

Reactions of N-Substituted 2,6(3,5)-Dialkyl-1,4-benzoquinone Imines with Arenesulfinic Acids

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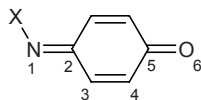
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Abstract—The regioselectivity in the reactions of *N*-arylsulfonyl-2,6-dialkyl-1,4-benzoquinone imines with arenesulfinic acids (1,6-, 6,1-, or 6,3-addition) is determined by steric factor, while in the reactions of *N*-aroyl-1,4-benzoquinone imines electronic effect of substituents in the quinoid ring is crucial. The reactions of *N*-arylsulfonyl-3,5-dimethyl-1,4-benzoquinone imines with arenesulfinic acids follow mainly the 1,4-addition pattern. *N*-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinone imines are capable of reacting in a way similar to both *N*-arylsulfonyl and *N*-aroyl derivatives.

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Reactions of various *N*-substituted 1,4-benzoquinone imines with arenesulfinic acids have been extensively studied [1, 2]. These reactions were found to follow four alternative patterns: 1,4-, 1,6-, 6,1-, and 6,3-addition, where the first number denotes the atom that takes up a proton (or other electrophile), and the second denotes the atom that takes up the corresponding acid anion (or other nucleophile); the atom numbering is shown below [2]:



While studying reactions of 2,6-dialkyl-*N*-(*p*-tolylsulfonyl)-1,4-benzoquinone imines with sodium 4-methylbenzenesulfinate we found that the regioselectivity in this process is determined by steric factor (among others) [2]. Depending on the size of the substituents in positions 2 and 6 of the quinoid ring, the most typical are 1,6- (for *N*-arylsulfonyl-2,6-diisopropyl-1,4-benzoquinone imines) and 6,1-additions (for *N*-arylsulfonyl-2,6-di-*tert*-butyl-1,4-benzoquinone imines), while 2,6-dimethyl-*N*-(4-tolylsulfonyl)-1,4-benzoquinone imine gives rise to 6,1- and 6,3-addition products. However, taking into account steric effect of substituents in the quinoid ring, formation of 1,6-ad-

dition product from 2,6-dimethyl-*N*-(4-tolylsulfonyl)-1,4-benzoquinone imine should be expected. Moreover, its fraction should be greater than in the reactions with 2,6-diisopropyl- and 2,6-di-*tert*-butyl-substituted analogs, for steric shielding of the oxygen atom in the former is minimal. Nevertheless, no 1,6-addition product was detected previously [2]. It should also be noted that the ¹H NMR spectra of the products were measured in different solvents, so that comparison of the spectral patterns and signal assignment were considerably complicated. In the present work we made an attempt to eliminate existing discrepancies in the description of reactions of 2,6-dialkyl-*N*-arylsulfonyl-1,4-benzoquinone imines with arenesulfinic acids.

The redox potential of quinone imines strongly depends on the substituent on the nitrogen atom, and it considerably affects the direction of nucleophilic addition to these compounds [3] since such reactions can formally be regarded as irreversible reduction processes. In the addition of a nucleophile at the quinone imine ring, the difference between its redox potential and that of *p*-benzoquinone is crucial, for this difference determines the structure of primary intermediate. Among known *p*-quinone imines, *N*-aroyl-1,4-benzoquinone imines are characterized by the highest redox potentials; therefore, such substrates should be expect-

ed to react with nucleophiles in a different way than *N*-arylsulfonyl derivatives. The latter occupy an intermediate place between *N*-aroyl-1,4-benzoquinone imines and *p*-benzoquinones with respect to their redox potentials.

N-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinone imines possess a bulky substituent on the nitrogen atom, which should hinder their reactions with nucleophiles according to the 6,1-addition scheme, whereas their redox potentials are intermediate between those of *N*-aroyl and *N*-arylsulfonyl analogs [3]. The reactivity of *N*-aroyl-1,4-benzoquinone imines and *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinone imines has been studied insufficiently. Their reactions with arenesulfinic acids have not been reported.

The present study was aimed at elucidating the relation between the redox potential of quinone imines (which is related in turn to electron-acceptor properties of the substituent on the nitrogen atom) and the regioselectivity in the addition of arenesulfinic acids to *N*-aroyl-, *N*-arylsulfonyl-, and *N*-(*N*-arylsulfonylbenzimidoyl)-2,6(3,5)-dialkyl-1,4-benzoquinone imines.

The reactions of *N*-arylsulfonyl-2,6(3,5)-dialkyl-1,4-benzoquinone imines **Ia**, **Ib**, **IVa**, **IVb**, **VIIa**, **VIIb**, **XLa**, and **XLb**, *N*-aroyl-2,6(3,5)-dialkyl-1,4-benzoquinone imines **IIa–IIc**, **Va–Vc**, **VIIIa**, **VIIIb**, and **XLIIa–XLIIe**, and *N*-(*N*-arylsulfonylbenzimidoyl)-2,6(3,5)-dialkyl-1,4-benzoquinone imines **IIIa–IIIId**, **VIa**, **VIb**, **IXa**, **IXb**, and **XLIIa–XLIIe** with sodium arenesulfonates **Xa–Xc** were carried out in acetic acid at a reactant ratio of 1:2. While planning experiments, the substituents in the *para* position of the aromatic fragments in the initial quinone imines and arenesulfonates (mainly Me and MeO groups) were selected so that to ensure unambiguous signal assignment in the ¹H NMR spectra.

The product mixtures were analyzed by ¹H NMR spectroscopy before recrystallization (after precipitation from the reaction solution with water). With a view to reliably determine the product structure and assign signals in the ¹H NMR spectra, a part of the product mixture obtained in each experiment was recrystallized, and both recrystallized product and that precipitated with water from the mother liquor were examined by ¹H NMR spectroscopy. As a result, we succeeded in identifying even those compounds whose fraction in the product mixture did not exceed a few percent. In some cases, repeated recrystallization was necessary to isolate individual compounds with a sufficient purity.

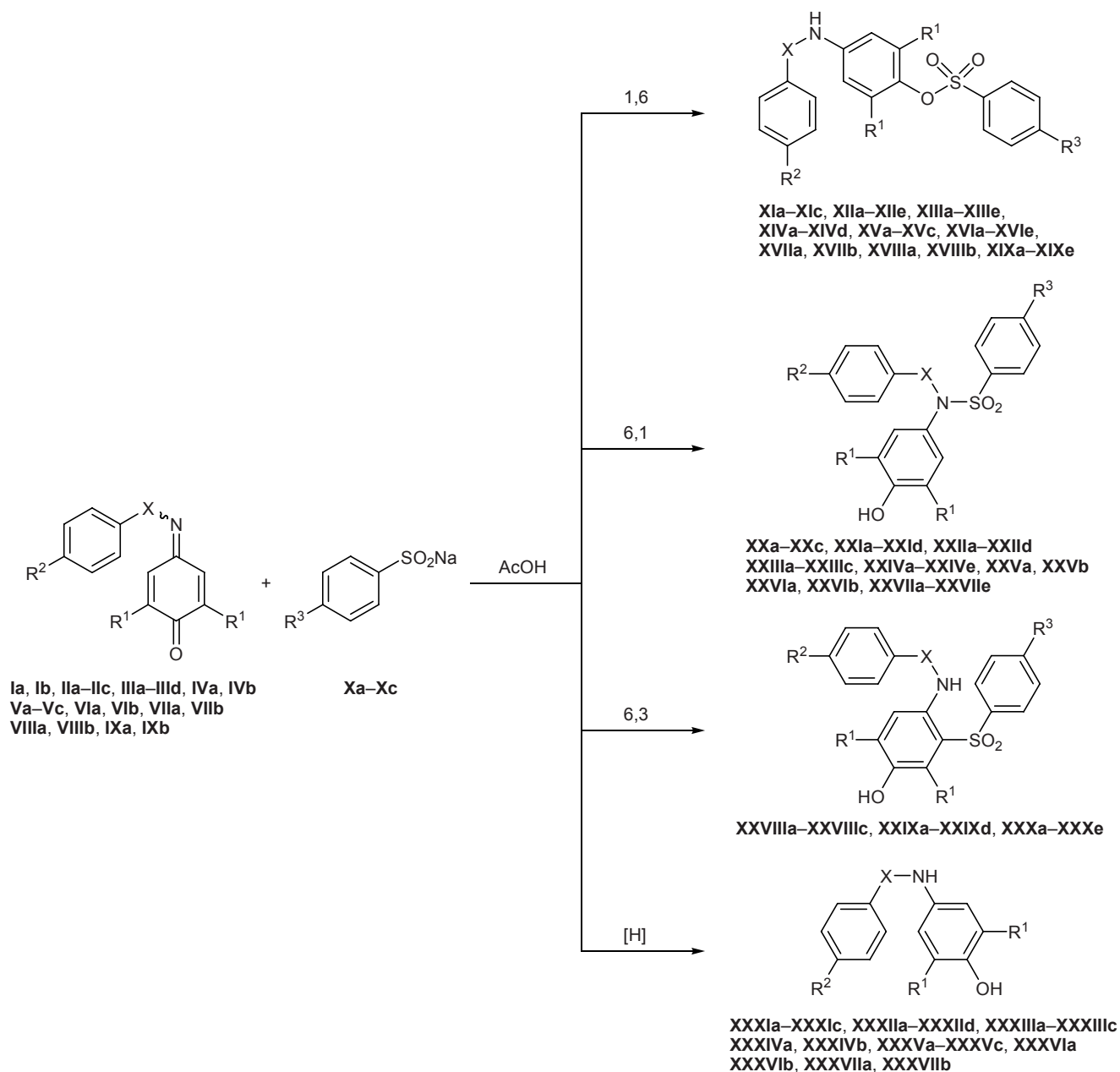
The results of the reactions of *N*-substituted 1,4-benzoquinone imines **I–IX** with arenesulfinic acids **Xa–Xc** are shown in Scheme 1, and the addition product ratios (with no account taken of the reduction products) are summarized in Table 1.

While analyzing the reaction mixtures obtained from *N*-arylsulfonyl derivatives, 4-amino-*N,N*-bis-(arylsulfonyl)-2,6-dimethyl(isopropyl, *tert*-butyl)phenols **XXa**, **XXIIa**, and **XXVa**, which were isolated as individual substances, were used as reference. These compounds possess two equivalent substituents on the nitrogen atom, and they display similar sets of signals in the ¹H NMR spectra; therefore, we succeeded in identifying 1,6-, 6,1-, and 6,3-addition products on the basis of only spectral data. Comparison of the ¹H NMR spectra of the product mixtures and individual compounds showed that aromatic protons in the aminophenol fragment of *N*-arylsulfonyl derivatives characteristically resonate at δ 6.56–6.69 (6,1-addition), 6.94–7.17 (1,6-addition), or 7.60–7.65 ppm (6,3-addition).

In the case of *N*-aroyl derivatives, assignment of signals from protons in the aminophenol ring in the 1,6- and 6,1-addition products was somewhat difficult. Even comparison of the ¹H NMR and IR spectra of individual compounds and product mixtures did not allow us to draw unambiguous conclusions. Therefore, the structure of the products obtained from *N*-aroyl-2,6-dialkyl-1,4-benzoquinone imines and arenesulfinic acids was determined by X-ray analysis of single crystals of 4-(4-methoxybenzoylamino)-2,6-dimethylphenyl 4-methylbenzenesulfonate (**XIIb**) (Fig. 1) and 4-(chlorobenzoylamino)-2,6-diisopropylphenyl 4-methoxybenzenesulfonate (**XVc**) (Fig. 2).

Due to the presence of substituents in positions 2 and 6 of the central ring in molecules **XIIb** and **XVc** the ordinary O–S bond is almost orthogonal to the aromatic ring plane [the torsion angles S¹O³C⁸C⁹ (**XIIb**) and S¹O²C¹¹C¹⁰ (**XVb**) are 77.4(2) and –92.8(3)°, respectively]. As a result, conjugation between the lone electron pair on the oxygen atom and the aromatic π -system is broken, and the O³–C⁸ (**XIIb**) and O²–C¹¹ bonds (**XVb**) are extended to 1.423(2) and 1.437(4) Å, respectively, relative to the standard value 1.401 Å [average C–O bond length in esters C*–C(=O)–O–C*] [2]. Extension of the C¹⁶–N¹ bond in molecule **XIIb** to 1.413(2) Å and of the N¹–C⁷ bond in molecule **XVc** to 1.419(4) Å relative to the average value 1.353 Å [4] should also be noted. Molecules of **XIIb** and **XVc** in crystal are linked to infinite chains through intermolecular hydrogen bonds N–H \cdots O between the

Scheme 1.



I, X = SO₂, R¹ = Me, R² = Me (**a**), Cl (**b**); **II**, X = CO, R¹ = R² = Me (**a**), R¹ = Me, R² = MeO (**b**), H (**c**); **III**, X = C(=NSO₂Ar), R¹ = Me, R² = H, Ar = 4-MeC₆H₄ (**a**), 4-MeOC₆H₄ (**b**), 4-ClC₆H₄ (**c**), 4-BrC₆H₄ (**d**); **IV**, X = SO₂, R¹ = *i*-Pr, R² = Me (**a**), Cl (**b**); **V**, X = CO, R¹ = *i*-Pr, R² = Me (**a**), MeO (**b**), Cl (**c**); **VI**, X = C(=NSO₂Ar), R¹ = *i*-Pr, R² = H, Ar = 4-MeC₆H₄ (**a**), 4-MeOC₆H₄ (**b**); **VII**, X = SO₂, R¹ = *t*-Bu, R² = Me (**a**), MeO (**b**); **VIII**, X = CO, R¹ = *t*-Bu, R² = Me (**a**), Cl (**b**); **IX**, X = C(=NSO₂Ar), R¹ = *t*-Bu, R² = H, Ar = 4-MeC₆H₄ (**a**), 4-MeOC₆H₄ (**b**); **X**, R³ = Me (**a**), MeO (**b**), Cl (**c**); **XI**, X = SO₂, R¹ = R² = R³ = Me (**a**), R¹ = R³ = Me, R² = Cl (**b**), R¹ = Me, R² = Cl, R³ = MeO (**c**); **XII**, X = CO, R¹ = R² = Me, R³ = MeO (**a**), R¹ = R³ = Me, R² = MeO (**b**), R¹ = Me, R² = MeO, R³ = Cl (**c**), R¹ = Me, R² = H, R³ = MeO (**d**); **XIII**, X = C(=NSO₂Ar), R¹ = Me, R² = H, Ar = 4-MeC₆H₄, R³ = MeO (**a**), Ar = 4-MeOC₆H₄, R³ = MeO (**b**), Ar = 4-MeOC₆H₄, R³ = Me (**c**), Ar = 4-ClC₆H₄, R³ = MeO (**d**), Ar = 4-BrC₆H₄, R³ = Me (**e**); **XIV**, X = SO₂, R¹ = *i*-Pr, R² = R³ = Me (**a**), R² = Me, R³ = MeO (**b**), R² = Cl, R³ = Me (**c**), R² = Cl, R³ = MeO (**d**); **XV**, X = CO, R¹ = *i*-Pr, R² = Me, R³ = MeO (**a**), R² = MeO, R³ = Me (**b**), R² = Cl, R³ = MeO (**c**); **XVI**, X = C(=NSO₂Ar), R¹ = *i*-Pr, R² = H, Ar = 4-MeC₆H₄, R³ = MeO (**a**), Ar = 4-MeOC₆H₄, R³ = MeO (**b**), Ar = 4-MeOC₆H₄, R³ = Me (**c**), Ar = 4-ClC₆H₄, R³ = MeO (**d**), Ar = 4-BrC₆H₄, R³ = Me (**e**); **XVII**, X = SO₂, R¹ = *t*-Bu, R² = R³ = Me (**a**), R² = MeO, R³ = Me (**b**); **XVIII**, X = CO, R¹ = *t*-Bu, R² = Cl, R³ = MeO (**a**), R² = Me, R³ = MeO (**b**); **XIX**, X = C(=NSO₂Ar), R¹ = *t*-Bu, R² = H, Ar = 4-MeC₆H₄, R³ = MeO (**a**), Ar = 4-MeOC₆H₄, R³ = MeO (**b**), Ar = 4-MeOC₆H₄, R³ = Me (**c**), Ar = 4-ClC₆H₄, R³ = MeO (**d**), Ar = 4-BrC₆H₄, R³ = Me (**e**); **XX**, X = SO₂, R¹ = R² = R³ = Me (**a**), R¹ =

Scheme 1. (Contd.)

