ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 9, pp. 1283–1291. © Pleiades Publishing, Ltd., 2014.
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Reaction of *N*-Acetyl- and *N*-[1-(Arylsulfonylimino)ethyl]-1,4-benzoquinone Imines with Sodium Arenesulfinates

S. A. Konovalova[a], A. P. Avdeenko[a], V. V. Pirozhenko[b], O. P. Ledeneva[c], and A. A. Santalova[a]

[a] *Donbass State Engineering Academy, ul. Shkadinova 72, Kramatorsk, 84313 Ukraine*
e-mail: chimist@dgma.donetsk.ua

[b] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02660 Ukraine*

[c] *Ukrainian Engineering and Pedagogical Academy, Slavyansk, Ukraine*

Received February 7, 2014

Abstract—*N*-Acetyl- and *N*-[1-(arylsulfonylimino)ethyl]-1,4-benzoquinone imines having no substituent in the 2- and/or 6-position of the quinoid ring react with sodium arenesulfinates preferentially according to the 1,4-addition pattern. The presence of an $ArSO_2N$ group favors radical ion reaction with formation of 1,6-addition products.

DOI: 10.1134/S1070428014090097

We previously showed that *N*-aryl- [1], *N*-aroyl- [2–4], *N*-arylsulfonyl- [2–7], and *N*-[α-(arylsulfonylimino)benzyl]-1,4-benzoquinone imines [2–4] react with sodium arenesulfinates to give four types of products. It was presumed that nucleophilic addition of arenesulfinate ion under charge or orbital control leads to the formation of 1,4- and 6,3-addition products and that 1,6- and 6,1-additions follow radical ion mechanism [2–4, 7]. The latter path becomes preferential for 1,4-benzoquinone imines characterized by a higher redox potential [2–4], and 1,4-addition is most typical of *N*-arylsulfonyl and *N*-[alkyl(or trifluoromethyl)sulfonyl] derivatives [2–4, 7] which contain a strong electron-withdrawing substituent on the nitrogen atom.

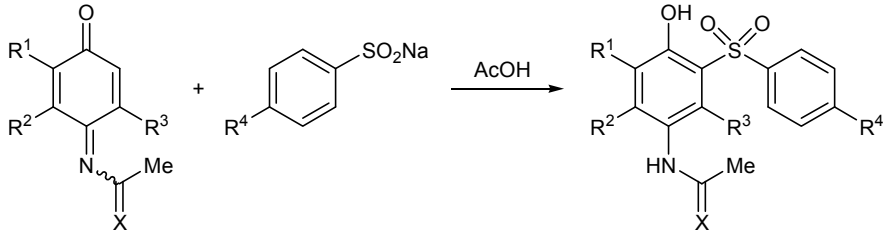
N-Acetyl- and *N*-[1-(arylsulfonylimino)ethyl]-1,4-benzoquinone imines are methyl analogs of *N*-aroyl and *N*-[(*N*-arylsulfonyl)benzimidoyl] derivatives. Replacement of the aryl group at the carbonyl carbon atom in *N*-aroyl and *N*-[1-(arylsulfonylimino)benzyl]-derivatives by methyl group changes their reactivity [8]. Reactions of *N*-acetyl- or *N*-[1-(arylsulfonylimino)ethyl]-1,4-benzoquinone imines with sodium arenesulfinates have not been studied previously.

The goal of the present work was to reveal specific features of the reaction of alkyl-substituted *N*-acetyl- and *N*-[1-(arylsulfonylimino)ethyl]-1,4-benzoquinone imines with sodium arenesulfinates. The reactions were carried out in boiling acetic acid using 2 equiv of the nucleophile. When the reaction mixture turned colorless, it was diluted with water until complete precipitation. A part of the solid product was filtered off and dried, and the other part was recrystallized. Both these parts, as well as the products isolated from the filtrate, were analyzed by ^{1}H NMR to identify all possible products.

In the reactions of *N*-[1-(arylsulfonylimino)ethyl]-(**Ia**–**If**) and *N*-acetyl-1,4-benzoquinone imines (**IIa**, **IIb**) with sodium arenesulfinates **IIIa**–**IIIc** we isolated only 1,4-addition products **IVa**–**IVk** and **Va**–**Vd** (Scheme 1). Their ^{1}H NMR spectra contained two doublets (**IVa**–**IVc**) or one singlet (**IVd**–**IVk**, **Va**–**Vd**) from protons in the aminophenol fragment, singlets from the NH and OH protons, and doublets from the former arenesulfinate, which indicated 1,4-addition of sulfinates **III**.

3-Methyl-1,4-benzoquinone imines **VIa** and **VIb** reacted with sodium arenesulfinates **IIIa** and **IIIb** to give mixtures of 1,4- (**VIIa**–**VIIc**, **VIIIa**–**VIIIc**) and 6,3-addition products (**IXa**–**IVc**) (Scheme 2; see table). Signals in their ^{1}H NMR spectra were assigned on the basis of published data [2–4]. 1,4-Addition products displayed two singlets at δ 6.72–6.76 and 7.74–7.76 ppm (**VIIa**–**VIIc**) or two doublets at δ 6.75–6.79 and 7.24–7.29 ppm with a vicinal coupling constant ^3J of 8.7 Hz (**VIIIa**–**VIIIc**); 6,3-addition products **IXa**–**IXc** were characterized by two broadened singlets

Scheme 1.



Ia–If, **IIa**, **IIb** **IIIa–IIIc** **IVa–IVk**, **Va–Vd**

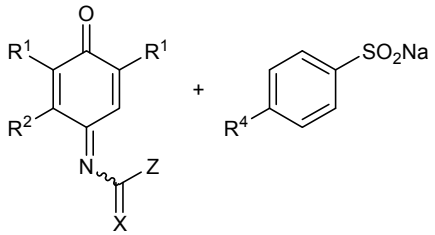
I, X = 4-$MeC_6H_4SO_2N$ (**a**, **c**, **e**), 4-$ClC_6H_4SO_2N$ (**b**, **d**, **f**); R^1 = Me, R^2 = R^3 = H (**a**, **b**); R^1 = R^2 = Me, R^3 = H (**c**, **d**); R^2 = R^3 = Me, R^1 = H (**e**, **f**); **II**, X = O: R^1 = R^2 = Me, R^3 = H (**a**); R^1 = Me, R^2 = H, R^3 = *i*-Pr (**b**); **III**, R^4 = Me (**a**), MeO (**b**), Cl (**c**); **IV**, X = 4-$MeC_6H_4SO_2N$ (**a**, **b**, **d**, **e**, **h**, **i**), 4-$ClC_6H_4SO_2N$ (**c**, **f**, **g**, **j**, **k**); R^1 = Me, R^2 = R^3 = H, R^4 = Me (**a**, **c**), MeO (**b**); R^1 = R^2 = Me, R^3 = H, R^4 = Me (**d**, **f**), MeO (**e**, **g**); R^1 = H, R^2 = R^3 = Me, R^4 = Me (**h**, **j**), MeO (**i**, **k**); **V**, X = O: R^1 = R^2 = Me, R^3 = H, R^4 = Me (**a**), MeO (**b**); R^1 = Me, R^2 = H, R^3 = *i*-Pr, R^4 = Me (**c**), MeO (**d**).

