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Reaction of *N*-[Aryl(benzylidene, phenoxy)acetyl]-1,4-benzoquinone Imines with Sodium 4-Methylbenzenesulfinate

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Abstract—The reaction of *N*-[aryl(phenoxy, benzylidene)acetyl]-1,4-benzoquinone imines with sodium 4-methylbenzenesulfinates takes different addition patterns, depending on the LUMO energy and charge distribution over the quinoid ring of the initial quinone imine.

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N-Substituted 1,4-benzoquinone imines react with sodium arenesulfinates to give 1,4-, 6,3-, 1,6-, and 6,1-addition products [1–6] whose ratio is determined by the substituent on the nitrogen atom [4–6], substitution pattern in the quinoid ring [4–5], and substituent in the aromatic ring of arenesulfinate [5]. We previously presumed that the 1,4- and 6,3-addition products are formed via nucleophilic addition of arenesulfinate ion and that 1,6- and 6,1-adducts result from addition of arenesulfonyl radical generated via single-electron transfer [6]. The relative contributions of these processes depend on the LUMO energy of the initial quinone imine. The radical ion mechanism was proved by the detection of radical anion species in the reaction of *N*-(4-methylbenzenesulfonyl)-1,4-benzoquinone imine with sodium 4-methylbenzenesulfinate by ESR spectroscopy [3]. Quantum chemical calculations also confirmed radical ion mechanism of the 1,6- and 6,1-additions [7].

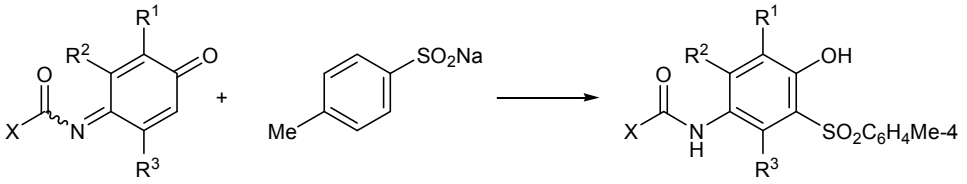
We previously synthesized *N*-[aryl(phenoxy, benzylidene)acetyl]-1,4-benzoquinone imines that are structural analogs of *N*-acetyl-1,4-benzoquinone imine where one or two hydrogen atoms in the acetyl group are replaced by aryl, benzylidene, or phenoxy group [8]. According to the results of quantum chemical calculations, the LUMO energy in the series of such quinone imines varies over a wide range, depending on the substituent on the nitrogen atom (Table 1), whereas the electron-withdrawing effects of these substituents on the quinoid ring differ insignificantly [8]. We presumed that the effect of the LUMO energy of *N*-substituted 1,4-benzoquinone imines on the direction of their reaction with sodium arenesulfinates may be estimated most clearly in the series of *N*-arylacetyl, *N*-benzylideneacetyl, and *N*-phenoxy derivatives.

The reactions of *N*-[aryl(phenoxy, benzylidene)-acetyl]-1,4-benzoquinone imines **I**–**VII** with sodium 4-methylbenzenesulfinate (**VIII**) were carried out using 2 equiv of the latter in acetic acid at room temperature. The products were isolated by precipitation with water. A part of the crude product mixture was recrystallized, the mother liquor was diluted with water, and all three samples (the crude product before and after recrystallization and the material precipitated from the mother liquor) were analyzed by ^{1}H NMR.

The results showed that *N*-substituted 2,3- and 2,5-dialkyl-1,4-benzoquinone imines **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, and **Va**–**Vd** reacted with sodium 4-methylbenzenesulfinate (**VIII**) following exclusively the 1,4-addition pattern with formation of compounds **IXa**, **IXb**, **Xa**, **Xb**, **XIa**, **XIb**, **XIIa**, and **XIIIa**–**XIIId**, respectively (Scheme 1), as reported previously for *N*-acetyl analogs [7]. The ^{1}H NMR spectra of **IX**–**XIII** contained a singlet from one proton in the aminophenol fragment and signals from protons in two aryl fragments and NH and OH groups, which confirmed the assumed structure. The signals were assigned on the basis of our previous data [4, 5, 7].

The reactions of 3,5-dimethyl derivatives **VIa**–**VIe** with sodium 4-methylbenzenesulfinate (**VIII**) gave mixtures of 6,1- and 1,4-addition products **XIVa**–**XIVe** and **XVa**–**XVc**, **XVe** (Scheme 2), the former prevailing (Table 1). Compounds **XIVa**–**XIVe** displayed in the

