ISSN 1070-4280, Russian Journal of Organic Chemistry, 2017, Vol. 53, No. 4, pp. 525–538. © Pleiades Publishing, Ltd., 2017.
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# Reaction of *N*-Sulfonyl-1,4-benzoquinone Imines with Enamines

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Received May 19, 2016

**Abstract**—*N*-Sulfonyl derivatives of 1,4-benzoquinone imine reacted with enamines to give 1,4-addition products and products of their subsequent cyclization, substituted 5-aminobenzofurans and 5-aminoindoles, depending on the solvent nature, electron-withdrawing power of the substituent on the quinone imine nitrogen atom, and enamine structure. The presence of strong electron-withdrawing trifluoromethanesulfonyl group on the quinone imine nitrogen atom favors formation of 1,4-addition products and benzofuran derivatives.

**DOI:** 10.1134/S1070428017040054

It was found previously that *N*-arenesulfonyl derivatives of 1,4-benzo- [1–5] and 1,4-naphthoquinone imines [5, 6] and 1,4-benzoquinone diimine [5, 7] react with enamines to give 1,4-addition products [2, 5] and derivatives of 5-aminobenzo(naphtho)furan [1, 2, 4–7], 5-aminoindole [4, 5, 7], and 6-aminoindole [4]. Analogous compounds obtained from 1,4-benzoquinone and its derivatives showed high antiviral activity [8–10] and are widely used as medicinal agents [11, 12]; examples are local anesthetic benzofurocain, antidepressant brofaromine, one of the most potent nonsteroidal anti-inflammatory drugs indometacin, radioprotector mexamine, antiviral drug umifenovir, monoamine neurotransmitter serotonin, and its derivative melatonin which is involved in sleep cycle synchronization.

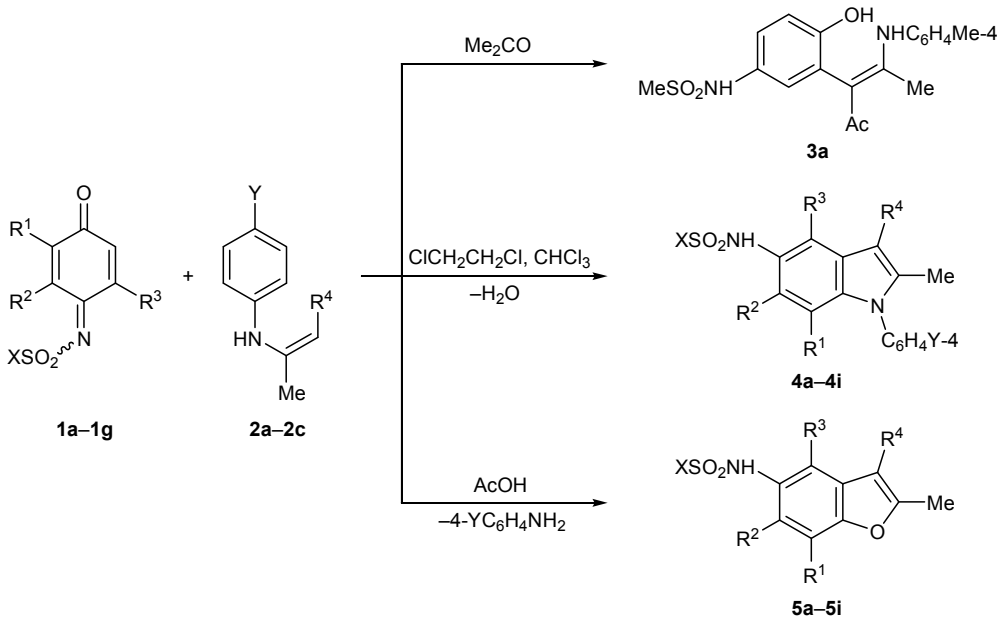
The product structure in the reactions of *N*-arenesulfonyl-1,4-benzoquinone imines with enamines is largely determined by the reaction conditions and enamine structure [5]; however, the effect of the X substituent in the $XSO_2N=$ fragment on the reaction course has not been studied so far.

We previously synthesized 1,4-benzoquinone imines containing a trifluoromethanesulfonyl group on the nitrogen atom [13]. The $CF_3SO_2$ group is a stronger acceptor than $ArSO_2$, which was demonstrated by reactions with potassium thiocyanate [13] and sodium sulfinates [14].

The goal of the present work was to elucidate how reaction conditions, substituent on the sulfonyl group, and enamine structure affect the direction of the reactions of *N*-methanesulfonyl-, *N*-trifluoromethanesulfonyl-, and *N*-arenesulfonyl-1,4-benzoquinone imines with 4-(4-methylanilino)pent-3-en-2-one and ethyl 3-(arylamino)but-2-enoates, as well as to obtain new benzofuran and indole derivatives expected to exhibit biological activity.

It is known that the solvent nature is the key factor determining the direction of the reactions of *N*-arenesulfonyl-1,4-benzoquinone imines with enamines [5]. Therefore, the reactions of *N*-sulfonyl quinone imines **1a**–**1g** with enamines **2a**–**2c** were carried out in acetone, chloroform, and acetic acid with a view to obtaining all possible products. In fact, in keeping with the data of [5], the reaction in acetone gave 1,4-addition product **3a**, indole derivatives **4a**–**4i** were formed in chloroform and 1,2-dichloroethane, and benzofuran derivatives **5a**–**5i** were isolated when acetic acid was used as solvent (Scheme 1).

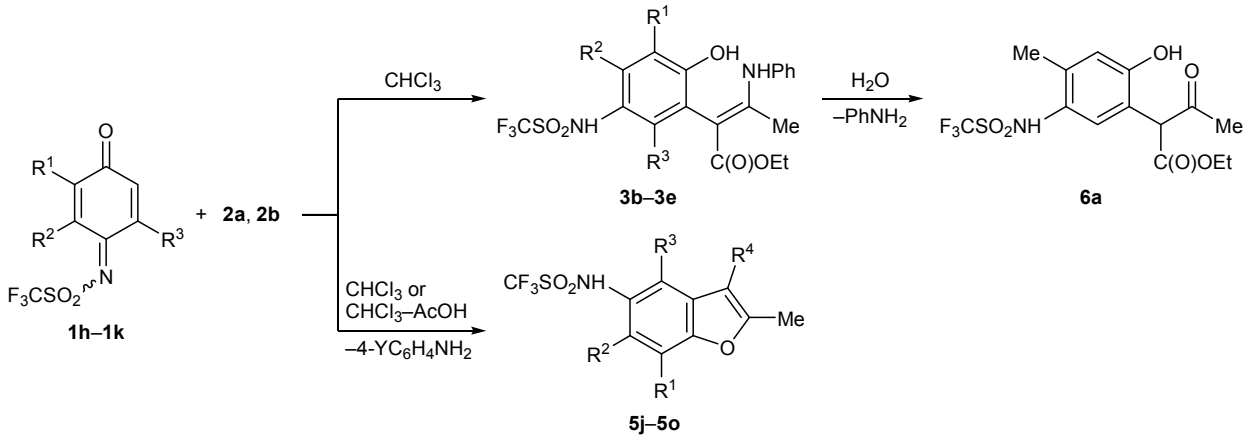
**Scheme 1.**




**1**, X = 4-$MeC_6H_4$ (**a**, **b**), Me (**c**–**g**); $R^1$ = Cl, $R^2$ = $R^3$ = H (**a**); $R^1$ = Me, $R^2$ = $R^3$= H (**b**, **d**); $R^1$ = $R^2$ = $R^3$ = H (**c**); $R^2$ = Me, $R^1$ = $R^3$ = H (**e**); $R^1$ = $R^2$ = Me, $R^3$ = H (**f**); $R^2$ = $R^3$ = Me, $R^1$ = H (**g**); **2**, $R^4$ = COMe, Y = Me (**a**); $R^4$ = COOEt, Y = H (**b**), $R^4$ = COOEt, Y = OMe (**c**); **4**, $R^1$ = Cl, $R^2$ = $R^3$ = Y = H, $R^4$ = COOEt, X = 4-$MeC_6H_4$ (**a**); $R^1$ = Me, $R^2$ = $R^3$ = Y = H, $R^4$ = COOEt, X = 4-$MeC_6H_4$ (**b**); $R^1$ = X = Y = Me, $R^2$ = $R^3$ = H, $R^4$ = COMe (**c**); $R^1$ = X = Me, $R^2$ = $R^3$ = Y = H, $R^4$ = COOEt (**d**); $R^2$ = X = Y = Me, $R^1$ = $R^3$ = H, $R^4$ = COMe (**e**); $R^2$ = X = Me, $R^1$ = $R^3$ = Y = H, $R^4$ = COOEt (**f**); $R^1$ = $R^2$ = X = Y = Me, $R^3$ = H, $R^4$ = COMe (**g**); $R^1$ = $R^2$ = X = Me, $R^3$ = Y = H, $R^4$ = COOEt (**h**); $R^1$ = $R^2$ = X = Me, $R^3$ = H, $R^4$ = COOEt, Y = OMe (**i**); **5**, $R^1$ = Cl, $R^2$ = $R^3$ = H, $R^4$ = COOEt, X = 4-$MeC_6H_4$ (**a**); $R^1$ = Me, $R^2$ = $R^3$ = H, $R^4$ = COOEt, X = 4-$MeC_6H_4$ (**b**); $R^1$ = $R^2$ = $R^3$ = H, $R^4$ = COMe, X = Me (**c**); $R^1$ = X = Me, $R^2$ = $R^3$ = H, $R^4$ = COMe (**d**); $R^2$ = X = Me, $R^1$ = $R^3$ = H, $R^4$ = COMe (**e**); $R^2$ = X = Me, $R^1$ = $R^3$ = H, $R^4$ = COOEt (**f**); $R^1$ = $R^2$ = X = Me, $R^3$ = H, $R^4$ = COMe (**g**); $R^1$ = $R^2$ = X = Me, $R^3$ = H, $R^4$ = COOEt (**h**); $R^2$ = $R^3$ = X = Me, $R^1$ = H, $R^4$ = COOEt (**i**).