at δ 6.61–6.62 and 7.09–7.12 ppm. The spectra of **IXa**–**IXc** revealed an appreciable upfield shift of the singlet signal from the methyl protons in the imidoyl fragment (δ 2.71 ppm) as a result of considerable shielding of that methyl group by the arylsulfonyl substituent in position *6* of the aminophenol fragment.

The reaction of *N*-[1-(arylsulfonylimino)ethyl]-2,6-dimethyl-1,4-benzoquinone imines **Xa** and **Xb** with sodium arenesulfinates **IIIa** and **IIIc** afforded only 1,6-addition products **XIIa** and **XIIb**, whereas *N*-acetyl-2,6-dimethyl-1,4-benzoquinone imine (**XI**) gave rise to mixtures of 1,6- (**XIIIa**, **XIIIb**) and 6,3-adducts (**XIVa**, **XIVb**); the yields of **XIVa** and **XIVb** were 15 and 10%, respectively (Scheme 3). We succeeded in isolating pure compounds **XIIIb** and **XIVa** after recrystallization of the reaction mixture. In the reactions with quinone imines **Xa** and **Xb** the reaction mixtures also contained their reduced derivatives, the corresponding aminophenols.

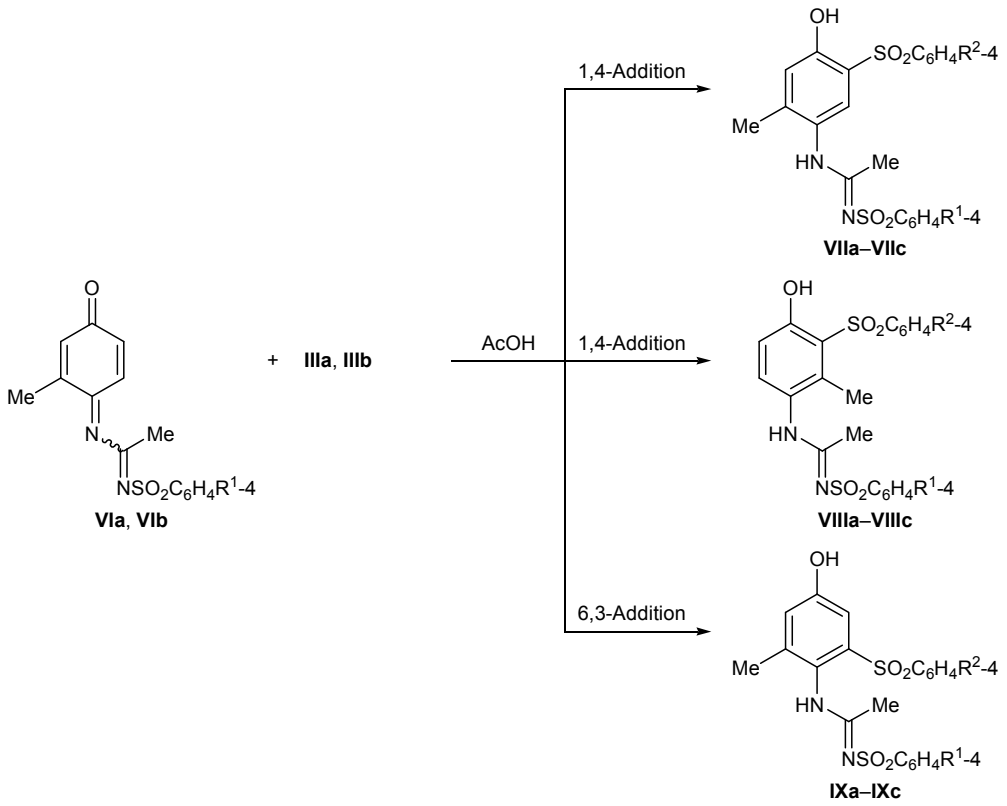
The structure of **XII**–**XIV** was determined on the basis of the ^{1}H NMR spectra. The spectra of **XIIa**, **XIIb**, **XIIIa**, and **XIIIb** characteristically contained

Reactions of *N*-acyl-, *N*-[α-(arenesulfonylimino)benzyl], and *N*-[1-(arenesulfonylimino)ethyl]-1,4-benzoquinone imines with sodium arenesulfinates