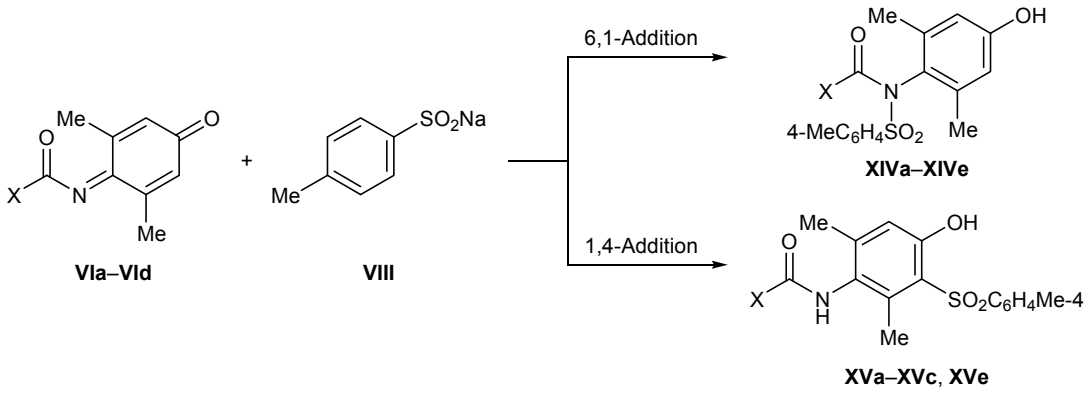
Scheme 1.



Ia, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIb** **IVa**, **Va–Vd** | **VIII** | **IXa**, **IXb**, **Xa**, **Xb**, **XIa**, **XIb** **XIIa**, **XIIIa–XIIId**

I, **IX**, X = $PhCH_2$; **II**, **X**, X = 4-$MeC_6H_4CH_2$; **III**, **XI**, X = 4-$ClC_6H_4CH_2$; **IV**, **XII**, X = $PhOCH_2$; **V**, **XIII**, X = PhCH=CH; **I–V**, **IX–XIII**, $R^1 = R^3 = Me$, $R^2 = H$ (**a**); $R^1 = R^2 = Me$, $R^3 = H$ (**b**); $R^1 = i$-Pr, $R^2 = H$, $R^3 = Me$ (**c**); $R^1 = Me$, $R^2 = H$, $R^3 = i$-Pr (**d**).

Scheme 2.



VIa–VId | **VIII** | **XIVa–XIVe** | **XVa–XVc**, **XVe**

X = $PhCH_2$ (**a**), 4-$MeC_6H_4CH_2$ (**b**), 4-$ClC_6H_4CH_2$ (**c**), $PhOCH_2$ (**d**), PhCH=CH (**e**).

^{1}H NMR spectra a singlet from the phenolic proton at δ 9.82–9.99 ppm and a singlet from 3-H and 5-H in the region δ 6.63–6.65 ppm, whereas no NH signal was present. The spectra of **XIVa–XIVc** were characterized by a strong downfield shift of the $COCH_2$ signal (δ 3.18–3.25 ppm) relative to the corresponding signals of **I–III**, **VIa–VIc**, **IX–XI**, **XIIIa–XIIIc**, and **XVa–XVc**. The OCH_2 signal of **XIVd** was displaced downfield (δ 4.24 ppm, s) relative to the corresponding signal of **IVa** and **XIIa**, and the CH=CH signals of **XIVe** (δ 5.98 and 7.65 ppm, d.d) were displaced relative to those in the spectra of **V**, **XIII**, and **XVe**.

Table 1. Product ratios in the reactions of *N*-[aryl(phenoxy, benzylidene)acetyl]-1,4-benzoquinone imines **VIa–VIe** and **VIIa–VIIe** with sodium 4-methylbenzenesulfinate (**VIII**) (Schemes 2, 3)

Initial quinone imine no.	LUMO energy, kJ/mol	ΔE,[a] kJ/mol	E_{rel}, kJ/mol	Product composition, %			
				6,1-addition	1,4-addition	1,6-addition	6,3-addition
VIa	–341.21	128.70	30.87	95	5	–	–
VIb				85	15	–	–
VIc				83	17	–	–
VId	–359.06	97.84	0	100	0	–	–
VIe	–331.68	120.34	22.51	75	25	–	–
VIIa	–340.97	132.35	13.28	–	–	75	25
VIIb				–	–	78	22
VIIc				–	–	85	15
VIId	–362.50	119.06	0	–	–	100	0
VIIe	–334.50	139.23	20.17	–	–	68	32

[a] ΔE is the change in the energy of formation of intermediate radical anions **XVIIIa–XVIIIc** and **XIXa–XIXc** (Scheme 4).

