

Reaction of N-Substituted 2,5-Dialkyl-1,4-benzoquinone Imines with Arenesulfinic Acids

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Abstract—Reactions of *N*-aroyl-, *N*-arylsulfonyl-, and *N*-(*N*-arylsulfonylbenzimidoyl)-2,5-dialkyl-1,4-benzoquinone imines with sodium aren sulfinate in acetic acid gave the corresponding 1,4-, 6,1-, and 1,6-addition products. Variation of the size and donor power of substituents in positions 2 and 5 of the quinoid ring almost does not affect the ratio of the addition products, which is determined mainly by the nature of substituent on the nitrogen atom.

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The present work continues our studies on reactions of various *N*-substituted 1,4-benzoquinone imines with aren sulfinic acids. We previously [1] examined reactions of symmetrical alkyl-substituted 1,4-benzoquinone imines with sodium aren sulfinate in acetic acid and found that the substituent on the nitrogen atom in initial quinone imines strongly affects their reactivity. In the reactions with *N*-arylsulfonyl derivatives, the addition pattern is determined by steric factor, i.e., by the size of substituents in the quinoid ring. The addition of sodium aren sulfinate to *N*-aroyl-1,4-benzoquinone imines, in which the substituent on the nitrogen atom is the strongest electron acceptor, is governed by the nature and position of substituents in the quinoid ring. *N*-(*N*-Arylsulfonylbenzimidoyl)-1,4-benzoquinone imines were found to occupy an intermediate place between *N*-aroyl and *N*-arylsulfonyl derivatives.

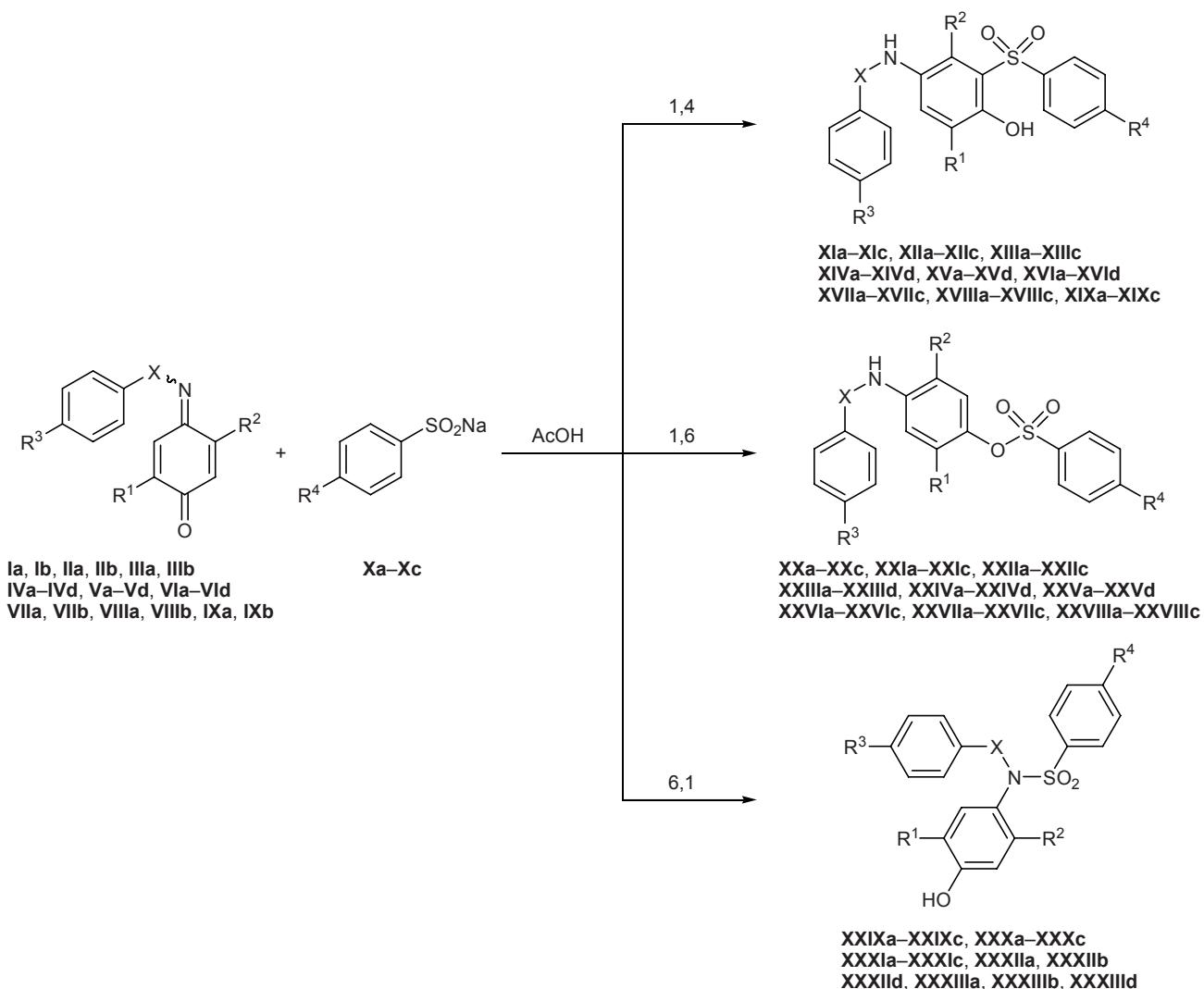
The goal of the present work was to compare the reactivities of analogous 2,5-substituted *N*-aroyl-, *N*-arylsulfonyl-, and *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinone imines **I–IX** toward sodium aren sulfinate **Xa–Xc**. The substrates and reagents were selected in such a way that the substituents in the *para* position of their aryl fragments (mainly methyl and methoxy groups) ensured unambiguous signal assignment in the ¹H NMR spectra of the products. The reactions were carried out in acetic acid using 2 equiv of sodium aren sulfinate **X** (Scheme 1). The product mixtures were analyzed by ¹H NMR spectroscopy both before and after recrystallization, and the correspond-

ing filtrates and mother liquors were also examined. We thus succeeded in identifying products whose fraction in the reaction mixture did not exceed a few percent. The results are summarized in table. It was found that reactions of quinone imines **I–IX** with sodium aren sulfinate **X** gave the corresponding 1,4-, 6,1-, and 1,6-addition products. No 6,3-adduct analogous to those obtained from 2,6-dimethyl-1,4-benzoquinone imines [1] were detected.

The product structure was determined by analysis of their ¹H NMR spectra with account taken of our previous data [1]. As reference structures for *N*-arylsulfonyl derivatives we used compounds **XI–XIII** having only one proton in the aminophenol ring and sulfonimides **XXIX–XXXI** with two equivalent substituents on the nitrogen atom. In most cases, 1,4-addition products were isolated as individual substances. Compounds **XIVb**, **XVc**, and **XVIb** were oxidized to the corresponding quinone imines **XXXIV–XXXVI** with lead tetraacetate in acetic acid (Scheme 2), for ¹H NMR spectra of quinone imines are more informative than the spectra of aminophenols.

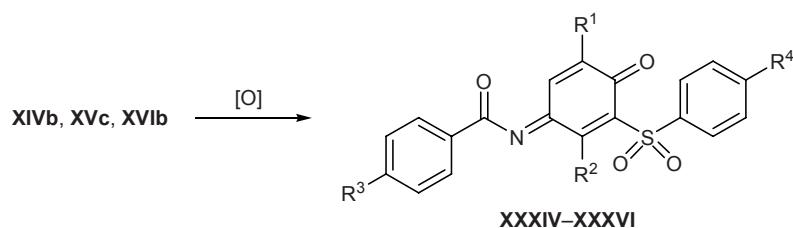
In the ¹H NMR spectrum of quinone imine **XXXIV**, signal from the only proton in the quinoid ring resonated as a quartet at δ 6.67 ppm, one methyl group gave a doublet at δ 1.88 ppm, and protons in the other methyl group appeared as a singlet at δ 2.92 ppm. The ¹H NMR spectrum of quinone imine **XXXV** contained a broadened singlet at δ 6.61 ppm from the proton in the quinoid ring, a multiplet at

Scheme 1.