$R^3 = \text{Me}$, $R^2 = \text{Cl}$ (**b**), $R^1 = \text{Me}$, $R^2 = \text{Cl}$, $R^3 = \text{MeO}$ (**c**); **XXI**, $X = \text{CO}$, $R^1 = R^2 = \text{Me}$, $R^3 = \text{MeO}$ (**a**), $R^1 = R^3 = \text{Me}$, $R^2 = \text{MeO}$ (**b**), $R^1 = \text{Me}$, $R^2 = \text{MeO}$, $R^3 = \text{Cl}$ (**c**), $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^3 = \text{MeO}$ (**d**); **XXII**, $X = \text{SO}_2$, $R^1 = i\text{-Pr}$, $R^2 = R^3 = \text{Me}$ (**a**), $R^2 = \text{Me}$, $R^3 = \text{MeO}$ (**b**), $R^2 = \text{Cl}$, $R^3 = \text{Me}$ (**c**), $R^2 = \text{Cl}$, $R^3 = \text{MeO}$ (**d**); **XXIII**, $X = \text{CO}$, $R^1 = i\text{-Pr}$, $R^2 = \text{Me}$, $R^3 = \text{MeO}$ (**a**), $R^2 = \text{MeO}$, $R^3 = \text{Me}$ (**b**), $R^2 = \text{Cl}$, $R^3 = \text{MeO}$ (**c**); **XXIV**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = i\text{-Pr}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**a**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**b**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{Me}$ (**c**), $\text{Ar} = 4\text{-ClC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**d**), $\text{Ar} = 4\text{-BrC}_6\text{H}_4$, $R^3 = \text{Me}$ (**e**); **XXV**, $X = \text{SO}_2$, $R^1 = t\text{-Bu}$, $R^2 = R^3 = \text{Me}$ (**a**), $R^2 = \text{Me}$, $R^3 = \text{MeO}$ (**b**); **XXVI**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = t\text{-Bu}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**a**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**b**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{Me}$ (**c**), $\text{Ar} = 4\text{-ClC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**d**), $\text{Ar} = 4\text{-BrC}_6\text{H}_4$, $R^3 = \text{Me}$ (**e**); **XXVIII**, $X = \text{SO}_2$, $R^1 = R^2 = R^3 = \text{Me}$ (**a**), $R^1 = R^3 = \text{Me}$, $R^2 = \text{Cl}$ (**b**), $R^1 = \text{Me}$, $R^2 = \text{Cl}$, $R^3 = \text{MeO}$ (**c**); **XXIX**, $X = \text{CO}$, $R^1 = R^2 = \text{Me}$, $R^3 = \text{MeO}$ (**a**), $R^1 = R^3 = \text{Me}$, $R^2 = \text{MeO}$ (**b**), $R^1 = \text{Me}$, $R^2 = \text{MeO}$, $R^3 = \text{Cl}$ (**c**), $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^3 = \text{MeO}$ (**d**); **XXX**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**a**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**b**), $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, $R^3 = \text{Me}$ (**c**), $\text{Ar} = 4\text{-ClC}_6\text{H}_4$, $R^3 = \text{MeO}$ (**d**), $\text{Ar} = 4\text{-BrC}_6\text{H}_4$, $R^3 = \text{Me}$ (**e**); **XXXI**, $X = \text{CO}$, $R^1 = \text{Me}$, $R^2 = \text{Me}$ (**a**), MeO (**b**), H (**c**); **XXXII**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = \text{Me}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ (**a**), $4\text{-MeOC}_6\text{H}_4$ (**b**), $4\text{-ClC}_6\text{H}_4$ (**c**), $4\text{-BrC}_6\text{H}_4$ (**d**); **XXXIII**, $X = \text{CO}$, $R^1 = i\text{-Pr}$, $R^2 = \text{Me}$ (**a**), MeO (**b**), Cl (**c**); **XXXIV**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = i\text{-Pr}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ (**a**), $4\text{-MeOC}_6\text{H}_4$ (**b**); **XXXV**, $X = \text{SO}_2$, $R^1 = t\text{-Bu}$, $R^2 = \text{Me}$ (**a**), MeO (**b**), Cl (**c**); **XXXVI**, $X = \text{CO}$, $R^1 = t\text{-Bu}$, $R^2 = \text{Me}$ (**a**), Cl (**b**); **XXXVII**, $X = \text{C}(=\text{NSO}_2\text{Ar})$, $R^1 = t\text{-Bu}$, $R^2 = \text{H}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$ (**a**), $4\text{-MeOC}_6\text{H}_4$ (**b**).

amide groups of the neighboring molecules [**XIIb**: $\text{N}^1\text{-H}^{1A}\cdots\text{O}^4$; x , $1 - y$, $-0.5 + z$; $\text{H}\cdots\text{O}$ 2.14 Å, $\angle\text{NHO}$ 154°; **XVc**: $\text{N}^1\text{-H}^{1A}\cdots\text{O}^{1'}$; $1.5 - x$, y , $0.5 + z$; $\text{H}\cdots\text{O}$ 2.09 Å, $\angle\text{NHO}$ 154°].

On the basis of the X-ray diffraction data, we were able to determine specificity of the spectral patterns of the addition products of arenesulfonates to *N*-aryloyl-2,6-dialkyl-1,4-benzoquinone imines. Protons in the aminophenol ring of 1,6-addition products are characterized by chemical shifts of δ 7.53–7.91 ppm, those in 6,1-addition products resonate in the region δ 6.67–6.82 ppm, and analogous protons in 6,3-adducts appear at δ 7.82–7.83 ppm. Compounds **XIIa–XIIId**, **XVa**, **XVc**, and **XVIa–XVIc** display in the IR spectra NH absorption band at 3310–3350 cm^{-1} .

According to the ^1H NMR data, addition products of arenesulfonates to 2,6-dialkyl-*N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinone imines are characterized by the following chemical shifts of protons in

the aminophenol ring, δ , ppm: 1,6-adducts, 7.25–7.72; 6,1-adducts, 6.68–6.96, and 6,3-adducts, 7.66–7.71.

Thus our experiments showed that all reactions of 1,4-benzoquinone imines **I–IX** with arenesulfonic acids are accompanied by formation of the corresponding 1,6-addition products (addition at the oxygen atom). We were the first to obtain 1,6-addition products not only from *N*-arylsulfonyl-2,6-diisopropyl-1,4-benzoquinone imines [4-amino-*N,O*-bis(arylsulfonyl)-2,6-diisopropylphenols **XIVa–XIVd**] but also from *N*-arylsulfonyl-2,6-dimethyl-1,4-benzoquinone imines [4-amino-*N,O*-bis(arylsulfonyl)-2,6-dimethylphenols **XIa–XIc**] and *N*-arylsulfonyl-2,6-di-*tert*-butyl-1,4-benzoquinone imines [4-amino-*N,O*-bis(arylsulfonyl)-2,6-di-*tert*-butylphenols **XVIIa** and **XVIIb**]. Compounds **XIa–XIc**, **XVIIa**, and **XVIIb** were not isolated previously. Addition products at the nitrogen atom (6,1-addition pattern) were isolated in all cases, except for *N*-(*N*-arylsulfonylbenzimidoyl)-2,6-dimethyl-1,4-benzoquinone imines **IIIa–IIIId**.

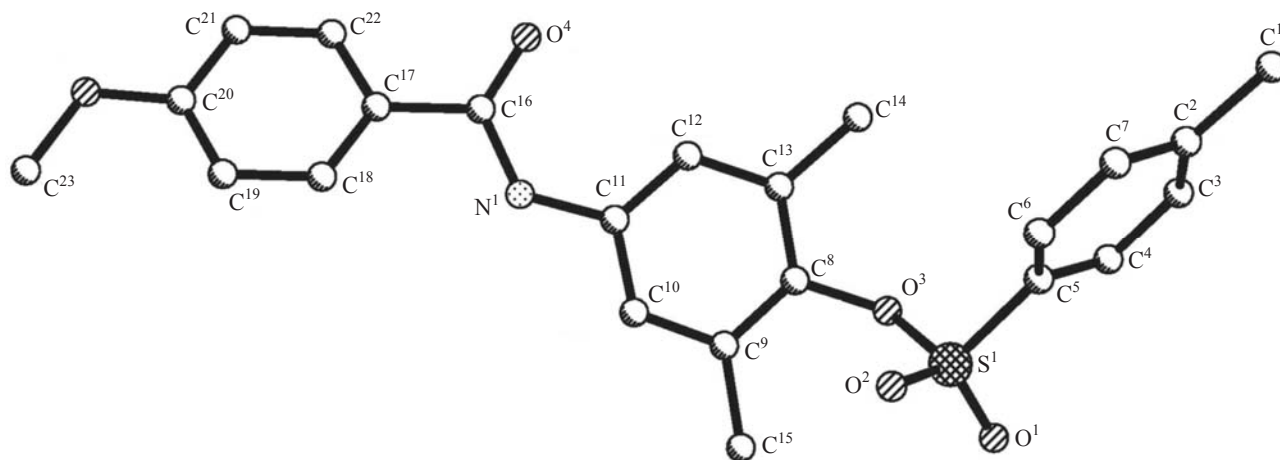


Fig. 1. Structure of the molecule of 2,6-dimethyl-4-(4-methoxybenzoylamino)phenyl 4-methylbenzenesulfonate (**XIIb**) according to the X-ray diffraction data.

Table 1. Product composition in the reactions of 2,6-dialkyl-1,4-benzoquinone imines **I–IX** with sodium arenesulfinates **Xa–Xc** (Scheme 1)

X	R ¹	R ³	R ⁴	Fraction of addition products, %		
				1,6	6,1	6,3
SO ₂	Me	Me	Me	44	26	30
SO ₂	Me	Cl	Me	40	24	36
SO ₂	Me	Cl	MeO	43	22	35
CO	Me	Me	MeO	52	14	34
CO	Me	MeO	Me	62.5	11	26.5
CO	Me	MeO	Cl	68	23	9
CO	Me	H	MeO	71	14	15
C(=NSO ₂ C ₆ H ₄ Me-4)	Me	H	MeO	95	–	5
C(=NSO ₂ C ₆ H ₄ Cl-4)	Me	H	MeO	93	–	7
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	H	MeO	94	–	6
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	H	Me	89	–	11
C(=NSO ₂ C ₆ H ₄ Br-4)	Me	H	Me	94	–	6
SO ₂	<i>i</i> -Pr	Me	Me	51	49	–
SO ₂	<i>i</i> -Pr	Me	MeO	53	47	–
SO ₂	<i>i</i> -Pr	Cl	Me	52	48	–
SO ₂	<i>i</i> -Pr	Cl	MeO	49	51	–
CO	<i>i</i> -Pr	Me	MeO	69	31	–
CO	<i>i</i> -Pr	MeO	Me	71	29	–
CO	<i>i</i> -Pr	Cl	MeO	67	33	–
C(=NSO ₂ C ₆ H ₄ Me-4)	<i>i</i> -Pr	H	MeO	89	11	–
C(=NSO ₂ C ₆ H ₄ OMe-4)	<i>i</i> -Pr	H	MeO	84	16	–
C(=NSO ₂ C ₆ H ₄ OMe-4)	<i>i</i> -Pr	H	Me	84	16	–
SO ₂	<i>t</i> -Bu	Me	Me	35	65	–
SO ₂	<i>t</i> -Bu	MeO	Me	45	55	–
CO	<i>t</i> -Bu	Me	MeO	87	13	–
CO	<i>t</i> -Bu	Cl	MeO	77	23	–
C(=NSO ₂ C ₆ H ₄ Me-4)	<i>t</i> -Bu	H	MeO	65	35	–
C(=NSO ₂ C ₆ H ₄ OMe-4)	<i>t</i> -Bu	H	MeO	80	20	–
C(=NSO ₂ C ₆ H ₄ OMe-4)	<i>t</i> -Bu	H	Me	60	40	–

In going from 2,6-dimethyl- (**Ia** and **Ib**) to 2,6-di-*tert*-butyl-substituted *N*-arylsulfonyl-1,4-benzoquinone imines **VIIa** and **VIIb**, the ratio of 1,6- and 6,1-addition products changes from 2 : 1 to 2 : 3, indicating steric effect of the substituents in positions 2 and 6 of the quinoid ring on the addition of arenesulfinic acids to these compounds.