The reactions of *N*-trifluoromethanesulfonyl derivatives **1h**–**1k** with enamines **2a** and **2b** were carried out on cooling to –10°C in chloroform or chloroform–acetic acid mixture. Unlike quinone imines **1a**–**1g**, compounds **1h**–**1k** reacted with 4-(4-methylanilino)-pent-3-en-2-one (**2a**) to produce only benzofurans **5j**–**5o**; the reactions of **1h**–**1k** with enamine **2b** in chloroform afforded 1,4-addition products **3b**–**3e**, whereas

**Scheme 2.**

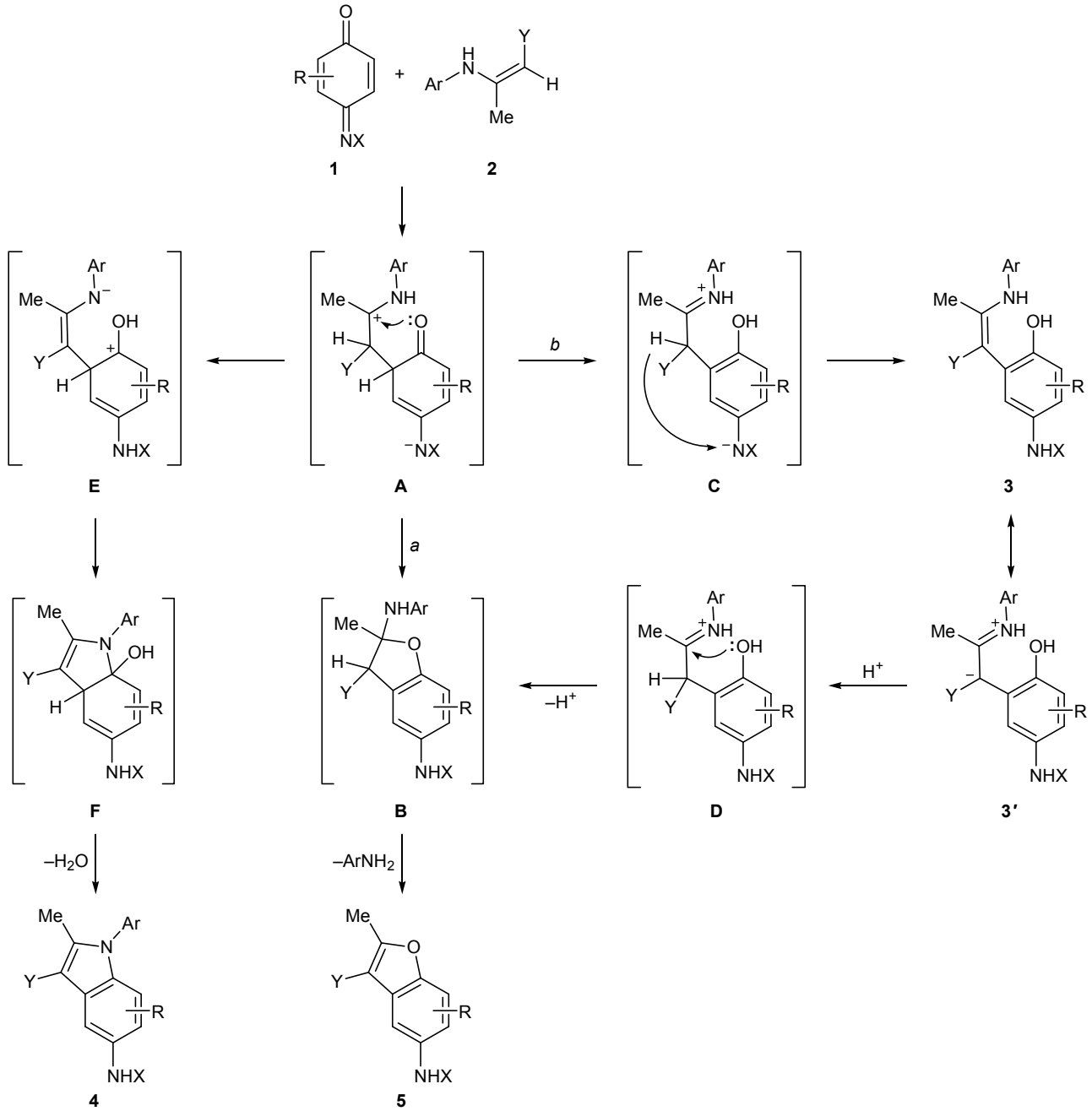



**1**, $R^1$ = $R^2$ = $R^3$ = H (**h**); $R^1$ = Me, $R^2$ = $R^3$ = H (**i**); $R^2$ = Me, $R^1$ = $R^3$ = H (**j**); $R^1$ = $R^2$ = Me, $R^3$ = H (**k**); **3**, $R^1$ = $R^2$ = $R^3$ = H (**b**); $R^1$ = Me, $R^2$ = $R^3$ = H (**c**); $R^2$ = Me, $R^1$ = $R^3$ = H (**d**); $R^1$ = $R^2$ = Me, $R^3$ = H (**e**); **5**, $R^1$ = $R^2$ = $R^3$ = H, $R^4$ = COMe (**j**); $R^1$ = Me, $R^2$ = $R^3$ = H, $R^4$ = COMe (**k**); $R^1$ = Me, $R^2$ = $R^3$ = H, $R^4$ = COOEt (**l**); $R^2$ = Me, $R^1$ = $R^3$ = H, $R^4$ = COMe (**m**); $R^1$ = $R^2$ = Me, $R^3$ = H, $R^4$ = COMe (**n**); $R^1$ = $R^2$ = Me, $R^3$ = H, $R^4$ = COOEt (**o**).

benzofuran derivatives **5j**–**5o** were obtained in a mixture of acetic acid with chloroform (Scheme 2). We failed to obtain indole derivatives from *N*-trifluoromethanesulfonyl derivatives **1h**–**1k**. Compound **3d** underwent hydrolysis during the isolation and purification procedures, so that the isolated product was compound **6a**. Analogous compound was obtained previously [2].

According to published data [5, 15, 16], the first stage of the Nenitzescu reaction of N-substituted 1,4-benzoquinone imines is Michael addition involving the electron-deficient carbon atom of quinone imine **1** and β-carbon atom of enamine **2** with formation of intermediate **A** (Scheme 3). Benzofurans **5** can be formed along two paths. The first path (*a*) includes intermediate **B** which is formed by attack of the lone electron pair on the carbonyl oxygen atom at the electron-deficient α-carbon atom of the enamine fragment, and the subsequent elimination of aromatic amine molecule yields final furan **5**. Following the second

**Scheme 3.**



path (*b*), intermediate **A** is converted to 1,4-addition product **3** through tautomeric structure **C**. Adduct **3** in the form of mesomeric structure **3′** undergoes protonation at the β-carbon atom of the enamine fragment, which bears a partial negative charge. Intermediate **D** thus formed is converted to structure **B** via attack on the α-carbon atom of the enamine fragment by the lone electron pair on the hydroxyl oxygen atom.

Our results suggest that benzofuran derivatives **5l** and **5o** are formed according to path *b*: **A** → **C** → **3** → **3′** → **D** → **B** → **5** (Scheme 3). In fact, compounds **5l** and **5o** were obtained from *N*-trifluoromethanesulfonyl derivatives **1i** and **1k** and ester **2b** only in the presence of acetic acid which favored protonation of the corresponding 1,4-addition products **3**. The formation of benzofurans **5j**, **5k**, **5m**, and **5n** in the absence of acid can be rationalized as follows. The acetyl group is a stronger electron acceptor than COOEt [17], so that the positive charge on the α-carbon atom of the enamine fragment in intermediate **A** derived from enamine **2a** is larger. This makes the attack by the carbonyl oxygen atom more probable, and compounds **5j**, **5k**, **5m**, and **5n** are formed along path *a*: **A** → **B** → **5** (Scheme 3).

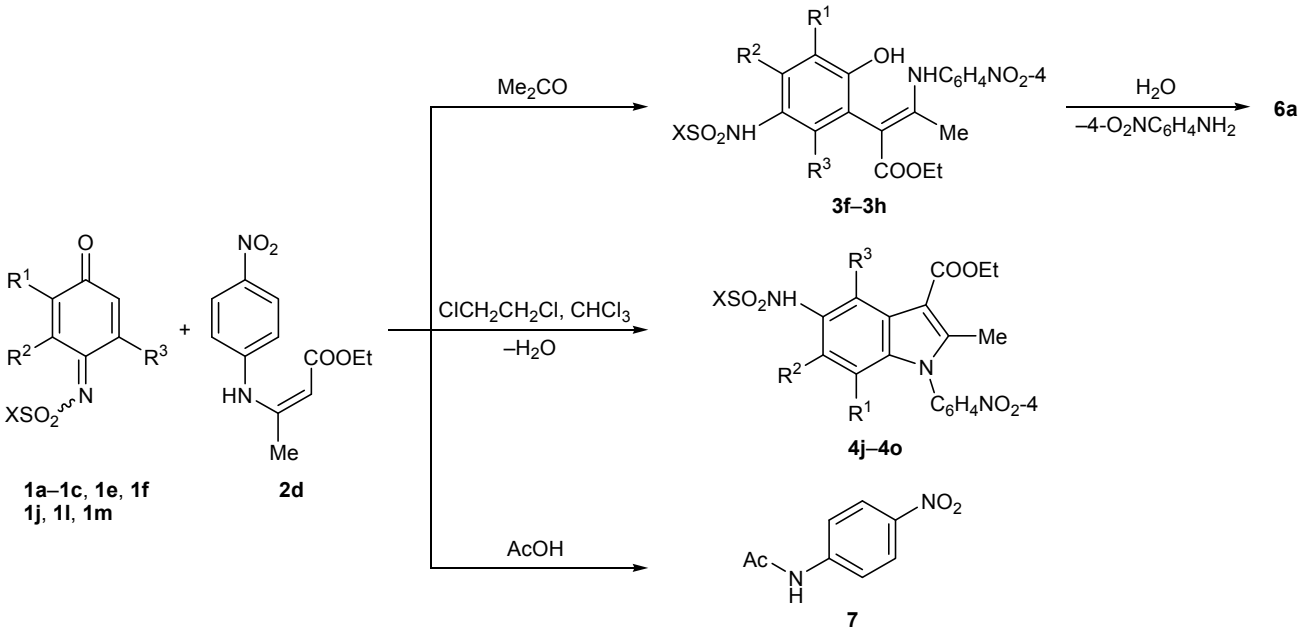
The cyclization to give indole derivatives also involves intermediate **A**. Proton transfer from the β-carbon atom of the enamine fragment to the nitrogen atom linked to the sulfonyl group and from the enamine nitrogen atom to the carbonyl oxygen atom leads to intermediate **E** which undergoes cyclization to structure **F**. Elimination of water molecule from the latter yields indole **4** (Scheme 3).

The fact that no indole derivatives were formed from *N*-trifluoromethanesulfonyl derivatives **1h**–**1k** may be accounted for by strong electron-withdrawing effect of the $CF_3SO_2$ group, which reduces the acidity of the NH proton in the enamine fragment of intermediate **A**, so that intramolecular protonation of the XN group is hindered. Therefore, intermediate **E** cannot be formed, and the formation of benzofuran derivatives **5** becomes predominant.

In keeping with published data, 1,4-benzoquinone imines react with enamines containing a Me, OMe, $NMe_2$, or NHCOMe group in the *para* position of the benzene ring attached to nitrogen to give 5-aminoindole derivatives [4, 5, 7], whereas acceptor substituents in the enamine favor formation of 6-aminoindoles [4].