I–III, XI–XIII, XX–XXII, XXIX–XXXI, $X = SO_2$; IV–VI, XIV–XVI, XXIII–XXV, XXXII, XXXIII, $X = CO$; VII–IX, XVII–XIX, XXVI–XXVIII, $X = C(=NSO_2Ar)$; I, IV, VII, XI, XIV, XVII, XX, XXIII, XXVI, XXIX, XXXII, $R^1 = R^2 = Me$; II, V, VIII, XII, XV, XVIII, XXI, XXIV, XXVII, XXX, XXXIII, $R^1 = i-Pr$, $R^2 = Me$; III, VI, IX, XIII, XVI, XIX, XXII, XXV, XXVIII, XXXI, $R^1 = Me$, $R^2 = i-Pr$; I–III, $R^3 = Me$ (a), MeO (b); IV–VI, $R^3 = H$ (a), Cl (b), MeO (c), Me (d); VII–IX, $R^3 = H$ (a, b), Ar = 4-MeC₆H₄ (a), 4-MeOC₆H₄ (b); X, $R^4 = Me$ (a), MeO (b), Cl (c); XI–XIII, XX–XXII, XXIX–XXXI, $R^3 = Me$ (a), MeO (b, c), $R^4 = MeO$ (a, c), Cl (b); XIV–XVI, XXIII–XXV, XXXII, XXXIII, $R^3 = H$ (a), Cl (b), MeO (c), Me (d), $R^4 = Me$ (a), MeO (b, d), Cl (c); XVII–XIX, XXVI–XXVIII, $R^3 = H$ (a, b, c), Ar = 4-MeC₆H₄ (a), 4-MeOC₆H₄ (b, c), $R^4 = MeO$ (a, b), Me (c).

Scheme 2.



XXXIV, $R^1 = R^2 = Me$, $R^3 = Cl$, $R^4 = MeO$; XXXV, $R^1 = i-Pr$, $R^2 = Me$, $R^3 = MeO$, $R^4 = Cl$;

XXXVI, $R^1 = Me$, $R^2 = i-Pr$, $R^3 = Cl$, $R^4 = OMe$.

Product composition in the reactions of 2,5-dialkyl-1,4-benzoquinone imines **I–IX** with sodium arenesulfinate **Xa–Xc** (Scheme 1)

X	R ¹	R ²	R ³	R ⁴	Fraction of addition products, %		
					1,4	6,1	1,6
SO ₂	Me	Me	Me	MeO	93	3	4
SO ₂	Me	Me	MeO	Cl	95	2	3
SO ₂	Me	Me	MeO	MeO	90	3	7
CO	Me	Me	H	Me	79	5	16
CO	Me	Me	Cl	MeO	64	7	29
CO	Me	Me	MeO	Cl	94	—	6
CO	Me	Me	Me	MeO	76	4	20
C(=NSO ₂ C ₆ H ₄ Me-4)	Me	Me	H	MeO	80	—	20
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	Me	H	MeO	78	—	22
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	Me	H	Me	79	—	21
SO ₂	i-Pr	Me	Me	MeO	90	2	8
SO ₂	i-Pr	Me	MeO	Cl	91	3	6
SO ₂	i-Pr	Me	MeO	MeO	93	2	5
CO	i-Pr	Me	H	Me	82	6	12
CO	i-Pr	Me	Cl	MeO	67	10	23
CO	i-Pr	Me	MeO	Cl	89	—	11
CO	i-Pr	Me	Me	MeO	79	6	15
C(=NSO ₂ C ₆ H ₄ Me-4)	i-Pr	Me	H	MeO	69	—	31
C(=NSO ₂ C ₆ H ₄ OMe-4)	i-Pr	Me	H	MeO	71	—	29
C(=NSO ₂ C ₆ H ₄ OMe-4)	i-Pr	Me	H	Me	73	—	27
SO ₂	Me	i-Pr	Me	MeO	75	9	16
SO ₂	Me	i-Pr	MeO	Cl	80	6	14
SO ₂	Me	i-Pr	MeO	MeO	79	7	14
CO	Me	i-Pr	H	Me	70	—	30
CO	Me	i-Pr	Cl	MeO	54	—	46
CO	Me	i-Pr	MeO	Cl	87	—	13
CO	Me	i-Pr	Me	MeO	79	—	21
C(=NSO ₂ C ₆ H ₄ Me-4)	Me	i-Pr	H	MeO	74	—	26
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	i-Pr	H	MeO	73	—	27
C(=NSO ₂ C ₆ H ₄ OMe-4)	Me	i-Pr	H	Me	72	—	28

δ 2.81–2.91 ppm from the isopropyl CH group, and a singlet at δ 2.93 ppm from the methyl group. Quinone imine **XXXVI** displayed in the ¹H NMR spectrum a quartet at δ 6.54 ppm from 6-H, and a doublet at δ 1.85 ppm from the methyl protons. These findings unambiguously indicate that the arylsulfonyl group in **XXXIV–XXXVI** occupies *ortho* position with respect to the carbonyl carbon atom in the quinoid ring.

Analysis of the results given in table shows that the second *ortho* position in the quinoid ring of *N*-arylsulfonyl-2,5-dialkyl-1,4-benzoquinone imines **I–III** is

more reactive toward arenesulfinate ions. In the reactions with *N*-(*N*-arylsulfonylbenzimidoyl) benzoquinone imines **VII–IX**, the main factor determining their reactivity is steric hindrance created by the substituent on the nitrogen atom [bulky ArSO₂N=C(Ph) group], so that no addition products at the nitrogen atom were isolated. In all cases, the size and electron-donor properties of the alkyl groups in positions 2 and 5 of the quinoid ring do not affect the product ratio to an appreciable extent, and the main factor is the nature and size of the substituent on the nitrogen atom.

EXPERIMENTAL

The ^1H NMR spectra were measured on a Varian VXR-300 spectrometer at 300 MHz from solutions in acetone- d_6 (**XI–XIII**, **XX–XXII**, **XXIX–XXXI**), DMSO- d_6 (**XIV–XIX**, **XXIII–XXVIII**, **XXXII**, **XXXIII**), and CDCl₃ (**XXXIV–XXXVI**); the chemical shifts were measured relative to TMS. Analytical thin-layer chromatography was performed on Silufol UV-254 plates; samples were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and spots were visualized under UV light.

Initial quinone imines **I–III** were synthesized according to the procedure reported in [2] by oxidation of the corresponding aminophenols with sodium dichromate in acetic acid. Quinone imines **IV–IX** and **XXXIV–XXXVI** were obtained as described in [3] by oxidation of the corresponding aminophenols with lead tetraacetate in acetic acid. The properties of compounds **Ia–IIIa** [4], **IVa**, **IVd**, **Va**, **Vd**, **VIa**, and **VIc** [5] were consistent with published data. Sodium arenesulfonates **Xa–Xc** were prepared as reported in [6].

N-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzenesulfonamide (Ib). Yield 72%, mp 111–112°C. Found, %: N 4.47, 4.83; S 10.23, 10.47. C₁₅H₁₅NO₄S. Calculated, %: N 4.59; S 10.50.

N-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzenesulfonamide (IIb). Yield 81%, mp 85–86°C. Found, %: N 4.09, 4.32; S 9.42, 9.45. C₁₇H₁₉NO₄S. Calculated, %: N 4.20; S 9.62.

N-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzenesulfonamide (IIIb). Yield 79%, mp 96–98°C. Found, %: N 4.02, 4.19; S 9.63, 9.71. C₁₇H₁₉NO₄S. Calculated, %: N 4.20; S 9.62.

4-Chloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (IVb). Yield 69%, mp 127–129°C. Found, %: N 5.00, 5.24. C₁₅H₁₂ClNO₂. Calculated, %: N 5.12.

N-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzamide (IVc). Yield 41%, mp 106–107°C. Found, %: N 5.23, 5.44. C₁₆H₁₅NO₃. Calculated, %: N 5.20.

4-Chloro-N-(5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (Vb). Yield 23%, mp 71–73°C. Found, %: N 4.47, 4.58. C₁₇H₁₆ClNO₂. Calculated, %: N 4.64.

N-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzamide (Vc). Yield 51%,

mp 81–83°C. Found, %: N 4.70, 4.86. C₁₈H₁₉NO₃. Calculated, %: N 4.71.

4-Chloro-N-(2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (VIb). Yield 61%, mp 96–98°C. Found, %: N 4.53, 4.78. C₁₇H₁₆ClNO₂. Calculated, %: N 4.64.

N-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxybenzamide (VIc). Yield 54%, mp 81–82°C. Found, %: N 4.42, 4.61. C₁₈H₁₉NO₃. Calculated, %: N 4.71.

N-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methylphenylsulfonyl)benzimidamide (VIIa). Yield 90%, mp 131.5–132°C. Found, %: N 7.07, 7.35; S 8.11, 8.34. C₂₂H₂₀N₂O₃S. Calculated, %: N 7.14; S 8.17.