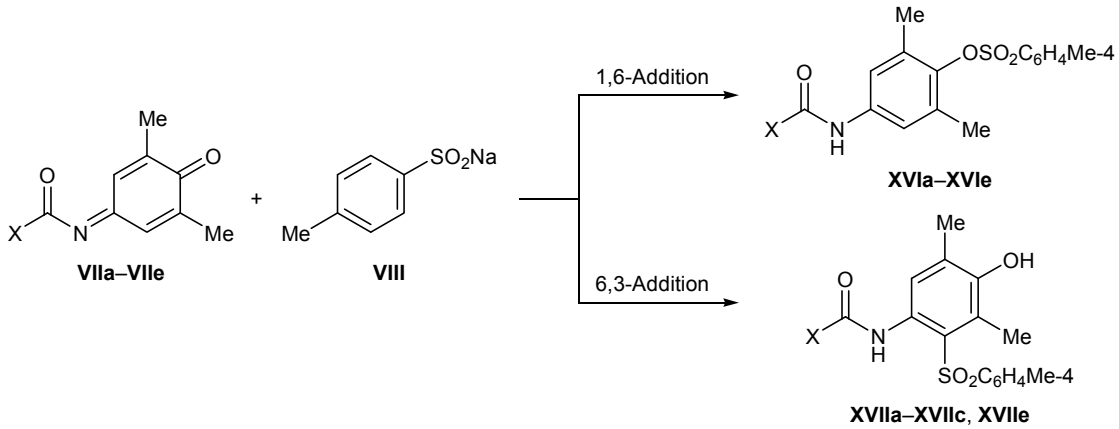
2,6-Dimethyl-1,4-bezoquinone imines **VIIa**–**VIIe** reacted with sodium arenesulfinate **VIII** to produce mixtures of 1,6- and 6,3-additon products **XVIa**–**XVIe** and **XVIIa**–**XVIIc**, **XVIIe** (Scheme 3); the products of addition to the oxygen atom were the major ones (Table 1). The ^{1}H NMR spectra of **XVIa**–**XVIe** contained a singlet from the NH proton at δ 10.09–10.21 ppm, a two-proton singlet from 3-H and 5-H at δ 7.31–7.43 ppm, a singlet from methyl groups on C^2 and C^6 at δ 1.99–2.03 ppm, and signals from protons in the two other aromatic fragments, while no OH signal was observed. Compounds **XVIIa**–**XVIIc** and **XVIIe** showed in the ^{1}H NMR spectra singlets from the NH and OH protons, a singlet from 6-H in the region δ 7.41–7.47 ppm, two singlets from methyl groups on C^2 (δ 2.30–2.32 ppm) and C^6 (δ 2.19–2.23 ppm), and signals from protons in the aromatic fragments.

Analysis of our experimental data shows that the fraction of 6,1-addition products increases in going from quinone imine **VIe** to **VIa**–**VIc** and then to **VId**; likewise, in going from **VIIe** to **VIIa**–**VIIc** and **VIId**, the contribution of 1,6-addition increases. In the reactions with compounds **VId** and **VIId**, the corresponding 6,1- and 1,6-addition products were formed exclusively (Table 1).

According to the results of quantum chemical calculations, the LUMO energy decreases in the series **VIe** > **VIa** > **VId** and **VIIe** > **VIIa** > **VIId**, the largest variations (ΔE_{LUMO} = 17.85 and 21.53 kJ/mol) being observed in going from *N*-phenylacetyl (**VIa**, **VIIa**) to *N*-phenoxyacetyl derivatives (**VId**, **VIId**; Table 1). Therefore, it may be presumed that the formation of radical anion pair from **VId** and **VIId** is the most favorable. To verify this assumption, we calculated the changes (ΔE) in the energy of formation of radical anions **XVIIIa**–**XVIIIc** and **XIXa**–**XIXc** in the reactions of quinone imines **VIa**, **VId**, **VIe** and **VIIa**, **VIId**, **VIIe** with 4-methylbenzenesulfinate ion (Scheme 4, Table 1).

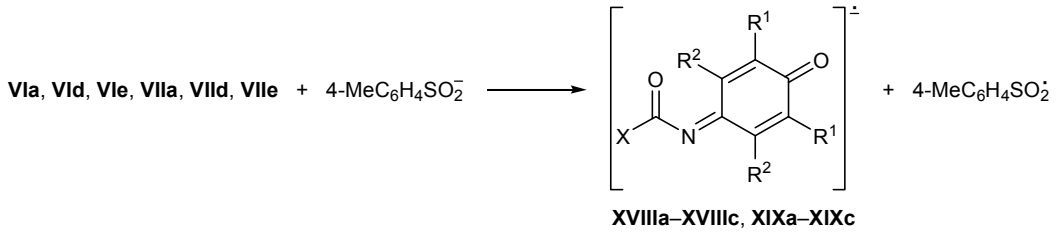
As might be expected, the calculated ΔE values correlate well with the LUMO energies and experimental data. Within the examined series, the formation of radical anion pair from *N*-phenoxyacetyl derivatives **VId** and **VIId** is most energetically favorable, so that these compounds gave rise only to 1,6- (2,6-dimethyl derivative **VIId**) and 6,1-addition products (3,5-dimethyl derivative **VId**) according to the radical ion mechanism (Table 1; E_{rel} = 0 kJ/mol). Increase of ΔE for the formation of radical anions **XVIIIa** and **XIXa** from *N*-phenylacetyl derivatives **VIa** and **VIIa** (E_{rel} =

Scheme 3.



X = $PhCH_2$ (**a**), 4-$MeC_6H_4CH_2$ (**b**), 4-$ClC_6H_4CH_2$ (**c**), $PhOCH_2$ (**d**), PhCH=CH (**e**).

Scheme 4.