In the reactions with *N*-aroyl-2,6-dialkyl-1,4-benzoquinone imines **IIa–IIc**, **Va–Vc**, **VIIIa**, and **VIIIb**, the corresponding 1,6-addition products, 4-(*N*-aroylamino)-2,6-dimethyl(*isopropyl*-, *tert*-butyl)phenyl

arenesulfonates **XIIa–XIIId**, **XVa–XVc**, **XVIIIa**, and **XVIIIb**, were formed as the major products, and the reaction mixtures also contained reduction products **XXXIa–XXXIc**, **XXXIIa–XXXIIc**, **XXXVIa**, and **XXXVIb**. Analysis of the product ratio showed that, unlike *N*-arylsulfonyl-1,4-benzoquinone imines, steric factor is not determining in the addition of arenesulfinates to *N*-aroyl-2,6-dialkyl-1,4-benzoquinone imines: as the size of the substituents in positions 2 and 6 of the quinoid ring of compounds **IIa–IIc**, **Va–Vc**, **VIIIa**, and **VIIIb** increases, the fraction of the

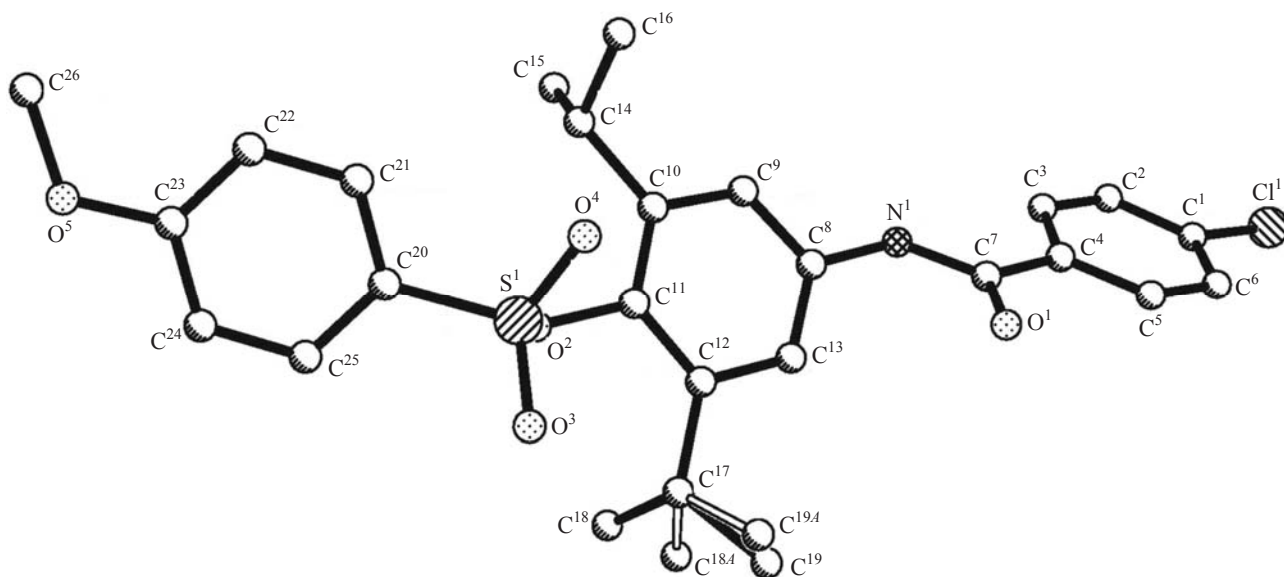


Fig. 2. Structure of the molecule of 4-(4-chlorobenzoylamino)-2,6-diisopropylphenyl 4-methoxybenzenesulfonate (**XVc**) according to the X-ray diffraction data.

corresponding 1,6-addition also increases (Table 1). This may be interpreted in terms of deactivation of the reaction center (nitrogen atom) by strong electron-withdrawing ArCO group and activation of the oxygen atom due to effect of donor alkyl groups in positions 2 and 6; here, increase in the donor properties of substituents in the series Me > *i*-Pr > *t*-Bu is accompanied by increase in the fraction of the 1,6-addition product.

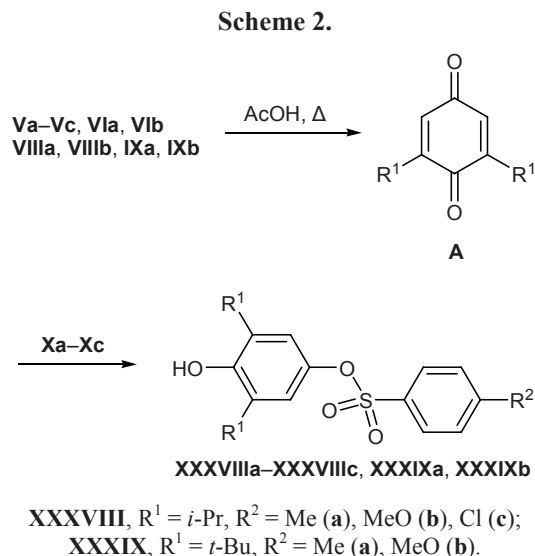
N-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinone imines **IIIa–III d**, **VIa**, **VIb**, **IXa**, and **IXb** are structural analogs of *N*-aroyl-1,4-benzoquinone imines [5]. They occupy an intermediate place between *N*-arylsulfonyl and *N*-aroyl derivatives with respect to electron-withdrawing effect of the substituent on the nitrogen atom and redox potential. Our experimental results showed that they behave similarly to both *N*-arylsulfonyl and *N*-aroyl analogs. As in *N*-aroyl-1,4-benzoquinone imines, the main reaction center in *N*-(*N*-arylsulfonylbenzimidoyl) derivatives is the oxygen atom. On the other hand, the fraction of 1,6-addition products decreases as the size of the substituents in positions 2 and 6 of the quinoid ring increases, as in the reactions with *N*-arylsulfonyl derivatives. It should be noted that quinone imines **IIIa–III d** did not give rise to addition products at the nitrogen atom, while the fraction of the 6,3-addition products was ~6–11%, presumably due to considerable steric hindrances created by the bulky CPh(=NSO₂Ar) substituent on the nitrogen atom.

6,3-Addition products were isolated only in the reactions with 2,6-dimethyl derivatives **Ia**, **Ib**, **IIa–IIc**,

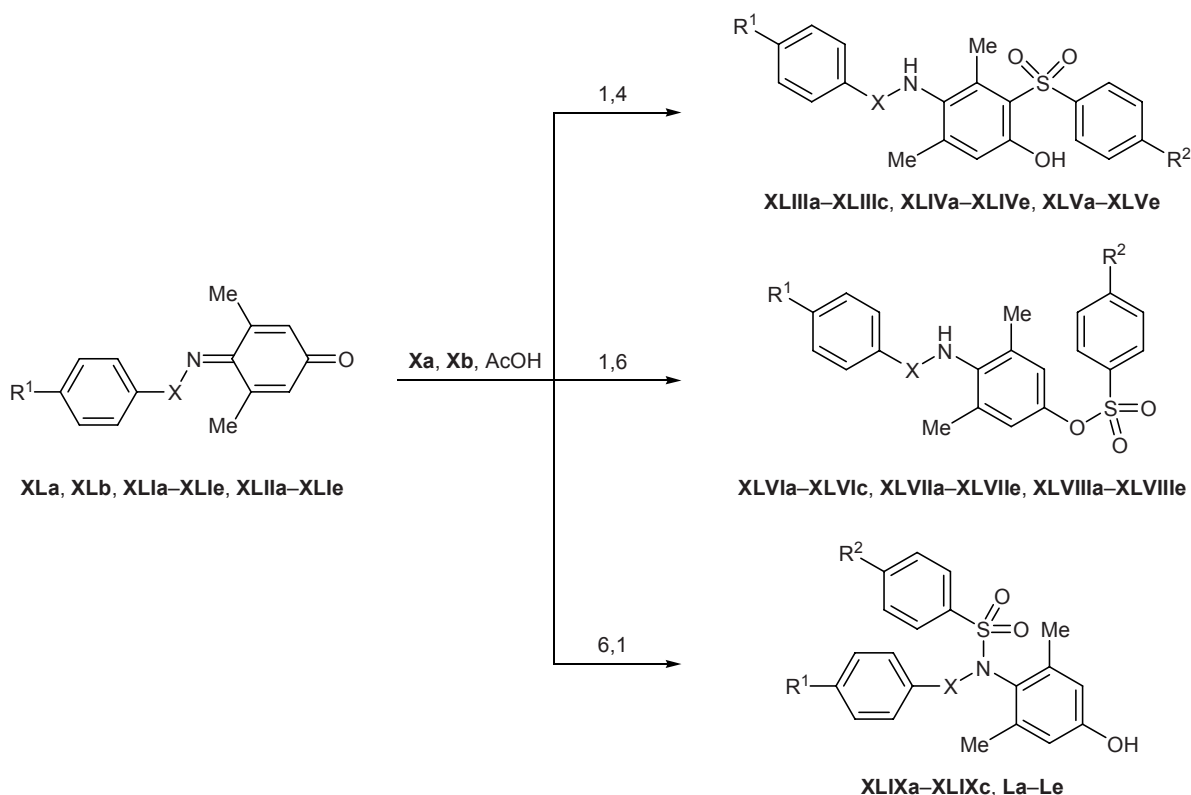
and **IIIa–III d**. The absence of analogous compounds among products of addition to quinone imines **IV–IX** may be rationalized in terms of steric effect of bulky isopropyl and *tert*-butyl groups in the quinoid ring.

In most cases, we isolated reduction products of the initial quinone imines, *N*-arylsulfonyl-, *N*-aroyl-, and *N*-(*N*-arylsulfonylbenzimidoyl)aminophenols **XXXI–XXXVII**, and their fraction in the reaction mixtures increased in parallel with the redox potential of the initial quinone imines [3].

The reaction mixtures obtained from quinone imines **Va–Vc**, **VIa**, **VIb**, **VIIIa**, **VIIIb**, **IXa**, and **IXb** and arenesulfinic acids also contained 3,5-dialkyl-4-



Scheme 3.



XL, X = SO₂, R¹ = Me (**a**), MeO (**b**); **XLI**, X = CO, R¹ = Me (**a**), MeO (**b**), Cl (**c**), Br (**d**), H (**e**); **XLII**, X = C(=NSO₂Ar), R¹ = H, Ar = Ph (**a**), 4-MeC₆H₄ (**b**), 4-MeOC₆H₄ (**c**), 4-ClC₆H₄ (**d**), 4-BrC₆H₄ (**e**); **XLIII**, X = SO₂, R¹ = Me, R² = MeO (**a**), R¹ = MeO, R² = Me (**b**), R¹ = R² = MeO (**c**); **XLIV**, X = CO, R¹ = Me, R² = MeO (**a**), R¹ = Cl, R² = MeO (**b**), R¹ = Br, R² = MeO (**c**), R¹ = MeO, R² = Me (**d**), R¹ = H, R² = Me (**e**); **XLV**, X = C(=NSO₂Ar), R¹ = H, Ar = 4-MeC₆H₄, R² = MeO (**a**), Ar = 4-MeOC₆H₄, R² = MeO (**b**), Ar = 4-BrC₆H₄, R² = MeO (**c**), Ar = 4-ClC₆H₄, R² = MeO (**d**), Ar = Ph, R² = Me (**e**); **XLVI**, X = SO₂, R¹ = Me, R² = MeO (**a**), R¹ = MeO, R² = Me (**b**), R¹ = R² = MeO (**c**); **XLVII**, X = CO, R¹ = Me, R² = MeO (**a**), R¹ = Cl, R² = MeO (**b**), R¹ = Br, R² = MeO (**c**), R¹ = MeO, R² = Me (**d**), R¹ = H, R² = Me (**e**); **XLVIII**, X = C(=NSO₂Ar), R¹ = H, Ar = 4-MeC₆H₄, R² = MeO (**a**), Ar = 4-MeOC₆H₄, R² = MeO (**b**), Ar = 4-BrC₆H₄, R² = MeO (**c**), Ar = 4-ClC₆H₄, R² = MeO (**d**), Ar = Ph, R² = Me (**e**); **XLIX**, X = SO₂, R¹ = Me, R² = MeO (**a**), R¹ = R² = MeO (**b**); **L**, X = CO, R¹ = Me, R² = MeO (**a**), R¹ = Cl, R² = MeO (**b**), R¹ = Br, R² = MeO (**c**), R¹ = MeO, R² = Me (**d**), R¹ = H, R² = Me (**e**).

hydroxyphenyl arenesulfonates **XXXVIIIa-XXXVIIIc**, **XXXIXa**, and **XXXIXb** formed via addition of arenesulfonic acids to 1,4-benzoquinones **A** resulting in turn from hydrolysis of the initial quinone imines (Scheme 2). 1,4-Benzoquinones **A** were not detected in the reaction mixtures. The structure of compounds **XXXVIIIa-XXXVIIIc**, **XXXIXa**, and **XXXIXb** was confirmed by independent synthesis from 2,6-diisopropyl(*tert*-butyl)-1,4-benzoquinones **A** and arenesulfonates **Xa-Xc**, as well as by elemental analyses and ¹H NMR data. In the ¹H NMR spectra of these compounds, the CH proton in the isopropyl groups resonated at δ 3.14–3.29 ppm, which is typical of 6,1-addition products.

Scheme 3 shows the results of the reactions of *N*-arylsulfonyl- (**XLa**, **XLb**), *N*-aroyl- (**XLIIa-XLIIe**),

and *N*-(*N*-arylsulfonylbenzimidoyl)-3,5-dimethyl-1,4-benzoquinone imines **XLIIIa-XLIIIe** with sodium arenesulfonates **Xa** and **Xb**, and the product ratios are collected in Table 2. The structure of the 1,6- and 6,1-addition products derived from *N*-arylsulfonyl derivatives **XLa** and **XLb** (compounds **XLVIa-XLVic** and **XLIXa-XLIXc**) was proved by analysis of the ¹H NMR spectra recorded from the filtrates obtained after recrystallization of the product mixtures. As described above for *N*-arylsulfonyl-2,6-dimethyl-1,4-benzoquinone imines, signals in their ¹H NMR spectra were assigned on the basis of the ¹H NMR spectrum of 6,1-addition product **XLIXc** having two equivalent substituents on the nitrogen atom.

The structure of *N*-aroyl-3,5-dimethyl-1,4-benzoquinone imines could not be assigned unambiguously

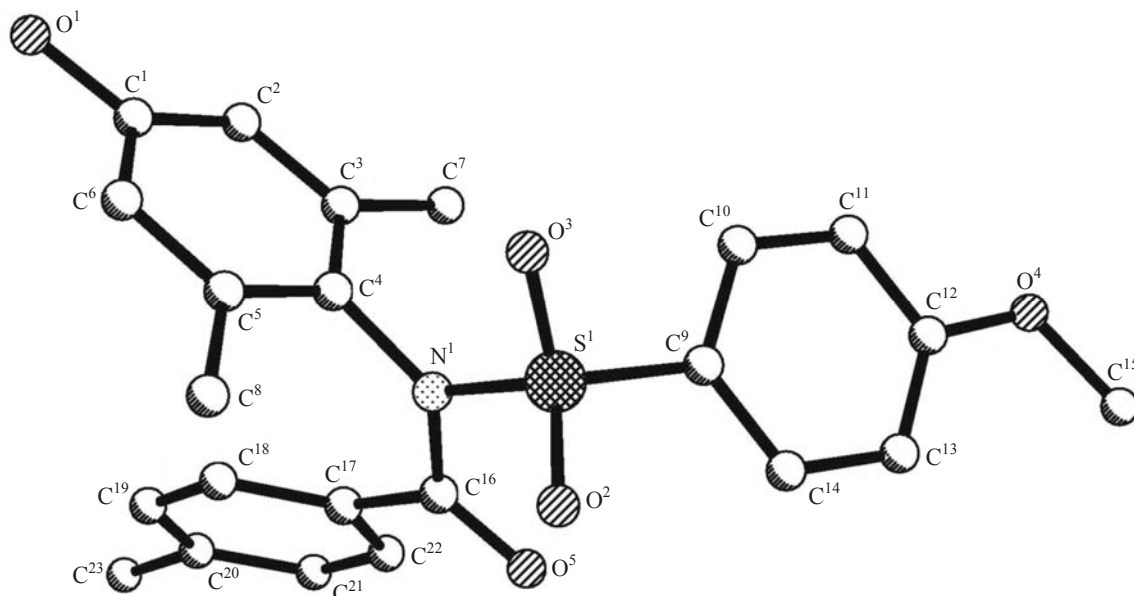
Table 2. Product composition in the reactions of 3,5-dimethyl-1,4-benzoquinone imines **XL–XLII** with sodium arenosulfonates **Xa** and **Xb** (Scheme 3)

X	R ¹	R ²	Fraction of addition products, %		
			1,4	6,1	1,6
SO ₂	Me	MeO	91	5	4
SO ₂	MeO	Me	81	15	4
SO ₂	MeO	MeO	83	14	3
CO	Me	Me	12	77	11
CO	Me	MeO	27	45	28
CO	Me	Cl	10	79	11
CO	MeO	Me	35	39	26
CO	Cl	MeO	24	55	21
CO	H	Me	29	51	20
CO	Br	MeO	26	56	18
C(=NSO ₂ Ph)	H	Me	81	–	19
C(=NSO ₂ C ₆ H ₄ Me-4)	H	MeO	81	–	19
C(=NSO ₂ C ₆ H ₄ Cl-4)	H	MeO	79	–	21
C(=NSO ₂ C ₆ H ₄ Br-4)	H	MeO	82	–	18
C(=NSO ₂ C ₆ H ₄ OMe-4)	H	MeO	90	–	10

on the basis of the ¹H NMR data. Therefore, one of these compounds, *N*-(2,6-dimethyl-4-hydroxyphenyl)-4-methoxyphenylsulfonyl)-4-methylbenzamide (**La**) was examined by X-ray diffraction (Fig. 3).