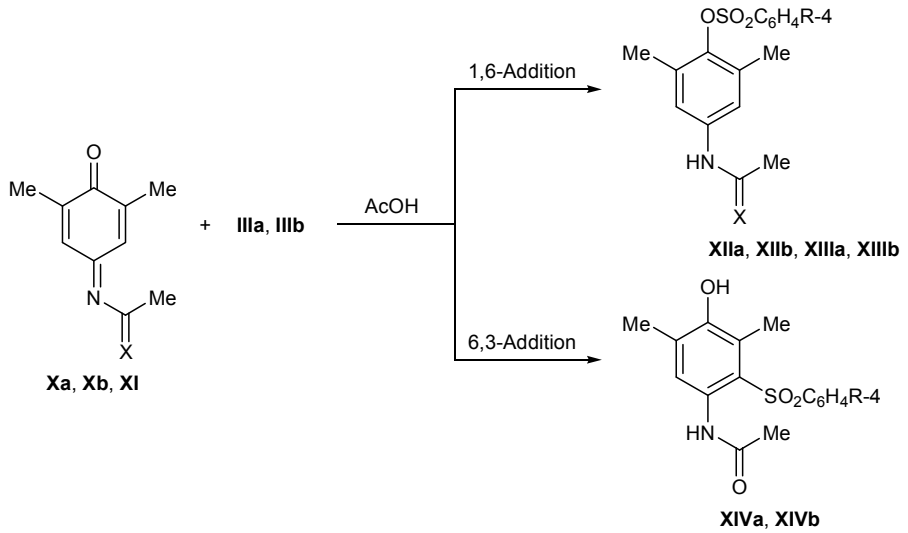
R^1	R^2	X	Z	R^4	Addition products, %			
					1,4 (**VII**/**VIII**)	6,3	6,1	1,6
H	Me	4-$MeC_6H_4SO_2N$	Me	Me	66/16	18	–	–
H	Me	4-$ClC_6H_4SO_2N$	Me	Me	47/17	36	–	–
H	Me	4-$ClC_6H_4SO_2N$	Me	MeO	35/5	60	–	–
Me	H	O	Me	Me	–	15	–	85
Me	H	O	Me	Cl	–	10	–	90
Me	H	4-$MeC_6H_4SO_2N$	Me	Me	–	–	–	100
Me	H	4-$ClC_6H_4SO_2N$	Me	Cl	–	–	–	100
Me	H	O	4-$MeOC_6H_4$	Me	–	26 [2]	11 [2]	63 [2]
Me	H	O	4-MeC_6H_4	MeO	–	34 [2]	14 [2]	52 [2]
Me	H	4-$MeC_6H_4SO_2N$	Ph	MeO	–	5 [2]	–	95 [2]
Me	H	4-$MeC_6H_4SO_2N$	Ph	Me	–	11 [2]	–	89 [2]

Scheme 2.



VI, R^1 = Me (**a**), Cl (**b**); **VII**–**IX**, $R^1 = R^2$ = Me (**a**); R^1 = Cl, R^2 = Me (**b**), MeO (**c**).

Scheme 3.

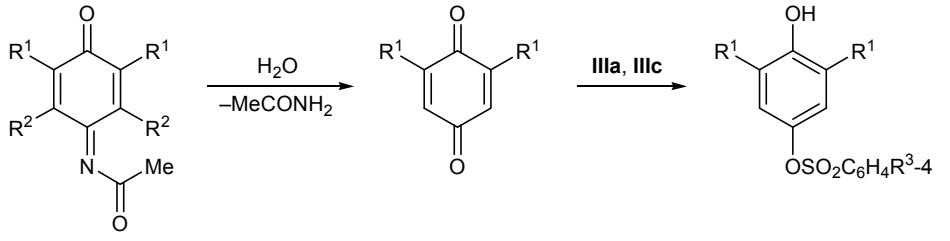


X, X = 4-$MeC_6H_4SO_2N$ (**a**), 4-$ClC_6H_4SO_2N$ (**b**); **XI**, X = O; **XII**, R = Me, X = 4-$MeC_6H_4SO_2N$ (**a**), 4-$ClC_6H_4SO_2N$ (**b**); **XIII**, X = O, R = Me (**a**), Cl (**b**); **XIV**, R = Me (**a**), Cl (**b**).

singlets from 3-H and 5-H at δ 7.27–7.32 ppm and from the NH proton at δ 9.92–10.49 ppm, while compounds **XIVa** and **XIVb** displayed singlets from 6-H at δ 7.37–7.38 ppm and from the NH and OH protons at δ 8.78–8.88 and 9.51–9.62 ppm, respectively.

Compounds **IIc** and **XV** failed to take up arenesulfinate ions. In the reactions of these compounds with sodium arenesulfinates **IIIa** and **IIIc** we isolated substituted hydroquinone derivatives **XVIIIa**, **XVIIIb**, **XIXa**, and **XIXb** (Scheme 4). Analysis of the ^{1}H NMR

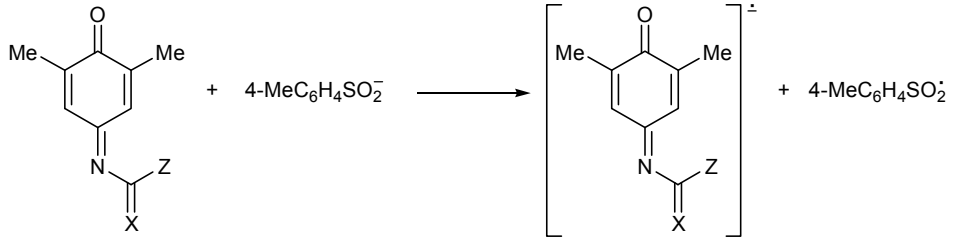
Scheme 4.



IIc, **XV** **XVI**, **XVII** **XVIIIa**, **XVIIIb**, **XIXa**, **XIXb**

IIc, R^1 = H, R^2 = Me; **XV**, R^1 = *i*-Pr, R^2 = H; **XVI**, R^1 = Me; **XVII**, R^1 = *i*-Pr; **XVIII**, R^1 = R^3 = Me (**a**); R^1 = Me, R^3 = Cl (**b**); **XIX**, R^1 = *i*-Pr, R^3 = Me (**a**), Cl (**b**).

Scheme 5.



Xc, **XI**, **XX**, **XXI**

Xc, X = $PhSO_2N$, Z = Me; **XI**, X = O, Z = Me; **XX**, X = $PhSO_2N$, Z = Ph; **XXI**, X = O, Z = Ph.

data showed that these compounds are products of addition of sodium arenesulfinates to the corresponding 1,4-benzoquinones **XVI** and **XVII** which were formed as a result of hydrolysis of initial quinone imines **IIc** and **XV**. Compounds **XIXa** and **XIXb** were identical to the products synthesized previously by reaction of *N*-aroyl- and *N*-[1-(arylsulfonylimino)-ethyl]-2,6-diisopropyl-1,4-benzoquinone imines with sodium arenesulfinates [2].

The results of our present study and those obtained in [2–4] show that 2,6-dimethyl derivatives **Xa**, **Xb**, and **XI** demonstrate the strongest difference in the reactivity of *N*-substituted 1,4-benzoquinone imines (see table, R^1 = Me, R^2 = H). 6,1-Addition products were formed only from *N*-aroyl-1,4-benzoquinone imines (X = O, Z = 4-$MeOC_6H_4$, 4-MeC_6H_4), and the contribution of 6,3-addition decreased in going from aryl- (Z = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4) to methyl-substituted derivatives (Z = Me). No 6,3-addition products were detected in the reactions with methylimidoyl analogs (X = 4-$MeC_6H_4SO_2N$, 4-$ClC_6H_4SO_2N$, Z = Me).