XVIIIa–**XVIIIc**, **XIXa**–**XIXc**

XVIII, R^1 = Me, R^2 = H; **XIX**, R^1 = H, R^2 = Me; X = $PhCH_2$ (**a**), $PhOCH_2$ (**b**), PhCH=CH (**c**).

30.87 and 13.28 kJ/mol, respectively; Table 1) is accompanied by increase of the contribution of the 1,4- and 6,3-addition paths implying direct nucleophilic addition of arenesulfinate ion; in this case, the determining factor is charge distribution over carbon atoms of the quinoid ring (Table 2).

Increase of the LUMO energy in the series of 2,6-dimethyl-1,4-benzoquinone imines **VIId** < **VIIa** < **VIIe** makes the radical ion mechanism (1,6-addition) less favorable, while partial negative charges on C^3 and C^5 decrease, which favor nucleophilic 6,3-addition (Tables 1, 2). Thus, consistent action of these two factors reduces the fraction of 1,6-addition products and increases the fraction of 6,3-addition products in the series of quinone imines **VIId**, **VIIa**, **VIIe**, which is in full agreement with the experimental data (Table 1).

Like 2,6-dimethyl derivatives, the LUMO energy of 3,5-dimethyl analogs increases in the series **VId** < **VIa** < **VIe**; on the other hand, the negative charges on C^2 and C^6 also increase (Table 2), i.e., in this series both radical ion (6,1-addition), and nucleophilic mechanisms (1,4-addition) become less favorable. The result is that there is no direct relation between the LUMO energy or charge on C^2/C^6 of the initial quinone imine and the product ratio which is determined by a complex combination of the above two factors.

In summary, we have found that the main factors determining the regioselectivity of the addition of sodium 4-methylbenzenesulfinate to *N*-[aryl(phenoxy, benzylidene)acetyl]-1,4-benzoquinone imines are the LUMO energy and charge distribution over the quinoid ring of the initial quinone imine.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Varian VXR-300 spectrometer at 300 MHz; the chemical shifts are given relative to tetramethylsilane. The purity of the isolated compounds was checked by TLC on Silufol UV-254 plates using benzene–hexane (10:1) or hexane–ethyl acetate (1:2) as eluent; spots were visualized under UV light.

Quantum chemical calculations were performed using Firefly QC [9] based in part on the GAMESS (US) code [10]. All geometric parameters of 1,4-benzoquinone imine molecules were optimized at the DFT B3LYP/6-31+G(*d*) level of theory.

Sodium 4-methylbenzenesulfinate (**VIII**) was prepared according to the procedure described in [11].

Table 2. Charge on atoms in the quinoid ring of compounds **VIa**, **VId**, **VIe**, **VIIa**, **VIId**, and **VIIe**

Compound no.	C^1	C^2	C^3	C^4	C^5	C^6
VIa	0.474	–0.250	–0.021	0.271	–0.003	–0.262
VId	0.474	–0.245	–0.026	0.279	–0.005	–0.258
VIe	0.474	–0.251	–0.020	0.270	–0.001	–0.264
VIIa	0.499	–0.041	–0.235	0.247	–0.209	–0.054
VIId	0.499	–0.036	–0.240	0.260	–0.212	–0.048
VIIe	0.499	–0.044	–0.231	0.249	–0.207	–0.055

Initial *N*-[aryl(phenoxy, benzylidene)acetyl]-1,4-benzoquinone imines **I**–**VII** were synthesized by oxidation of the corresponding *N*-substituted 4-aminophenols with lead tetraacetate in acetic acid as described in [8]. Quinone imines **Ia**, **Ib**, **IIa**, **IIb**, **IVa**, **Va**–**Vc**, **VIa**–**VIc**, **VIe**, **VIIa**–**VIIc**, and **VIIe** were reported previously [8].

2-(4-Chlorophenyl)-*N*-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (IIIa). Yield 86%, mp 149–150°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.81 d (3H, 2-Me, J = 1.2 Hz), 2.10 d (3H, 5-Me, J = 1.2 Hz), 3.80 s (2H, CH_2), 6.19 q (1H, 6-H, J = 1.5 Hz), 6.46 q (1H, 3-H, J = 1.2 Hz), 7.22 d (2H, 2′-H, 6′-H, J = 8.6 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.6 Hz). Found, %: N 4.65, 4.53. $C_{16}H_{14}ClNO_2$. Calculated, %: N 4.87.

2-(4-Chlorophenyl)-*N*-(2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (IIIb). Yield 54%, mp 92–93°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 d (3H, 2-Me), 2.04 d (3H, 3-Me), 3.78 s (2H, CH_2), 6.59 d (1H, 6-H, J = 8.4 Hz), 6.79 s (1H, 5-H, J = 8.4 Hz), 7.42 br.s (4H, C_6H_4). Found, %: N 5.10, 5.18. $C_{16}H_{14}ClNO_2$. Calculated, %: N 4.87.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-yliden)-3-phenylprop-2-enamide (Vd).** Yield 72%, mp 115–116°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 d [6H, 2-CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.24 d (3H, 5-Me, J = 1.5 Hz), 2.97–3.06 m [1H, 2-C**H**(CH$_3$)$_2$], 6.58 q (1H, 3-H, J = 1.5 Hz), 6.62 d (1H, 6-H, J = 1.2 Hz), 6.70 d and 7.57 d (1H each, CH=CH, J = 16.2 Hz), 7.44–7.59 m (5H, Ph). Found, %: N 4.89, 5.03. $C_{19}H_{19}NO_2$. Calculated, %: N 4.77.