N-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methoxyphenylsulfonyl)benzimidamide (VIIb). Yield 93%, mp 106–108°C. Found, %: N 6.66, 6.93; S 7.91, 7.98. C₂₂H₂₀N₂O₄S. Calculated, %: N 6.86; S 7.85.

N-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methylphenylsulfonyl)benzimidamide (VIIIa). Yield 93%, mp 102–104°C. Found, %: N 6.62, 6.75; S 7.54, 7.76. C₂₄H₂₄N₂O₃S. Calculated, %: N 6.66; S 7.62.

N-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methoxyphenylsulfonyl)benzimidamide (VIIIb). Yield 88%, mp 74–76°C. Found, %: N 6.45, 6.61; S 7.37, 7.44. C₂₄H₂₄N₂O₄S. Calculated, %: N 6.42; S 7.35.

N-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methylphenylsulfonyl)benzimidamide (IXa). Yield 74%, mp 78–80°C. Found, %: N 6.63, 6.84; S 7.55, 7.69. C₂₄H₂₄N₂O₃S. Calculated, %: N 6.66; S 7.62.

N-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(4-methoxyphenylsulfonyl)benzimidamide (IXb). Yield 87%, mp 86–88°C. Found, %: N 6.45, 6.69; S 7.46, 7.83. C₂₄H₂₄N₂O₄S. Calculated, %: N 6.42; S 7.35.

Reaction of quinone imines I–IX with sodium arenesulfonates Xa–Xc (general procedure). A solution of 2 mmol of quinone imine **I–IX** in 20 ml of glacial acetic acid was heated to the boiling point, 4 mmol of sodium arenesulfonate **Xa–Xc** was added, and the mixture was heated until it became colorless, cooled, and diluted with water 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. All three samples were analyzed by ^1H NMR spectroscopy.

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]-4-methylbenzenesulfonamide (XIa). Yield 69%, mp 149–151°C. ^1H NMR spectrum, δ , ppm: 1.76 s (3H, 5-CH₃), 2.19 s (3H, 2-CH₃), 2.34 s (3H, CH₃C₆H₄), 3.97 s (3H, MeO), 7.18 s (1H, 6-H), 7.17–7.78 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.20–7.36 d.d (4H, CH₃C₆H₄, J = 8.7 Hz), 8.31 s (1H, OH), 10.92 s (1H, NH). Found, %: N 2.79, 3.12; S 13.54, 13.98. C₂₂H₂₃NO₆S₂. Calculated, %: N 3.03; S 13.89.

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-2,5-dimethylphenyl]-4-methoxybenzenesulfonamide (XIb). ^1H NMR spectrum, δ , ppm: 1.87 s (3H, 5-CH₃), 2.09 s (3H, 2-CH₃), 3.80 s (3H, MeO), 6.97–7.30 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.09 s (1H, 6-H), 7.70–7.79 d.d (4H, ClC₆H₄, J = 8.7 Hz), 9.43 s (1H, OH), 10.24 s (1H, NH).

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]-4-methoxybenzenesulfonamide (XIc). ^1H NMR spectrum, δ , ppm: 1.77 s (3H, 5-CH₃), 2.11 s (3H, 2-CH₃), 3.79 s and 3.87 s (3H each, MeO), 6.94–7.39 d.d (4H, C₆H₄, J = 9.0 Hz), 7.08 s (1H, 6-H), 7.14–7.72 d.d (4H, C₆H₄, J = 9.0 Hz), 9.38 s (1H, OH), 10.52 s (1H, NH).

N-[4-Hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]-4-methylbenzenesulfonamide (XIIa). Yield 70%, mp 146–148°C. ^1H NMR spectrum, δ , ppm: 1.06 d (6H, Me₂CH, J = 6.9 Hz), 2.02 s (3H, 2-CH₃), 2.37 s (3H, CH₃C₆H₄), 3.20–3.34 m (1H, 5-CH), 3.96 s (3H, MeO), 6.99 s (1H, 6-H), 7.19–7.81 d.d (4H, MeOC₆H₄, J = 8.1 Hz), 7.25–7.42 d.d (4H, MeC₆H₄, J = 8.7 Hz), 8.18 s (1H, OH), 10.97 s (1H, NH). Found, %: N 2.64, 2.77; S 13.07, 13.54. C₂₄H₂₇NO₆S₂. Calculated, %: N 2.86; S 13.10.

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-5-isopropyl-2-methylphenyl]-4-methoxybenzenesulfonamide (XIIb). ^1H NMR spectrum, δ , ppm: 0.95 d (6H, Me₂CH, J = 6.9 Hz), 2.07 s (3H, 2-CH₃), 3.07–3.21 m (1H, 5-CH), 3.81 s (3H, MeO), 6.78 s (1H, 6-H), 7.02–7.45 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.72–7.82 d.d (4H, ClC₆H₄, J = 8.7 Hz), 9.29 s (1H, OH), 10.34 s (1H, NH).

N-[4-Hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]-4-methoxybenzenesulfonamide (XIIc). ^1H NMR spectrum, δ , ppm: 0.97 d

(6H, Me₂CH, J = 6.9 Hz), 2.01 s (3H, 2-CH₃), 3.10–3.23 m (1H, 5-CH), 3.80 s and 3.87 s (3H each, MeO), 6.76 s (1H, 6-H), 7.04–7.43 d.d (4H, C₆H₄, J = 8.4 Hz), 7.17–7.75 d.d (4H, C₆H₄, J = 8.7 Hz), 9.26 s (1H, OH), 10.61 s (1H, NH).

N-[4-Hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]-4-methylbenzenesulfonamide (XIIIa). Yield 55%, mp 172–173°C. ^1H NMR spectrum, δ , ppm: 1.03 d (6H, Me₂CH, J = 6.9 Hz), 2.02 s (3H, 5-CH₃), 2.46 s (3H, CH₃C₆H₄), 3.67–3.80 m (1H, 2-CH), 3.93 s (3H, MeO), 6.79 s (1H, 6-H), 7.19–7.81 d.d (4H, MeC₆H₄, J = 8.7 Hz), 7.45–7.73 d.d (4H, MeOC₆H₄, J = 8.1 Hz), 8.98 s (1H, OH), 11.15 s (1H, NH). Found, %: N 2.69, 2.91; S 12.96, 13.28. C₂₄H₂₇NO₆S₂. Calculated, %: N 2.86; S 13.10.

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-2-isopropyl-5-methylphenyl]-4-methoxybenzenesulfonamide (XIIIb). ^1H NMR spectrum, δ , ppm: 1.06 d (6H, Me₂CH, J = 6.6 Hz), 1.95 s (3H, 5-CH₃), 3.59–3.73 m (1H, 2-CH), 3.87 s (3H, MeO), 6.57 s (1H, 6-H), 7.17–7.73 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.73–7.85 d.d (4H, ClC₆H₄, J = 8.7 Hz), 9.04 s (1H, OH), 10.53 s (1H, NH).

N-[4-Hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]-4-methoxybenzenesulfonamide (XIIIc). ^1H NMR spectrum, δ , ppm: 1.00 d (6H, Me₂CH, J = 6.6 Hz), 1.95 s (3H, 5-CH₃), 3.63–3.77 m (1H, 2-CH), 3.86 s and 3.87 s (3H each, MeO), 6.52 s (1H, 6-H), 7.17–7.74 d.d and 7.17–7.77 d.d (4H each, C₆H₄, J = 8.7 Hz), 8.96 s (1H, OH), 10.85 s (1H, NH).

N-[4-Hydroxy-2,5-dimethyl-3-(4-methylphenylsulfonyl)-2-methylphenyl]benzamide (XIVa). Yield 55%, mp 209–210°C. ^1H NMR spectrum, δ , ppm: 2.21 s (6H, 2-CH₃, 5-CH₃), 2.41 s (3H, CH₃C₆H₄), 7.41 s (1H, 6-H), 7.45–7.57 m (5H, Ph), 7.80–7.93 d.d (4H, C₆H₄, J = 8.1 Hz), 9.81 s (1H, OH), 10.41 br.s (1H, NH). Found, %: N 3.28, 3.48; S 7.86, 7.98. C₂₂H₂₁NO₄S. Calculated, %: N 3.54; S 8.11.

4-Chloro-N-[4-hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]benzamide (XIVb). Yield 42%, mp 177–178°C. ^1H NMR spectrum, δ , ppm: 2.20 s (6H, CH₃), 3.85 s (3H, MeO), 7.39 s (1H, 6-H), 7.17–7.86 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.58–7.95 d.d (4H, ClC₆H₄, J = 8.7 Hz), 9.93 s (1H, OH), 10.45 br.s (1H, NH). Found, %: N 3.02, 3.28; S 7.05, 7.39. C₂₂H₂₀ClNO₅S. Calculated, %: N 3.14; S 7.19.