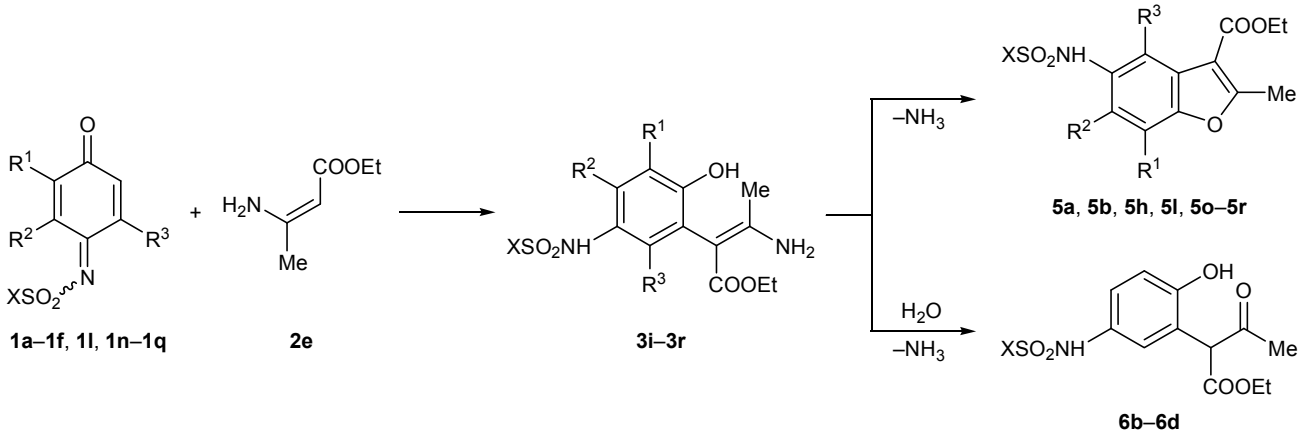
We examined reactions of benzoquinone imines **1a**–**1c**, **1e**, **1f**, **1l**, and **1m** with enamine **2d** containing an electron-withdrawing nitro group in the *para* position of the benzene ring. The reactions in acetone,

**Scheme 4.**




**1**, X = 4-$MeC_6H_4$, $R^1 = R^2 = R^3$ = H (**l**); $R^1 = R^3$ = H, $R^2$ = Me (**m**); **3**, $R^1 = R^2 = R^3$ = H, X = 4-$MeC_6H_4$ (**f**); $R^1 = R^3$ = H, $R^2$ = Me, X = 4-$MeC_6H_4$ (**g**); $R^2$ = Me, $R^1 = R^3$ = H, X = $CF_3$ (**h**); **4**, $R^1 = R^2 = R^3$ = H, X = Me (**j**); $R^1$ = Cl, $R^2 = R^3$ = H, X = 4-$MeC_6H_4$ (**k**); $R^1$ = Me, $R^2 = R^3$ = H, X = 4-$MeC_6H_4$ (**l**); $R^1 = R^3$ = H, $R^2$ = Me, X = 4-$MeC_6H_4$ (**m**); $R^1 = R^3$ = H, $R^2$ = X = Me (**n**); $R^1 = R^2$ = X = Me, $R^3$ = H (**o**).

**Scheme 5.**




**1**, X = 4-MeC$_6$H$_4$ (**n**), Ph (**o**–**q**); $R^1 = R^2 = R^3 = H$ (**o**); $R^1 = H$, $R^2 = R^3 = Me$ (**n**, **p**); $R^1 = R^2 = Me$, $R^3 = H$ (**q**); **3**, X = Ph (**i**), 4-MeC$_6$H$_4$ (**j**, **k**, **r**), Me (**l**–**n**), CF$_3$ (**o**–**q**); $R^1 = R^2 = R^3 = H$ (**i**, **l**, **o**, **r**); $R^1 = Me$, $R^2 = R^3 = H$ (**m**, **p**); $R^1 = Cl$, $R^2 = R^3 = H$ (**j**); $R^1 = R^2 = Me$, $R^3 = H$ (**n**, **q**); $R^1 = H$, $R^2 = R^3 = Me$ (**k**); **5**, X = Ph, $R^1 = R^2 = Me$, $R^3 = H$ (**p**); $R^1 = H$, $R^2 = R^3 = Me$ (**q**); X = Me, $R^1 = Me$, $R^2 = R^3 = H$ (**r**); **6**, X = Ph (**b**), 4-MeC$_6$H$_4$ (**c**), CF$_3$ (**d**).

chloroform, and dichloroethane afforded 1,4-addition products **3f**–**3h** and indoles **4j**–**4o** (Scheme 4). Enamine **2d** in acetic acid underwent hydrolysis followed by acetylation, and the product was *p*-nitroacetanilide **7**. No benzofuran derivatives were obtained from enamine **2d**. In the reaction of quinone imine **1j** with enamine **2d** we isolated a mixture of compound **6a** and *p*-nitroaniline which were formed as a result of hydrolysis of compound **3h**. The reactions of **2d** with quinone imines **1i** and **1k** lead to the formation of noncrystallizable oily products, from which we succeeded in isolating only *p*-nitroaniline. We failed to isolate pure compounds **3g** and **4m**.

Thus, in no case were 6-aminoindole derivatives isolated in the reactions of quinone imines with enamine **2d**: 1,4-addition products and 5-aminoindoles **4** were formed in all solvents, except for acetic acid.

Some *N*-arenesulfonyl-1,4-benzoquinone imines were previously reported to react with ethyl 3-aminobut-2-enoate to give 1,4-addition products [1, 2] whose subsequent treatment with sulfuric, hydrochloric, or acetic acid at different concentrations led to the formation of 2,3-dihydrobenzofuran or benzofuran derivatives, or 2-[1-acetyl-1-(ethoxycarbonyl)methyl]-4-(arenesulfonylamino)phenols analogous to **6a.**

Taking into account that the molecule of ethyl 3-aminobut-2-enoate possesses a free amino group, this enamine was expected to add through the nitrogen atom to quinone imines. We studied the reactions of ethyl 3-aminobut-2-enoate (**2e**) with *N*-arenesulfonyl- and *N*-methanesulfonyl-1,4-benzoquinone imines **1a**–**1f**, **1l**, and **1n**–**1q** in chloroform and acetic acid and with *N*-trifluoromethanesulfonyl analogs **1h**, **1i**, and **1k** in chloroform and chloroform–acetic acid mixture. As reported in [1, 2], all quinone imines in chloroform gave rise to 1,4-addition products **3i**–**3r**. The reactions of substituted quinone imines **1a**, **1b**, **1d**–**1f**, **1i**, **1k**, **1p**, and **1q** with **2e** in acetic acid afforded benzofuran derivatives **5a**, **5b**, **5h**, **5l**, **5o**, and **5p**–**5r**, whereas compounds **1h**, **1l**, and **1o** having no substituents in the quinoid ring were converted to phenols **6b**–**6d** through 1,4-addition products **3i**, **3o**, and **3r** (Scheme 5). Presumably, the hydrolysis of 1,4-addition products **3i**, **3o**,

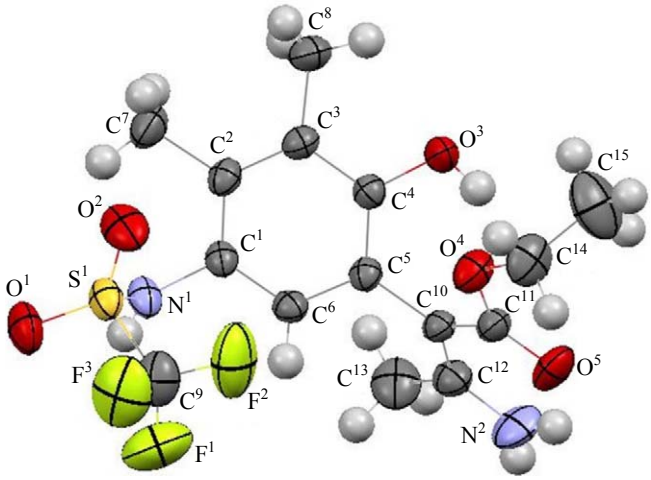



**Fig. 1.** Structure of the molecule of ethyl 3-amino-2-{2-hydroxy-3,4-dimethyl-5-[(trifluoromethanesulfonyl)amino]-phenyl}but-2-enoate (**3q**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

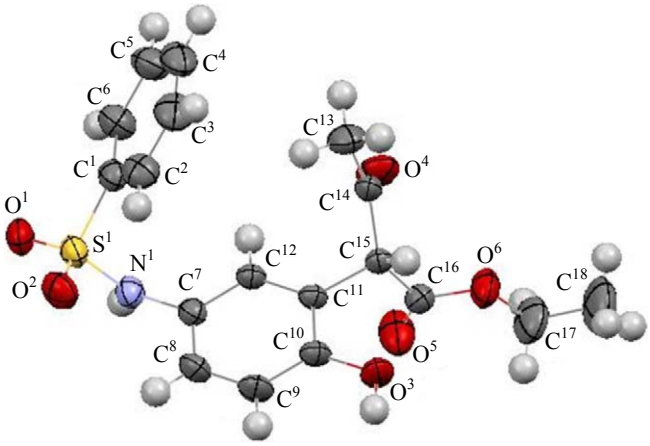



**Fig. 2.** Structure of the molecule of ethyl 2-[5-(benzenesulfonyl)amino]-2-hydroxyphenyl}-3-oxobutanoate (**6b**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

and **3r** derived from unsubstituted quinone imines **1h**, **1l**, and **1o** is faster than the attack of the aromatic hydroxy group on the α-carbon atom of the enamine fragment. Compound **3r** was not isolated.

The structure of compounds **3**–**7** was determined on the basis of their elemental analyses and $^1$H and $^{19}$F NMR and IR spectra. The $^1$H NMR spectra of **4a**–**4o** displayed signals from protons in the $ArSO_2$ or $MeSO_2$ and ArN groups, protons and alkyl substituents in the indole ring, NH proton, and $R^4$. Likewise, signals from the $Ar(Me)SO_2$ group, protons and alkyl substituents in the benzofuran fragment, NH proton, and $R^4$ group were observed in the $^1$H NMR spectra of **5a**–**5o**. In the

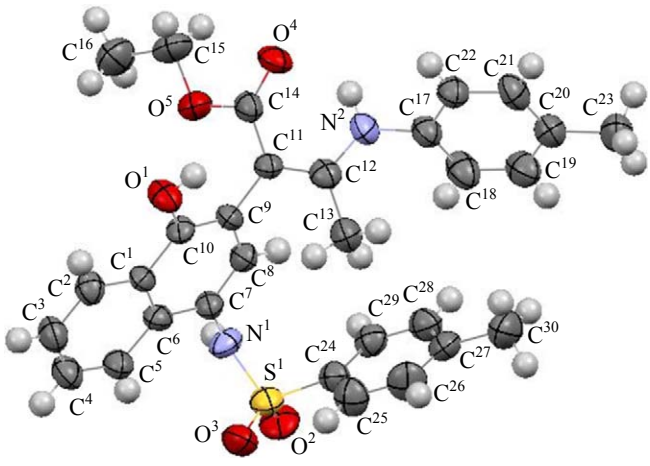



**Fig. 3.** Structure of the molecule of ethyl 2-(1-hydroxy-4-[(4-methylbenzenesulfonyl)amino]naphthalen-2-yl)-3-(4-methylanilino)but-2-enoate (**8**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

$^{19}$F NMR spectra, the $CF_3$ signal of **3b**, **3c**, and **3e** was located at $\delta_F$ –74.59 to –75.53 ppm, and of **5j**–**5o**, at δ –74.89 to –75.96 ppm. Methylene protons of the ester group of **3i**–**3r** appeared in the $^1$H NMR spectra as two quartets at δ 3.81–3.88 and 3.92–4.09 ppm, and the amino group gave two broadened singlets at δ 6.94–7.20 and 7.85–8.41 ppm. The IR spectra of **4a**–**4o**, and **5a**–**5o** contained absorption bands at 3160–3280, 1670–1690, and 1620–1630 cm$^{-1}$ due to stretching vibrations of the NH and ester and ketone carbonyl groups, respectively, whereas no absorption at 3350–3450 cm$^{-1}$ typical of hydroxy group was observed.