We previously presumed that 1,6- and 6,1-addition products are formed according to radical ion mechanism. Taking into account that just these adducts were mainly obtained from imidoyl derivatives (X = 4-$MeC_6H_4SO_2N$, 4-$ClC_6H_4SO_2N$), introduction of an $ArSO_2N$ fragment favors more facile formation of radical anion species from the initial 1,4-benzoquinone imine and increases the contribution of the radical ion path. To verify this assumption we calculated the change in the energy of the system (ΔE) upon generation of radical ions from initial model quinone imines **Xc**, **XI**, **XX**, and **XXI** during their reactions with sodium 4-methylbenzenesulfinate (Scheme 5). The formation of radical anion from quinone imines **Xc** and **XX** turned out to be more favorable (ΔE = 105.73 and 93.17 kJ/mol, respectively) than from quinone imines **XI** and **XXI** (ΔE = 124.07 and 113.80 kJ/mol, respectively), which was fully consistent with the experimental data (see table).

Thus, the experimental data and results of quantum chemical calculations showed that the presence of an $ArSO_2N$ group in *N*-[α-(arylsulfonylimino)benzyl]- or *N*-[1-(arylsulfonylimino)ethyl]-2,6-dimethyl-1,4-benzoquinone imines favors their reaction with sodium arenesulfinates to follow radical ion path, which is determined by decrease of the energy of formation of intermediate radical ion from the initial quinone imine. These compounds gave rise to the largest number of 1,6-addition products.

Among the examined quinone imines, only *N*-aroyl derivatives (X = O, Z = 4-$MeOC_6H_4$, 4-MeC_6H_4) reacted with sodium arenesulfinates to give 6,1-addition products (see table). The most probable reason for the

lack of analogous adducts in the reactions with *N*-imidoyl quinone imines **X** and **XX** is steric hindrances created by bulky sybstituents on the nitrogen atom. Methyl groups in the *ortho* positions with respect to the carbonyl carbon atom in *N*-acetyl-1,4-benzoquinone imine **XI** are likely to stabilize the radical center on the oxygen atom to a greater extent than in *N*-aroyl derivative **XXI**, so that 1,6-addition products are mainly formed.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using tetramethylsilane as internal reference. Thin-layer chromatography was performed on Silufol UV-254 plates; spots were applied from solutions in chloroform, the plates were eluted with benzene–hexane (10 : 1), and the chromatograms were developed under UV light.

Quantum-chemical calculations were performed using Firefly QC software package [9] based in part on the program code of GAMESS (US) [10]. The molecular structures were calculated in terms of the density functional theory with the B3LYP potential using standard 6-31+G(*d*) basis set.

Initial *N*-[1-(arylsulfonylimino)ethyl]-1,4-benzoquinone imines **Ia**–**If**, **VIa**, **VIb**, **Xa**, and **Xb** were synthesized by oxidation of the corresponding *N*-substituted 4-aminophenols with lead(IV) acetate in glacial acetic acid according to the procedure described in [11] and were recrystallized from glacial acetic acid.

N-Acetyl-1,4-benzoquinone imines **IIa**–**IIc** and **XI** were prepared by oxidation of the corresponding *N*-(4-hydroxyphenyl)acetamides with silver(I) oxide in chloroform as reported in [11], and *N*-acetyl-1,4-benzoquinone imine (**XV**) was obtained by oxidation of the corresponding *N*-(4-hydroxyphenyl)acetamide with 4-(diacetoxy-λ^3-iodanyl)toluene in dichloroethane according to [12]. The spectral parameters and elemental analyses of quinone imines **Ib**, **Id**–**If**, **Xa**, **Xb** [8], **IIb** [13], **IIc**, and **XI** [14] were reported previously. Sodium arenesulfinates **IIIa**–**IIIc** were prepared as described in [15].

General procedure for the reaction of quinone imines Ia–If, IIa–IIc, VIa, VIb, Xa, and Xb with sodium arenesulfinates IIIa–IIIc. A solution of 2 mmol of quinone imine **Ia**–**If**, **IIa**–**IIc**, **VIa**, **VIb**, **Xa**, or **Xb** in 20 mL of glacial acetic acid was heated to the boiling point, 4 mmol of sodium arenesulfinate **IIIa**–**IIIc** was added, and the mixture was heated for 5 min under reflux and left to stand for 12 h at room temperature. When the mixture turned colorless, 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 crude product was recrystallized from glacial acetic acid. The mother liquor was diluted with water, and the precipitate was filtered off. All three portions of the solid product were analyzed by ^{1}H NMR.

General procedure for the reaction of quinone imines XI and XV with sodium arenesulfinates IIIa and IIIc. Sodium arenesulfinate **IIIa** or **IIIc**, 4 mmol, was added to a solution of 2 mmol of quinone imine **XI** or **XV** in 20 mL of glacial acetic acid, the mixture was heated to the boiling point, kept boiling for 5 min, and left to stand for 6 h at room temperature. When the mixture turned colorless, an ice–water mixture was added until a solid began to separate from the solution. The colorless precipitate was filtered off, and a part of it was recrystallized from glacial acetic acid. The mother liquor was diluted with water, and the precipitate was filtered off. All three portions of the solid product were analyzed by ^{1}H NMR.

***N′*-(4-Methylbenzenesulfonyl)-*N*-(3-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetimidamide (Ia).** Yield 58%, mp 140–142°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer (79%): 2.07 br.s (3H, 3-Me), 2.27 s (3H, Me), 2.43 s (3H, **Me**C_6H_4), 6.66 d (1H, 5-H, J = 10.2 Hz), 6.71 q (1H, 2-H), 6.89–6.93 d.d (1H, 6-H, J = 10.2, 2.7 Hz), 7.30 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.78 d (2H, 3′-H, 5′-H, J = 8.4 Hz); *Z* isomer (21%): 2.05 br.s (3H, 3-Me), 2.43 s (3H, **Me**C_6H_4), 2.70 br.s (3H, Me), 6.64 d (1H, 5-H, J = 10.2 Hz), 6.81 q (1H, 2-H), 6.97–7.01 d.d (1H, 6-H, J = 10.2, 2.7 Hz), 7.30 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.86 d (2H, 3′-H, 5′-H, J = 8.4 Hz). Found, %: N 8.57, 8.89; S 10.08, 10.24. $C_{16}H_{16}N_2O_3S$. Calculated, %: N 8.85; S 10.14.