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-2,5-dimethylphenyl]-4-methoxybenzamide (XIVc). Yield

67%, mp 168–170°C. ^1H NMR spectrum, δ , ppm: 2.18 s (3H, 5-H₃), 2.27 s (3H, 2-CH₃), 3.82 s (3H, MeO), 7.39 s (1H, 6-H), 7.04–7.93 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.72–7.91 d.d (4H, ClC₆H₄, J = 8.4 Hz), 9.73 s (1H, OH), 10.09 br.s (1H, NH). Found, %: N 3.06, 3.23; S 7.02, 7.16. $\text{C}_{22}\text{H}_{20}\text{ClNO}_5\text{S}$. Calculated, %: N 3.14; S 7.19.

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]-4-methylbenzamide (XIVd). Yield 49%, mp 196–197°C. ^1H NMR spectrum, δ , ppm: 2.23 s (3H, 5-CH₃), 2.24 s (3H, 2-CH₃), 2.38 s (3H, CH₃C₆H₄), 3.91 s (3H, MeO), 7.46 s (1H, 6-H), 7.17–7.87 d.d (4H, MeC₆H₄, J = 9.0 Hz), 7.29–8.87 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 9.03 s (1H, OH), 10.83 s (1H, NH). Found, %: N 3.28, 3.44; S 7.50, 7.81. $\text{C}_{23}\text{H}_{23}\text{NO}_5\text{S}$. Calculated, %: N 3.29; S 7.54.

N-[4-Hydroxy-5-isopropyl-2-methyl-3-(4-methylphenylsulfonyl)phenyl]benzamide (XVa). Yield 58%, mp 208–209°C. ^1H NMR spectrum, δ , ppm: 1.20 d (6H, Me₂CH), 2.16 s (3H, 2-CH₃), 2.40 s (3H, CH₃C₆H₄), 3.28–3.41 m (1H, 5-CH), 7.42 s (1H, 6-H), 7.47–7.57 m (5H, Ph), 7.80–7.94 d.d (4H, MeC₆H₄, J = 8.1 Hz), 9.87 s (1H, OH), 10.55 br.s (1H, NH). Found, %: N 3.28, 3.46; S 7.52, 7.85. $\text{C}_{24}\text{H}_{25}\text{NO}_4\text{S}$. Calculated, %: N 3.31; S 7.57.

4-Chloro-N-[4-hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]benzamide (XVb). ^1H NMR spectrum, δ , ppm: 1.20 d (6H, Me₂CH, J = 6.9 Hz), 2.16 s (3H, 2-CH₃), 3.25–3.39 m (1H, 5-CH), 3.86 s (3H, MeO), 7.40 s (1H, 6-H), 7.18–7.85 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.58–7.95 d.d (4H, 4-ClC₆H₄, J = 8.7 Hz), 9.94 s (1H, OH), 10.65 br.s (1H, NH).

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-5-isopropyl-2-methylphenyl]-4-methoxybenzamide (XVc). Yield 62%, mp 164–166°C. ^1H NMR spectrum, δ , ppm: 1.17 d (6H, Me₂CH, J = 6.9 Hz), 2.20 s (3H, 2-CH₃), 3.24–3.38 m (1H, 5-CH), 3.82 s (3H, MeO), 7.41 s (1H, 6-H), 7.03–7.92 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.74–7.92 d.d (4H, ClC₆H₄, J = 9.0 Hz), 9.75 s (1H, OH), 10.19 br.s (1H, NH). Found, %: N 3.01, 3.24; S 6.70, 6.84. $\text{C}_{24}\text{H}_{24}\text{ClNO}_5\text{S}$. Calculated, %: N 2.96; S 6.76.

N-[4-Hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]-4-methylbenzamide (XVd). Yield 54%, mp 173–174°C. ^1H NMR spectrum, δ , ppm: 1.24 d (6H, Me₂CH, J = 6.9 Hz), 2.24 s (3H, 2-CH₃), 2.39 s (3H, CH₃C₆H₄), 3.33–3.47 m (1H, 5-CH), 3.91 s (3H, MeO), 7.53 s (1H, 6-H), 7.17–

7.88 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.29–7.88 d.d (4H, MeC₆H₄, J = 8.1 Hz), 9.11 s (1H, OH), 10.95 s (1H, NH). Found, %: N 3.06, 3.19; S 7.03, 7.09. $\text{C}_{25}\text{H}_{27}\text{NO}_5\text{S}$. Calculated, %: N 3.09; S 7.07.

N-[4-Hydroxy-2-isopropyl-5-methyl-3-(4-methylphenylsulfonyl)phenyl]benzamide (XVIa). Yield 48%, mp 167–168°C. ^1H NMR spectrum, δ , ppm: 0.90 d (6H, Me₂CH, J = 6.9 Hz), 2.21 s (3H, 5-CH₃), 2.41 s (3H, CH₃C₆H₄), 3.58–3.72 m (1H, 2-CH), 7.27 s (1H, 6-H), 7.48–7.59 m (5H, Ph), 7.75–7.91 d.d (4H, C₆H₄, J = 8.7 Hz), 9.60 s (1H, OH), 10.66 br.s (1H, NH). Found, %: N 3.12, 3.41; S 7.27, 7.63. $\text{C}_{24}\text{H}_{25}\text{NO}_4\text{S}$. Calculated, %: N 3.31; S 7.57.

4-Chloro-N-[4-hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]benzamide (XVIb). ^1H NMR spectrum, δ , ppm: 0.94 d (6H, Me₂CH, J = 6.9 Hz), 2.21 s (3H, 5-CH₃), 3.61–3.75 m (1H, 2-CH), 3.86 s (3H, MeO), 7.27 s (1H, 6-H), 7.19–7.82 m (4H, MeOC₆H₄, J = 9.0 Hz), 7.60–7.93 d.d (4H, ClC₆H₄, J = 8.4 Hz), 9.73 s (1H, OH), 10.90 s (1H, NH).

N-[3-(4-Chlorophenylsulfonyl)-4-hydroxy-2-isopropyl-5-methylphenyl]-4-methoxybenzamide (XVIc). Yield 56%, mp 188–189°C. ^1H NMR spectrum, δ , ppm: 0.94 d (6H, Me₂CH, J = 6.9 Hz), 2.19 s (3H, 5-CH₃), 3.82 s (3H, MeO), 3.61–3.75 m (1H, 2-CH), 7.26 s (1H, 6-H), 7.04–7.90 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.74–7.89 d.d (4H, ClC₆H₄, J = 8.4 Hz), 9.44 s (1H, OH), 10.37 br.s (1H, NH). Found, %: N 3.05, 3.17; S 6.59, 6.80. $\text{C}_{24}\text{H}_{24}\text{ClNO}_5\text{S}$. Calculated, %: N 2.96; S 6.76.

N-[4-Hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]-4-methylbenzamide (XVID). ^1H NMR spectrum, δ , ppm: 1.05 d (6H, Me₂CH, J = 7.2 Hz), 2.15 s (3H, 5-CH₃), 2.41 s (3H, CH₃C₆H₄), 3.10–3.24 m (1H, 2-CH), 3.96 s (3H, MeO), 7.34 s (1H, 6-H), 7.21–7.83 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.32–7.91 d.d (4H, MeC₆H₄, J = 8.1 Hz), 8.07 s (1H, OH), 9.06 br.s (1H, NH).

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]-N'-(4-methylphenylsulfonyl)benzimidamide (XVIIa). ^1H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.21 s (3H, 2-CH₃), 2.33 s (3H, CH₃C₆H₄), 3.85 s (3H, MeO), 7.34 br.s (1H, 6-H), 7.15–7.82 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.16–7.54 m (5H, Ph), 7.18–7.53 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 10.17 s (1H, OH), 10.43 br.s (1H, NH).

N-[4-Hydroxy-3-(4-methoxyphenylsulfonyl)-2,5-dimethylphenyl]-N'-(4-methoxyphenylsulfonyl)-

benzimidamide (XVIIb). ^1H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.19 s (3H, 2-CH₃), 3.79 s and 3.85 s (3H each, MeO), 6.91–7.47 d.d and 7.14–7.80 d.d (4H each, MeOC₆H₄, J = 8.4 Hz), 7.40–7.82 m (5H, Ph), 7.33 br.s (1H, 6-H), 10.07 br.s (1H, OH), 10.38 br.s (1H, NH).