The amide nitrogen atom in molecule **La** bears three bulky substituents, which induce considerable steric strain. As a result, there are shortened intra-

molecular contacts H^{7C}...C¹⁶ 2.74 Å (the sum of the corresponding van der Waals radii is 2.87 Å [6]), C⁴...C¹⁸ 2.99 Å (3.42 Å), C⁵...H¹⁸ 2.58 Å (2.87 Å), and S¹...C⁸ 3.44 Å (3.58 Å), while the bond angles C⁴C³C⁷ 123.2(2)°, C⁴C⁵C⁸ 122.70(19)°, and C¹⁶C¹⁷C¹⁸ 126.62(19)° are increased as compared to C²C³C⁷ 119.2(2)°, C⁶C⁵C⁸ 118.72(19)°, and C¹⁶C¹⁷C²²

**Fig. 3.** Structure of the molecule of *N*-(4-hydroxy-2,6-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)-4-methylbenzamide (**La**) according to the X-ray diffraction data.

115.56(18)°, respectively. Steric strain in molecule **La** leads to rupture of conjugation between the π -electron system of the phenol ring and lone electron pair on the nitrogen atom [the torsion angle $C^4C^3N^1C^{16}$ is $-72.4(3)^\circ$]. Molecules **La** in crystal give rise to chains along the crystallographic (*100*) axis due to intermolecular hydrogen bonds $O^1-H^{1A}\cdots O^{3'}$ ($0.5 + x, 0.5 - y, 0.5 + z$) ($H\cdots O$ 1.99 Å, $\angle OHO$ 168.8°).

Addition products of arenesulfinates to 3,5-dimethyl-1,4-benzoquinone imines are characterized by the following chemical shifts of aromatic protons in the aminophenol fragment: 1,4-adducts: δ 6.84–6.85 ppm for *N*-arylsulfonyl derivatives and δ 6.68–6.82 ppm for *N*-aroyl- and *N*-(*N*-arylsulfonylbenzimidoyl) derivatives; 6,1-adducts: δ 6.56 ppm for *N*-arylsulfonyl and δ 6.44–6.48 ppm for *N*-aroyl derivatives; 1,6-adducts: δ 6.71 ppm for *N*-arylsulfonyl and δ 6.82–6.86 ppm for *N*-aroyl and *N*-(*N*-arylsulfonylbenzimidoyl) derivatives. In the IR spectrum of **La**, the OH group gave rise to absorption at 3450 cm^{-1} . 1,4-Addition products **XLIIa–XLIIIc** characteristically displayed absorption bands at 3210–3250 (NH) and 3290–3300 cm^{-1} (OH).

The reactions of *N*-arylsulfonyl-3,5-dimethyl-1,4-benzoquinone imines **XLa** and **XLb** with arenesulfinates afforded mainly 1,4-addition products **XLIIa–XLIIIc**. In the reactions with *N*-aroyl-3,5-dimethyl-1,4-benzoquinone imines **XLIIa–XLIIe** the major products were compounds **La–Le** formed via addition at the nitrogen atom. The direction of arenesulfinate addition to *N*-aroyl-1,4-benzoquinone imines depends on the electronic properties of substituents in the quinoid ring. The presence of electron-donating substituents in positions 3 and 5 of the quinoid ring makes the nitrogen atom more reactive toward arenesulfinates (Table 2). If alkyl groups are present in positions 2 and 6 of the quinoid ring (quinone imines **IIa–IIc**, **Va–Vc**, **VIIa**, and **VIIb**), the oxygen atom becomes more reactive. It should be noted that the fraction of the 1,4-addition products derived from *N*-aroyl derivatives is considerably smaller than that in the reactions with *N*-arylsulfonyl derivatives, i.e., positions 2 and 6 in the quinoid ring of 3,5-dimethyl-substituted *N*-arylsulfonyl-1,4-benzoquinone imines are more reactive than those in the corresponding *N*-aroyl derivatives.

The reactions of *N*-(*N*-arylsulfonylbenzimidoyl)-3,5-dimethyl-1,4-benzoquinone imines **XLIIa–XLIIe** with arenesulfinates **Xa** and **Xb** gave only 1,6- and 1,4-addition products, the latter prevailing (as with *N*-arylsulfonyl derivatives), while the fraction of the 1,6-ad-

dition products is similar to that found in the reactions with *N*-aroyl derivatives. The absence of addition products at the nitrogen atom is likely to result from considerable steric hindrances due to the presence of substituents in positions 3 and 5 of the quinoid ring and bulky substituent on the nitrogen atom.

Thus in the present work we determined the following general relations holding in the reactions of symmetrically substituted 1,4-benzoquinone imines with arenesulfonic acids:

(1) *N*-Substituted 1,4-benzoquinone imines react with arenesulfonic acids according to 1,6-, 6,1-, 6,3-, and 1,4-addition patterns, and the regioselectivity of the addition is determined by the reactivity ratio of the N, C²/C⁶, C³/C⁵, and O centers in the quinoid ring;

(2) The most reactive centers in *N*-arylsulfonyl-1,4-benzoquinone imines with respect to arenesulfinates are positions 2 and 6 in the quinoid ring; when these positions are occupied, the addition direction is determined by steric factor, i.e., by the size of substituents therein;

(3) The addition of arenesulfinates to *N*-aroyl-1,4-benzoquinone imines (in which the substituent on the nitrogen atom is the strongest electron acceptor among the examined ones) is governed by electronic effect of the substituents in the quinoid ring: electron-donating substituents favor addition at the nearest reaction center, nitrogen or oxygen atom;

(4) *N*-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinone imines whose redox potential and electronic properties of the substituent on the nitrogen atom are intermediate between those of analogous *N*-arylsulfonyl- and *N*-aroyl-1,4-benzoquinone imines exhibit reactivity typical of both *N*-arylsulfonyl and *N*-aroyl derivatives.

On the basis of the above stated we can conclude that increase in the electron-withdrawing properties of the substituent on the nitrogen atom is accompanied by change of the effect of the substituents in the quinoid ring on the addition of arenesulfonic acids: in going from *N*-arylsulfonyl to *N*-aroyl derivatives, steric factor becomes less important whereas electronic effect of the substituents and their position become crucial.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz from solutions in acetone-*d*₆ (compounds **XI**, **XIV**, **XVII**, **XX**, **XXII**, **XXV**, **XXVIII**, **XXXV**, **XLIII**, **XLVI**, and **XLIX**),

DMSO- d_6 (XII, XIII, XV, XVI, XVIII, XIX, XXI, XXIII, XXIV, XXVI, XXVII, XXIX–XXXIV, XXXVI–XXXIX, XLIV, XLV, XLVII, XLVIII, L), or CDCl_3 (XLb, XLIIId) using tetramethylsilane as reference. The IR spectra were measured in KBr on a UR-20 instrument. Thin-layer chromatography was performed on Silufol UV-254 plates; spots were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and the chromatograms were developed under UV light.

The X-ray diffraction data for compounds XIIb, XVc, and La were acquired on an Xcalibur-3 diffractometer at 293 K (MoK_α irradiation, CCD detector, graphite monochromator, ω scanning, $2\theta_{\text{max}} = 50^\circ$). Compound XIIb: monoclinic crystals, $\text{C}_{23}\text{H}_{23}\text{NO}_5\text{S}$; unit cell parameters: $a = 14.7415(9)$, $b = 16.8436(8)$, $c = 9.7969(5)$ Å; $\beta = 118.886(6)^\circ$; $V = 2129.9(2)$ Å³; $M_r = 425.48$; $Z = 4$; space group Cc ; $d_{\text{calc}} = 1.327$ g \times cm⁻³; $\mu(\text{MoK}_\alpha) = 0.186$ mm⁻¹; $F(000) = 896$. Total of 7032 reflections were measured, 3236 of which were independent ($R_{\text{int}} = 0.024$).

Compound XVc: rhombic crystals, $\text{C}_{26}\text{H}_{29}\text{ClNO}_5\text{S}$; $a = 26.432(1)$, $b = 9.579(1)$, $c = 10.055(1)$ Å; $V = 2545.8(2)$ Å³; $M_r = 503.01$; $Z = 4$; space group $Pca2_1$; $d_{\text{calc}} = 1.312$ g/cm³; $\mu(\text{MoK}_\alpha) = 0.269$ mm⁻¹; $F(000) = 1060$. Total of 17558 reflections were measured, 5658 of which were independent ($R_{\text{int}} = 0.065$).

Compound La: rhombic crystals, $\text{C}_{23}\text{H}_{23}\text{NO}_5\text{S}$; $a = 12.1988(3)$, $b = 13.4836(4)$, $c = 25.8824(8)$ Å; $V = 4257.2(2)$ Å³; $M_r = 425.48$; $Z = 4$; space group $Pbca$; $d_{\text{calc}} = 1.328$ g/cm³; $\mu(\text{MoK}_\alpha) = 0.187$ mm⁻¹; $F(000) = 1792$. Total of 24160 reflections were measured, 3724 of which were independent ($R_{\text{int}} = 0.028$).

The structures were solved by the direct method using SHELXTL software package [7]. The positions of hydrogen atoms were determined by difference synthesis of electron density and were refined using the riding model with $U_{\text{iso}} = nU_{\text{equiv}}$ (where U_{equiv} refers to the non-hydrogen atom to which the given hydrogen atom is attached; $n = 1.5$ for methyl hydrogen atoms and 1.2 for other hydrogen atoms). The structures were refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. In the refinement of structure XVc, the C–C bond lengths in the disordered isopropyl group were restricted to 1.52(1) Å. The final divergence factors were as follows: structure XIIb: $wR_2 = 0.069$ (3202 reflections) and $R_1 = 0.047$ [2990 reflections with $F > 4\sigma(F)$, $S = 1.037$]; structure XVc: $wR_2 = 0.089$ (5638 reflections) and $R_1 = 0.047$ [2632 reflec-

tions with $F > 4\sigma(F)$, $S = 0.959$]; structure La: $wR_2 = 0.109$ (3992 reflections) and $R_1 = 0.042$ (2860 reflections with $F > 4\sigma(F)$, $S = 1.086$). The complete sets of crystallographic data for compounds XIIb, XVc, and La (coordinates of atoms and geometric parameters of molecules) were deposited to the Cambridge Crystallographic Data Center (entry nos. CCDC 666669, CCDC 666671, and CCDC 666670, respectively).

Quinone imines I, IV, and VII were synthesized according to the procedure described in [8] by oxidation of the corresponding aminophenols with sodium dichromate in acetic acid. Quinone imines II, III, V, VI, IX, and XL–XLII were prepared as reported in [9] by oxidation of the corresponding aminophenols with lead tetraacetate in acetic acid, and quinone imines VIII were obtained by oxidation of *N*-aroylaminophenols with diacetoxy- λ^3 -iodanylbenzene as described in [10]. The properties of compounds Ia, Ib [11], IIa–IIc [12], IIIId [5], IVa, IVb [13], Va–Vc [14], VIIa, VIIb [15], VIIIa, VIIIb [10], XLa [16], XLIa–XLIIe [12], and XLIIe [5] were consistent with published data. Sodium arenesulfonates Xa–Xc were synthesized as described in [17].

***N*-(3,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methylphenylsulfonyl)benzimidamide (IIIa).** Yield 88%, mp 172–174°C. Found, %: N 7.01, 7.23; S 8.03, 8.27. $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$. Calculated, %: N 7.14; S 8.17.

***N*-(3,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (IIIb).** Yield 84%, mp 140–142°C. Found, %: N 6.82, 6.97; S 7.54, 7.78. $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$. Calculated, %: N 6.86; S 7.85.

***N'*-(4-Chlorophenylsulfonyl)-*N*-(3,5-dimethyl-4-oxocyclohexa-2,5-dienylidene)benzimidamide (IIIc).** Yield 84%, mp 175–177°C. Found, %: N 6.79, 6.94; S 7.49, 7.82. $\text{C}_{21}\text{H}_{17}\text{ClN}_2\text{O}_3\text{S}$. Calculated, %: N 6.78; S 7.77.

***N*-(3,5-Diisopropyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methylphenylsulfonyl)benzimidamide (VIa).** Yield 65%, mp 101–103°C. Found, %: N 6.21, 6.44; S 7.04, 7.19. $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_3\text{S}$. Calculated, %: N 6.24; S 7.15.

***N*-(3,5-Diisopropyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (VIb).** Yield 66%, mp 115–117°C. Found, %: N 6.05, 6.42; S 6.73, 6.99. $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_4\text{S}$. Calculated, %: N 6.03; S 6.90.

***N*-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methylphenylsulfonyl)benzimidamide**

(IXa). Yield 88%, mp 156–157°C. Found, %: N 5.76, 5.88; S 6.58, 6.73. C₂₈H₃₂N₂O₃S. Calculated, %: N 5.88; S 6.73.

***N*-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (IXb).** Yield 78%, mp 147–148°C. Found, %: N 5.47, 5.64; S 6.39, 6.48. C₂₈H₃₂N₂O₄S. Calculated, %: N 5.69; S 6.51.

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-methoxybenzenesulfonamide (XLb).** Yield 74%, mp 117–118°C. ¹H NMR spectrum, δ, ppm: 7.18–7.91 d.d (4H), 6.55 s (2H), 3.88 s (3H, MeO), 2.24 s (6H, Me). Found, %: N 4.62, 4.68; S 10.48, 10.62. C₁₅H₁₅NO₄S. Calculated, %: N 4.59; S 10.50.

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(phenylsulfonyl)benzimidamide (XLIIa).** Yield 69%, mp 134–136°C. Found, %: N 7.34, 7.45; S 8.40, 8.67. C₂₁H₁₈N₂O₃S. Calculated, %: N 7.40; S 8.47.

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XLIIb).** Yield 61%, mp 122–124°C. Found, %: N 7.06, 7.28; S 8.01, 8.15. C₂₂H₂₀N₂O₃S. Calculated, %: N 7.14; S 8.17.

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XLIIc).** Yield 84%, mp 113–115°C. Found, %: N 6.75, 6.92; S 7.57, 7.78. C₂₂H₂₀N₂O₄S. Calculated, %: N 6.86; S 7.85.