***N*-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylbenzenesulfonyl)acetimidamide (Ic).** Yield 70%, mp 171–173°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer (78%): 2.07 br.s (3H, 3-Me), 2.12 br.s (3H, 2-Me), 2.28 s (3H, Me), 2.43 s (3H, **Me**C_6H_4), 6.56 d (1H, 5-H, J = 9.6 Hz), 6.69 d (1H, 6-H, J = 9.6 Hz), 7.29 d (2H, 2′-H, 6′-H, J = 9.0 Hz), 7.77 d (2H, 3′-H, 5′-H, J = 9.0 Hz); *Z* isomer (22%): 2.03 br.s (3H, 3-Me), 2.12 br.s (3H, 2-Me), 2.70 br.s (3H, Me), 2.42 s (3H, **Me**C_6H_4), 6.56 d (1H, 5-H, J = 9.6 Hz), 6.92 d (1H, 6-H, J = 9.6 Hz), 7.29 d

(2H, 2′-H, 6′-H, J = 9.0 Hz), 7.86 d (2H, 3′-H, 5′-H, J = 9.0 Hz). Found, %: N 8.13, 8.42; S 9.46, 9.74. $C_{17}H_{18}N_2O_3S$. Calculated, %: N 8.48; S 9.70.

***N*-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (IIa).** Yield 57%, mp 73–74°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.07 br.s (3H, 3-Me), 2.11 br.s (3H, 2-Me), 2.31 s (3H, Me), 6.54 d (1H, 6-H, J = 9.6 Hz), 6.81 d (1H, 5-H, J = 9.6 Hz). Found, %: N 7.99, 8.23. $C_{10}H_{11}NO_2$. Calculated, %: N 7.90.

***N*-[4-Hydroxy-3-methyl-5-(4-methylbenzenesulfonyl)phenyl]-*N*′-(4-methylbenzenesulfonyl)acetimidamide (IVa).** Yield 67%, mp 216–217°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.08 s (3H, 3-Me), 2.37 s (3H, 4′-Me), 2.37 s (3H, 4″-Me), 2.47 s (3H, Me), 7.35 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.36 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.51 d (1H, 2-H, J = 1.2 Hz), 7.68 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 7.76 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 8.05 d (1H, 6-H, J = 1.2 Hz), 9.67 s (1H, NH), 10.38 s (1H, OH). Found, %: N 5.80, 6.02; S 13.47, 13.60. $C_{23}H_{24}N_2O_5S_2$. Calculated, %: N 5.93; S 13.57.

***N*-[4-Hydroxy-3-(4-methoxybenzenesulfonyl)-5-methylphenyl]-*N*′-(4-methylbenzenesulfonyl)acetimidamide (IVb).** Yield 75%, mp 150–152°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 s (3H, 5-Me), 2.37 s (3H, 4′-Me), 2.46 s (3H, Me), 3.82 s (3H, MeO), 7.14 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.37 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.53 d (1H, 6-H, J = 1.2 Hz), 7.79 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.79 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.98 d (1H, 2-H, J = 1.2 Hz), 9.94 br.s (1H, NH), 10.35 br.s (1H, OH). Found, %: N 5.51, 5.84; S 13.00, 13.21. $C_{23}H_{24}N_2O_6S_2$. Calculated, %: N 5.73; S 13.13.

***N*′-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-3-methyl-5-(4-methylbenzenesulfonyl)phenyl]acetimidamide (IVc).** Yield 69%, mp 208–210°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.08 s (3H, 3-Me), 2.38 s (3H, **Me**C_6H_4), 2.48 s (3H, Me), 7.38 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.47 d (1H, 2-H, J = 1.5 Hz), 7.63 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.68 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.88 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 8.04 d (1H, 6-H, J = 1.5 Hz), 9.72 s (1H, NH), 10.52 br.s (1H, OH). Found, %: N 5.47, 5.69; S 13.16, 13.34. $C_{22}H_{21}ClN_2O_5S_2$. Calculated, %: N 5.68; S 13.01.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]-*N*′-(4-methylbenzenesulfonyl)acetimidamide (IVd).** Yield 68%, mp 211–212°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 s (3H, 3-Me), 2.03 s (3H, 2-Me), 2.35 s (3H, 4′-Me), 2.38 s (3H, 4″-Me), 2.46 s (3H, Me), 7.31 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.36 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.61 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.64 s (1H, 6-H), 7.70 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.64 s (1H, NH), 10.16 s (1H, OH). Found, %: N 5.72, 5.94; S 13.15, 13.32. $C_{24}H_{26}N_2O_5S_2$. Calculated, %: N 5.76; S 13.18.

***N*-[4-Hydroxy-5-(4-methoxybenzenesulfonyl)-2,3-dimethylphenyl]-*N*′-(4-methylbenzenesulfonyl)acetimidamide (IVe).** Yield 65%, mp 139–140°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 s (3H, 3-Me), 2.04 s (3H, 2-Me), 2.35 s (3H, 4′-Me), 2.45 s (3H, Me), 3.83 s (3H, MeO), 7.08 d (2H, 2″-H, 6″-H, J = 9.0 Hz), 7.32 d (2H, 2′-H, 6′-H, J = 9.0 Hz), 7.61 d (2H, 3′-H, 5′-H, J = 9.0 Hz), 7.62 s (1H, 6-H), 7.76 d (2H, 3″-H, 5″-H, J = 9.0 Hz), 9.62 br.s (1H, NH), 10.11 s (1H, OH). Found, %: N 5.50, 5.64; S 12.70, 12.84. $C_{24}H_{26}N_2O_6S_2$. Calculated, %: N 5.57; S 12.76.

***N*′-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]acetimidamide (IVf).** Yield 63%, mp 209–210°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.04 br.s (6H, 2-Me, 3-Me), 2.38 s (3H, 4″-Me), 2.48 s (3H, Me), 7.36 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.58 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.64 s (1H, 6-H), 7.67 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.74 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 9.69 br.s (1H, NH), 10.42 br.s (1H, OH). Found, %: N 5.61, 5.69; S 12.44, 12.69. $C_{23}H_{23}ClN_2O_5S_2$. Calculated, %: N 5.53; S 12.65.