***N*-[4-Hydroxy-2,5-dimethyl-3-(4-methylphenylsulfonyl)phenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XVIIc).** ^1H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.20 s (3H, 2-CH₃), 2.40 s (3H, CH₃C₆H₄), 3.80 s (3H, MeO), 6.91–7.43 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.34 br.s (1H, 6-H), 7.42–7.74 m (5H, Ph), 7.48–7.73 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 10.06 s (1H, OH), 10.31 br.s (1H, NH).

***N*-[4-Hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XVIIIa).** ^1H NMR spectrum, δ , ppm: 1.08 d (6H, Me₂CH, J = 6.9 Hz), 2.17 s (3H, 2-CH₃), 2.33 s (3H, CH₃C₆H₄), 3.18–3.31 m (1H, 5-CH), 3.84 s (3H, MeO), 7.40 br.s (1H, 6-H), 7.14–7.83 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.18–7.84 m (5H, Ph), 7.19–7.48 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 10.08 s (1H, OH), 10.62 br.s (1H, NH).

***N*-[4-Hydroxy-5-isopropyl-3-(4-methoxyphenylsulfonyl)-2-methylphenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XVIIIb).** ^1H NMR spectrum, δ , ppm: 1.08 d (6H, Me₂CH, J = 6.9 Hz), 2.16 s (3H, 2-CH₃), 3.18–3.32 m (1H, 5-CH), 3.79 s and 3.85 s (3H each, MeO), 6.89–7.83 m (5H, Ph), 6.90–7.48 d.d and 7.15–7.82 d.d (4H each, C₆H₄, J = 8.4 Hz), 7.38 br.s (1H, 6-H), 10.03 s (1H, OH), 10.53 br.s (1H, NH).

***N*-[4-Hydroxy-5-isopropyl-2-methyl-3-(4-methylphenylsulfonyl)phenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XVIIIc).** ^1H NMR spectrum, δ , ppm: 1.08 d (6H, Me₂CH, J = 6.9 Hz), 2.15 s (3H, 2-CH₃), 2.39 s (3H, CH₃C₆H₄), 3.16–3.30 m (1H, 5-CH), 3.79 s (3H, MeO), 6.89–7.76 m (5H, Ph), 6.90–7.44 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.39 br.s (1H, 6-H), 7.45–7.76 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 10.01 s (1H, OH), 10.47 br.s (1H, NH).

***N*-[4-Hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XIXa).** ^1H NMR spectrum, δ , ppm: 0.88 d (6H, Me₂CH, J = 6.6 Hz), 2.21 s (3H, 5-CH₃), 2.31 s (3H, CH₃C₆H₄), 3.61–3.74 m (1H, 2-CH), 3.85 s (3H, MeO), 7.14–7.55 m (5H, Ph), 7.15–7.80 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.17–7.48 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 7.37 br.s (1H, 6-H), 10.06 s (1H, OH), 10.93 s (1H, NH).

***N*-[4-Hydroxy-2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methylphenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XIXb).** Yield 45%, mp 157–158°C. ^1H NMR spectrum, δ , ppm: 0.88 d (6H, Me₂CH, J = 6.6 Hz), 2.21 s (3H, 5-CH₃), 3.60–3.73 m (1H, 2-CH), 3.78 s and 3.86 s (3H, MeO), 6.86–7.46 d.d and 7.16–7.79 d.d (4H each, C₆H₄, J = 8.4 Hz), 7.22–7.52 m (5H, Ph), 7.34 br.s (1H, 6-H), 9.99 s (1H, OH), 10.92 br.s (1H, NH). Found, %: N 4.40, 4.62; S 10.56, 10.60. C₃₁H₃₂N₂O₇S. Calculated, %: N 4.60; S 10.53.

***N*-[4-Hydroxy-2-isopropyl-5-methyl-3-(4-methylphenylsulfonyl)phenyl]-*N'*-(4-methoxyphenylsulfonyl)benzimidamide (XIXc).** Yield 46%, mp 192–194°C. ^1H NMR spectrum, δ , ppm: 0.87 d (6H, Me₂CH, J = 6.6 Hz), 2.21 s (3H, 5-CH₃), 2.41 s (3H, CH₃C₆H₄), 3.57–3.71 m (1H, 2-CH), 3.79 s (3H, MeO), 6.86–7.43 d.d (4H, MeOC₆H₄, J = 8.4 Hz), 7.36 br.s (1H, 6-H), 7.43–7.52 m (5H, Ph), 7.46–7.73 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 9.99 br.s (1H, OH), 10.84 br.s (1H, NH). Found, %: N 4.57, 4.65; S 10.63, 10.78. C₃₁H₃₂N₂O₆S₂. Calculated, %: N 4.73; S 10.82.

2,5-Dimethyl-4-(4-methylphenylsulfonylamino)-phenyl 4-methoxybenzenesulfonate (XXa). ^1H NMR spectrum, δ , ppm: 1.84 s (3H, 2-CH₃), 1.91 s (3H, 5-CH₃), 2.41 s (3H, CH₃C₆H₄), 3.95 s (3H, MeO), 6.82 s (1H, 6-H), 7.02 s (1H, 3-H), 7.16–7.75 d.d (4H, MeOC₆H₄, J = 8.7 Hz), 7.25–7.46 d.d (4H, CH₃C₆H₄, J = 8.7 Hz), 8.78 s (1H, NH).

4-(4-Methoxyphenylsulfonylamino)-2,5-dimethylphenyl 4-chlorobenzenesulfonate (XXb). ^1H NMR spectrum, δ , ppm: 1.84 s (3H, 2-CH₃), 1.90 s (3H, 5-CH₃), 3.95 s (3H, MeO), 6.84 s (1H, 6-H), 7.05 s (1H, 3-H), 7.06–7.45 d.d (4H, MeOC₆H₄, J = 9.0 Hz), 7.76–7.89 d.d (4H, ClC₆H₄, J = 8.7 Hz), 8.69 s (1H, NH).

4-(4-Methoxyphenylsulfonylamino)-2,5-dimethylphenyl 4-methoxybenzenesulfonate (XXc). ^1H NMR spectrum, δ , ppm: 1.83 s (3H, 2-CH₃), 1.91 s (3H, 5-CH₃), 3.95 s (6H, MeO), 6.82 s (1H, 6-H), 7.00–7.42 d.d (4H, C₆H₄, J = 9.0 Hz), 7.03 s (1H, 3-H), 7.07–7.69 d.d (4H, C₆H₄, J = 8.7 Hz), 8.74 s (1H, NH).

2-Isopropyl-5-methyl-4-(4-methylphenylsulfonylamino)phenyl 4-methoxybenzenesulfonate (XXIa). ^1H NMR spectrum, δ , ppm: 1.00 d (6H, Me₂CH, J = 6.6 Hz), 3.23–3.37 m (1H, 2-CH), 2.10 s (3H, 5-CH₃), 2.49 s (3H, CH₃C₆H₄), 3.96 s (3H, MeO), 6.85 s (1H, 6-H), 6.90 s (1H, 3-H), 7.16–7.77 d.d (4H, MeOC₆H₄,

J = 8.7 Hz), 7.23–7.48 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, *J* = 8.7 Hz), 8.81 s (1H, NH).

2-Isopropyl-4-(4-methoxyphenylsulfonylamino)-5-methylphenyl 4-chlorobenzenesulfonate (XXIb). ^1H NMR spectrum, δ , ppm: 1.00 d (6H, Me_2CH , *J* = 6.6 Hz), 2.08 s (3H, 5-CH₃), 3.21–3.35 m (1H, 2-CH), 3.95 s (3H, MeO), 6.83 s (1H, 6-H), 6.89 s (1H, 3-H), 7.00–7.42 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz), 7.70–7.86 d.d (4H, ClC_6H_4 , *J* = 8.4 Hz), 8.65 s (1H, NH).

2-Isopropyl-4-(4-methoxyphenylsulfonylamino)-5-methylphenyl 4-methoxybenzenesulfonate (XXIc). ^1H NMR spectrum, δ , ppm: 0.99 d (6H, Me_2CH , *J* = 6.6 Hz), 2.09 s (3H, 5-CH₃), 3.24–3.36 m (1H, 2-CH), 3.95 s (6H, MeO), 6.85 s (1H, 6-H), 6.92 s (1H, 3-H), 7.02–7.39 d.d and 7.19–7.82 d.d (4H each, C_6H_4 , *J* = 8.7 Hz), 8.76 s (1H, NH).

5-Isopropyl-2-methyl-4-(4-methylphenylsulfonylamino)phenyl 4-methoxybenzenesulfonate (XXIIa). ^1H NMR spectrum, δ , ppm: 1.03 d (6H, Me_2CH , *J* = 6.6 Hz), 2.02 s (3H, 2-CH₃), 2.41 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.23–3.36 m (1H, 5-CH), 3.95 s (3H, MeO), 6.84 s (1H, 6-H), 6.97 s (1H, 3-H), 7.19–7.82 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz), 7.47–7.76 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, *J* = 8.4 Hz), 8.73 s (1H, NH).