***N'*-(4-Chlorophenylsulfonyl)-*N*-(2,6-dimethyl-4-oxocyclohexa-2,5-dienylidene)benzimidamide (XLIIId).** Yield 68%, mp 175°C. ¹H NMR spectrum, δ, ppm: 7.45–7.63 m (5H, Ph), 7.31–7.80 d.d (4H), 6.46 br.s (2H), 2.12 s (6H, Me). Found, %: N 6.63, 6.81; S 7.82, 7.98. C₂₁H₁₇ClN₂O₃S. Calculated, %: N 6.78; S 7.77.

Reactions of quinone imines I–IX and XL–XLII with sodium arenesulfonates Xa–Xc (general procedure). A solution of 2 mmol of quinone imine I–IX or XL–XLII in 20 ml of glacial acetic acid was heated to the boiling point, and 4 mmol of the corresponding sodium arenesulfinate Xa–Xc was added in one portion. When the solution turned colorless, it was cooled, and water was added until complete precipitation. The colorless precipitate was filtered off and washed first with cold and then with warm water. A part of the product was recrystallized from acetic acid. The mother liquor was diluted with water, and the precipitate was filtered off. The three portions of the product were analyzed by ¹H NMR spectroscopy.

2,6-Dimethyl-4-(4-methylphenylsulfonylamino)phenyl 4-methylbenzenesulfonate (XIa). ¹H NMR spectrum, δ, ppm: 7.52–7.83 d.d (4H, C₆H₄, *J* = 8.1 Hz), 7.35–7.71 d.d (4H, C₆H₄, *J* = 8.7 Hz), 6.94 s (2H, 3-H, 5-H), 2.49 s and 2.38 s (3H each, MeC₆H₄), 2.01 s (6H, 2-Me, 6-Me).

4-(4-Chlorophenylsulfonylamino)-2,6-dimethylphenyl 4-methylbenzenesulfonate (XIb). ¹H NMR spectrum, δ, ppm: 7.60–7.83 d.d (4H, ClC₆H₄, *J* = 8.4 Hz), 7.52–7.83 d.d (4H, MeC₆H₄, *J* = 8.1 Hz), 6.94 s (2H, 3-H, 5-H), 2.49 s (3H, MeC₆H₄), 2.02 s (6H, 2-Me, 6-Me).

4-(4-Chlorophenylsulfonylamino)-2,6-dimethylphenyl 4-methoxybenzenesulfonate (XIc). ¹H NMR spectrum, δ, ppm: 7.59–7.84 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 7.19–7.87 d.d (4H, MeOC₆H₄, *J* = 8.1 Hz), 6.94 s (2H, 3-H, 5-H), 2.95 s (3H, MeO), 2.03 s (6H, 2-Me, 6-Me).

2,6-Dimethyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XIIa). Yield 40%, mp 165–167°C. ¹H NMR spectrum, δ, ppm: 10.13 s (1H, NH), 7.33–7.86 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 7.23–7.90 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.54 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 2.38 s (3H, MeC₆H₄), 2.05 s (6H, 2-Me, 6-Me). Found, %: N 3.25, 3.36; S 7.48, 7.83. C₂₃H₂₃NO₅S. Calculated, %: N 3.29; S 7.54.

2,6-Dimethyl-4-(4-methoxybenzoylamino)phenyl 4-methylbenzenesulfonate (XIIb). Yield 45%, mp 230–232°C. ¹H NMR spectrum, δ, ppm: 10.07 s (1H, NH), 7.54–7.87 d.d (4H, MeC₆H₄, *J* = 8.1 Hz), 7.06–7.95 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.53 s (2H, 3-H, 5-H), 3.84 s (3H, MeO), 2.46 s (3H, MeC₆H₄), 2.04 s (6H, 2-Me, 6-Me). Found, %: N 3.17, 3.28; S 7.44, 7.59. C₂₃H₂₃NO₅S. Calculated, %: N 3.29; S 7.54.

2,6-Dimethyl-4-(4-methoxybenzoylamino)phenyl 4-chlorobenzenesulfonate (XIIc). Yield 48%, mp 207–208°C. ¹H NMR spectrum, δ, ppm: 10.07 s (1H, NH), 7.82–8.02 d.d (4H, MeC₆H₄, *J* = 8.1 Hz), 7.06–7.95 d.d (4H, 4-MeOC₆H₄, *J* = 8.7 Hz), 7.55 s (2H, 3-H, 5-H), 3.84 s (3H, MeO), 2.06 s (6H, MeC₆H₄). Found, %: N 3.09, 3.18; S 7.15, 7.32. C₂₂H₂₀ClNO₅S. Calculated, %: N 3.14; S 7.19.

4-Benzoylamino-2,6-dimethylphenyl 4-methoxybenzenesulfonate (XIIId). Yield 50%, mp 149–151°C. ¹H NMR spectrum, δ, ppm: 10.21 s (1H, NH), 7.51–7.92 m (5H, Ph), 7.23–7.94 d.d (4H, C₆H₄, *J* = 9.0 Hz), 7.54 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 2.05 s (6H,

Me). Found, %: N 3.33, 3.42; S 7.77, 7.96. $C_{22}H_{21}NO_5S$. Calculated, %: N 3.40; S 7.79.

2,6-Dimethyl-4-[(4-methylphenylsulfonylimino)-(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XIIIa). Yield 77%, mp 185–187°C. 1H NMR spectrum, δ , ppm: 10.53 s (1H, NH), 7.23–7.88 d.d (4H, $MeOC_6H_4$, $J = 8.7$ Hz), 7.32–7.61 d.d (4H, MeC_6H_4 , $J = 7.8$ Hz), 7.49–7.63 m (5H, Ph), 7.28 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 2.36 s (3H, MeC_6H_4), 1.91 s (6H, 2-Me, 6-Me). Found, %: N 4.87, 5.10; S 11.31, 11.48. $C_{29}H_{28}N_2O_6S_2$. Calculated, %: N 4.96; S 11.36.

4-[(4-Methoxyphenylsulfonylimino)(phenyl)methylamino]-2,6-dimethylphenyl 4-methoxybenzenesulfonate (XIIIb). Yield 79%, mp 177–179°C. 1H NMR spectrum, δ , ppm: 10.48 s (1H, NH), 7.22–7.88 d.d (4H, $MeOC_6H_4$, $J = 9.3$ Hz), 7.03–7.64 d.d (4H, $MeOC_6H_4$, $J = 8.7$ Hz), 7.46–7.60 m (5H, Ph), 7.29 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 3.81 s (3H, MeO), 1.92 s (6H, 2-Me, 6-Me). Found, %: N 4.83, 4.91; S 10.89, 10.96. $C_{29}H_{28}N_2O_7S_2$. Calculated, %: N 4.82; S 11.04.

4-[(4-Methoxyphenylsulfonylimino)(phenyl)methylamino]-2,6-dimethylphenyl 4-methylbenzenesulfonate (XIIIc). Yield 74%, mp 199–200°C. 1H NMR spectrum, δ , ppm: 10.46 s (1H, NH), 7.53–7.85 d.d (4H, MeC_6H_4 , $J = 8.1$ Hz), 7.03–7.64 d.d (4H, $MeOC_6H_4$, $J = 8.7$ Hz), 7.48–7.60 m (5H, Ph), 7.30 s (2H, 3-H, 5-H), 3.81 s (3H, MeO), 2.46 s (3H, MeC_6H_4), 1.92 s (6H, 2-Me, 6-Me). Found, %: N 4.76, 4.94; S 11.23, 11.29. $C_{29}H_{28}N_2O_6S_2$. Calculated, %: N 4.96; S 11.36.

4-[(4-Chlorophenylsulfonylimino)(phenyl)methylamino]-2,6-dimethylphenyl 4-methoxybenzenesulfonate (XIII d). 1H NMR spectrum, δ , ppm: 10.65 s (1H, NH), 7.23–7.89 d.d (4H, $MeOC_6H_4$, $J = 8.7$ Hz), 7.58–7.71 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 7.49–7.62 m (5H, Ph), 7.26 s (2H, 3-H, 5-H), 3.91 s (3H, MeO), 1.92 s (6H, 2-Me, 6-Me).

4-[(4-Bromophenylsulfonylimino)(phenyl)methylamino]-2,6-dimethylphenyl 4-methylbenzenesulfonate (XIII e). 1H NMR spectrum, δ , ppm: 10.66 s (1H, NH), 7.54–7.85 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 7.63–7.72 d.d (4H, BrC_6H_4 , $J = 8.7$ Hz), 7.49–7.60 m (5H, Ph), 7.25 s (2H, 3-H, 5-H), 2.46 s (3H, MeC_6H_4), 1.91 s (6H, 2-Me, 6-Me).

2,6-Diisopropyl-4-(4-methylphenylsulfonylamino)phenyl 4-methylbenzenesulfonate (XIVa). 1H NMR spectrum, δ , ppm: 7.54–7.85 d.d (4H, C_6H_4 , $J = 8.4$ Hz), 7.34–7.67 d.d (4H, C_6H_4 , $J = 8.1$ Hz),

6.99 s (2H, 3-H, 5-H), 3.02–3.15 m (2H, CH in *i*-Pr), 2.49 s and 2.37 s (3H each, MeC_6H_4), 0.99 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

2,6-Diisopropyl-4-(4-methylphenylsulfonylamino)phenyl 4-methoxybenzenesulfonate (XIVb). 1H NMR spectrum, δ , ppm: 7.22–7.90 d.d (4H, $MeOC_6H_4$, $J = 8.4$ Hz), 7.34–7.67 d.d (4H, MeC_6H_4 , $J = 7.8$ Hz), 6.99 s (2H, 3-H, 5-H), 3.02–3.17 m (2H, CH in *i*-Pr), 3.96 s (3H, MeO), 2.37 s (3H, MeC_6H_4), 1.00 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-(4-Chlorophenylsulfonylamino)-2,6-diisopropylphenyl 4-methylbenzenesulfonate (XIVc). 1H NMR spectrum, δ , ppm: 7.54–7.86 d.d (4H, MeC_6H_4 , $J = 8.1$ Hz), 7.59–7.76 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 6.98 s (2H, 3-H, 5-H), 3.02–3.15 m (2H, CH in *i*-Pr), 2.50 s (3H, MeC_6H_4), 0.99 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-(4-Chlorophenylsulfonylamino)-2,6-diisopropylphenyl 4-methoxybenzenesulfonate (XIVd). 1H NMR spectrum, δ , ppm: 7.59–7.76 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 7.23–7.74 d.d (4H, $MeOC_6H_4$, $J = 9.0$ Hz), 6.98 s (2H, 3-H, 5-H), 3.05–3.17 m (2H, CH in *i*-Pr), 3.96 s (3H, MeO), 1.00 d (12H, Me in *i*-Pr, $J = 6.6$ Hz).

2,6-Diisopropyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XV a). Yield 51%, mp 217–219°C. 1H NMR spectrum, δ , ppm: 10.09 s (1H, NH), 7.25–7.93 d.d (4H, $MeOC_6H_4$, $J = 9.0$ Hz), 7.34–7.90 d.d (4H, MeC_6H_4 , $J = 8.1$ Hz), 7.70 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 3.02–3.16 m (2H, CH in *i*-Pr), 2.39 s (3H, MeC_6H_4), 1.07 d (12H, Me in *i*-Pr, $J = 6.6$ Hz). Found, %: N 2.74, 2.90; S 6.57, 6.83. $C_{27}H_{31}NO_5S$. Calculated, %: N 2.91; S 6.66.

2,6-Diisopropyl-4-(4-methoxybenzoylamino)phenyl 4-methylbenzenesulfonate (XV b). 1H NMR spectrum, δ , ppm: 10.09 s (1H, NH), 7.50–7.88 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 7.07–7.97 d.d (4H, $MeOC_6H_4$, $J = 9.0$ Hz), 7.68 s (2H, 3-H, 5-H), 3.85 s (3H, MeO), 2.99–3.12 m (2H, CH in *i*-Pr), 2.46 s (3H, MeC_6H_4), 1.067 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-(4-Chlorobenzoylamino)-2,6-diisopropylphenyl 4-methoxybenzenesulfonate (XV c). Yield 49%, mp 195–197°C. 1H NMR spectrum, δ , ppm: 10.31 s (1H, NH), 7.25–7.93 d.d (4H, $MeOC_6H_4$, $J = 9.0$ Hz), 7.62–8.00 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 7.68 s (2H, 3-H, 5-H), 3.90 s (3H, MeO), 3.02–3.15 m (2H, CH in *i*-Pr), 1.07 d (12H, Me in *i*-Pr, $J = 6.9$ Hz). Found, %: N 2.78, 2.91; S 6.38, 6.52. $C_{26}H_{28}ClNO_5S$. Calculated, %: N 2.79; S 6.39.

2,6-Diisopropyl-4-[(4-methylphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XVIa). Yield 69%, mp 191–192.5°C. ¹H NMR spectrum, δ , ppm: 10.47 s (1H, NH), 7.23–7.88 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.33–7.88 d.d (4H, MeC₆H₄, J = 8.4 Hz), 7.51–7.70 m (5H, Ph), 7.47 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 2.88–3.01 m (2H, CH in *i*-Pr), 2.36 s (3H, MeC₆H₄), 0.82 d (12H, Me in *i*-Pr, J = 6.9 Hz). Found, %: N 4.50, 4.62; S 10.35, 10.47. C₃₃H₃₆N₂O₆S₂. Calculated, %: N 4.51; S 10.33.

2,6-Diisopropyl-4-[(4-methoxyphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XVIb). Yield 60%, mp 179–180.5°C. ¹H NMR spectrum, δ , ppm: 10.43 s (1H, NH), 7.22–7.88 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.04–7.1 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.52–7.68 m (5H, Ph), 7.47 s (2H, 3-H, 5-H), 3.89 s and 3.81 s (3H each, MeO), 2.89–3.03 m (2H, CH in *i*-Pr), 0.85 d (12H, Me in *i*-Pr, J = 6.6 Hz). Found, %: N 4.25, 4.37; S 10.01, 10.17. C₃₃H₃₆N₂O₇S₂. Calculated, %: N 4.40; S 10.07.

2,6-Diisopropyl-4-[(4-methoxyphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methylbenzenesulfonate (XVIc). Yield 62%, mp 195–196°C. ¹H NMR spectrum, δ , ppm: 10.42 s (1H, NH), 7.66–7.84 d.d (4H, MeC₆H₄, J = 8.1 Hz), 7.04–7.70 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.52–7.60 m (5H, Ph), 7.49 s (2H, 3-H, 5-H), 3.81 s (3H, MeO), 2.86–3.00 m (2H, CH in *i*-Pr), 2.45 s (3H, MeC₆H₄), 0.84 d (12H, Me in *i*-Pr, J = 6.9 Hz). Found, %: N 4.52, 4.60, S 10.34, 10.45. C₃₃H₃₆N₂O₆S₂. Calculated, %: N 4.51; S 10.33.