***N*′-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-5-(4-methoxybenzenesulfonyl)-2,3-dimethylphenyl]acetimidamide (IVg).** Yield 42%, mp 127–129°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 s (3H, 3-Me), 2.04 s (3H, 2-Me), 2.48 s (3H, Me), 3.83 s (3H, MeO), 7.08 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.58 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.63 s (1H, 6-H), 7.73 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.74 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 9.63 br.s (1H, NH), 10.23 br.s (1H, OH). Found, %: N 5.31, 5.47; S 12.05, 12.38. $C_{23}H_{23}ClN_2O_6S_2$. Calculated, %: N 5.36; S 12.26.

***N*-[4-Hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-*N*′-(4-methylbenzenesulfonyl)acetimidamide (IVh).** Yield 41%, mp 244–245°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.42 s (3H, Me), 2.01 s (3H, 2-Me), 2.33 s (3H, 6-Me), 2.35 s (3H, 4′-Me), 2.38 s (3H, 4″-Me), 6.65 s (1H, 5-H), 7.31 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.39 d (2H, 2-H, 6-H, J = 8.1 Hz), 7.52 d (2H, 3-H, 5-H, J = 8.1 Hz), 7.72 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.92 s (1H, NH), 10.56 br.s (1H, OH). Found, %: N 5.70, 5.92; S 12.94, 13.15. $C_{24}H_{26}N_2O_5S_2$. Calculated, %: N 5.76; S 13.18.

***N*-[4-Hydroxy-3-(4-methoxybenzenesulfonyl)-2,6-dimethylphenyl]-*N′*-(4-methylbenzenesulfonyl)-acetimidamide (IVi).** Yield 48%, mp 234–235°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (3H, 2-Me), 2.33 s (3H, 6-Me), 2.35 s (3H, 4′-Me), 2.42 s (3H, Me), 3.84 s (3H, MeO), 6.68 s (1H, 5-H), 7.10 d (2H, 2″-H, 6″-H, *J* = 8.1 Hz), 7.29 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.51 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 7.78 d (2H, 3″-H, 5″-H, *J* = 8.1 Hz), 9.84 br.s (1H, NH), 10.57 br.s (1H, OH). Found, %: N 5.21, 5.41; S 12.46, 12.68. $C_{24}H_{26}N_2O_6S_2$. Calculated, %: N 5.57; S 12.76.

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]acetimidamide (IVj).** Yield 44%, mp 227–229°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00 s (3H, 2-Me), 2.34 s (3H, 6-Me), 2.38 s (3H, 4″-Me), 2.47 s (3H, Me), 6.67 s (1H, 5-H), 7.37 d (2H, 2″-H, 6″-H, *J* = 7.5 Hz), 7.57 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.64 d (2H, 3″-H, 5″-H, *J* = 7.5 Hz), 7.70 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 10.20 br.s (1H, NH), 10.86 br.s (1H, OH). Found, %: N 6.93, 7.18; S 12.54, 12.70. $C_{23}H_{23}ClN_2O_5S_2$. Calculated, %: N 5.53; S 12.65.

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-3-(4-methoxybenzenesulfonyl)-2,6-dimethylphenyl]-acetimidamide (IVk).** Yield 49%, mp 226–227°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (3H, 2-Me), 2.32 s (3H, 6-Me), 2.45 s (3H, Me), 3.84 s (3H, MeO), 6.68 s (1H, 5-H), 7.09 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.56 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.62 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 7.77 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 9.96 br.s (1H, NH), 10.53 br.s (1H, OH). Found, %: N 5.09, 5.32; S 11.92, 12.39. $C_{23}H_{23}ClN_2O_6S_2$. Calculated, %: N 5.36; S 12.26.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]acetamide (Va).** Yield 55%, mp 180–181°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (3H, Me), 2.14 s (3H, 2-Me), 2.16 s (3H, 3-Me), 2.39 s (3H, **Me**C_6H_4), 7.32 s (1H, 6-H), 7.46 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.78 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 9.34 s (1H, NH), 10.35 s (1H, OH). Found, %: N 4.06, 4.29; S 9.53, 9.81. $C_{17}H_{19}NO_4S$. Calculated, %: N 4.20; S 9.62.

***N*-[4-Hydroxy-5-(4-methoxybenzenesulfonyl)-2,3-dimethylphenyl]acetamide (Vb).** Yield 68%, mp 191–192°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (3H, Me), 2.14 s (3H, 2-Me), 2.16 s (3H, 3-Me), 3.85 s (3H, MeO), 7.16 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.30 s (1H, 6-H), 7.84 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 9.31 s (1H, NH), 10.39 s (1H, OH). Found, %: N 4.15, 4.33; S 9.05, 9.39. $C_{17}H_{19}NO_5S$. Calculated, %: N 4.01; S 9.18.

***N*-[4-Hydroxy-2-isopropyl-5-methyl-3-(4-methylbenzenesulfonyl)phenyl]acetamide (Vc).** Yield 74%, mp 210–211°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.86 d [6H, CH(C**H**$_3$)$_2$, *J* = 6.9 Hz], 1.96 s (3H, Me), 2.16 s (3H, 5-Me), 2.40 s (3H, **Me**C_6H_4), 3.55–3.64 m [1H, C**H**(CH$_3$)$_2$], 7.15 s (1H, 6-H), 7.47 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.74 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 9.05 s (1H, NH), 10.83 br.s (1H, OH). Found, %: N 4.00, 4.17; S 8.68, 8.83. $C_{19}H_{23}NO_4S$. Calculated, %: N 3.88; S 8.87.

***N*-[4-Hydroxy-2-isopropyl-3-(4-methoxybenzenesulfonyl)-5-methylphenyl]acetamide (Vd).** Yield 30%, mp 172–173°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.87 d [6H, CH(C**H**$_3$)$_2$, *J* = 6.0 Hz], 1.96 s (3H, Me), 2.17 s (3H, 5-Me), 3.56–3.65 m [1H, C**H**(CH$_3$)$_2$], 3.85 s (3H, MeO), 7.16 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.19 s (1H, 6-H), 7.80 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 9.07 br.s (1H, NH), 10.84 br.s (1H, OH). Found, %: N 3.59, 3.89; S 8.53, 8.64. $C_{19}H_{23}NO_5S$. Calculated, %: N 3.71; S 8.50.