5-Isopropyl-4-(4-methoxyphenylsulfonylamino)-2-methylphenyl 4-chlorobenzenesulfonate (XXIIb). ^1H NMR spectrum, δ , ppm: 1.02 d (6H, Me_2CH , *J* = 6.6 Hz), 2.00 s (3H, 2-CH₃), 3.20–3.34 m (1H, 5-CH), 3.95 s (3H, MeO), 6.80 s (1H, 6-H), 6.92 s (1H, 3-H), 7.12–7.75 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz), 7.69–7.80 d.d (4H, ClC_6H_4 , *J* = 8.7 Hz), 8.62 s (1H, NH).

5-Isopropyl-4-(4-methoxyphenylsulfonylamino)-2-methylphenyl 4-methoxybenzenesulfonate (XXIIc). ^1H NMR spectrum, δ , ppm: 1.02 d (6H, Me_2CH , *J* = 6.6 Hz), 2.02 s (3H, 2-CH₃), 3.22–3.35 m (1H, 5-CH), 3.95 s (6H, MeO), 6.83 s (1H, 6-H), 6.95 s (1H, 3-H), 7.14–7.72 d.d (4H, C_6H_4 , *J* = 8.7 Hz), 7.20–7.81 d.d (4H, C_6H_4 , *J* = 9.0 Hz), 8.70 s (1H, NH).

4-Benzoylamino-2,5-dimethylphenyl 4-methylbenzenesulfonate (XXIIIa). ^1H NMR spectrum, δ , ppm: 1.97 s (3H, 2-CH₃), 2.16 s (3H, 5-CH₃), 2.45 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.93 s (1H, 6-H), 7.27 s (1H, 3-H), 7.45–7.60 m (5H, Ph), 7.80–7.96 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, *J* = 8.7 Hz), 9.86 s (1H, NH).

4-(4-Chlorobenzoylamino)-2,5-dimethylphenyl 4-methoxybenzenesulfonate (XXIIIb). ^1H NMR spectrum, δ , ppm: 1.97 s (3H, 2-CH₃), 2.15 s (3H, 5-CH₃), 3.89 s (3H, MeO), 6.93 s (1H, 6-H), 7.19 s (1H, 3-H), 7.24–7.83 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz),

7.61–7.97 d.d (4H, ClC_6H_4 , *J* = 8.1 Hz), 9.95 s (1H, NH).

4-(4-Methoxybenzoylamino)-2,5-dimethylphenyl 4-chlorobenzenesulfonate (XXIIIc). ^1H NMR spectrum, δ , ppm: 1.99 s (3H, 2-CH₃), 2.16 s (3H, 5-CH₃), 3.76 s (3H, MeO), 6.93 s (1H, 6-H), 7.27 s (1H, 3-H), 7.08–7.65 d.d (4H, MeOC_6H_4 , *J* = 9.0 Hz), 7.79–7.95 d.d (4H, ClC_6H_4 , *J* = 8.7 Hz), 9.92 s (1H, NH).

2,5-Dimethyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XXIIId). ^1H NMR spectrum, δ , ppm: 2.01 s (3H, 2-CH₃), 2.23 s (3H, 5-CH₃), 2.40 s (3H, 4-CH₃ C_6H_4), 3.94 s (3H, MeO), 6.93 s (1H, 6-H), 7.34 s (1H, 3-H), 7.15–7.83 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz), 7.31–7.90 d.d (4H, MeC_6H_4 , *J* = 8.4 Hz), 8.96 s (1H, NH).

4-Benzoylamino-2-isopropyl-5-methylphenyl 4-methylbenzenesulfonate (XXIVa). ^1H NMR spectrum, δ , ppm: 0.99 d (6H, Me_2CH , *J* = 6.9 Hz), 2.15 s (3H, 5-CH₃), 2.44 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.88–3.02 m (1H, 5-CH), 6.93 s (1H, 6-H), 7.32 s (1H, 3-H), 7.40–7.60 m (5H, Ph), 7.81–7.97 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, *J* = 9.0 Hz), 9.90 s (1H, NH).

4-(4-Chlorobenzoylamino)-2-isopropyl-5-methylphenyl 4-methoxybenzenesulfonate (XXIVb). ^1H NMR spectrum, δ , ppm: 1.00 d (6H, Me_2CH , *J* = 6.9 Hz), 2.14 s (3H, 5-CH₃), 2.91–3.04 m (1H, 2-CH), 3.89 s (3H, MeO), 6.94 s (1H, 6-H), 7.21–7.89 d.d (4H, MeOC_6H_4 , *J* = 9.0 Hz), 7.31 s (1H, 3-H), 7.60–7.99 d.d (4H, ClC_6H_4 , *J* = 8.7 Hz), 9.97 s (1H, NH).

2-Isopropyl-4-(4-methoxybenzoylamino)-5-methylphenyl 4-chlorobenzenesulfonate (XXIVc). ^1H NMR spectrum, δ , ppm: 1.00 d (6H, Me_2CH , *J* = 6.9 Hz), 2.15 s (3H, 5-CH₃), 2.79–2.93 m (1H, 2-CH), 3.84 s (3H, MeO), 6.94 s (1H, 6-H), 7.03–7.67 d.d (4H, MeOC_6H_4 , *J* = 9.0 Hz), 7.32 s (1H, 3-H), 7.75–7.96 d.d (4H, ClC_6H_4 , *J* = 8.7 Hz), 9.79 s (1H, NH).

2-Isopropyl-5-methyl-4-(4-methylbenzoylamino)phenyl 4-methoxybenzenesulfonate (XXIVd). ^1H NMR spectrum, δ , ppm: 1.05 d (6H, Me_2CH , *J* = 6.9 Hz), 2.26 s (3H, 5-CH₃), 2.41 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.00–3.13 m (1H, 2-CH), 3.95 s (3H, MeO), 6.96 s (1H, 6-H), 7.05 s (1H, 3-H), 7.18–7.86 d.d (4H, MeOC_6H_4 , *J* = 8.7 Hz), 7.34–7.92 d.d (4H, MeC_6H_4 , *J* = 8.4 Hz), 9.04 s (1H, NH).

4-Benzoylamino-5-isopropyl-2-methylphenyl 4-methylbenzenesulfonate (XXVa). ^1H NMR spectrum, δ , ppm: 0.94 d (6H, Me_2CH , *J* = 6.9 Hz), 2.10 s (3H, 2-CH₃), 2.98–3.11 m (1H, 5-CH), 2.44 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.59 s (1H, 6-H), 7.19 s (1H, 3-H), 7.42–

7.64 m (5H, Ph), 7.78–7.94 d.d (4H, C₆H₄, *J* = 8.4 Hz), 9.86 s (1H, NH).

4-(4-Chlorobenzoylamino)-5-isopropyl-2-methylphenyl 4-methoxybenzenesulfonate (XXVb).

¹H NMR spectrum, δ , ppm: 0.95 d (6H, Me₂CH, *J* = 6.9 Hz), 2.11 s (3H, 2-CH₃), 2.96–3.10 m (1H, 5-CH), 3.88 s (3H, MeO), 6.61 s (1H, 6-H), 7.19 s (1H, 3-H), 7.22–7.83 d.d (4H, MeOC₆H₄, *J* = 9.0 Hz), 7.60–7.97 d.d (4H, ClC₆H₄, *J* = 8.7 Hz), 9.95 s (1H, NH).

5-Isopropyl-4-(4-methoxybenzoylamino)-2-methylphenyl 4-chlorobenzenesulfonate (XXVc).

¹H NMR spectrum, δ , ppm: 0.87 d (6H, Me₂CH, *J* = 6.9 Hz), 2.13 s (3H, 2-CH₃), 2.98–3.12 m (1H, 5-CH), 3.83 s (3H, MeO), 6.60 s (1H, 6-H), 7.05–7.50 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.20 s (1H, 3-H), 7.80–7.93 d.d (4H, ClC₆H₄, *J* = 8.74 Hz), 9.69 s (1H, NH).

5-Isopropyl-2-methyl-4-(4-methylbenzoylamino)-phenyl 4-methoxybenzenesulfonate (XXVd).

¹H NMR spectrum, δ , ppm: 1.13 d (6H, Me₂CH, *J* = 6.9 Hz), 2.15 s (3H, 2-CH₃), 2.23 s (3H, CH₃C₆H₄), 2.91–3.05 m (1H, 5-CH), 3.92 s (3H, MeO), 6.81 s (1H, 6-H), 6.97 s (1H, 3-H), 7.16–8.07 d.d (4H, CH₃C₆H₄, *J* = 8.4 Hz), 7.26–7.88 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 8.64 s (1H, NH).