2,6-Di-*tert*-butyl-4-(4-methylphenylsulfonylamino)phenyl 4-methylbenzenesulfonate (XVIIa). ¹H NMR spectrum, δ , ppm: 7.47–7.65 d.d (4H, MeC₆H₄, J = 9.0 Hz), 7.37–7.57 d.d (4H, MeC₆H₄, J = 8.4 Hz), 17 s (2H, 3-H, 5-H), 2.47 s and 2.37 s (3H each, MeC₆H₄), 1.31 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-(4-methoxyphenylsulfonylamino)phenyl 4-methylbenzenesulfonate (XVIIb). ¹H NMR spectrum, δ , ppm: 7.47–7.69 d.d (4H, MeC₆H₄, J = 8.7 Hz), 7.05–7.62 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.17 s (2H, 3-H, 5-H), 3.84 s (3H, MeO), 2.47 s (3H, MeC₆H₄), 1.31 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-(4-chlorobenzoylamino)phenyl 4-methoxybenzenesulfonate (XVIIIa). ¹H NMR spectrum, δ , ppm: 10.27 s (1H, NH), 7.63–8.01 d.d (4H, ClC₆H₄, J = 8.4 Hz), 7.24–7.81 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.89 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 1.33 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XVIIIb). ¹H NMR spectrum, δ , ppm: 10.11 s (1H, NH), 7.35–7.90 d.d (4H, MeC₆H₄, J = 9.0 Hz), 7.24–7.81 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.91 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 2.40 s (3H, MeC₆H₄), 1.32 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-[(4-methylphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XIXa). ¹H NMR spectrum, δ , ppm: 10.43 s (1H, NH), 7.71–7.80 d.d (4H, MeOC₆H₄, J = 7.8 Hz), 7.36–7.56 d.d (4H, MeC₆H₄, J = 8.1 Hz), 7.71 s (2H, 3-H, 5-H), 7.65–7.76 m (5H, Ph), 3.88 s (3H, MeO), 2.37 s (3H, MeC₆H₄), 1.12 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-[(4-methoxyphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XIXb). ¹H NMR spectrum, δ , ppm: 10.39 s (1H, NH), 7.71–7.77 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.04–7.22 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.72 s (2H, 3-H, 5-H), 7.53–7.66 m (5H, Ph), 3.88 s and 3.82 s (3H each, MeO), 1.14 s (18H, *t*-Bu).

2,6-Di-*tert*-butyl-4-[(4-methoxyphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methylbenzenesulfonate (XIXc). ¹H NMR spectrum, δ , ppm: 10.38 s (1H, NH), 7.66–7.76 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.05–7.52 d.d (4H, MeC₆H₄, J = 8.7 Hz), 7.69 s (2H, 3-H, 5-H), 7.51–7.76 m (5H, Ph), 3.82 s (3H, MeO), 2.44 s (3H, MeC₆H₄), 1.14 s (18H, *t*-Bu).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-4-methyl-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXa).** ¹H NMR spectrum, δ , ppm: 7.46–7.77 d.d (8H, C₆H₄, J = 8.7 Hz), 6.60 s (2H, 2-H, 6-H), 2.49 s (6H, MeC₆H₄), 2.16 s (6H, 3-Me, 5-Me).

4-Chloro-*N*-(4-hydroxy-3,5-dimethylphenyl)-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXb). ¹H NMR spectrum, δ , ppm: 7.79–7.91 d.d (4H, ClC₆H₄, J = 9.0 Hz), 7.35–7.48 d.d (4H, MeC₆H₄, J = 7.8 Hz), 6.64 s (2H, 2-H, 6-H), 2.49 s (3H, MeC₆H₄), 2.17 s (6H, 3-Me, 5-Me).

4-Chloro-*N*-(4-hydroxy-3,5-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXc). Yield 16%, mp 214°C (decomp.). ¹H NMR spectrum, δ , ppm: 7.82–7.91 d.d (4H, ClC₆H₄, J = 9.0 Hz), 7.16–7.71 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 6.64 s (2H, 2-H, 6-H), 3.90 s (3H, MeO), 2.17 s (6H, 3-Me, 5-Me). Found, %: N 2.84, 2.99; S 13.07, 13.28. C₂₁H₂₀ClNO₆S₂. Calculated, %: N 2.91; S 13.31.

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)-4-methylbenzamide (XXIa).** ¹H NMR spectrum, δ , ppm: 8.65 s (1H, OH), 7.07–

7.81 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 7.16–7.38 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 6.78 s (2H, 2-H, 6-H), 3.87 s (3H, MeO), 2.38 s (3H, MeC₆H₄), 2.06 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-4-methoxy-*N*-(4-methylphenylsulfonyl)benzamide (XXIb).** ¹H NMR spectrum, δ , ppm: 8.67 s (1H, OH), 7.49–7.73 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 6.81–7.43 d.d (4H, MeC₆H₄, $J = 8.4$ Hz), 6.79 s (2H, 2-H, 6-H), 3.72 s (3H, MeO), 2.42 s (3H, MeC₆H₄), 2.06 s (6H, 3-Me, 5-Me).

***N*-(4-Chlorophenylsulfonyl)-*N*-(4-hydroxy-3,5-dimethylphenyl)-4-methoxybenzamide (XXIc).** ¹H NMR spectrum, δ , ppm: 8.69 s (1H, OH), 7.64–7.84 d.d (4H, ClC₆H₄, $J = 8.1$ Hz), 7.52–7.72 d.d (4H, MeOC₆H₄, $J = 8.7$ Hz), 6.82 s (2H, 2-H, 6-H), 3.73 s (3H, MeO), 2.08 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)benzamide (XXId).** ¹H NMR spectrum, δ , ppm: 8.62 s (1H, OH), 7.74–7.78 d.d (4H, MeOC₆H₄, $J = 8.7$ Hz), 7.51–7.92 m (5H, Ph), 6.79 s (2H, 2-H, 6-H), 3.88 s (3H, MeO), 2.07 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-4-methyl-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXIIa).** Yield 38%, mp 200–202°C. ¹H NMR spectrum, δ , ppm: 7.48–7.76 d.d (8H, C₆H₄, $J = 8.4$ Hz), 6.56 s (2H, 2-H, 6-H), 3.23–3.36 m (2H, CH in *i*-Pr), 2.49 s (6H, MeC₆H₄), 1.09 s (12H, Me in *i*-Pr, $J = 6.9$ Hz). Found, %: N 2.58, 2.71; S 12.48, 12.70. C₂₆H₃₁NO₅S₂. Calculated, %: N 2.79; S 12.78.

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-4-methoxy-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXIIb).** ¹H NMR spectrum, δ , ppm: 7.48–7.77 d.d (4H, MeC₆H₄, $J = 8.4$ Hz), 7.17–7.80 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 6.57 s (2H, 2-H, 6-H), 3.96 s (3H, MeO), 3.24–3.36 m (2H, CH in *i*-Pr), 2.49 s (3H, MeC₆H₄), 1.09 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-Chloro-*N*-(4-hydroxy-3,5-diisopropylphenyl)-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXIIc). Yield 34%, mp 200–202°C. ¹H NMR spectrum, δ , ppm: 7.74–7.90 d.d (4H, ClC₆H₄, $J = 8.7$ Hz), 7.50–7.78 d.d (4H, MeC₆H₄, $J = 8.4$ Hz), 6.59 s (2H, 2-H, 6-H), 3.25–3.37 m (2H, CH in *i*-Pr), 2.50 s (3H, MeC₆H₄), 1.10 d (12H, Me in *i*-Pr, $J = 6.9$ Hz). Found, %: N 2.69, 2.85; S 11.94, 12.41. C₂₅H₂₈ClNO₅S₂. Calculated, %: N 2.68; S 12.28.

4-Chloro-*N*-(4-hydroxy-3,5-diisopropylphenyl)-*N*-(4-methoxyphenylsulfonyl)benzenesulfonamide

(XXIId). ¹H NMR spectrum, δ , ppm: 7.74–7.91 d.d (4H, ClC₆H₄, $J = 9.0$ Hz), 7.18–7.82 d.d (4H, MeOC₆H₄, $J = 9.3$ Hz), 6.59 s (2H, 2-H, 6-H), 3.96 s (3H, MeO), 3.24–3.36 m (2H, CH in *i*-Pr), 1.10 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N*-(4-methoxyphenylsulfonyl)-4-methylbenzamide (XXIIIa).** ¹H NMR spectrum, δ , ppm: 8.49 s (1H, OH), 7.16–7.75 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 7.04–7.45 d.d (4H, MeC₆H₄, $J = 8.4$ Hz), 6.67 s (2H, 2-H, 6-H), 3.87 s (3H, MeO), 3.14–3.27 m (2H, CH in *i*-Pr), 2.20 s (3H, MeC₆H₄), 0.99 d (12H, Me in *i*-Pr, $J = 6.6$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-4-methoxy-*N*-(4-methylphenylsulfonyl)benzamide (XXIIIb).** ¹H NMR spectrum, δ , ppm: 8.50 s (1H, OH), 6.76–7.45 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 7.43–7.70 d.d (4H, MeC₆H₄, $J = 8.4$ Hz), 6.67 s (2H, 2-H, 6-H), 3.70 s (3H, MeO), 3.12–3.25 m (2H, CH in *i*-Pr), 2.42 s (3H, MeC₆H₄), 1.00 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-Chloro-*N*-(4-hydroxy-3,5-diisopropylphenyl)-*N*-(4-methoxyphenylsulfonyl)benzamide (XXIIIc). ¹H NMR spectrum, δ , ppm: 8.51 s (1H, OH), 7.17–7.80 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 7.27–7.43 d.d (4H, ClC₆H₄, $J = 9.0$ Hz), 6.80 s (2H, 2-H, 6-H), 3.88 s (3H, MeO), 3.11–3.24 m (2H, CH in *i*-Pr), 0.99 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N*-(4-methoxyphenylsulfonyl)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXIVa).** ¹H NMR spectrum, δ , ppm: 8.39 s (1H, OH), 7.14–7.72 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 7.00–7.42 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 7.47–7.73 m (5H, Ph), 6.68 s (2H, 2-H, 6-H), 3.93 s (3H, MeO), 3.14–3.27 m (2H, CH in *i*-Pr), 2.44 s (3H, MeC₆H₄), 0.89 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N,N'*-bis-(4-methoxyphenylsulfonyl)benzimidamide (XXIVb).** ¹H NMR spectrum, δ , ppm: 8.42 s (1H, OH), 7.16–7.71 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 7.01–7.49 d.d (4H, MeOC₆H₄, $J = 8.7$ Hz), 7.50–7.74 m (5H, Ph), 6.68 s (2H, 2-H, 6-H), 3.93 s and 3.84 s (3H each, MeO), 3.13–3.27 m (2H, CH in *i*-Pr), 0.91 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N*-(4-methylphenylsulfonyl)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXIVc).** ¹H NMR spectrum, δ , ppm: 8.42 s (1H, OH), 7.44–7.79 m (5H, Ph), 7.39–7.76 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 7.24–7.46 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 6.70 s (2H, 2-H, 6-H), 3.84 s (3H,

MeO), 3.13–3.26 m (2H, CH in *i*-Pr), 2.40 s (3H, MeC₆H₄), 0.91 d (12H, Me in *i*-Pr, *J* = 6.9 Hz).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methyl-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXVa).** Yield 35%, mp 173–174°C. ¹H NMR spectrum, δ, ppm: 7.48–7.74 d.d (8H, C₆H₄, *J* = 8.1 Hz), 6.68 s (2H, 2-H, 6-H), 2.49 s (6H, MeC₆H₄), 1.82 s (18H, *t*-Bu). Found, %: N 2.54, 2.73; S 12.02, 12.23. C₂₈H₃₅NO₅S₂. Calculated, %: N 2.64; S 12.11.

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methoxy-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XXVb).** ¹H NMR spectrum, δ, ppm: 7.17–7.79 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.20–7.75 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 6.69 s (2H, 2-H, 6-H), 3.96 s (3H, MeO), 2.49 s (3H, MeC₆H₄), 1.33 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-chloro-*N*-(4-methoxyphenylsulfonyl)benzamide (XXVIa).** ¹H NMR spectrum, δ, ppm: 9.23 s (1H, OH), 7.52–7.89 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 6.99–7.49 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.76 s (2H, 2-H, 6-H), 3.87 s (3H, MeO), 1.39 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenylsulfonyl)-4-methylbenzamide (XXVIb).** ¹H NMR spectrum, δ, ppm: 9.28 s (1H, OH), 7.09–7.78 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 6.99–7.48 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.75 s (2H, 2-H, 6-H), 3.87 s (3H, MeO), 2.38 s (3H, *t*-Bu), 1.39 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-(4-methoxyphenylsulfonyl)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXVIIa).** ¹H NMR spectrum, δ, ppm: 9.04 s (1H, OH), 7.50–7.84 m (5H, Ph), 7.09–7.77 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 7.00–7.48 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.96 s (2H, 2-H, 6-H), 3.86 s (3H, MeO), 2.37 s (3H, MeC₆H₄), 1.19 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N,N'*-bis-(4-methoxyphenylsulfonyl)benzimidamide (XXVIIb).** ¹H NMR spectrum, δ, ppm: 9.04 s (1H, OH), 7.50–7.80 m (5H, Ph), 7.17–7.78 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.00–7.49 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.95 s (2H, 2-H, 6-H), 3.86 s and 3.80 s (3H each, MeO), 1.19 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N'*-(4-methoxyphenylsulfonyl)-*N*-(4-methylphenylsulfonyl)benzimidamide (XXVIIc).** ¹H NMR spectrum, δ, ppm: 9.04 s (1H, OH), 7.42–7.77 m (5H, Ph), 7.16–7.95 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.21–7.82 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 6.94 s (2H, 2-H, 6-H), 3.80 s (3H, MeO), 2.38 s (3H, MeC₆H₄), 1.19 s (18H, *t*-Bu).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylphenylsulfonyl)phenyl]-4-methylbenzenesulfonamide (XXVIIIa).** ¹H NMR spectrum, δ, ppm: 7.65 s (1H, 6-H), 7.32–7.75 d.d (4H, MeC₆H₄, *J* = 7.8 Hz), 7.28–7.38 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 2.41 s and 2.44 s (3H each, MeC₆H₄), 2.32 s (3H, 3-Me), 2.10 s (3H, 5-Me).

4-Chloro-*N*-[4-hydroxy-3,5-dimethyl-2-(4-methylphenylsulfonyl)phenyl]benzenesulfonamide (XXVIIIb). ¹H NMR spectrum, δ, ppm: 7.60–7.82 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 7.62 s (1H, 6-H), 7.32–7.72 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 2.42 s (3H, MeC₆H₄), 2.34 s (3H, 3-Me), 2.10 s (3H, 5-Me).

4-Chloro-*N*-[4-hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]benzenesulfonamide (XXVIIIc). ¹H NMR spectrum, δ, ppm: 7.61–7.82 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 7.60 s (1H, 6-H), 7.02–7.34 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 3.95 s (3H, MeO), 2.33 s (3H, 3-Me), 2.12 s (3H, 5-Me).

***N*-[4-Hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]-4-methoxybenzamide (XXIXa).** ¹H NMR spectrum, δ, ppm: 10.61 s (1H, NH), 8.81 s (1H, OH), 7.83 s (1H, 6-H), 7.36–7.73 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 7.06–7.85 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 3.80 s (3H, MeO), 2.38 s (3H, MeC₆H₄), 2.29 s (3H, 3-Me), 2.26 s (3H, 5-Me).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylphenylsulfonyl)phenyl]-4-methoxybenzamide (XXIXb).** ¹H NMR spectrum, δ, ppm: 10.52 s (1H, NH), 8.80 s (1H, OH), 7.82 s (1H, 6-H), 7.35–7.67 d.d (4H, MeC₆H₄, *J* = 8.1 Hz), 7.08–7.91 d.d (4H, MeOC₆H₄, *J* = 8.74 Hz), 3.84 s (3H, MeO), 2.35 s (3H, MeC₆H₄), 2.27 s (3H, 3-Me), 2.25 s (3H, 5-Me).