***N*-(2-Methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylbenzenesulfonyl)acetimidamide (VIa).** Yield 64%, mp 151–152°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer (74%): 2.15 br.s (3H, 2-Me), 2.29 s (3H, Me), 2.43 s (3H, **Me**C_6H_4), 6.53–6.56 d.d (1H, 5-H, *J* = 9.3, 1.5 Hz), 6.56 br.s (1H, 3-H), 6.73 d (1H, 6-H, *J* = 9.3 Hz), 7.30 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.78 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz); *Z* isomer (26%): 2.09 br.s (3H, 2-Me), 2.43 s (3H, **Me**C_6H_4), 2.71 br.s (3H, Me), 6.53–6.56 d.d (1H, 5-H, *J* = 9.3, 1.5 Hz), 6.56 br.s (1H, 3-H), 6.97 d (1H, 6-H, *J* = 9.3 Hz), 7.31 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.86 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz). Found, %: N 8.55, 8.72; S 10.15, 10.26. $C_{16}H_{16}N_2O_3S$. Calculated, %: N 8.85; S 10.14.

***N′*-(4-Chlorobenzenesulfonyl)-*N*-(2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetimidamide (VIb).** Yield 46%, mp 152–153°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer (75%): 2.17 br.s (3H, 2-Me), 2.31 s (3H, Me), 6.58 br.s (1H, 3-H), 6.58–6.61 d.d (1H, 5-H, *J* = 10.2, 1.5 Hz), 6.76 d (1H, 6-H, *J* = 10.2 Hz), 7.50 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.85 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz); *Z* isomer (25%): 2.09 br.s (3H, 2-Me), 2.74 br.s (3H, Me), 6.55–6.58 d.d (1H, 5-H, *J* = 10.2, 1.5 Hz), 6.58 br.s (1H, 3-H), 6.96 d (1H, 6-H, *J* = 10.2 Hz), 7.50 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.92 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz). Found, %: N 7.99, 8.30; S 9.48, 9.77. $C_{15}H_{13}ClN_2O_3S$. Calculated, %: N 8.32; S 9.52.

***N*-[4-Hydroxy-2-methyl-5-(4-methylbenzenesulfonyl)phenyl]-*N′*-(4-methylbenzenesulfonyl)acet-**

imidamide (VIIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 2-Me), 2.35 s (3H, 4′-Me), 2.37 s (3H, 4″-Me), 2.47 s (3H, Me), 6.76 s (1H, 3-H), 7.32 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.35 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.64 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.68 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 7.75 s (1H, 6-H), 10.09 br.s (1H, NH), 10.85 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2-methyl-5-(4-methylbenzenesulfonyl)phenyl]acetimidamide (VIIb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.10 s (3H, 2-Me), 2.37 s (3H, 4″-Me), 2.48 s (3H, Me), 6.72 s (1H, 3-H), 7.36 d (2H, 2″-H, 6″-H, *J* = 8.4 Hz), 7.57 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.65 d (2H, 3″-H, 5″-H, *J* = 8.4 Hz), 7.74 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 7.76 s (1H, 6-H), 10.10 br.s (1H, NH), 10.80 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-5-(4-methoxybenzenesulfonyl)-2-methylphenyl]acetimidamide (VIIc).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 2-Me), 2.46 s (3H, Me), 3.83 s (3H, MeO), 6.72 s (1H, 3-H), 7.08 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.59 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.71 d (2H, 3″-H, 5′-H, *J* = 8.7 Hz), 7.74 s (1H, 6-H), 7.76 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 10.10 br.s (1H, NH), 10.78 br.s (1H, OH).

***N*-[4-Hydroxy-2-methyl-3-(4-methylbenzenesulfonyl)phenyl]-*N′*-(4-methylbenzenesulfonyl)acetimidamide (VIIIa).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, 2-Me), 2.38 s (3H, 4′-Me), 2.39 s (3H, 4″-Me), 2.42 s (3H, Me), 6.75 d (1H, 5-H, *J* = 8.7 Hz), 7.24 d (1H, 6-H, *J* = 8.4 Hz), 7.29 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.34 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.55 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.70 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 10.06 br.s (1H, NH), 10.68 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2-methyl-3-(4-methylbenzenesulfonyl)phenyl]acetimidamide (VIIIb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, 2-Me), 2.38 s (3H, 4″-Me), 2.45 s (3H, Me), 6.76 d (1H, 5-H, *J* = 8.7 Hz), 7.27 d (1H, 6-H, *J* = 8.4 Hz), 7.36 d (2H, 2″-H, 6″-H, *J* = 8.4 Hz), 7.58 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.65 d (2H, 3″-H, 5″-H, *J* = 8.4 Hz), 8.00 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 10.31 br.s (1H, NH), 10.70 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-3-(4-methoxybenzenesulfonyl)-2-methylphenyl]acetimidamide (VIIIc).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, 2-Me), 2.46 s (3H, Me), 3.83 s (3H, MeO), 6.79 d (1H, 5-H, *J* = 8.7 Hz), 7.08 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.29 d (1H, 6-H, *J* = 8.1 Hz), 7.59 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.71 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 7.98 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 10.25 br.s (1H, NH), 10.69 br.s (1H, OH).

***N*-[4-Hydroxy-2-methyl-6-(4-methylbenzenesulfonyl)phenyl]-*N′*-(4-methylbenzenesulfonyl)acetimidamide (IXa).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, 2-Me), 2.38 s (3H, 4′-Me), 2.38 s (3H, 4″-Me), 2.71 s (3H, Me), 6.61 br.s (1H, 3-H), 7.12 br.s (1H, 5-H), 7.32 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.46 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.63 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.87 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 9.56 br.s (1H, NH), 10.85 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2-methyl-6-(4-methylbenzenesulfonyl)phenyl]acetimidamide (IXb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, 2-Me), 2.38 s (3H, 4″-Me), 2.71 s (3H, Me), 6.62 br.s (1H, 3-H), 7.09 br.s (1H, 5-H), 7.57 d (2H, 2″-H, 6″-H, *J* = 8.4 Hz), 7.58 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.99 d (2H, 3″-H, 5″-H, *J* = 8.4 Hz), 8.00 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 9.60 br.s (1H, NH), 10.86 br.s (1H, OH).