The structure of compounds **3q** (Fig. 1) and **6b** (Fig. 2) was unambiguously determined by X-ray analysis. The trifluoromethanesulfonyl group in molecule **3q** is orthogonal to the aromatic ring plane, and the trifluoromethyl group is almost orthogonal to the $C^1$–$N^1$ bond: the torsion angles $C^6C^1N^1S^1$ and $C^1N^1S^1C^9$ are 95.4(2) and –79.2(2)°, respectively. The substituent on $C^5$ is oriented in such a way that its planar conjugated fragment is turned through an appreciable angle with respect to the benzene ring plane [torsion angle $C^6C^5C^{10}C^{12}$ 73.8(2)°], and fairly weak intramolecular hydrogen bond $O^3$–H$\cdots C^{11}$ ($H^{3A}\cdots C^{11}$ 2.79 Å, $\angle O^3HC^{11}$ 128°) is formed. The amino group appears in *s-trans* configuration with respect to the $C^5$–$C^{10}$ bond [torsion angle $C^5C^{10}C^{12}N^2$ –178.9(2)°], which is favored by intramolecular hydrogen bond $N^2$–$H^{2b}\cdots O^5$ ($H^{2b}\cdots O^5$ 1.82 Å, $\angle N^2H^{2b}O^5$ 132°). Furthermore, the amino group is involved in intermolecular hydrogen bond $N^2$–$H^{2A}\cdots O^{2'}$ (1 + *x*, *y*, *z*; $H^{2A}\cdots O^{2'}$ 2.27 Å, $\angle N^2H^{2A}O^{2'}$ 150°). This is likely to be responsible for nonequivalence of the $NH_2$ protons which appear as two broadened singlets in the $^1$H NMR spectrum. The ester ethyl group is *syn-periplanar* with respect to the $C^{11}$–$O^5$ carbonyl group, and the $C^{14}$–$C^{15}$ bond is orthogonal to the planar fragment of the substituent [torsion angles $O^5C^{11}O^4C^{14}$ 5.8(3), $C^{11}O^4C^{14}C^{15}$ 81.9(2)°]. The OH and NH groups participate in intermolecular hydrogen bonds $O^3$–$H^{3A}\cdots O^{1'}$ (0.5 + *x*, 0.5 – *y*, –0.5 + *z*; $H^{3A}\cdots O^{1'}$ 2.26 Å, $\angle O^3H^{3A}O^{1'}$ 149°) and $N^1$–$H^{1A}\cdots O^{5'}$ (1.5 – *x*, –0.5 + *y*, 1.5 – *z*; $H^{1A}\cdots O^{5'}$ 1.88 Å, $\angle N^1H^{1A}O^{5'}$ 166°).

The benzenesulfonyl group in molecule **6b** is oriented in such a way that the torsion angle $C^8C^7N^1S^1$ is 77.9(1)°. The phenyl substituent appears in +*sc* conformation with respect to the $C^7$–$N^1$ bond and is turned with respect to the $N^1$–$S^1$ bond [torsion angles $C^7N^1S^1C^1$ 61.9(1), $N^1S^1C^1C^6$ 78.9(1)°]. The ester fragment is almost orthogonal to the $C^7$–$C^{12}$ aromatic ring and is turned through some angle with respect to the

Crystallographic data and parameters of X-ray diffraction experiments for compounds **3q**, **6b**, and **8**

| Parameter | **3q** | **6b** | **8** |
|---|---|---|---|
| Unit cell parameters | | | |
| *a*, Å | 10.8717(7) | 7.7533(4) | 10.661(3) |
| *b*, Å | 12.4884(9) | 7.9756(5) | 12.306(4) |
| *c*, Å | 13.975(1) | 15.4074(8) | 12.609(3) |
| α, deg | 90.0 | 79.900(5) | 68.55(3) |
| β, deg | 104.357(9) | 81.035(4) | 69.56(3) |
| γ, deg | 90.0 | 77.745(5) | 67.88(3) |
| *V*, Å$^3$ | 1838.1(2) | 909.62(9) | 1382.7(7) |
| *F*(000) | 824 | 396 | 560 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ |
| *Z* | 4 | 2 | 2 |
| Temperature, K | 293 | 293 | 293 |
| μ, mm$^{-1}$ | 0.233 | 0.212 | 0.159 |
| $d_{calc}$, g/cm$^3$ | 1.432 | 1.378 | 1.274 |
| $2\Theta_{max}$, deg | 50 | 60 | 50 |
| Total number of reflections | 6517 | 8370 | 9221 |
| Number of independent reflections | 3194 | 5217 | 4647 |
| $R_{int}$ | 0.032 | 0.017 | 0.130 |
| Number of reflections with $F > 4\sigma(F)$ | 2043 | 4025 | 1807 |
| Number of variables | 253 | 237 | 348 |
| $R_1$ | 0.050 | 0.045 | 0.073 |
| $wR_2$ | 0.150 | 0.145 | 0.141 |
| Goodness of fit *S* | 1.000 | 0.995 | 0.843 |
| CCDC entry no. | 1473884 | 1473885 | 1473886 |

$C^{11}$–$C^{15}$ bond [torsion angles $C^{10}C^{11}C^{15}C^{16}$ 78.0(1), $C^{11}C^{15}C^{16}O^5$ 28.8(2)°]. The orientation of the acyl group with respect to the endocyclic $C^{10}$–$C^{11}$ bond is close to *antiperiplanar* [torsion angle $C^{10}C^{11}C^{15}C^{14}$ –157.9(1)°], and the torsion angle $C^{11}C^{15}C^{14}O^4$ is –108.2(1)°. The acetyl methyl group and the π-system of the phenyl substituent on the sulfur atom are oriented pseudo-*cis* with respect to the $C^7\cdots C^{12}$ ring and are located close to each other. As a result, the methyl proton singlet of **6b** and **6c** is observed in a stronger field (δ 1.96 ppm) relative to the corresponding signal of trifluoromethanesulfonyl derivatives **6a** or **6d** (δ 2.13–2.14 ppm). Molecules **6b** in crystal are linked to form chains through intermolecular hydrogen bonds $O^3$–$H^{3A}\cdots O^{4'}$ ($x-1$, $y$, $z$; $H^{3A}\cdots O^{4'}$ 1.90 Å, $\angle O^3H^{3A}O^{4'}$ 171°) and $N^1$–$H^{1A}\cdots O^{1'}$ ($2-x$, $1-y$, $-z$; $H^{1A}\cdots O^{1'}$ 2.35 Å, $\angle N^1H^{1A}O^{1'}$ 125°).

We also performed X-ray analysis of ethyl 3-(4-methylanilino)-2-[1-hydroxy-4-(4-methylbenzenesulfonylamino)naphthalen-2-yl]but-2-enoate (**8**) synthesized previously [5] (Fig. 3) in order to compare structural parameters of 1,4-addition products derived from *N*-substituted 1,4-benzoquinone imine and 1,4-naphthoquinone imine. The tosyl group in molecule **8** is orthogonal to the naphthalene plane [torsion angle $C^6C^7N^1S^1$ –88.0(5)°]. The tolyl substituent appears in –*sc* conformation with respect to the $C^7$–$N^1$ bond and is turned with respect to the $N^1$–$S^1$ bond [torsion angles $C^7N^1S^1C^{24}$ –59.3(4), $N^1S^1C^{24}C^{29}$ –63.5(4)°]. The planar fragment of the substituent on $C^9$ (including the $C^{11}$=$C^{12}$ double bond and ester, methyl, and NH groups) is additionally stabilized by intramolecular hydrogen bond $N^2$–$H^{2A}\cdots O^4$ ($H^{2A}\cdots O^4$ 1.98 Å, $\angle N^2H^{2A}O^4$ 135°) and is oriented almost ortho-

gonally to the naphthalene fragment [torsion angle $C^{10}C^{9}C^{11}C^{12}$ 112.2(5)°]. The tolyl substituent on $N^2$ is *antiperiplanar* with respect to the $C^{11}=C^{12}$ bond and is turned relative to the above planar fragment to form torsion angles $C^{11}C^{12}N^{2}C^{17}$ –167.1(4) and $C^{12}N^{2}C^{17}C^{18}$ 43.6(7)°. As in molecule **6b**, the $C^{13}$ methyl group in **8** is spatially close to the $C^{24}$–$C^{29}$ aromatic π-system, so that protons on $C^{13}$ resonate in a strong field (δ 1.61–1.66 ppm) in the $^1$H NMR spectrum [5]. The $C^{11}=C^{12}$, $C^{12}$–$N^2$, and $C^{11}$–$C^{14}$ bond lengths in molecule **8** are 1.367, 1.360, and 1.445 Å, respectively (cf. the $C^{10}=C^{12}$, $C^{12}$–$N^2$, and $C^{10}$–$C^{11}$ bond lengths in **3q**: 1.372, 1.338, and 1.441 Å, respectively); these values are typical of such compounds. Molecules **8** in crystal are linked to chains through intermolecular hydrogen bonds $O^1$–$H^{1B}\cdots O^{4'}$ (1 – *x*, –*y*, 1 – *z*; $H^{1B}\cdots O^{4'}$ 2.11 Å, $\angle O^1H^{1B}O^{4'}$ 146°) and $N^1$–$H^{1A}\cdots O^{2'}$ (–*x*, 2 – *y*, 2 – *z*; $H^{1A}\cdots O$ 2.26 Å, $\angle NH^{1A}O$ 148°).

PASS online prediction [18] of biological activity of compounds **3**–**7** revealed antiarrhythmic, cardiotonic, and antineoplastic (brain cancer, colorectal cancer) activities with probabilities of 0.805–0.901, 0.805–0.876, and 0.707–0.880, respectively.

In summary, reactions of *N*-methanesulfonyl-, *N*-trifluoromethanesulfonyl-, and *N*-arenesulfonyl-1,4-benzoquinone imines gave 1,4-addition products and indole and benzofuran derivatives. The reaction direction is determined by the solvent nature, electron-withdrawing power of the substituent on the quinone imine nitrogen atom, and enamine structure. Introduction of a strong electron-withdrawing trifluoromethanesulfonyl group to the nitrogen atom favors formation of 1,4-addition products and benzofuran derivatives.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz) using tetramethylsilane as internal standard and DMSO-$d_6$ as solvent. The $^{19}$F NMR spectra of compounds **3b**–**3e**, **5j**–**5o**, **6a**, and **6d** were measured on a Varian Gemini-200 instrument at 188.14 MHz relative to trichloro(fluoro)methane. The IR spectra were recorded in KBr on a UR-20 spectrometer. The purity of the initial compounds and reaction products was checked by TLC on Silufol UV-254 plates; samples were applied from solutions in acetone or THF, and ethanol–chloroform (1 : 10) and hexane–ethyl acetate (1 : 2) were used as eluents; spots were visualized under UV light.

Initial quinone imines **1a**, **1o** [19], **1b**, **1m** [20], **1c**–**1k** [13], **1l** [21], **1q** [22], **1n**, and **1p** [23] were described previously.

The X-ray diffraction data for compounds **3q**, **6b**, and **8** were obtained on an Xcalibur-3 diffractometer (Mo $K_\alpha$ radiation, CCD detector, graphite monochromator, ω-scanning). The structures were solved by the direct method implemented in SHELXTL [24]. The positions of hydrogen atoms were determined from the difference electron density maps and were refined according to the riding model ($U_{iso} = nU_{eq}$, where $n$ = 1.5 for methyl and hydroxy groups, and $n$ = 1.2 for other hydrogen atoms). The crystallographic data and experimental parameters are given in table. The coordinates of atoms and complete tables of bond lengths and bond angles for compounds **3q**, **6b**, and **8** were deposited to the Cambridge Crystallographic Data Centre (e-mail: deposit@ccdc.cam.ac.uk); CCDC entry numbers are given in table.

