hz), 9.22 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –75.70 s (CF_3).

***N*-[3,5-Dimethyl-4-(4-methylphenoxy)phenyl]-1,1,1-trifluoromethanesulfonamide (Xb).** ^{1}H NMR spectrum, δ, ppm: 2.06 s (6H, 3,5-Me), 2.39 s (3H, Me in Ts), 7.00 s (1H, H^{2,6}), 7.39 d (2H, H$^{3',5'}$, Ts, *J* 8.1 Hz), 7.72 d (2H, H$^{2',6'}$, Ts, *J* 8.1 Hz), 9.22 s (1H, NH). ^{19}F NMR spectrum, δ, ppm: –75.69 s (CF_3).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methoxyphenylsulfonyl)phenyl]methanesulfonamide (XIa).** ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, 5-Me), 2.24 s (3H, 3-Me), 3.16 s (3H, $MeSO_2$), 3.85 s (3H, MeO), 7.02 s (1H, H^{6}), 7.29 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 7.8 Hz), 7.81 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 7.8 Hz), 8.91 s (1H, NH), 9.52 s (1H, OH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-chlorophenylsulfonyl)phenyl]methanesulfonamide (XIb).** ^{1}H NMR spectrum, δ, ppm: 2.19 s (3H, 5-Me), 2.27 s (3H, 3-Me), 3.16 s (3H, $MeSO_2$), 7.26 s (1H, H^{6}), 7.70 d (2H, H$^{3',5'}$, 4-ClC_6H_4, *J* 7.8 Hz), 7.93 d (2H, H$^{2',6'}$, 4-ClC_6H_4, *J* 7.8 Hz), 8.96 s (1H, NH), 9.49 s (1H, OH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methoxyphenylsulfonyl)phenyl]-1,1,1-trifluoromethanesulfonamide (XIIa).** ^{1}H NMR spectrum, δ, ppm: 2.14 s (3H, 5-Me), 2.22 s (3H, 3-Me), 3.89 s (3H, MeO), 7.03 s (1H, H^{6}), 7.21 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 7.8 Hz), 7.89 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 7.8 Hz), 9.24 s (1H, NH), 11.43 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.34 s (CF_3).

***N*-(4-Hydroxy-3,5-dimethyl-2-tosylphenyl)-1,1,1-trifluoromethanesulfonamide (XIIb).** ^{1}H NMR spectrum, δ, ppm: 2.12 s (3H, 5-Me), 2.23 s (3H, 3-Me), 2.46 s (3H, Me in Ts), 7.04 s (1H, H^{6}), 7.52 d (2H, H$^{3',5'}$, Ts, *J* 7.8 Hz), 7.86 d (2H, H$^{2',6'}$, Ts, *J* 7.8 Hz), 9.31 s (1H, NH), 11.40 s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.36 s (CF_3).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)methanesulfonamide (XIII),** mp 139–141°C. ^{1}H NMR spectrum, δ, ppm: 1.34 s (18H, 3,5-CMe_3), 2.82 s (3H, $MeSO_2$), 6.12 s (2H, H^{2,6}), 8.72 br.s (1H, NH), 9.40 br.s (1H, OH). Found, %: N 4.69, 4.72. $C_{15}H_{25}NO_3S$. Calculated, %: N 4.68.

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1,1,1-trifluoromethanesulfonamide (XIV),** mp 106–109°C. ^{1}H NMR spectrum, δ, ppm: 1.38 s (18H, 3,5-CMe_3), 7.00 s (2H, H^{2,6}), 7.19 br.s (1H, NH), 11.32 br.s (1H, OH). ^{19}F NMR spectrum, δ, ppm: –75.11 s (CF_3). Found, %: N 3.93, 3.95. $C_{15}H_{22}F_3NO_3S$. Calculated, %: N 3.96.

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