***N′*-(4-Chlorobenzenesulfonyl)-*N*-[4-hydroxy-2-(4-methoxybenzenesulfonyl)-6-methylphenyl]-acetimidamide (IXc).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, 6-Me), 2.71 s (3H, Me), 3.82 s (3H, MeO), 6.62 br.s (1H, 5-H), 7.09 br.s (1H, 3-H), 7.47 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.59 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.76 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.99 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 9.60 br.s (1H, NH), 10.78 br.s (1H, OH).

2,6-Dimethyl-4-[1-(4-methylbenzenesulfonylimino)ethylamino]phenyl 4-methylbenzenesulfonate (XIIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (6H, 2-Me, 6-Me), 2.38 (3H, 4′-Me), 2.45 s (3H, Me), 2.45 s (3H, 4″-Me), 7.30 s (2H, 3-H, 5-H), 7.38 d (2H, 2′-H, 6′-H, *J* = 7.5 Hz), 7.53 d (2H, 2″-H, 6″-H, *J* = 7.8 Hz), 7.74 d (2H, 3′-H, 5′-H, *J* = 7.5 Hz), 7.86 d (2H, 3″-H, 5″-H, *J* = 7.8 Hz), 10.40 br.s (1H, NH).

4-[1-(4-Chlorobenzenesulfonylimino)ethylamino]-2,6-dimethylphenyl 4-methylbenzenesulfonate (XIIb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (6H, 2-Me, 6-Me), 2.45 s (3H, Me), 2.47 s (3H, 4″-Me), 7.27 s (2H, 3-H, 5-H), 7.53 d (2H, 2″-H, 6″-H, *J* = 8.1 Hz), 7.65 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.86 d (2H, 3″-H, 5″-H, *J* = 8.1 Hz), 7.86 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 10.49 br.s (1H, NH).

4-Acetylamino-2,6-dimethylphenyl 4-methylbenzenesulfonate (XIIIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 s (6H, 2-Me, 6-Me), 2.02 s (3H, Me), 2.44 s (3H, 4′-Me), 7.31 s (2H, 3-H, 5-H),

7.52 d (2H, 2′-H, 6′-H, J = 6.3 Hz), 7.85 d (2H, 3′-H, 5′-H, J = 6.3 Hz), 9.92 s (1H, NH).

4-Acetylamino-2,6-dimethylphenyl 4-chlorobenzenesulfonate (XIIIb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03 s (3H, Me), 2.01 s (6H, 2-Me, 6-Me), 7.32 s (2H, 3-H, 5-H), 7.79 d (2H, 2′-H, 6′-H, J = 6.3 Hz), 7.99 d (2H, 3′-H, 5′-H, J = 6.3 Hz), 9.93 s (1H, NH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylbenzenesulfonyl)phenyl]acetamide (XIVa).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.98 s (3H, 3-Me), 2.20 s (3H, 5-Me), 2.30 s (3H, Me), 2.37 s (3H, 4′-Me), 7.37 s (1H, 6-H), 7.39 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.68 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 8.78 br.s (1H, NH), 9.62 s (1H, OH).

***N*-[2-(4-Chlorobenzenesulfonyl)-4-hydroxy-3,5-dimethylphenyl]acetamide (XIVb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.96 s (3H, 3-Me), 2.21 s (3H, 5-Me), 2.34 s (3H, Me), 7.38 s (1H, 6-H), 7.66 d (2H, 2′-H, 6′-H, J = 6.9 Hz), 7.81 d (2H, 3′-H, 5′-H, J = 6.9 Hz), 8.88 br.s (1H, NH), 9.51 s (1H, OH).

***N*-(3,5-Diisopropyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (XV).** Yield 53%, mp 34–35°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d [12H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.31 s (3H, Me), 3.05–3.14 m [2H, C**H**(CH$_3$)$_2$], 6.64 br.s (2H, 2-H, 6-H). Found, %: N 6.05, 6.18. $C_{14}H_{19}NO_2$. Calculated, %: N 6.00.

4-Hydroxy-3,5-dimethylphenyl 4-methylbenzenesulfonate (XVIIIa). Yield 71%, mp 159–160°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (6H, 3-Me, 5-Me), 2.37 s (3H, 4′-Me), 6.58 br.s (2H, 2-H, 6-H), 7.39 d (2H, 2′-H, 6′-H, J = 7.5 Hz), 7.70 d (2H, 3′-H, 5′-H, J = 7.5 Hz), 9.50 br.s (1H, OH). Found, %: S 10.52, 10.88. $C_{15}H_{16}O_4S$. Calculated, %: S 10.97.

4-Hydroxy-3,5-dimethylphenyl 4-chlorobenzenesulfonate (XVIIIb). Yield 75%, mp 82–83°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.07 s (6H, 3-Me, 5-Me), 6.62 br.s (2H, 2-H, 6-H), 7.39 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.57 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 9.82 br.s (1H, OH). Found, %: S 9.73, 10.18. $C_{14}H_{13}ClO_4S$. Calculated, %: S 10.25.

4-Hydroxy-3,5-diisopropylphenyl 4-methylbenzenesulfonate (XIXa). Yield 60%, mp 113°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.98 d [12H, CH(C**H**$_3$)$_2$, J = 5.1 Hz], 2.40 s (3H, 4′-Me), 3.16–3.23 m [2H, C**H**(CH$_3$)$_2$], 6.44 s (2H, 2-H, 6-H), 7.45 d (2H, 2′-H, 6′-H, J = 6.3 Hz), 7.67 d (2H, 3′-H, 5′-H, J = 6.3 Hz), 8.32 s (1H, OH). Found, %: S 8.81, 9.17. $C_{19}H_{24}O_4S$. Calculated, %: S 9.20.

4-Hydroxy-3,5-diisopropylphenyl 4-chlorobenzenesulfonate (XIXb). Yield 50%, mp 119–120°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.99 d [12H, CH(C**H**$_3$)$_2$, J = 5.1 Hz], 3.17–3.24 m [2H, C**H**(CH$_3$)$_2$], 6.47 s (2H, 2-H, 6-H), 7.38 d (2H, 2′-H, 6′-H, J = 6.3 Hz), 7.56 d (2H, 3′-H, 5′-H, J = 6.3 Hz), 8.38 br.s (1H, OH). Found, %: S 8.34, 8.72. $C_{18}H_{21}ClO_4S$. Calculated, %: S 8.69.

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