**Reaction of quinone imines 1a–1q with enamines 2a–2e (***general procedures***).** *a*. A mixture of 1.5 mmol of quinone imine **1a**–**1e**, **1l**, or **1m** and 1.7 mmol of enamine **2a**–**2d** in 40 mL of 1,2-dichloroethane was refluxed for 1 h. The solvent was distilled off under reduced pressure, a few drops of ethanol were added to the brown oily residue, and the light brown precipitate was filtered off and washed with a small amount of ethanol.

*b*. A solution of 1.7 mmol of enamine **2a**–**2e** in 10 mL of acetone or chloroform was added to a solution of 1.5 mmol of quinone imine **1a**–**1q** in 10 mL of the same solvent. The solution immediately turned dark brown. Evaporation of the mixture left a light solid. If the residue was oily, it was treated with a few drops of ethanol, the mixture was stirred, and the precipitate was filtered off and washed with a small amount of ethanol.

*c*. Enamine **2a**–**2e**, 1.7 mmol, was added to a suspension or solution of 1.5 mmol of quinone imine **1a**–**1i**, **1l**, or **1m**–**1q** in 10 mL of glacial acetic acid. The mixture immediately turned dark brown. After a time (several minutes to several hours), a light solid precipitated. In same cases, water was added dropwise to initiate precipitation. The product was filtered off and washed with a small amount of ethanol.

*d*. A solution of 1.7 mmol of enamine **2a**–**2e** in 10 mL of glacial acetic acid was added at room temperature or on cooling to –10°C to a solution of 1.5 mmol of quinone imine **1h**–**1k** in 10 mL of chloroform or chloroform–acetic acid mixture. The solution

immediately turned dark brown or violet. After 24 h, the mixture was evaporated, and the light precipitate was filtered off and washed with a small amount of ethanol.

All isolated compounds were recrystallized from ethanol, hexane, aqueous ethanol (1:1), or benzene–hexane (1:2).

***N*-{4-Hydroxy-3-[2-(4-methylanilino)-4-oxopent-2-en-3-yl]phenyl}methanesulfonamide (3a).** Yield 65%, mp 151–153°C. $^1$H NMR spectrum, δ, ppm: 1.71 s (3H, COMe), 1.78 s (3H, C=CMe), 2.31 s (3H, **Me**$C_6H_4$), 2.87 s (3H, $MeSO_2$), 6.86 d (1H, 6-H, $J_{6,5}$ = 8.4 Hz), 6.95 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 7.01–7.03 d.d (1H, 5-H), 7.10 d (2H, 3′-H, 5′-H, $J$ = 8.0 Hz), 7.23 d (2H, 2′-H, 6′-H, $J$ = 8.0 Hz), 9.21 br.s (2H, NH), 13.51 s (1H, OH). Found, %: N 7.40, 7.45; S 8.54, 8.60. $C_{19}H_{22}N_2O_4S$. Calculated, %: N 7.48; S 8.56.

**Ethyl 3-anilino-2-{2-hydroxy-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3b).** Yield 37%, mp 68–70°C. $^1$H NMR spectrum, δ, ppm: 1.07 t (3H, $CH_2$**Me**, $J$ = 6.8 Hz), 1.70 s (3H, C=CMe), 4.01 q (2H, $OCH_2$), 6.69 d (1H, 6-H, $J_{6,5}$ = 8.1 Hz), 6.72 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 7.00–7.02 d.d (1H, 5-H), 7.19–7.42 m (5H, Ph), 8.40 s (1H, NH), 10.01 br.s (1H, NH), 11.33 s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.48 ppm, s. Found, %: N 6.25, 6.55; S 8.50, 8.62. $C_{19}H_{19}F_3N_2O_5S$. Calculated, %: N 6.30; S 8.56.

**Ethyl 3-anilino-2-{2-hydroxy-3-methyl-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3c).** Yield 54%, mp 137–139°C. $^1$H NMR spectrum, δ, ppm: 1.07 t (3H, $CH_2$**Me**, $J$ = 7.2 Hz), 1.70 s (3H, C=CMe), 2.17 s (3H, 2-Me), 4.00 q (2H, $OCH_2$), 6.73 d (1H, 5-H, $J_{5,3}$ = 1.4 Hz), 6.91 d (1H, 3-H), 7.18–7.41 m (5H, Ph), 8.32 s (1H, NH), 8.44 s (1H, NH), 11.31 s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –74.59 ppm, s. Found, %: N 6.07, 6.12; S 6.90, 6.95. $C_{20}H_{21}F_3N_2O_5S$. Calculated, %: N 6.11; S 6.99.

**Ethyl 3-anilino-2-{2-hydroxy-3,4-dimethyl-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3e).** Yield 62%, mp 81–83°C. $^1$H NMR spectrum, δ, ppm: 1.07 t (3H, $CH_2$**Me**, $J$ = 6.8 Hz), 1.70 s (3H, C=CMe), 2.14 s (3H, 2-Me), 2.20 s (3H, 3-Me), 3.99 q (2H, $OCH_2$), 6.72 s (1H, 5-H), 7.16–7.41 m (5H, Ph), 8.39 s (1H, NH), 10.32 br.s (1H, NH), 11.32 s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.53 ppm, s. Found, %: N 5.89, 5.95; S 6.80, 6.85. $C_{21}H_{23}F_3N_2O_5S$. Calculated, %: N 5.93; S 6.79.

**Ethyl 2-{2-hydroxy-5-[(4-methylbenzenesulfonyl)amino]phenyl}-3-(4-nitroanilino)but-2-enoate (3f).** Yield 71%, mp 158–159°C. $^1$H NMR spectrum, δ, ppm: 1.02 t (3H, $CH_2$**Me**, $J$ = 5.4 Hz), 1.72 s (3H, C=CMe), 2.32 s (3H, **Me**$C_6H_4$), 3.99 q (2H, $OCH_2$), 6.67 d (1H, 6-H, $J_{6,5}$ = 7.8 Hz), 6.70 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 6.79–6.81 d.d (1H, 5-H), 7.28 d (2H, 3″-H, 5″-H, $J$ = 7.8 Hz), 7.33 d (2H, 2″-H, 6″-H, $J$ = 7.8 Hz), 7.53 d (2H, 3′-H, 5′-H, $J$ = 6.8 Hz), 8.18 d (2H, 2′-H, 6′-H, $J$ = 6.8 Hz), 9.10 s (1H, NH), 9.61 s (1H, NH), 11.34 s (1H, OH). Found, %: N 8.17, 8.25; S 6.20, 6.24. $C_{25}H_{25}N_3O_7S$. Calculated, %: N 8.21; S 6.27.

**Ethyl 2-{2-hydroxy-5-[(4-methylbenzenesulfonyl)amino]-4-methylphenyl)-3-(4-nitroanilino)-but-2-enoate (3g).** $^1$H NMR spectrum, δ, ppm: 1.05 t (3H, $CH_2$**Me**, $J$ = 6.4 Hz), 1.75 s (3H, C=CMe), 1.93 s (3H, 3-Me), 2.36 s (3H, **Me**$C_6H_4$), 3.99 q (2H, $OCH_2$), 6.53 s (1H, 2-H), 6.58 s (1H, 5-H), 7.27 d (2H, 3″-H, 5″-H, $J$ = 8.7 Hz), 7.34 d (2H, 2″-H, 6″-H, $J$ = 8.7 Hz), 7.51 d (2H, 3′-H, 5′-H, $J$ = 8.4 Hz), 8.19 d (2H, 2′-H, 6′-H, $J$ = 8.4 Hz), 9.15 s (1H, NH), 9.16 s (1H, NH), 11.30 s (1H, OH).

**Ethyl 3-amino-2-{5-[(benzenesulfonyl)amino]-2-hydroxyphenyl}but-2-enoate (3i).** Yield 68%, mp 120–122°C. $^1$H NMR spectrum, δ, ppm: 0.98 t (3H, $CH_2$**Me**, $J$ = 7.2 Hz), 1.37 s (3H, MeC=C), 3.86 m and 3.92 m (1H each, $OCH_2$), 6.53 d (1H, 3-H, $J_{3,5}$ = 2.4 Hz), 6.60 d (1H, 6-H, $J_{6,5}$ = 7.8 Hz), 6.75–6.77 d.d (1H, 5-H), 7.47–7.64 m (5H, Ph), 8.35 br.s (2H, $NH_2$), 8.76 s (1H, NH), 9.60 br.s (1H, OH). Found, %: N 7.32, 7.55; S 8.48, 8.54. $C_{18}H_{20}N_2O_5S$. Calculated, %: N 7.44; S 8.52.

**Ethyl 3-amino-2-{3-chloro-2-hydroxy-5-[(4-methylbenzenesulfonyl)amino]phenyl}but-2-enoate (3j).** Yield 61%, mp 102–104°C. $^1$H NMR spectrum, δ, ppm: 0.98 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.37 s (3H, MeC=C), 2.33 s (3H, **Me**$C_6H_4$), 3.88 m and 4.09 m (1H each, $OCH_2$), 6.52 s (1H, 4-H), 6.93 s (1H, 6-H), 7.20 br.s (1H, $NH_2$), 7.37 d (2H, 3″-H, 5″-H, $J$ = 8.1 Hz), 7.52 d (2H, 2″-H, 6″-H, $J$ = 8.1 Hz), 8.45 br.s (1H, $NH_2$), 8.71 s (1H, NH), 9.77 br.s (1H, OH). Found, %: N 6.51, 6.64; S 7.48, 7.54. $C_{19}H_{21}ClN_2O_5S$. Calculated, %: N 6.59; S 7.55.

**Ethyl 3-amino-2-{6-hydroxy-2,4-dimethyl-3-[(4-methylbenzenesulfonyl)amino]phenyl}but-2-enoate (3k).** Yield 85%, mp 210–212°C. $^1$H NMR spectrum, δ, ppm: 0.98 t (3H, $CH_2$**Me**, $J$ = 7.2 Hz), 1.45 s (3H, MeC=C), 1.53 s (3H, 3-Me), 1.93 s (3H, 5-Me), 3.94 m (2H, $OCH_2$), 6.44 s (1H, 6-H), 6.94 br.s (1H, $NH_2$), 7.32 d (2H, 3″-H, 5″-H, $J$ = 8.4 Hz), 7.47 d (2H, 2″-H, 6″-H, $J$ = 8.4 Hz), 8.36 br.s (1H, $NH_2$), 8.60 s (1H, NH), 8.90 br.s (1H, OH). Found, %: N 6.51,

6.64; S 7.58, 7.64. $C_{21}H_{26}N_2O_5S$. Calculated, %: N 6.69; S 7.66.

**Ethyl 3-amino-2-{2-hydroxy-5-[(methanesulfonyl)amino]phenyl}but-2-enoate (3l).** Yield 72%, mp 174–175°C. $^1$H NMR spectrum, δ, ppm: 1.02 t (3H, $CH_2$**Me**, $J$ = 7.2 Hz), 1.62 s (3H, MeC=C), 2.82 s (3H, $MeSO_2$), 3.86 m and 3.95 m (1H each, $OCH_2$), 6.71 d (1H, 3-H, $J_{3,4}$ = 8.4 Hz), 6.81 d (1H, 6-H, $J_{4,6}$ = 1.8 Hz), 6.88–6.91 d.d (1H, 4-H, $J$ = 1.8, 8.4 Hz), 7.02 br.s and 8.41 br.s (1H each, $NH_2$), 8.81 s (1H, NH), 9.05 br.s (1H, OH). Found, %: N 8.71, 8.95; S 10.09, 10.16. $C_{13}H_{18}N_2O_5S$. Calculated, %: N 8.91; S 10.20.