2-(4-Chlorophenyl)-*N*-(2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (VIc). Yield 69%, mp 145–146°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.97 s (6H, 2-Me, 6-Me), 3.78 s (2H, CH_2), 6.53 s (2H, 3-H, 5-H), 7.20 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.29 d

(2H, 3′-H, 5′-H, J = 8.4 Hz). Found, %: N 4.71, 4.60. $C_{16}H_{14}ClNO_2$. Calculated, %: N 4.87.

2-(4-Chlorophenyl)-*N*-(3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetamide (VIIc). Yield 80%, mp 153–154°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 s (6H, 3-Me, 5-Me), 6.64 s (2H, 2-H, 6-H), 3.72 s (2H, CH_2), 7.18 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.26 d (2H, 3′-H, 5′-H, J = 8.4 Hz). Found, %: N 4.64, 4.75. $C_{16}H_{14}ClNO_2$. Calculated, %: N 4.87.

Reaction of quinone imines I–VII with sodium 4-methylbenzenesulfinate (VIII). Sodium 4-methylbenzenesulfinate (**VIII**), 4 mmol, was added in one portion under stirring at room temperature to a solution of 2 mmol of quinone imine **I**–**VII** in 10 mL of glacial acetic acid, and the mixture was stirred until it became colorless. If the mixture did not lose its color in 2 h after addition of **VIII**, it was heated until decoloration. The solution was cooled and poured onto ice under vigorous stirring. 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 acetic acid, the mother liquor was diluted with water, and the precipitate was filtered off and dried. All three samples were analyzed by ^{1}H NMR. Compounds **XVa**–**XVc**, **XVe**, **XVIb**, **XVIe**, **XVIIa**–**XVIIc**, and **XVIIe** were not isolated in the pure state, and their structure was determined on the basis of spectral data.

***N*-[4-Hydroxy-2,5-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-2-phenylacetamide (IXa).** Yield 97%, mp 172–173°C. ^{1}H NMR spectrum* (DMSO-d_6), δ, ppm: 2.08 s (3H, 5-Me), 2.16 s (3H, 2-Me), 2.38 s (3H, 4″-CH_3), 3.57 s (2H, CH_2), 7.22–7.30 m (5H, Ph), 7.29 s (1H, 6-H), 7.43 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.75 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.46 br.s (1H, NH), 10.34 br.s (1H, OH). Found, %: N 3.10, 3.22; S 7.69, 7.57. $C_{23}H_{23}NO_4S$. Calculated, %: N 3.42; S 7.83.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]-2-phenylacetamide (IXb).** Yield 98%, mp 155–156°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 3-Me), 2.16 s (3H, 2-Me), 2.39 s (3H, 4″-CH_3), 3.57 s (2H, CH_2), 7.24–7.34 m (5H, Ph), 7.30 s (1H, 6-H), 7.44 d (2H, 2″-H, 6″-H, J = 7.5 Hz), 7.75 d (2H, 3″-H, 5″-H, J = 6.6 Hz), 9.54 br.s (1H, NH), 10.35 br.s (1H, OH). Found, %: N 3.31, 3.56; S 7.77, 7.95. $C_{23}H_{23}NO_4S$. Calculated, %: N 3.31; S 7.57.

***N*-[4-Hydroxy-2,5-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-2-(4-methylphenyl)acetamide (Xa).** Yield 96%, mp 164–165°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, 5-Me), 2.15 s (3H, 2-Me), 2.26 s (3H, 4′-CH_3), 2.38 s (3H, 4″-CH_3), 3.52 s (2H, CH_2), 7.11 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.18 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.28 s (1H, 6-H), 7.43 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.76 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.52 br.s (1H, NH), 10.46 br.s (1H, OH). Found, %: N 3.52, 3.60; S 7.41, 7.36. $C_{24}H_{25}NO_4S$. Calculated, %: N 3.42; S 7.83.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]-2-(4-methylphenyl)acetamide (Xb).** Yield 99%, mp 194–195°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 d (3H, 3-Me), 2.04 d (3H, 2-Me), 2.29 s (3H, 4′-CH_3), 2.36 s (3H, 4″-CH_3), 3.59 s (2H, CH_2), 7.15 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.25 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.38 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.63 s (1H, 6-H), 7.75 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.43 br.s (1H, NH), 9.65 br.s (1H, OH). Found, %: N 3.28, 3.17; S 7.41, 7.36. $C_{24}H_{25}NO_4S$. Calculated, %: N 3.31; S 7.57.