***N*-[2-(4-Chlorophenylsulfonyl)-4-hydroxy-3,5-dimethylphenyl]-4-methoxybenzamide (XXIXc).** ¹H NMR spectrum, δ, ppm: 10.30 s (1H, NH), 8.88 s (1H, OH), 7.83 s (1H, 6-H), 7.39–7.67 d.d (4H, ClC₆H₄, *J* = 8.4 Hz), 7.09–7.89 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 3.84 s (3H, MeO), 2.28 s (3H, 3-Me), 2.22 s (3H, 5-Me).

***N*-[4-Hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]benzamide (XXIXd).** ¹H NMR spectrum, δ, ppm: 10.62 s (1H, NH), 8.81 s (1H, OH), 7.82 s (1H, 6-H), 7.50–7.60 m (5H, Ph), 7.05–7.83 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 3.83 s (3H, MeO), 2.28 s (3H, 3-Me), 2.26 s (3H, 5-Me).

***N*-[4-Hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXXa).** ¹H NMR spectrum, δ, ppm:

10.40 s (1H, NH), 9.03 s (1H, OH), 7.71 s (1H, 6-H), 7.45–7.62 m (5H, Ph), 7.39–7.67 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 6.94–7.78 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 3.89 s (3H, MeO), 2.36 s (3H, MeC₆H₄), 2.31 s (3H, 3-Me), 2.01 s (3H, 5-Me).

***N*-[4-Hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXXb).** ¹H NMR spectrum, δ , ppm: 10.36 s (1H, NH), 9.06 s (1H, OH), 7.69 s (1H, 6-H), 7.47–7.65 m (5H, Ph), 7.20–7.49 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 6.91–7.72 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 3.93 s and 3.76 s (3H each, MeO), 2.01 s (3H, 3-Me), 1.87 s (3H, 5-Me).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylphenylsulfonyl)phenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXXc).** ¹H NMR spectrum, δ , ppm: 10.34 s (1H, NH), 9.03 s (1H, OH), 7.66 s (1H, 6-H), 7.49–7.68 m (5H, Ph), 7.37–7.64 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 7.19–7.49 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 3.78 s (3H, MeO), 2.40 s (3H, MeC₆H₄), 2.14 s (3H, 3-Me), 1.87 s (3H, 5-Me).

***N'*-(4-Chlorophenylsulfonyl)-*N*-[4-hydroxy-2-(4-methoxyphenylsulfonyl)-3,5-dimethylphenyl]benzimidamide (XXXd).** ¹H NMR spectrum, δ , ppm: 10.48 s (1H, NH), 9.06 s (1H, OH), 7.67 s (1H, 6-H), 7.49–7.66 m (5H, Ph), 7.48–7.85 d.d (4H, ClC₆H₄, $J = 8.4$ Hz), 6.98–7.70 d.d (4H, MeOC₆H₄, $J = 8.4$ Hz), 3.89 s (3H, MeO), 1.99 s (3H, 3-Me), 1.90 s (3H, 5-Me).

***N'*-(4-Bromophenylsulfonyl)-*N*-[4-hydroxy-3,5-dimethyl-2-(4-methylphenylsulfonyl)phenyl]benzimidamide (XXXe).** ¹H NMR spectrum, δ , ppm: 10.49 s (1H, NH), 9.05 s (1H, OH), 7.50–7.84 d.d (4H, BrC₆H₄, $J = 8.4$ Hz), 7.48–7.66 m (5H, Ph), 7.36–7.63 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 7.68 s (1H, 6-H), 2.38 s (3H, MeC₆H₄), 1.99 s (3H, 3-Me), 1.91 s (3H, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-4-methylbenzamide (XXXIa).** ¹H NMR spectrum, δ , ppm: 9.80 s (1H, NH), 8.04 s (1H, OH), 7.30–7.85 d.d (4H, C₆H₄, $J = 8.1$ Hz), 7.30 s (2H, 2-H, 6-H), 2.37 s (3H, MeC₆H₄), 2.17 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-4-methoxybenzamide (XXXIb).** ¹H NMR spectrum, δ , ppm: 9.74 s (1H, NH), 8.26 s (1H, OH), 7.29 s (2H, 2-H, 6-H), 7.03–7.93 d.d (4H, C₆H₄, $J = 8.7$ Hz), 3.83 s (3H, MeO), 2.16 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)benzamide (XXXIc).** ¹H NMR spectrum, δ , ppm: 9.75 s (1H, NH),

8.09 s (1H, OH), 7.31 s (2H, 2-H, 6-H), 7.06–7.83 m (5H, Ph), 2.17 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXXIIa).** ¹H NMR spectrum, δ , ppm: 10.27 s (1H, NH), 8.30 s (1H, OH), 7.45–7.55 m (5H, Ph), 7.31–7.58 d.d (4H, C₆H₄, $J = 7.8$ Hz), 7.10 s (2H, 2-H, 6-H), 2.36 s (3H, MeC₆H₄), 2.05 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-dimethylphenyl)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXXIIb).** ¹H NMR spectrum, δ , ppm: 10.22 s (1H, NH), 8.28 s (1H, OH), 7.46–7.60 m (5H, Ph), 7.23–7.61 d.d (4H, MeOC₆H₄, $J = 8.1$ Hz), 7.10 s (2H, 2-H, 6-H), 3.80 s (3H, MeO), 2.05 s (6H, 3-Me, 5-Me).

***N'*-(4-Chlorophenylsulfonyl)-*N*-(4-hydroxy-3,5-dimethylphenyl)benzimidamide (XXXIIc).** ¹H NMR spectrum, δ , ppm: 10.40 s (1H, NH), 8.31 s (1H, OH), 7.49–7.62 m (5H, Ph), 7.24–7.58 d.d (4H, ClC₆H₄, $J = 8.1$ Hz), 7.07 s (2H, 2-H, 6-H), 2.05 s (6H, 3-Me, 5-Me).

***N'*-(4-Bromophenylsulfonyl)-*N*-(4-hydroxy-3,5-dimethylphenyl)benzimidamide (XXXIId).** ¹H NMR spectrum, δ , ppm: 10.39 s (1H, NH), 8.31 s (1H, OH), 7.53–7.66 m (5H, Ph), 7.24–7.60 d.d (4H, BrC₆H₄, $J = 8.1$ Hz), 7.08 s (2H, 2-H, 6-H), 2.04 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-4-methylbenzamide (XXXIIIa).** ¹H NMR spectrum, δ , ppm: 9.86 s (1H, NH), 8.34 s (1H, OH), 7.42 s (2H, 2-H, 6-H), 7.22–7.93 d.d (4H, MeC₆H₄, $J = 8.7$ Hz), 3.23–3.36 m (2H, CH), 2.39 s (3H, MeC₆H₄), 1.17 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-4-methoxybenzamide (XXXIIIb).** ¹H NMR spectrum, δ , ppm: 9.77 s (1H, NH), 7.71 s (1H, OH), 7.41 s (2H, 2-H, 6-H), 7.04–7.95 d.d (4H, MeOC₆H₄, $J = 9.0$ Hz), 3.27–3.42 m (2H, CH in *i*-Pr), 3.83 s (3H, MeO), 1.15 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

4-Chloro-*N*-(4-hydroxy-3,5-diisopropylphenyl)benzamide (XXXIIIc). ¹H NMR spectrum, δ , ppm: 10.01 s (1H, NH), 8.31 s (1H, OH), 7.41 s (2H, 2-H, 6-H), 7.18–7.99 d.d (4H, ClC₆H₄, $J = 8.7$ Hz), 3.19–3.33 m (2H, CH in *i*-Pr), 1.16 d (12H, Me in *i*-Pr, $J = 6.9$ Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXXIVa).** ¹H NMR spectrum, δ , ppm: 10.24 s (1H, NH), 8.09 s (1H, OH), 7.47–7.73 m (5H, Ph), 7.35–7.79 d.d (4H, MeC₆H₄, $J = 7.8$ Hz), 7.25 s (2H, 2-H, 6-H), 3.14–

3.28 m (2H, CH in *i*-Pr), 2.35 s (3H₃), 0.94 d (12H, Me in *i*-Pr, *J* = 6.9 Hz).

***N*-(4-Hydroxy-3,5-diisopropylphenyl)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXXIVb).** ¹H NMR spectrum, δ, ppm: 10.18 s (1H, NH), 8.06 s (1H, OH), 7.49–7.72 m (5H, Ph), 7.26 s (2H, 2-H, 6-H), 7.24–7.60 d.d (4H, MeOC₆H₄, *J* = 7.8 Hz), 3.13–3.27 m (2H, CH), 3.85 s (3H, MeO), 0.96 d (12H, Me in *i*-Pr, *J* = 6.9 Hz).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methylbenzenesulfonamide (XXXVa).** ¹H NMR spectrum, δ, ppm: 8.38 s (1H, NH), 6.66 s (1H, OH), 7.31–7.47 d.d (4H, MeC₆H₄, *J* = 8.1 Hz), 6.91 s (2H, 2-H, 6-H), 2.37 s (3H₃), 1.32 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methoxybenzenesulfonamide (XXXVb).** ¹H NMR spectrum, δ, ppm: 8.33 s (1H, NH), 6.00 s (1H, OH), 7.02–7.62 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.92 s (2H, 2-H, 6-H), 3.85 s (3H, MeO), 1.33 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methylbenzamide (XXXVIa).** ¹H NMR spectrum, δ, ppm: 9.85 s (1H, NH), 8.31 s (1H, OH), 7.58 s (2H, 2-H, 6-H), 7.41–7.78 d.d (4H, MeC₆H₄, *J* = 7.8 Hz), 2.38 s (3H, MeC₆H₄), 1.24 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-methoxybenzamide (XXXVIb).** ¹H NMR spectrum, δ, ppm: 9.79 s (1H, NH), 8.28 s (1H, OH), 7.59 s (2H, 2-H, 6-H), 7.42–7.83 d.d (4H, MeOC₆H₄, *J* = 8.1 Hz), 3.83 s (3H, MeO), 1.23 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N'*-(4-methylphenylsulfonyl)benzimidamide (XXXVIIa).** ¹H NMR spectrum, δ, ppm: 10.24 s (1H, NH), 8.23 s (1H, OH), 7.50–7.82 m (5H, Ph), 7.40 s (2H, 2-H, 6-H), 7.34–7.48 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 2.37 s (3H, MeC₆H₄), 1.24 s (18H, *t*-Bu).

***N*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XXXVIIb).** ¹H NMR spectrum, δ, ppm: 10.19 s (1H, NH), 8.20 s (1H, OH), 7.42–7.77 m (5H, Ph), 7.40 s (2H, 2-H, 6-H), 7.23–7.89 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 3.82 s (3H, MeO), 1.24 s (18H, *t*-Bu).

4-Hydroxy-3,5-diisopropylphenyl arenesulfonates XXXVIIIa–XXXVIIIc (general procedure). A solution of 0.01 mol of 2,6-diisopropyl-1,4-benzoquinone in 20 ml of acetic acid was heated to the boiling point, 0.02 mol of sodium arenesulfinate **Xa–Xc** was added, and the mixture was heated for 20–30 min under reflux until it turned colorless. The mixture was cooled and poured into water, and the precipitate was filtered off, washed first with cold and then with warm water, and recrystallized from glacial acetic acid.

itate was filtered off, washed first with cold and then with warm water, and recrystallized from glacial acetic acid.

4-Hydroxy-3,5-diisopropylphenyl 4-methylbenzenesulfonate (XXXVIIIa). Yield 66%, mp 105–106°C. ¹H NMR spectrum, δ, ppm: 8.32 s (1H, OH), 7.45–7.67 d.d (4H, MeC₆H₄, *J* = 7.8 Hz), 6.45 s (2H, 2-H, 6-H), 3.14–3.27 m (2H, CH in *i*-Pr), 2.40 s (3H, MeC₆H₄), 0.99 d (12H, Me in *i*-Pr, *J* = 6.6 Hz). Found, %: S 9.02, 9.36. C₁₉H₂₅O₄S. Calculated, %: S 9.17.

4-Hydroxy-3,5-diisopropylphenyl 4-methoxybenzenesulfonate (XXXVIIIb). Yield 63%, mp 110–112°C. ¹H NMR spectrum, δ, ppm: 8.31 s (1H, OH), 7.15–7.70 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.45 s (2H, 2-H, 6-H), 3.85 s (3H, MeO), 3.14–3.27 m (2H, CH in *i*-Pr), 1.00 d (12H, Me in *i*-Pr, *J* = 6.6 Hz). Found, %: S 8.57, 8.89. C₁₉H₂₅O₄S. Calculated, %: S 8.80.

4-Hydroxy-3,5-diisopropylphenyl 4-chlorobenzenesulfonate (XXXVIIIc). ¹H NMR spectrum, δ, ppm: 8.38 s (1H, OH), 7.39–7.69 d.d (4H, ClC₆H₄, *J* = 7.8 Hz), 6.48 s (2H, 2-H, 6-H), 3.17–3.29 m (2H, CH), 1.00 d (12H, Me in *i*-Pr, *J* = 6.6 Hz).

3,5-Di-*tert*-butyl-4-hydroxyphenyl arenesulfonates XXXIXa and XXXIXb (general procedure). A solution of 0.01 mol of 2,6-di-*tert*-butyl-1,4-benzoquinone and 0.03 mol of sodium arenesulfinate **Xa** or **Xb** in 30 ml of acetic acid was heated under reflux for several hours until it became colorless. The mixture was cooled and poured into water, and the precipitate was filtered off, washed with cold and warm water, and recrystallized from glacial acetic acid.

3,5-Di-*tert*-butyl-4-hydroxyphenyl 4-methylbenzenesulfonate (XXXIXa). ¹H NMR spectrum, δ, ppm: 7.20 s (1H, OH), 7.21–7.67 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 6.55 s (2H, 2-H, 6-H), 2.42 s (3H, MeC₆H₄), 1.24 s (18H, *t*-Bu).

3,5-Di-*tert*-butyl-4-hydroxyphenyl 4-methoxybenzenesulfonate (XXXIXb). Yield 58%, mp 150–152°C. ¹H NMR spectrum, δ, ppm: 7.21 s (1H, OH), 7.16–7.70 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.55 s (2H, 2-H, 6-H), 3.85 s (3H, MeO), 1.25 s (18H, *t*-Bu). Found, %: S 8.15, 8.32. C₂₁H₂₈O₅S. Calculated, %: S 8.17.

***N*-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]-4-methylbenzenesulfonamide (XLIIIa).** Yield 70%, mp 179–180.5°C. ¹H NMR spectrum, δ, ppm: 10.58 s (1H, NH), 8.15 s (1H, OH), 7.21–7.44 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 7.19–7.79 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.84 s (1H, 5-H),

3.98 s (3H, MeO), 2.37 s (3H, MeC₆H₄), 2.20 s (3H, 2-Me), 1.81 s (3H, 6-Me). Found, %: N 2.87, 2.94; S 13.77, 13.90. C₂₂H₂₃NO₆S₂. Calculated, %: N 3.03; S 13.89.