2,5-Dimethyl-4-[(4-methylphenylsulfonylimino)-(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XXVIa). ¹H NMR spectrum, δ , ppm: 1.86 s (3H, 2-CH₃), 2.13 s (3H, 5-CH₃), 2.33 s (3H, CH₃C₆H₄), 3.88 s (3H, MeO), 6.93 s (1H, 6-H), 7.16 s (1H, 3-H), 7.17–7.79 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.25–7.58 d.d (4H, CH₃C₆H₄, *J* = 8.1 Hz), 7.48–7.72 m (5H, Ph), 10.21 br.s (1H, NH).

4-[(4-Methoxyphenylsulfonylimino)(phenyl)-methylamino]-2,5-dimethylphenyl 4-methoxybenzenesulfonate (XXVIb). ¹H NMR spectrum, δ , ppm: 1.88 s (3H, 2-CH₃), 2.11 s (3H, 5-CH₃), 3.78 s and 3.88 s (3H each, MeO), 6.92 s (1H, 6-H), 6.93–7.38 d.d (4H, MeOC₆H₄, *J* = 8.1 Hz), 7.16 s (1H, 3-H), 7.17–7.79 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.51–7.70 m (5H, Ph), 10.14 br.s (1H, NH).

4-[(4-Methoxyphenylsulfonylimino)(phenyl)-methylamino]-2,5-dimethylphenyl 4-methylbenzenesulfonate (XXVIc). ¹H NMR spectrum, δ , ppm: 1.86 s (3H, 2-CH₃), 2.10 s (3H, 5-CH₃), 2.44 s (3H, CH₃C₆H₄), 3.78 s (3H, MeO), 6.92 s (1H, 6-H), 6.94–7.36 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.11 s (1H, 3-H), 7.31–7.70 d.d (4H, CH₃C₆H₄, *J* = 8.1 Hz), 7.54–7.69 m (5H, Ph), 10.16 s (1H, NH).

2-Isopropyl-5-methyl-4-[(4-methylphenylsulfonylimino)(phenyl)methylamino]phenyl 4-meth-

oxybenzenesulfonate (XXVIIa). ¹H NMR spectrum, δ , ppm: 0.89 d (6H, Me₂CH, *J* = 6.9 Hz), 2.13 s (3H, 5-CH₃), 2.33 s (3H, CH₃C₆H₄), 2.79–2.93 m (1H, 2-CH), 3.87 s (3H, MeO), 6.92 s (1H, 6-H), 7.12 s (1H, 3-H), 7.17–7.82 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.24–7.61 d.d (4H, CH₃C₆H₄, *J* = 8.4 Hz), 7.32–7.56 m (5H, Ph), 10.13 s (1H, NH).

2-Isopropyl-4-[(4-methoxyphenylsulfonylimino)-(phenyl)methylamino]-5-methylphenyl 4-methoxybenzenesulfonate (XXVIIb). ¹H NMR spectrum, δ , ppm: 0.89 d (6H, Me₂CH, *J* = 6.9 Hz), 2.12 s (3H, 5-CH₃), 2.78–2.91 m (1H, 2-CH), 3.78 s and 3.88 s (3H each, MeO), 6.92 s (1H, 6-H), 6.93–7.40 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.12 s (1H, 3-H), 7.17–7.79 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.28–7.64 m (5H, Ph), 10.14 s (1H, NH).

2-Isopropyl-4-[(4-methoxyphenylsulfonylimino)-(phenyl)methylamino]-5-methylphenyl 4-methylbenzenesulfonate (XXVIIc). ¹H NMR spectrum, δ , ppm: 0.89 d (6H, Me₂CH, *J* = 6.9 Hz), 2.12 s (3H, 5-CH₃), 2.43 s (3H, CH₃C₆H₄), 2.79–2.92 m (1H, 2-CH), 3.77 s (3H, MeO), 6.93–7.41 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 6.94 s (1H, 6-H), 7.12 s (1H, 3-H), 7.29–7.65 m (5H, Ph), 7.30–7.72 d.d (4H, CH₃C₆H₄, *J* = 8.1 Hz), 10.09 s (1H, NH).

5-Isopropyl-2-methyl-4-[(4-methylphenylsulfonylimino)(phenyl)methylamino]phenyl 4-methoxybenzenesulfonate (XXVIIIa). ¹H NMR spectrum, δ , ppm: 0.91 d (6H, Me₂CH, *J* = 6.9 Hz), 2.05 s (3H, 2-CH₃), 2.31 s (3H, CH₃C₆H₄), 2.87–3.00 m (1H, 5-CH), 3.87 s (3H, MeO), 6.58 s (1H, 6-H), 7.13 s (1H, 3-H), 7.17–7.77 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.24–7.59 d.d (4H, CH₃C₆H₄, *J* = 8.1 Hz), 7.31–7.56 m (5H, Ph), 10.26 s (1H, NH).

5-Isopropyl-4-[(4-methoxyphenylsulfonylimino)-(phenyl)methylamino]-2-methylphenyl 4-methoxybenzenesulfonate (XXVIIIb). ¹H NMR spectrum, δ , ppm: 0.91 d (6H, Me₂CH, *J* = 6.9 Hz), 2.05 s (3H, 2-CH₃), 2.86–3.00 m (1H, 5-CH), 3.77 s and 3.87 s (3H each, MeO), 6.56 s (1H, 6-H), 6.91–7.41 d.d (4H, MeOC₆H₄, *J* = 8.7 Hz), 7.14 s (1H, 3-H), 7.18–7.77 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.21–7.54 m (5H, Ph), 10.21 s (1H, NH).

5-Isopropyl-4-[(4-methoxyphenylsulfonylimino)-(phenyl)methylamino]-2-methylphenyl 4-methylbenzenesulfonate (XXVIIIc). ¹H NMR spectrum, δ , ppm: 0.90 d (6H, Me₂CH, *J* = 6.9 Hz), 2.04 s (3H, 2-CH₃), 2.44 s (3H, CH₃C₆H₄), 2.86–2.99 m (1H, 5-CH), 3.77 s (3H, MeO), 6.56 s (1H, 6-H), 6.91–7.41 d.d (4H, MeOC₆H₄, *J* = 8.4 Hz), 7.14 s (1H, 3-H),

7.20–7.50 m (5H, Ph), 7.34–7.70 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.1$ Hz), 10.19 br.s (1H, NH).

N-(4-Hydroxy-2,5-dimethylphenyl)-4-methoxy-N-(4-methylphenylsulfonyl)benzenesulfonamide (XXIXa). ^1H NMR spectrum, δ , ppm: 1.84 s (3H, 5- CH_3), 1.94 s (3H, 2- CH_3), 2.49 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.96 s (3H, MeO), 6.52 s (1H, 3-H), 6.72 s (1H, 6-H), 7.19–7.43 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.7$ Hz), 7.27–7.84 d.d (4H, MeOC_6H_4 , $J = 8.4$ Hz), 8.33 s (1H, OH).

4-Chloro-N-(4-hydroxy-2,5-dimethylphenyl)-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXIXb). ^1H NMR spectrum, δ , ppm: 1.84 s (3H, 5- CH_3), 1.95 s (3H, 2- CH_3), 3.96 s (3H, MeO), 6.55 s (1H, 3-H), 6.74 s (1H, 6-H), 7.08–7.49 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.72–7.87 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 8.19 s (1H, OH).

N-(4-Hydroxy-2,5-dimethylphenyl)-4-methoxy-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXIXc). ^1H NMR spectrum, δ , ppm: 1.83 s (3H, 5- CH_3), 1.94 s (3H, 2- CH_3), 3.96 s (6H, MeO), 6.52 s (1H, 3-H), 6.71 s (1H, 6-H), 7.23–7.81 d.d (8H, C_6H_4 , $J = 8.7$ Hz), 8.29 s (1H, OH).

N-(4-Hydroxy-5-isopropyl-2-methylphenyl)-4-methoxy-N-(4-methylphenylsulfonyl)benzenesulfonamide (XXXa). ^1H NMR spectrum, δ , ppm: 0.84 d (6H, Me_2CH , $J = 6.9$ Hz), 1.99 s (3H, 2- CH_3), 2.49 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.84–2.98 m (1H, 5-CH), 3.96 s (3H, MeO), 6.33 s (1H, 3-H), 6.75 s (1H, 6-H), 7.20–7.35 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.7$ Hz), 7.31–7.90 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 8.30 s (1H, OH).