**Ethyl 3-amino-2-{2-hydroxy-5-[(methanesulfonyl)amino]-3-methylphenyl}but-2-enoate (3m).** Yield 74%, mp 165–167°C. $^1$H NMR spectrum, δ, ppm: 1.02 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.59 s (3H, MeC=C), 2.12 s (3H, 3-Me), 2.82 s (3H, $MeSO_2$), 3.86 m and 3.97 m (1H each, $OCH_2$), 6.64 d (1H, 4-H, $J_{4,6}$ = 1.8 Hz), 6.81 d (1H, 6-H), 7.12 br.s and 7.83 s (1H each, $NH_2$), 8.49 br.s (1H, NH), 9.00 br.s (1H, OH). Found, %: N 8.31, 8.52; S 9.68, 9.74. $C_{14}H_{20}N_2O_5S$. Calculated, %: N 8.53; S 9.76.

**Ethyl 3-amino-2-{2-hydroxy-5-[(methanesulfonyl)amino]-3,4-dimethylphenyl}but-2-enoate (3n).** Yield 68%, mp 197–199°C. $^1$H NMR spectrum, δ, ppm: 1.02 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.59 s (3H, MeC=C), 2.09 s (3H, 3-Me), 2.17 s (3H, 4-Me), 2.83 s (3H, $MeSO_2$), 3.97 m (2H, $CH_2$Me), 6.67 s (1H, 6-H), 7.14 br.s and 7.85 s (1H each, $NH_2$), 8.52 br.s (1H, NH), 8.61 br.s (1H, OH). Found, %: N 8.01, 8.19; S 9.28, 9.35. $C_{15}H_{22}N_2O_5S$. Calculated, %: N 8.18; S 9.36.

**Ethyl 3-amino-2-{2-hydroxy-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3o).** Yield 53%, mp 124–126°C. $^1$H NMR spectrum, δ, ppm: 1.01 t (3H, $CH_2$**Me**, $J$ = 7.2 Hz), 1.60 s (3H, MeC=C), 3.87 m and 3.95 m (1H each, $OCH_2$), 6.77 d (1H, 3-H, $J_{3,4}$ = 8.4 Hz), 6.78 d (1H, 6-H, $J_{4,6}$ = 1.8 Hz), 6.92–6.94 d.d (1H, 4-H, $J$ = 1.8, 8.4 Hz), 7.06 br.s and 8.41 br.s (1H each, $NH_2$), 9.11 s (1H, NH), 11.32 br.s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.96 ppm, s. Found, %: N 7.54, 7.77; S 8.59, 8.72. $C_{13}H_{15}F_3N_2O_5S$. Calculated, %: N 7.61; S 8.71.

**Ethyl 3-amino-2-{2-hydroxy-3-methyl-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3p).** Yield 71%, mp 178–179°C. $^1$H NMR spectrum, δ, ppm: 1.01 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.56 s (3H, MeC=C), 2.13 s (3H, 3-Me), 3.86 m and 3.99 m (1H each, $OCH_2$), 6.63 d (1H, 4-H, $J_{4,6}$ = 1.8 Hz), 6.85 d (1H, 6-H), 7.18 br.s and 8.14 s (1H each, $NH_2$), 8.51 br.s (1H, NH), 11.23 br.s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.33 ppm, s. Found, %: N 7.21, 7.45; S 8.30, 8.42. $C_{14}H_{17}F_3N_2O_5S$. Calculated, %: N 7.33; S 8.39.

**Ethyl 3-amino-2-{2-hydroxy-3,4-dimethyl-5-[(trifluoromethanesulfonyl)amino]phenyl}but-2-enoate (3q).** Yield 83%, mp 203–204°C. $^1$H NMR spectrum, δ, ppm: 1.01 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.56 s (3H, MeC=C), 2.11 s (3H, 3-Me), 2.17 s (3H, 4-Me), 3.86 m and 3.96 m (1H each, $OCH_2$), 6.61 s (1H, 6-H), 7.16 br.s and 8.07 s (1H each, $NH_2$), 8.52 br.s (1H, NH), 10.91 br.s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.79 ppm, s. Found, %: N 6.98, 7.10; S 7.97, 8.11. $C_{15}H_{19}F_3N_2O_5S$. Calculated, %: N 7.07; S 8.09.

**Ethyl 7-chloro-2-methyl-5-[(4-methylbenzenesulfonyl)amino]-1-phenyl-1*H*-indole-3-carboxylate (4a).** Yield 68%, mp 229–231°C. $^1$H NMR spectrum, δ, ppm: 1.37 t (3H, $CH_2$**Me**, $J$ = 6.9 Hz), 2.32 s (3H, **Me**$C_6H_4$), 2.33 s (3H, 2-Me), 4.30 q (2H, $OCH_2$), 6.93 s (1H, 6-H), 7.35 d (2H, 3″-H, 5″-H, $J$ = 7.8 Hz), 7.39–7.55 m (5H, Ph), 7.67 d (2H, 2″-H, 6″-H, $J$ = 7.8 Hz), 7.92 s (1H, 4-H), 10.02 br.s (1H, NH). Found, %: N 5.79, 5.81; S 6.60, 6.66. $C_{25}H_{23}ClN_2O_4S$. Calculated, %: N 5.80; S 6.64.

**Ethyl 2,7-dimethyl-5-[(4-methylbenzenesulfonyl)amino]-1-phenyl-1*H*-indole-3-carboxylate (4b).** Yield 53%, mp 207–209°C. $^1$H NMR spectrum, δ, ppm: 1.35 t (3H, $CH_2$**Me**, $J$ = 6.9 Hz), 1.64 s (3H, 7-Me), 2.32 s (3H, 2-Me), 4.29 q (2H, $OCH_2$), 6.67 s (1H, 6-H), 7.33 d (2H, 3″-H, 5″-H, $J$ = 8.1 Hz), 7.41–7.58 m (5H, Ph), 7.66 d (2H, 2″-H, 6″-H, $J$ = 8.1 Hz), 7.76 s (1H, 4-H), 10.02 br.s (1H, NH). Found, %: N 6.01, 6.10; S 6.88, 6.95. $C_{26}H_{26}N_2O_4S$. Calculated, %: N 6.06; S 6.93.

***N*-[3-Acetyl-2,7-dimethyl-1-(4-methylphenyl)-1*H*-indol-5-yl]methanesulfonamide (4c).** Yield 89%, mp 186–189°C. $^1$H NMR spectrum, δ, ppm: 1.74 s (3H, 7-Me), 2.37 s (3H, 2-Me), 2.45 s (3H, **Me**$C_6H_4$), 2.56 s (3H, COMe), 2.91 (3H, $MeSO_2$), 6.82 br.s (1H, 6-H), 7.34 d (2H, 3′-H, 5′-H, $J$ = 8.2 Hz), 7.40 d (2H, 2′-H, 6′-H, $J$ = 8.2 Hz), 7.98 br.s (1H, 4-H), 9.42 br.s (1H, NH). Found, %: N 7.50, 7.58; S 7.08, 7.16. $C_{20}H_{22}N_2O_3S$. Calculated, %: N 7.56; S 7.15.

**Ethyl 5-[(methanesulfonyl)amino]-2,7-dimethyl-1-phenyl-1*H*-indole-3-carboxylate (4d).** Yield 41%, mp 191–193°C. $^1$H NMR spectrum, δ, ppm: 1.38 t

(3H, $CH_2$**Me**, *J* = 6.8 Hz), 1.73 s (3H, 7-Me), 2.38 s (3H, 2-Me), 2.91 s (3H, $MeSO_2$), 4.31 q (2H, $OCH_2$), 6.81 br.s (1H, 6-H), 7.48–7.62 m (5H, Ph), 7.94 br.s (1H, 4-H), 9.47 br.s (1H, NH). Found, %: N 7.20, 7.26; S 8.28, 8.36. $C_{20}H_{22}N_2O_4S$. Calculated, %: N 7.25; S 8.30.

***N*-[3-Acetyl-2,6-dimethyl-1-(4-methylphenyl)-1*H*-indol-5-yl]methanesulfonamide (4e).** Yield 85%, mp 211–213°C. $^1$H NMR spectrum, δ, ppm: 2.33 s (3H, 2-Me), 2.44 s (3H, **Me**$C_6H_4$), 2.48 s (3H, 6-Me), 2.58 s (3H, COMe), 2.97 s (3H, $MeSO_2$), 6,81 s (1H, 7-H), 7.31 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.45 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 8.04 s (1H, 4-H), 9.01 br.s (1H, NH). Found, %: N 7.54, 7.58; S 8.61, 8.65. $C_{20}H_{22}N_2O_3S$. Calculated, %: N 7.56; S 8.66.

**Ethyl 5-[(methanesulfonyl)amino]-2,6-dimethyl-1-phenyl-1*H*-indole-3-carboxylate (4f).** Yield 90%, mp 167–168°C. $^1$H NMR spectrum, δ, ppm: 1.38 t (3H, $CH_2$**Me**, *J* = 5.4 Hz), 2.33 s (3H, 2-Me), 2.50 s (3H, 6-Me), 2.97 s (3H, $MeSO_2$), 4.33 q (2H, $OCH_2$), 6.84 s (1H, 7-H), 7.45–7.67 m (5H, Ph), 8.01 s (1H, 4-H), 9.00 br.s (1H, NH). Found, %: N 7.18, 7.25; S 8.24, 8.28. $C_{20}H_{22}N_2O_4S$. Calculated, %: N 7.25; S 8.30.

***N*-[3-Acetyl-2,6,7-trimethyl-1-(4-methylphenyl)-1*H*-indol-5-yl]methanesulfonamide (4g).** Yield 83%, mp 165–167°C. $^1$H NMR spectrum, δ, ppm: 1.67 s (3H, 7-Me), 2.20 s (3H, 6-Me), 2.31 s (3H, 2-Me), 2.40 s (3H, **Me**$C_6H_4$), 2.52 s (3H, COMe), 2.91 s (3H, $MeSO_2$), 7.24 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.36 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.96 s (1H, 4-H), 8.99 br.s (1H, NH). Found, %: N 7.28, 7.31; S 8.34, 8.38. $C_{21}H_{24}N_2O_3S$. Calculated, %: N 7.29; S 8.34.

**Ethyl 5-[(methanesulfonyl)amino]-2,6,7-trimethyl-1-phenyl-1*H*-indole-3-carboxylate (4h).** Yield 87%, mp 154–155°C. $^1$H NMR spectrum, δ, ppm: 1.38 t (3H, $CH_2$**Me**, *J* = 6.4 Hz), 1.70 s (3H, 7-Me), 2.24 s (3H, 6-Me), 2.37 s (3H, 2-Me), 2.95 s (3H, $MeSO_2$), 4.32 q (2H, $OCH_2$), 7.44–7.61 m (5H, Ph), 7.96 s (1H, 4-H), 9.03 br.s (1H, NH). Found, %: N 6.95, 7.02; S 7.97, 8.02. $C_{21}H_{24}N_2O_4S$. Calculated, %: N 6.99; S 8.01.

**Ethyl 5-[(methanesulfonyl)amino]-1-(4-methoxyphenyl)-2,6,7-trimethyl-1*H*-indole-3-carboxylate (4i).** Yield 84%, mp 174–176°C. $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, $CH_2$**Me**, *J* = 6.8 Hz), 1.74 s (3H, 7-Me), 2.23 s (3H, 6-Me), 2.36 s (3H, 2-Me), 2.94 s (3H, $MeSO_2$), 3.86 s (3H, MeO), 4.30 q (2H, $OCH_2$), 7.14 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 7.36 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz), 7.94 s (1H, 4-H), 9.03 br.s (1H, NH). Found, %: N 6.45, 6.50; S 7.39, 7.43. $C_{22}H_{26}N_2O_5S$. Calculated, %: N 6.51; S 7.45.