2-(4-Chlorophenyl)-*N*-[4-hydroxy-2,5-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]acetamide (XIa). Yield 98%, mp 189–190°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.13 s (3H, 5-Me), 2.19 s (3H, 2-Me), 2.36 s (3H, 4″-CH_3), 3.61 s (2H, CH_2), 7.12 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.20 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.30 s (1H, 6-H), 7.43 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.76 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.66 br.s (1H, NH), 10.08 br.s (1H, OH). Found, %: N 3.08, 3.25; S 7.12, 7.25. $C_{23}H_{22}ClNO_4S$. Calculated, %: N 3.16; S 7.22.

2-(4-Chlorophenyl)-*N*-[4-hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]acetamide (XIb). Yield 97%, mp 174–175°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03 s (3H, 3-Me), 2.05 s (3H, 2-Me), 2.36 s (3H, 4″-CH_3), 3.67 s (2H, CH_2), 7.37 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.36 s (1H, 6-H), 7.39 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.42 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.76 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 9.67 br.s (1H, NH), 10.12 br.s (1H, OH). Found, %: N 3.21, 3.38; S 7.49, 7.35. $C_{23}H_{22}ClNO_4S$. Calculated, %: N 3.16; S 7.22.

***N*-[4-Hydroxy-2,5-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-2-phenoxyacetamide (XIIa).** Yield 100%, mp 190–191°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.11 s (3H, 5-Me), 2.17 s (3H, 2-Me), 2.39 s

* Hereinafter, unprimed locants refer to the quinoid (phenol) fragment, primed locants refer to the aromatic ring in the acetamide fragment, and double primed locants refer to the 4-methylbenzenesulfonyl fragment.

(3H, 4″-CH_3), 4.65 s (2H, OCH_2), 6.97–7.34 m (5H, Ph), 7.28 s (1H, 6-H), 7.45 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.77 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.58 br.s (1H, NH), 10.36 br.s (1H, OH). Found, %: N 3.14, 3.37; S 7.56, 7.63. $C_{24}H_{27}NO_5S$. Calculated, %: N 3.17; S 7.76.

***N*-[4-Hydroxy-2,5-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XIIIa).** Yield 97%, mp 199–200°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (6H, 2-Me, 5-Me), 2.40 s (3H, 4″-CH_3), 6.81 d (1H, CH=CH, J = 15.6 Hz), 7.42–7.62 m (5H, Ph), 7.45 s (1H, 6-H), 7.46 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.53 d (1H, CH=CH, J = 15.9 Hz), 7.80 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 9.61 br.s (1H, NH), 10.39 br.s (1H, OH). Found, %: N 3.41, 3.53; S 7.74, 7.85. $C_{24}H_{23}NO_4S$. Calculated, %: N 3.32; S 7.61.

***N*-[4-Hydroxy-2,3-dimethyl-5-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XIIIb).** Yield 96%, mp 250–251°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 d (3H, 3-Me), 2.13 d (3H, 2-Me), 2.38 s (3H, 4″-CH_3), 6.92 d (1H, CH=CH, J = 15.6 Hz), 7.39–7.65 m (5H, Ph), 7.40 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.59 d (1H, CH=CH, J = 15.6 Hz), 7.78 s (1H, 6-H), 7.82 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.43 br.s (1H, NH), 9.69 br.s (1H, OH). Found, %: N 3.22, 3.56; S 7.43, 7.55. $C_{24}H_{23}NO_4S$. Calculated, %: N 3.32; S 7.61.

***N*-[4-Hydroxy-5-isopropyl-2-methyl-3-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XIIIc).** Yield 97%, mp 185–186°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.18 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.15 s (3H, 2-Me), 2.41 s (3H, 4″-CH_3), 3.23–3.32 m [1H, C**H**$(CH_3)_2$], 6.80 d (1H, CH=CH, J = 15.9 Hz), 7.43 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.46 s (1H, 6-H), 7.49–7.61 m (5H, Ph), 7.53 d (1H, CH=CH, J = 15.9 Hz), 7.79 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.63 br.s (1H, NH), 10.50 br.s (1H, OH). Found, %: N 3.34, 3.45; S 6.94, 7.03. $C_{26}H_{27}NO_4S$. Calculated, %: N 3.12; S 7.13.

***N*-[4-Hydroxy-2-isopropyl-5-methyl-3-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XIIId).** Yield 99%, mp 246–247°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.89 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.20 s (3H, 5-Me), 2.42 s (3H, 4″-CH_3), 3.59–3.68 m [1H, C**H**$(CH_3)_2$], 6.92 d (1H, CH=CH, J = 15.6 Hz), 7.27 s (1H, 6-H), 7.43 d (2H, 2″-H, 6″-H, J = 6.9 Hz), 7.49–7.61 m (5H, Ph), 7.53 d (1H, CH=CH, J = 15.9 Hz), 7.77 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.28 br.s (1H, NH), 10.82 br.s (1H, OH). Found, %: N 2.98, 3.15; S 7.32, 7.57. $C_{26}H_{27}NO_4S$. Calculated, %: N 3.12; S 7.13.