4-Chloro-N-(4-hydroxy-5-isopropyl-2-methylphenyl)-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXXb). ^1H NMR spectrum, δ , ppm: 0.85 d (6H, Me_2CH , $J = 6.9$ Hz), 2.00 s (3H, 2- CH_3), 2.82–2.95 m (1H, 5-CH), 3.96 s (3H, MeO), 6.38 s (1H, 3-H), 6.77 s (1H, 6-H), 7.15–7.43 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.72–7.91 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 8.18 s (1H, OH).

N-(4-Hydroxy-5-isopropyl-2-methylphenyl)-4-methoxy-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXXc). ^1H NMR spectrum, δ , ppm: 0.84 d (6H, Me_2CH , $J = 6.9$ Hz), 2.00 s (3H, 2- CH_3), 2.84–2.97 m (1H, 5-CH), 3.96 s (6H, MeO), 6.36 s (1H, 3-H), 6.74 s (1H, 6-H), 7.28–7.86 d.d (8H, 4- MeOC_6H_4 , $J = 8.7$ Hz), 8.27 s (1H, OH).

N-(4-Hydroxy-2-isopropyl-5-methylphenyl)-4-methoxy-N-(4-methylphenylsulfonyl)benzenesulfonamide (XXXIa). ^1H NMR spectrum, δ , ppm: 0.77 d (6H, Me_2CH , $J = 6.9$ Hz), 2.02 s (3H, 5- CH_3),

2.49 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.94–3.08 m (1H, 2-CH), 3.96 s (3H, MeO), 6.36 s (1H, 3-H), 6.64 s (1H, 6-H), 7.16–7.74 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.7$ Hz), 7.26–7.49 d.d (4H, MeOC_6H_4 , $J = 8.4$ Hz), 8.40 s (1H, OH).

4-Chloro-N-(4-hydroxy-2-isopropyl-5-methylphenyl)-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXXIb). ^1H NMR spectrum, δ , ppm: 0.76 d (6H, Me_2CH , $J = 6.9$ Hz), 2.02 s (3H, 5- CH_3), 2.92–3.05 m (1H, 2-CH), 3.96 s (3H, MeO), 6.35 s (1H, 3-H), 6.60 s (1H, 6-H), 7.05–7.41 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.67–7.83 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 8.23 s (1H, OH).

N-(4-Hydroxy-2-isopropyl-5-methylphenyl)-4-methoxy-N-(4-methoxyphenylsulfonyl)benzenesulfonamide (XXXIc). ^1H NMR spectrum, δ , ppm: 0.77 d (6H, Me_2CH , $J = 6.9$ Hz), 2.01 s (3H, 5- CH_3), 2.94–3.07 m (1H, 2-CH), 3.96 s (6H, MeO), 6.34 s (1H, 3-H), 6.62 s (1H, 6-H), 7.15–7.79 d.d (8H, C_6H_4 , $J = 8.7$ Hz), 8.34 s (1H, OH).

N-(4-Hydroxy-2,5-dimethylphenyl)-N-(4-methylphenylsulfonyl)benzamide (XXXIIa). ^1H NMR spectrum, δ , ppm: 1.91 s (3H, 5- CH_3), 2.03 s (3H, 2- CH_3), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.49 s (1H, 3-H), 7.05 s (1H, 6-H), 7.20–7.35 m (5H, Ph), 7.43–7.88 d.d (4H, C_6H_4 , $J = 8.7$ Hz), 9.65 s (1H, OH).

4-Chloro-N-(4-hydroxy-2,5-dimethylphenyl)-N-(4-methoxyphenylsulfonyl)benzamide (XXXIIb). ^1H NMR spectrum, δ , ppm: 1.87 s (3H, 5- CH_3), 2.03 s (3H, 2- CH_3), 3.89 s (3H, MeO), 6.51 s (1H, 3-H), 7.03 s (1H, 6-H), 7.18–7.90 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.67–7.82 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 9.70 s (1H, OH).

N-(4-Hydroxy-2,5-dimethylphenyl)-N-(4-methoxyphenylsulfonyl)-4-methylbenzamide (XXXIIId). ^1H NMR spectrum, δ , ppm: 8.68 s (1H, OH), 7.14–7.98 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.03–7.46 d.d (4H, MeC_6H_4 , $J = 8.7$ Hz), 7.01 s (1H, 6-H), 6.59 s (1H, 3-H), 3.94 s (3H, MeO), 2.24 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.10 s (3H, 2- CH_3), 1.96 s (3H, 5- CH_3).

N-(4-Hydroxy-5-isopropyl-2-methylphenyl)-N-(4-methylphenylsulfonyl)benzamide (XXXIIIa). ^1H NMR spectrum, δ , ppm: 1.08 d (6H, Me_2CH , $J = 6.9$ Hz), 2.00 s (3H, 2- CH_3), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.96–3.10 m (1H, 5-CH), 6.52 s (1H, 3-H), 6.76 s (1H, 6-H), 7.20–7.37 m (5H, Ph), 7.43–7.84 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.7$ Hz), 9.60 s (1H, OH).

4-Chloro-N-(4-hydroxy-5-isopropyl-2-methylphenyl)-N-(4-methoxyphenylsulfonyl)benzamide (XXXIIIb). ^1H NMR spectrum, δ , ppm: 1.08 d (6H,

Me_2CH , $J = 6.9$ Hz), 1.98 s (3H, 2- CH_3), 2.97–3.11 m (1H, 5-CH), 3.80 s (3H, MeO), 6.54 s (1H, 3-H), 6.75 s (1H, 6-H), 7.27–7.81 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 7.64–7.85 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz), 9.64 s (1H, OH).

N-(4-Hydroxy-5-isopropyl-2-methylphenyl)-N-(4-methoxyphenylsulfonyl)-4-methylbenzamide (XXXIIIId). ^1H NMR spectrum, δ , ppm: 1.20 d (6H, Me_2CH , $J = 6.9$ Hz), 2.09 s (3H, 2- CH_3), 2.23 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 3.09–3.23 m (1H, 5-CH), 3.95 s (3H, MeO), 6.63 s (1H, 3-H), 6.84 s (1H, 6-H), 7.20–7.35 d.d (4H, MeOC_6H_4 , $J = 8.4$ Hz), 7.31–7.96 d.d (4H, MeOC_6H_4 , $J = 8.7$ Hz), 8.69 s (1H, OH).

4-Chloro-N-[3-(4-methoxyphenylsulfonyl)-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene]benzamide (XXXIV). Yield 74%, mp 175–177°C. ^1H NMR spectrum, δ , ppm: 1.88 s (3H, 5- CH_3), 2.92 s (3H, 2- CH_3), 3.89 s (3H, MeO), 6.67 s (1H, 6-H), 7.03–8.04 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.48–7.81 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz). Found, %: N 3.02, 3.46; S 7.01, 7.34. $\text{C}_{22}\text{H}_{18}\text{ClNO}_5\text{S}$. Calculated, %: N 3.16; S 7.22.

N-[3-(4-Chlorophenylsulfonyl)-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene]-4-methoxybenzamide (XXXV). Yield 68%, mp 93–95°C. ^1H NMR spectrum, δ , ppm: 0.92 d (6H, Me_2CH , $J = 6.9$ Hz), 2.79–2.93 m (1H, 5-CH), 2.93 s (3H, 2- CH_3), 3.89 s (3H, MeO), 6.61 s (1H, 6-H), 6.98–8.03 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.53–7.82 d.d (4H,

ClC_6H_4 , $J = 8.7$ Hz). Found, %: N 2.64, 2.95; S 6.72, 6.90. $\text{C}_{24}\text{H}_{22}\text{ClNO}_5\text{S}$. Calculated, %: N 2.97; S 6.79.

4-Chloro-N-[2-isopropyl-3-(4-methoxyphenylsulfonyl)-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene]benzamide (XXXVI). Yield 66%, mp 142–143°C.

^1H NMR spectrum, δ , ppm: 1.58 d (6H, Me_2CH , $J = 6.9$ Hz), 1.85 s (3H, 5- CH_3), 3.89 s (3H, MeO), 4.76–4.90 m (1H, 2-CH), 6.54 s (1H, 6-H), 7.03–8.03 d.d (4H, MeOC_6H_4 , $J = 9.0$ Hz), 7.50–7.79 d.d (4H, ClC_6H_4 , $J = 8.4$ Hz). Found, %: N 2.73, 3.08; S 6.57, 6.86. $\text{C}_{24}\text{H}_{22}\text{ClNO}_5\text{S}$. Calculated, %: N 2.97; S 6.79.

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