N-[4-Hydroxy-2,6-dimethyl-3-(4-methylphenylsulfonyl)phenyl]-4-methoxybenzenesulfonamide (XLIIIb). Yield 60%, mp 185–186°C. ¹H NMR spectrum, δ, ppm: 10.54 s (1H, NH), 8.10 s (1H, OH), 7.50–7.74 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 6.91–7.50 d.d (4H, 4-MeOC₆H₄, *J* = 9.0 Hz), 6.85 s (1H, 5-H), 3.88 s (3H, MeO), 2.49 s (3H, MeC₆H₄), 2.19 s (3H, 2-Me), 1.88 s (3H, 6-Me). Found, %: N 3.08, 3.13; S 13.76, 13.95. C₂₂H₂₃NO₆S₂. Calculated, %: N 3.03; S 13.89.

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]-4-methoxybenzenesulfonamide (XLIIIc). Yield 62%, mp 173–175°C. ¹H NMR spectrum, δ, ppm: 10.59 s (1H, NH), 8.10 s (1H, OH), 7.19–7.80 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 6.92–7.49 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.84 s (1H, 5-H), 3.96 s and 3.88 s (3H each, MeO), 2.20 s (3H, 2-Me), 1.87 s (3H, 6-Me). Found, %: N 2.91, 3.01; S 13.14, 13.34. C₂₂H₂₃NO₇S₂. Calculated, %: N 2.93; S 13.43.

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]-4-methylbenzamide (XLIVa). ¹H NMR spectrum, δ, ppm: s 10.46 s (1H, NH), 9.64 s (1H, OH), 7.33–7.88 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 7.20–7.84 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 6.76 s (1H, 5-H), 3.84 s (3H, MeO), 2.41 s (3H, MeC₆H₄), 2.38 s (3H, 2-Me), 2.11 s (3H, 6-Me).

4-Chloro-N-[4-hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]benzamide (XLIVb). ¹H NMR spectrum, δ, ppm: 10.47 s (1H, NH), 9.80 s (1H, OH), 7.61–8.00 d.d (4H, ClC₆H₄, *J* = 9.0 Hz), 7.13–7.84 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.77 s (1H, 5-H), 3.84 s (3H, MeO), 2.42 s (3H, 2-Me), 2.12 s (3H, 6-Me).

4-Bromo-N-[4-hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]benzamide (XLIVc). ¹H NMR spectrum, δ, ppm: 10.49 s (1H, NH), 9.81 s (1H, OH), 7.45–7.91 d.d (4H, BrC₆H₄, *J* = 8.4 Hz), 7.13–7.84 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.76 s (1H, 5-H), 3.84 s (3H, MeO), 2.42 s (3H, 2-Me), 2.11 s (3H, 6-Me).

N-[4-Hydroxy-2,6-dimethyl-3-(4-methylphenylsulfonyl)phenyl]-4-methoxybenzamide (XLIVd). ¹H NMR spectrum, δ, ppm: 10.43 s (1H, NH), 9.68 s (1H, OH), 7.47–7.78 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 7.05–7.95 d.d (4H, MeC₆H₄, *J* = 8.7 Hz), 6.76 s (1H,

5-H), 3.83 s (3H, MeO), 2.41 s (3H, MeC₆H₄), 2.39 s (3H, 2-Me), 2.11 s (3H, 6-Me).

N-[4-Hydroxy-2,6-dimethyl-3-(4-methylphenylsulfonyl)phenyl]benzamide (XLIVe). ¹H NMR spectrum, δ, ppm: 10.45 s (1H, NH), 9.71 s (1H, OH), 7.49–7.77 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 7.19–7.52 m (5H, Ph), 6.75 s (1H, 5-H), 2.43 s (3H, MeC₆H₄), 2.39 s (3H, 2-Me), 2.12 s (3H, 6-Me).

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]-N'-(4-methylphenylsulfonyl)benzimidamide (XLVa). ¹H NMR spectrum, δ, ppm: 10.61 s (1H, NH), 10.02 s (1H, OH), 7.16–7.25 d.d (4H, MeC₆H₄, *J* = 7.8 Hz), 7.14–7.58 m (5H, Ph), 7.10–7.79 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 6.71 s (1H, 5-H), 3.84 s (3H, MeO), 2.48 s (3H, MeC₆H₄), 2.32 s (3H, 2-Me), 2.13 s (3H, 6-Me).

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]-N'-(4-methoxyphenylsulfonyl)benzimidamide (XLVb). Yield 90%, mp 146–148°C. ¹H NMR spectrum, δ, ppm: 10.53 s (1H, NH), 9.91 s (1H, OH), 7.42–7.57 m (5H, Ph), 7.09–7.78 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 6.87–7.28 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 6.72 s (1H, 5-H), 3.84 s and 3.78 s (3H each, MeO), 2.45 s (3H, 2-Me), 2.13 s (3H, 6-Me). Found, %: N 4.86, 5.11; S 11.05, 11.28. C₂₉H₂₈N₂O₇S₂. Calculated, %: N 4.82; S 11.04.

N'-(4-Bromophenylsulfonyl)-N-[4-hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]benzimidamide (XLVc). ¹H NMR spectrum, δ, ppm: 10.71 s (1H, NH), 10.19 s (1H, OH), 7.46–7.58 m (5H, Ph), 7.29–7.57 d.d (4H, BrC₆H₄, *J* = 8.7 Hz), 7.10–7.78 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 6.72 s (1H, 5-H), 3.85 s (3H, MeO), 2.48 s (3H, 2-Me), 2.13 s (3H, 6-Me).

N'-(4-Chlorophenylsulfonyl)-N-[4-hydroxy-3-(4-methoxyphenylsulfonyl)-2,6-dimethylphenyl]benzimidamide (XLVd). ¹H NMR spectrum, δ, ppm: 10.78 s (1H, NH), 10.18 s (1H, OH), 7.47–7.58 m (5H, Ph), 7.36–7.43 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 7.10–7.78 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 6.72 s (1H, 5-H), 3.84 s (3H, MeO), 2.48 s (3H, 2-Me), 2.12 s (3H, 6-Me).

N-[4-Hydroxy-2,6-dimethyl-3-(4-methylphenylsulfonyl)phenyl]-N'-(phenylsulfonyl)benzimidamide (XLVe). ¹H NMR spectrum, δ, ppm: 10.65 s (1H, NH), 10.05 s (1H, OH), 7.46–7.57 m (5H, Ph), 7.37–7.70 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 7.36–7.57 m (5H, Ph), 6.68 s (1H, 5-H), 2.48 s (3H, MeC₆H₄), 2.39 s (3H, 2-Me), 2.12 s (3H, 6-Me).

3,5-Dimethyl-4-(4-methylphenylsulfonylamino)phenyl 4-methoxybenzenesulfonate (XLVIa). ^1H NMR spectrum, δ , ppm: 7.55–7.66 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.37–7.75 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 6.71 s (2H, 2-H, 6-H), 3.95 s (3H, MeO), 2.43 s (3H, MeC_6H_4), 1.97 s (6H, 3-Me, 5-Me).

4-(4-Methoxyphenylsulfonylamino)-3,5-dimethylphenyl 4-methylbenzenesulfonate (XLVIb). ^1H NMR spectrum, δ , ppm: 7.47–7.60 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.07–7.76 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 6.71 s (2H, 2-H, 6-H), 3.91 s (3H, MeO), 2.49 s (3H, MeC_6H_4), 1.99 s (6H, 3-Me, 5-Me).

4-(4-Methoxyphenylsulfonylamino)-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIc). ^1H NMR spectrum, δ , ppm: 7.27–7.43 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 6.97–7.59 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 6.71 s (2H, 2-H, 6-H), 3.91 s and 3.90 s (3H each, MeO), 1.98 s (6H, 3-Me, 5-Me).

3,5-Dimethyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XLVIIa). ^1H NMR spectrum, δ , ppm: 9.69 s (1H, NH), 7.33–7.88 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 7.12–7.84 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 6.82 s (2H, 2-H, 5-H), 3.89 s (3H, MeO), 2.38 s (3H, MeC_6H_4), 2.11 s (6H, 3-Me, 5-Me).

4-(4-Chlorobenzoylamino)-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIIb). ^1H NMR spectrum, δ , ppm: 9.85 s (1H, NH), 7.61–8.00 d.d (4H, ClC_6H_4 , $J = 9.0$ Hz), 7.20–7.84 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 6.83 s (2H, 2-H, 6-H), 3.89 s (3H, MeO), 2.12 s (6H, 3-Me, 5-Me).

4-(4-Bromobenzoylamino)-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIIc). ^1H NMR spectrum, δ , ppm: 9.86 s (1H, NH), 7.45–7.91 d.d (4H, BrC_6H_4 , $J = 8.4$ Hz), 7.20–7.84 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 6.83 s (2H, 2-H, 6-H), 3.89 s (3H, MeO), 2.11 s (6H, 3-Me, 5-Me).

4-(4-Methoxybenzoylamino)-3,5-dimethylphenyl 4-methylbenzenesulfonate (XLVIIId). ^1H NMR spectrum, δ , ppm: 9.56 s (1H, NH), 7.50–7.80 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 6.83 s (2H, 2-H, 6-H), 6.77–7.96 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 3.83 s (3H, MeO), 2.43 s (3H, MeC_6H_4), 2.11 s (6H, 3-Me, 5-Me).

4-Benzoylamino-3,5-dimethylphenyl 4-methylbenzenesulfonate (XLVIIe). ^1H NMR spectrum, δ , ppm: 9.76 s (1H, NH), 7.41–7.80 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 7.34–7.62 m (5H, Ph), 6.84 s (2H, 2-H, 6-H), 2.44 s (3H), 2.12 s (6H, 3-Me, 5-Me).

3,5-Dimethyl-4-[(4-methylphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzene-

sulfonate (XLVIIIa). ^1H NMR spectrum, δ , ppm: 10.10 s (1H, NH), 7.40–7.54 m (5H, Ph), 7.32–7.76 d.d (4H, MeC_6H_4 , $J = 8.7$ Hz), 7.18–7.80 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 6.84 s (2H, 2-H, 6-H), 3.88 s (3H, MeO), 2.32 s (3H, MeC_6H_4), 2.13 s (6H, 3-Me, 5-Me).

4-[(4-Methoxyphenylsulfonylimino)(phenyl)methylamino]-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIIIb). ^1H NMR spectrum, δ , ppm: 10.00 s (1H, NH), 7.42–7.51 m (5H, Ph), 7.09–7.78 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 6.88 s (2H, 2-H, 6-H), 3.88 s and 3.79 s (3H each, MeO), 2.13 s (6H, 3-Me, 5-Me).

4-[(4-Bromophenylsulfonylimino)(phenyl)methylamino]-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIIIc). ^1H NMR spectrum, δ , ppm: 10.25 s (1H, NH), 7.50 m (5H, Ph), 7.48–7.82 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.25–7.48 d.d (4H, BrC_6H_4 , $J = 8.7$ Hz), 6.86 s (2H, 2-H, 6-H), 3.88 s (3H, MeO), 2.13 s (6H, 3-Me, 5-Me).

4-[(4-Chlorophenylsulfonylimino)(phenyl)methylamino]-3,5-dimethylphenyl 4-methoxybenzenesulfonate (XLVIIIId). ^1H NMR spectrum, δ , ppm: 10.24 s (1H, NH), 7.47–7.58 m (5H, Ph), 7.18–7.82 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 6.91–7.43 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 6.86 s (2H, 2-H, 6-H), 3.88 s (3H, MeO), 2.13 s (6H, 3-Me, 5-Me).

3,5-Dimethyl-4-[(phenyl)(phenylsulfonylimino)methylamino]phenyl 4-methylbenzenesulfonate (XLVIIIe). ^1H NMR spectrum, δ , ppm: 10.26 s (1H, NH), 7.46–7.60 m (10H, Ph), 7.11–7.20 d.d (4H, MeC_6H_4 , $J = 8.1$ Hz), 6.84 s (2H, 2-H, 6-H), 2.44 s (3H, MeC_6H_4), 2.13 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-2,6-dimethylphenyl)-4-methoxy-*N*-(4-methylphenylsulfonyl)benzenesulfonamide (XLIXa).** ^1H NMR spectrum, δ , ppm: 7.48–7.87 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz), 7.17–7.91 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 6.56 s (2H, 3-H, 5-H), 3.97 s (3H, MeO), 2.49 s (3H, MeC_6H_4), 1.78 s (6H, 3-Me, 5-Me).

***N*-(4-Hydroxy-2,6-dimethylphenyl)-4-methoxy-*N*-(4-methoxyphenylsulfonyl)benzenesulfonamide (XLIXb).** ^1H NMR spectrum, δ , ppm: 7.17–7.92 d.d (8H, C_6H_4 , $J = 9.0$ Hz), 6.56 s (2H, 3-H, 5-H), 3.96 s (6H, MeO), 1.79 s (6H, 2-Me, 6-Me).

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methoxyphenylsulfonyl)-4-methylbenzamide (La).** Yield 30%, mp 210.5–211°C. ^1H NMR spectrum, δ , ppm: 9.65 s (1H, OH), 7.19–8.01 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.03–7.11 d.d (4H, MeC_6H_4 , $J = 8.4$ Hz),

6.45 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 2.21 s (3H, MeC₆H₄), 2.04 s (6H, 3-Me, 5-Me). Found, %: N 3.33, 3.41; S 7.47, 7.66. C₂₃H₂₃NO₅S. Calculated, %: N 3.29; S 11.04.

4-Chloro-N-(4-hydroxy-2,6-dimethylphenyl)-N-(4-methoxyphenylsulfonyl)benzamide (Lb). ¹H NMR spectrum, δ, ppm: 9.69 s (1H, OH), 7.20–8.03 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.20–7.31 d.d (4H, ClC₆H₄, *J* = 8.4 Hz), 6.47 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 2.05 s (6H, 3-Me, 5-Me).

4-Bromo-N-(4-hydroxy-2,6-dimethylphenyl)-N-(4-methoxyphenylsulfonyl)benzamide (Lc). ¹H NMR spectrum, δ, ppm: 9.71 s (1H, OH), 7.20–8.02 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.13–7.75 d.d (4H, BrC₆H₄, *J* = 8.4 Hz), 6.46 s (2H, 3-H, 5-H), 3.89 s (3H, MeO), 2.04 s (6H, 3-Me, 5-Me).

N-(4-Hydroxy-2,6-dimethylphenyl)-4-methoxy-N-(4-methylphenylsulfonyl)benzamide (Ld). ¹H NMR spectrum, δ, ppm: 9.55 s (1H, OH), 7.19–7.96 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.05–7.41 d.d (4H, MeC₆H₄, *J* = 8.4 Hz), 6.48 s (2H, 3-H, 5-H), 3.70 s (3H, MeO), 2.43 s (3H, MeC₆H₄), 2.05 s (6H, 3-Me, 5-Me).

N-(4-Hydroxy-2,6-dimethylphenyl)-N-(4-methylphenylsulfonyl)benzamide (Le). ¹H NMR spectrum, δ, ppm: 9.64 s (1H, OH), 7.96–7.99 d (4H, MeC₆H₄, *J* = 8.1 Hz), 7.20–7.55 m (5H, Ph), 6.44 s (2H, 3-H, 5-H), 2.44 s (3H, MeC₆H₄), 2.06 s (6H, 3-Me, 5-Me).

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