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methylbenzenesulfonyl)-2-phenylacetamide (XIVa).** Yield 95%, mp 194–195°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (6H, 2-Me, 6-Me), 2.41 s (3H, 4″-CH_3), 3.24 s (2H, CH_2), 6.63 s (2H, 3-H, 5-H), 6.92–7.24 m (5H, Ph), 7.44 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.95 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.83 s (1H, OH). Found, %: N 3.54, 3.62; S 7.95, 8.00. $C_{23}H_{23}NO_4S$. Calculated, %: N 3.42; S 7.83.

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methylbenzenesulfonyl)-2-(4-methylphenyl)acetamide (XIVb).** Yield 96%, mp 250–251°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (6H, 2-Me, 6-Me), 2.24 s (3H, 4′-CH_3), 2.41 s (3H, 4″-CH_3), 3.18 s (2H, CH_2), 6.63 s (2H, 3-H, 5-H), 6.81 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.04 d (2H, 3′-H, 5′-H, J = 7.5 Hz), 7.43 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.93 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 9.82 br.s (1H, OH). Found, %: N 3.41, 3.53; S 7.43, 7.55. $C_{24}H_{23}NO_4S$. Calculated, %: N 3.32; S 7.61.

2-(4-Chlorophenyl)-*N*-(4-hydroxy-2,6-dimethylphenyl)-*N*-(4-methylbenzenesulfonyl)acetamide (XIVc). Yield 83%, mp 220–221°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.04 d (6H, 2-Me, 6-Me), 2.41 s (3H, 4″-CH_3), 3.25 s (2H, CH_2), 6.64 s (2H, 3-H, 5-H), 6.99 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.44 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.93 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.85 br.s (1H, OH). Found, %: N 2.93, 3.05; S 6.98, 7.04. $C_{23}H_{22}ClNO_4S$. Calculated, %: N 3.16; S 7.22.

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methylbenzenesulfonyl)-2-phenoxyacetamide (XIVd).** Yield 100%, mp 194–195°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.13 s (6H, 2-Me, 6-Me), 2.43 s (3H, 4″-CH_3), 4.24 s (2H, OCH_2), 6.65 s (2H, 3-H, 5-H), 6.70–7.27 m (5H, Ph), 7.47 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.98 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 9.90 br.s (1H, OH). Found, %: N 3.17, 3.38; S 7.40, 7.65. $C_{23}H_{23}NO_5S$. Calculated, %: N 3.29; S 7.54.

***N*-(4-Hydroxy-2,6-dimethylphenyl)-*N*-(4-methylbenzenesulfonyl)-3-phenylprop-2-enamide (XIVe).** Yield 75%, mp 140–141°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 s (6H, 2-Me, 6-Me), 2.44 s (3H, 4″-CH_3), 5.98 d (1H, CH=CH, J = 15.3 Hz), 6.65 s (2H, 3-H, 5-H), 7.32–7.42 m (5H, Ph), 7.48 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.65 d (1H, CH=CH, J = 15.6 Hz), 8.02 d (2H, 3″-H, 5″-H, J = 8.1 Hz),

9.99 br.s (1H, OH). Found, %: N 3.37, 3.48; S 7.50, 7.54. $C_{24}H_{23}NO_4S$. Calculated, %: N 3.32; S 7.61.

***N*-[4-Hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-2-phenylacetamide (XVa).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (3H, 6-Me), 2.32 s (3H, 2-Me), 2.37 s (3H, 4″-CH_3), 3.62 s (2H, CH_2), 6.74 s (1H, 5-H), 6.92–7.26 m (5H, Ph), 7.38 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.74 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.40 s (1H, NH), 10.40 s (1H, OH).

***N*-[4-Hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-2-(4-methylphenyl)acetamide (XVb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 s (3H, 6-Me), 2.28 s (3H, 4′-CH_3), 2.32 s (3H, 2-Me), 2.37 s (3H, 4″-CH_3), 3.56 s (2H, CH_2), 6.74 s (1H, 5-H), 7.13 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.23 d (2H, 3′-H, 5′-H, J = 7.5 Hz), 7.38 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.73 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.36 s (1H, NH), 10.40 br.s (1H, OH).

2-(4-Chlorophenyl)-*N*-[4-hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]acetamide (XVc). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 s (3H, 6-Me), 2.34 s (3H, 2-Me), 2.40 s (3H, 4″-CH_3), 3.64 s (2H, CH_2), 6.75 s (1H, 5-H), 7.23 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.38 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.39 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.77 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 9.42 s (1H, NH), 10.37 s (1H, OH).

***N*-[4-Hydroxy-2,6-dimethyl-3-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XVe).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 s (3H, 6-Me), 2.39 s (3H, 2-Me), 2.41 s (3H, 4″-CH_3), 6.72 s (1H, 5-H), 6.86 d (1H, CH=CH, J = 15.6 Hz), 7.39 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.42–7.62 m (5H, Ph), 7.77 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.92 d (1H, CH=CH, J = 15.9 Hz), 9.48 s (1H, NH), 10.10 s (1H, OH).