**Ethyl 5-[(methanesulfonyl)amino]-2-methyl-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate 4(j).** Yield 74%, mp 217–219°C. $^1$H NMR spectrum, δ, ppm: 1.40 t (3H, $CH_2$**Me**, *J* = 6.8 Hz), 2.57 s (3H, 2-Me), 2.92 s (3H, $MeSO_2$), 4.33 q (2H, $OCH_2$), 7.07 d (1H, 7-H, $J_{7,6}$ = 8.4 Hz), 7.10–7.13 d.d (1H, 6-H, $J_{6,4}$ = 1.2 Hz), 7.83 d (2H, 3′-H, 5′-H, *J* = 8.0 Hz), 8.04 d (1H, 4-H), 8.47 d (2H, 2′-H, 6′-H, *J* = 8.0 Hz), 9.59 br.s (1H, NH). Found, %: N 10.01, 10.10; S 7.59, 7.65. $C_{19}H_{19}N_3O_6S$. Calculated, %: N 10.07; S 7.68.

**Ethyl 7-chloro-2-methyl-5-[(4-methylbenzenesulfonyl)amino]-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate (4k).** Yield 69%, mp 229–230°C. $^1$H NMR spectrum, δ, ppm: 1.39 t (3H, $CH_2$**Me**, *J* = 6.1 Hz), 2.34 s (3H, **Me**$C_6H_4$), 2.38 s (3H, 2-Me), 4.33 q (2H, $OCH_2$), 6.98 br.s (1H, 6-H), 7.37 d (2H, 3″-H, 5″-H, *J* = 7.5 Hz), 7.68 d (2H, 2″-H, 6″-H, *J* = 7.5 Hz), 7.79 d (2H, 3′-H, 5′-H, *J* = 7.8 Hz), 7.95 br.s (1H, 4-H), 8.40 d (2H, 2′-H, 6′-H, *J* = 7.8 Hz), 10.36 br.s (1H, NH). Found, %: N 7.91, 7.95; S 6.01, 6.08. $C_{25}H_{22}ClN_3O_6S$. Calculated, %: N 7.96; S 6.07.

**Ethyl 2,7-dimethyl-5-[(4-methylbenzenesulfonyl)amino]-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate (4l).** Yield 51%, mp 244–246°C. $^1$H NMR spectrum, δ, ppm: 1.34 t (3H, $CH_2$**Me**, *J* = 6.1 Hz), 1.67 s (3H, 7-Me), 2.32 s (3H, **Me**$C_6H_4$), 2.33 s (3H, 2-Me), 4.29 q (2H, $OCH_2$), 6.70 br.s (1H, 6-H), 7.32 d (2H, 3″-H, 5″-H, *J* = 7.5 Hz), 7.64 d (2H, 2″-H, 6″-H, *J* = 7.5 Hz), 7.75 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.78 br.s (1H, 4-H), 8.37 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 10.05 br.s (1H, NH). Found, %: N 8.21, 8.27; S 6.27, 6.34. $C_{26}H_{25}N_3O_6S$. Calculated, %: N 8.28; S 6.32.

**Ethyl 2,6-dimethyl-5-[(4-methylbenzenesulfonyl)amino]-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate (4m).** $^1$H NMR spectrum, δ, ppm: 1.24 t (3H, $CH_2$**Me**, *J* = 6.8 Hz), 2.13 s (3H, 2-Me), 2.38 s (3H, **Me**$C_6H_4$), 2.52 s (3H, 6-Me), 4.23 q (2H, $OCH_2$), 6.90 s (1H, 7-H), 7.07 s (1H, 4-H), 7.36 d (2H, 3″-H, 5″-H, *J* = 7.5 Hz), 7.57 d (2H, 2″-H, 6″-H, *J* = 7.5 Hz), 7.80 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 8.45 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 9.43 br.s (1H, NH).

**Ethyl 5-[(methanesulfonyl)amino]-2,6-dimethyl-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate (4n).** Yield 67%, mp 210–212°C. $^1$H NMR spectrum, δ, ppm: 1.38 t (3H, $CH_2$**Me**, *J* = 7.6 Hz), 2.34 s (3H, 2-Me), 2.56 s (3H, 6-Me), 2.97 s (3H, $MeSO_2$), 4.33 q (2H, $OCH_2$), 6.98 s (1H, 7-H), 7.83 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 8.02 s (1H, 4-H), 8.47 d (2H, 2′-H, 6′-H,

*J* = 8,4 Hz), 9.03 br.s (1H, NH). Found, %: N 9.68, 9.77; S 7.39, 7.42. $C_{20}H_{21}N_3O_6S$. Calculated, %: N 9.74; S 7.43.

**Ethyl 5-[(methanesulfonyl)amino]-2,6,7-trimethyl-1-(4-nitrophenyl)-1*H*-indole-3-carboxylate (4o).** Yield 55%, mp 196–197°C. $^1$H NMR spectrum, δ, ppm: 1.38 t (3H, $CH_2$**Me**, *J* = 6.4 Hz), 1.73 s (3H, 7-Me), 2.26 s (3H, 6-Me), 2.40 s (3H, 2-Me), 2.95 (3H, $MeSO_2$), 4.32 q (2H, $OCH_2$), 7.77 d (2H, 3′-H, 5′-H, *J* = 7.5 Hz), 7.97 s (1H, 4-H), 8.43 d (2H, 2′-H, 6′-H, *J* = 7.5 Hz), 9.05 br.s (1H, NH). Found, %: N 9.38, 9.45; S 7.17, 7.22. $C_{21}H_{23}N_3O_6S$. Calculated, %: N 9.43; S 7.20.

**Ethyl 7-chloro-2-methyl-5-[(4-methylbenzenesulfonyl)amino]-1-benzofuran-3-carboxylate (5a).** Yield 68%, mp 182–184°C. $^1$H NMR spectrum, δ, ppm: 1.37 t (3H, $CH_2$**Me**, *J* = 7.5 Hz), 2.33 s (3H, **Me**$C_6H_4$), 2.72 s (3H, 2-Me), 4.32 q (2H, $OCH_2$), 7.15 d (1H, 6-H, $J_{6,4}$ = 1.5 Hz), 7.36 d (2H, 3″-H, 5″-H, *J* = 8.1 Hz), 7.65 d (1H, 4-H), 7.66 d (2H, 2″-H, 6″-H, *J* = 8.1 Hz), 10.49 br.s (1H, NH). Found, %: N 3.38, 3.45; S 7.79, 7.86. $C_{19}H_{18}ClNO_5S$. Calculated, %: N 3.43; S 7.86.

**Ethyl 2,7-dimethyl-5-[(4-methylbenzenesulfonyl)amino]-1-benzofuran-3-carboxylate (5b).** Yield 72%, mp 167–169°C. $^1$H NMR spectrum, δ, ppm: 1.34 t (3H, $CH_2$**Me**, *J* = 6.9 Hz), 2.31 s (3H, 7-Me), 2.34 s (3H, **Me**$C_6H_4$), 2.68 s (3H, 2-Me), 4.29 q (2H, $OCH_2$), 6.90 d (1H, 6-H, $J_{6,4}$ = 1.5 Hz), 7.36 d (2H, 3″-H, 5″-H, *J* = 7.8 Hz), 7.47 d (1H, 4-H), 7.66 d (2H, 2″-H, 6″-H, *J* = 7.8 Hz), 10.16 br.s (1H, NH). Found, %: N 3.59, 3.68; S 8.19, 8.26. $C_{20}H_{21}NO_5S$. Calculated, %: N 3.62; S 8.28.

***N*-(3-Acetyl-2-methyl-1-benzofuran-5-yl)methanesulfonamide (5c).** Yield 75%, mp 170–171°C. $^1$H NMR spectrum, δ, ppm: 2.58 s (3H, COMe), 2.79 s (3H, 2-Me), 2.94 s (3H, $MeSO_2$), 7.21–7.23 d.d (1H, 6-H, $J_{6,7}$ = 8.8, $J_{6,4}$ = 1.2 Hz), 7.57 d (1H, 7-H), 7.92 d (1H, 4-H), 9.65 br.s (1H, NH). Found, %: N 5.15, 5.22; S 11.97, 12.03. $C_{12}H_{13}NO_4S$. Calculated, %: N 5.24; S 12.00.

***N*-(3-Acetyl-2,7-dimethyl-1-benzofuran-5-yl)methanesulfonamide (5d).** Yield 48%, mp 207–209°C. $^1$H NMR spectrum, δ, ppm: 2.46 s (3H, 7-Me), 2.58 s (3H, COMe), 2.80 s (3H, 2-Me), 2.95 s (3H, $MeSO_2$), 7.07 br.s (1H, 6-H), 7.76 br.s (1H, 4-H), 9.58 br.s (1H, NH). Found, %: N 4.85, 4.90; S 11.34, 11.41. $C_{13}H_{15}NO_4S$. Calculated, %: N 4.98; S 11.40.

***N*-(3-Acetyl-2,6-dimethyl-1-benzofuran-5-yl)methanesulfonamide (5e).** Yield 82%, mp 213–215°C. $^1$H NMR spectrum, δ, ppm: 2.43 s (3H, 6-Me), 2.59 s (3H, COMe), 2.77 s (3H, 2-Me), 3.00 (3H, $MeSO_2$), 7.51 s (1H, 7-H), 7.91 s (1H, 4-H), 9.11 br.s (1H, NH). Found, %: N 4.95, 4.99; S 11.41, 11.44. $C_{13}H_{15}NO_4S$. Calculated, %: N 4.98; S 11.40.

**Ethyl 5-[(methanesulfonyl)amino]-2,6-dimethyl-1-benzofuran-3-carboxylate (5f).** Yield 61%, mp 172–173°C. $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, $CH_2$**Me**, *J* = 5.1 Hz), 2.41 s (3H, 6-Me), 2.72 s (3H, 2-Me), 2.97 s (3H, $MeSO_2$), 4.32 q (2H, $OCH_2$), 7.50 s (1H, 7-H), 7.81 s (1H, 4-H), 9.10 br.s (1H, NH). Found, %: N 4.45, 4.51; S 10.28, 10.32. $C_{14}H_{17}NO_5S$. Calculated, %: N 4.50; S 10.30.

***N*-(3-Acetyl-2,6,7-trimethyl-1-benzofuran-5-yl)methanesulfonamide (5g).** Yield 55%, mp 190–191°C. $^1$H NMR spectrum, δ, ppm: 2.34 s (3H, 6-Me), 2.42 s (3H, 7-Me), 2.60 s (3H, COMe), 2.81 s (3H, 2-Me), 2.97 s (3H, $MeSO_2$), 7.77 s (1H, 4-H), 9.13 br.s (1H, NH). Found, %: N 4.65, 4.70; S 10.86, 10.89. $C_{14}H_{17}NO_4S$. Calculated, %: N 4.74; S 10.86.

**Ethyl 5-[(methanesulfonyl)amino]-2,6,7-trimethyl-1-benzofuran-3-carboxylate (5h).** Yield 70%, mp 184–185°C. $^1$H NMR spectrum, δ, ppm: 1.37 t (3H, $CH_2$**Me**, *J* = 6.8 Hz), 2.32 s (3H, 6-Me), 2.40 s (3H, 7-Me), 2.74 s (3H, 2-Me), 2.95 s (3H, $MeSO_2$), 4.34 q (2H, $CH_2$Me), 7.67 s (1H, 4-H), 9.12 br.s (1H, NH). Found, %: N 4.20, 4.28; S 9.78, 9.84. $C_{15}H_{19}NO_5S$. Calculated, %: N 4.30; S 9.85.