2,6-Dimethyl-4-(2-phenylacetylamino)phenyl 4-methylbenzenesulfonate (XVIa). Yield 75%, mp 134–135°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 s (6H, 2-Me, 6-Me), 2.45 s (3H, 4″-CH_3), 3.61 s (2H, CH_2), 7.24–7.35 m (5H, Ph), 7.33 s (2H, 3-H, 5-H), 7.51 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.84 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 10.17 br.s (1H, NH). Found, %: N 3.15, 3.38; S 7.65, 7.73. $C_{24}H_{25}NO_4S$. Calculated, %: N 3.31; S 7.57.

2,6-Dimethyl-4-[2-(4-methylphenyl)acetylamino]-phenyl 4-methylbenzenesulfonate (XVIb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 s (6H, 2-Me, 6-Me), 2.28 s (3H, 4′-CH_3), 2.43 s (3H, 4″-CH_3), 3.61 s (2H, CH_2), 7.13 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.23 d (2H, 3′-H, 5′-H, J = 7.5 Hz), 7.31 s (2H, 3-H, 5-H), 7.52 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.86 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 10.12 br.s (1H, NH).

4-[2-(4-Chlorophenyl)acetylamino]-2,6-dimethylphenyl 4-methylbenzenesulfonate (XVIc). Yield 85%, mp 166–167°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 d (6H, 2-Me, 6-Me), 2.45 s (3H, 4″-CH_3), 3.63 s (2H, CH_2), 7.32 s (2H, 3-H, 5-H), 7.33 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.39 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.52 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.84 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 10.21 br.s (1H, NH). Found, %: N 2.54, 2.87; S 6.85, 6.93. $C_{24}H_{24}ClNO_4S$. Calculated, %: N 3.06; S 7.00.

2,6-Dimethyl-4-(2-phenoxyacetylamino)phenyl 4-methylbenzenesulfonate (XVId). Yield 100%, mp 168–169°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01 s (6H, 2-Me, 6-Me), 2.45 s (3H, 4″-CH_3), 4.68 s (2H, OCH_2), 6.95–7.34 m (5H, Ph), 7.39 s (2H, 3-H, 5-H), 7.53 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.85 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 10.09 br.s (1H, NH). Found, %: N 3.12, 3.99; S 7.10, 7.23. $C_{24}H_{25}NO_5S$. Calculated, %: N 3.19; S 7.30.

2,6-Dimethyl-4-[(1-oxo-3-phenylprop-2-en-1-yl)-amino]phenyl 4-methylbenzenesulfonate (XVIe). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03 s (6H, 2-Me, 6-Me), 2.46 s (3H, 4″-CH_3), 6.80 d (1H, CH=CH, J = 15.6 Hz), 7.43 s (2H, 3-H, 5-H), 7.42–7.65 m (5H, Ph), 7.53 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.69 d (1H, CH=CH, J = 15.6 Hz), 7.86 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 10.18 br.s (1H, OH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylbenzenesulfonyl)phenyl]-2-phenylacetamide (XVIIa).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, 5-Me), 2.30 s (3H, 3-Me), 2.36 s (3H, 4″-CH_3), 3.65 s (2H, CH_2), 7.24–7.35 m (5H, Ph), 7.34 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.46 s (1H, 6-H), 7.59 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 9.80 br.s (1H, NH), 9.85 br.s (1H, OH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylbenzenesulfonyl)phenyl]-2-(4-methylphenyl)acetamide (XVIIb).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, 5-Me), 2.29 s (3H, 4′-CH_3), 2.31 s (3H, 3-Me), 2.36 s (3H, 4″-CH_3), 3.55 s (2H, CH_2), 7.15 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.25 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.35 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.46 s (1H, 6-H), 7.62 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 8.77 br.s (1H, NH), 9.83 br.s (1H, OH).

2-(4-Chlorophenyl)-*N*-[4-hydroxy-3,5-dimethyl-2-(4-methylbenzenesulfonyl)phenyl]acetamide (XVIIc). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, 5-Me), 2.30 s (3H, 3-Me), 2.36 s (3H,

4″-CH_3), 3.65 s (2H, CH_2), 7.33 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.34 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.41 s (1H, 6-H), 7.39 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.59 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 8.84 br.s (1H, NH), 9.84 br.s (1H, OH).

***N*-[4-Hydroxy-3,5-dimethyl-2-(4-methylbenzenesulfonyl)phenyl]-3-phenylprop-2-enamide (XVIIe).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, 5-Me), 2.32 s (3H, 3-Me), 2.32 s (3H, 4″-CH_3), 6.88 d (1H, CH=CH, J = 15.6 Hz), 7.35 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.42–7.65 m (5H, Ph), 7.47 s (1H, 6-H), 7.62 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 7.71 d (1H, CH=CH, J = 15.6 Hz), 8.81 br.s (1H, NH), 9.90 br.s (1H, OH).

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