**Ethyl 5-[(methanesulfonyl)amino]-2,4,6-trimethyl-1-benzofuran-3-carboxylate (5i).** Yield 62%, mp 154–156°C. $^1$H NMR spectrum, δ, ppm: 1.34 t (3H, $CH_2$**Me**, *J* = 6.4 Hz), 2.44 s (3H, 6-Me), 2.55 s (3H, 4-Me), 2.61 s (3H, 2-Me), 3.05 s (3H, $MeSO_2$), 4.34 q (2H, $OCH_2$), 7.35 s (1H, 7-H), 8.89 br.s (1H, NH). Found, %: N 4.29, 4.35; S 9.82, 9.88. $C_{15}H_{19}NO_5S$. Calculated, %: N 4.30; S 9.85.

***N*-(3-Acetyl-2-methyl-1-benzofuran-5-yl)trifluoromethanesulfonamide (5j).** Yield 30%, mp 164–165°C. $^1$H NMR spectrum, δ, ppm: 2.59 s (3H, COMe), 2.81 s (3H, 2-Me), 7.22–7.24 d.d (1H, 6-H, $J_{6,7}$ = 8.7, $J_{6,4}$ = 1.2 Hz), 7.63 d (1H, 7-H), 7.96 d (1H, 4-H), 11.82 br.s (1H, NH). $^{19}$F NMR spectrum: $\delta_F$ –74.89 ppm, s. Found, %: N 4.30, 4.37; S 9.92, 9.97. $C_{12}H_{10}F_3NO_4S$. Calculated, %: N 4.36; S 9.98.

***N*-(3-Acetyl-2,7-dimethyl-1-benzofuran-5-yl)trifluoromethanesulfonamide (5k).** Yield 35%, mp 197–198°C. $^1$H NMR spectrum, δ, ppm: 2.50 s (3H, 7-Me), 2.59 s (3H, COMe), 2.84 s (3H, 2-Me), 7.09 br.s (1H, 6-H), 7.81 br.s (1H, 4-H), 11.82 br.s (1H,

NH). $^{19}$F NMR spectrum: $\delta_F$ –74.91 ppm, s. Found, %: N 4.11, 4.19; S 9.49, 9.55. $C_{13}H_{12}F_3NO_4S$. Calculated, %: N 4.18; S 9.56.

**Ethyl 2,7-dimethyl-5-[(trifluoromethanesulfonyl)amino]-1-benzofuran-3-carboxylate (5l).** Yield 54%, mp 145–147°C. $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, $CH_2$**Me**, $J$ = 6.8 Hz), 2.46 s (3H, 7-Me), 2.75 s (3H, 2-Me), 4.34 q (2H, $OCH_2$), 7.06 d (1H, 6-H, $J_{6,4}$ = 1.2 Hz), 7.66 d (1H, 4-H), 11.85 br.s (1H, NH). $^{19}$F NMR spectrum: $\delta_F$ –75.16 ppm, s. Found, %: N 3.78, 3.85; S 8.73, 8.79. $C_{14}H_{14}F_3NO_5S$. Calculated, %: N 3.83; S 8.78.

***N*-(3-Acetyl-2,6-dimethyl-1-benzofuran-5-yl)-trifluoromethanesulfonamide (5m).** Yield 71%, mp 145–167°C. $^1$H NMR spectrum, δ, ppm: 2.41 s (3H, 6-Me), 2.57 s (3H, COMe), 2.79 s (3H, 2-Me), 7.56 s (1H, 7-H), 7.89 s (1H, 4-H), 11.80 br.s (1H, NH). $^{19}$F NMR spectrum: $\delta_F$ –75.96 ppm, s. Found, %: N 4.13, 4.19; S 9.51, 9.58. $C_{13}H_{12}F_3NO_4S$. Calculated, %: N 4.18; S 9.56.

***N*-(3-Acetyl-2,6,7-trimethyl-1-benzofuran-5-yl)-trifluoromethanesulfonamide (5n).** Yield 65%, mp 183–185°C. $^1$H NMR spectrum, δ, ppm: 2.32 s (3H, 6-Me), 2.42 s (3H, 7-Me), 2.56 s (3H, COMe), 2.79 s (3H, 2-Me), 7.76 s (1H, 4-H), 11.53 br.s (1H, NH). $^{19}$F NMR spectrum: $\delta_F$ –75.11 ppm, s. Found, %: N 3.95, 3.99; S 9.11, 9.18. $C_{14}H_{14}F_3NO_4S$. Calculated, %: N 4.01; S 9.18.

**Ethyl 2,6,7-trimethyl-5-[(trifluoromethanesulfonyl)amino]-1-benzofuran-3-carboxylate (5o).** Yield 57%, mp 118–120°C. $^1$H NMR spectrum, δ, ppm: 1.23 t (3H, $CH_2$**Me**, $J$ = 6.8 Hz), 2.10 s (3H, 6-Me), 2.13 s (3H, 7-Me), 2.19 s (3H, 2-Me), 4.29 q (2H, $OCH_2$), 7.17 s (1H, 4-H), 11.14 br.s (1H, NH). $^{19}$F NMR spectrum: $\delta_F$ –75.76 ppm, s. Found, %: N 3.61, 3.72; S 8.38, 8.44. $C_{15}H_{16}F_3NO_5S$. Calculated, %: N 3.69; S 8.45.

**Ethyl 5-[(benzenesulfonyl)amino]-2,6,7-trimethyl-1-benzofuran-3-carboxylate (5p).** Yield 88%, mp 174–175°C. $^1$H NMR spectrum, δ, ppm: 1.23 t (3H, $CH_2$**Me**, $J$ = 6.9 Hz), 2.11 s (3H, 7-Me), 2.33 s (3H, 6-Me), 2.69 s (3H, 2-Me), 4.21 q (2H, $OCH_2$), 7.11 s (1H, 4-H), 7.53–7.65 m (5H, Ph), 9.58 s (1H, NH). Found, %: N 3.58, 3.75; S 8.28, 8.36. $C_{20}H_{21}NO_5S$. Calculated, %: N 3.62; S 8.28.

**Ethyl 5-[(benzenesulfonyl)amino]-2,4,6-trimethyl-1-benzofuran-3-carboxylate (5q).** Yield 75%, mp 185–186°C. $^1$H NMR spectrum, δ, ppm: 1.28 t (3H, $CH_2$**Me**, $J$ = 6.9 Hz), 2.01 s (3H, 6-Me), 2.11 s (3H, 4-Me), 2.58 s (3H, 2-Me), 4.27 q (2H, $OCH_2$), 7.26 s (1H, 7-H), 7.54–7.69 m (5H, Ph), 9.43 br.s (1H, NH). Found, %: N 3.45, 3.68; S 8.23, 8.30. $C_{20}H_{21}NO_5S$. Calculated, %: N 3.62; S 8.28.

**Ethyl 5-[(methanesulfonyl)amino]-2,7-dimethyl-1-benzofuran-3-carboxylate (5r).** Yield 61%, mp 172–173°C. $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, $CH_2$**Me**, $J$ = 5.1 Hz), 2.41 s (3H, 6-Me), 2.72 s (3H, 2-Me), 2.97 s (3H, $MeSO_2$), 4.32 q (2H, $OCH_2$), 7.50 s (1H, 7-H), 7.81 s (1H, 5-H), 9.10 br.s (1H, NH). Found, %: N 4.35, 4.51; S 10.23, 10.32. $C_{14}H_{17}NO_5S$. Calculated, %: N 4.00; S 10.30.

**Ethyl 2-{2-hydroxy-4-methyl-5-[(trifluoromethanesulfonyl)amino]phenyl}-3-oxobutanoate (6a).** Yield 40%, mp 135–136°C. $^1$H NMR spectrum, δ, ppm: 1.18 t (3H, $CH_2$**Me**, $J$ = 6.4 Hz), 2.13 s (3H, 4-Me), 2.23 s (3H, MeCO), 4.15 q (2H, $OCH_2$), 5.10 s (1H, CH), 6.78 s (1H, 3-H), 6.93 s (1H, 6-H), 10.16 br.s (1H, NH), 11.11 br.s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.58 ppm, s. Found, %: N 3.58, 3.64; S 8.31, 8.38. $C_{14}H_{16}F_3NO_6S$. Calculated, %: N 3.65; S 8.36.

**Ethyl 2-{5-[(benzenesulfonyl)amino]-2-hydroxyphenyl}-3-oxobutanoate (6b).** Yield 67%, mp 175–177°C. $^1$H NMR spectrum, δ, ppm: 1.15 t (3H, $CH_2$**Me**, $J$ = 6.2 Hz), 1.96 s (3H, MeCO), 4.04 m (2H, $OCH_2$), 4.99 s (1H, CH), 6.72 d (1H, 6-H, $J_{6,5}$ = 7.8 Hz), 6.75 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 6.86–6.90 d.d (1H, 5-H), 7.48–7.64 m (5H, Ph), 9.80 s (1H, NH), 9.86 s (1H, OH). Found, %: N 3.65, 3.82; S 8.42, 8.61. $C_{18}H_{19}NO_6S$. Calculated, %: N 3.71; S 8.50.

**Ethyl 2-{2-hydroxy-5-[(4-methylbenzenesulfonyl)amino]phenyl}-3-oxobutanoate (6c).** Yield 71%, mp 139–141°C. $^1$H NMR spectrum, δ, ppm: 1.15 t (3H, $CH_2$**Me**, $J$ = 6.4 Hz), 1.96 s (3H, MeCO), 4.07 m (2H, $OCH_2$), 4.98 s (1H, CH), 6.72 d (1H, 6-H, $J_{6,5}$ = 7.8 Hz), 6.74 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 6.86–6.90 d.d (1H, 5-H), 7.30 d (2H, 3″-H, 5″-H, $J$ = 8.1 Hz), 7.50 d (2H, 2″-H, 6″-H, $J$ = 8.1 Hz), 9.67 s (1H, NH), 9.79 s (1H, OH). Found, %: N 3.42, 3.65; S 8.13, 8.23. $C_{19}H_{21}NO_6S$. Calculated, %: N 3.58; S 8.19.

**Ethyl 2-{2-hydroxy-5-[(trifluoromethanesulfonyl)amino]phenyl}-3-oxobutanoate (6d).** Yield 55%, mp 127–129°C. $^1$H NMR spectrum, δ, ppm: 1.18 t (3H, $CH_2$**Me**, $J$ = 6.4 Hz), 2.14 s (3H, MeCO), 4.12 m (2H, $OCH_2$), 5.14 s (1H, CH), 6.90 d (1H, 6-H, $J_{6,5}$ = 7.8 Hz), 6.98 d (1H, 3-H, $J_{3,5}$ = 1.2 Hz), 7.07–7.09 d.d (1H, 5-H), 10.21 s (1H, NH), 11.51 br.s (1H, OH). $^{19}$F NMR spectrum: $\delta_F$ –75.84 ppm, s. Found, %: N 3.61, 3.81; S 8.56, 8.66. $C_{14}H_{16}F_3NO_6S$. Calculated, %: N 3.79; S 8.68.

***N*-(4-Nitrophenyl)acetamide (7).** Yield 48%, mp 210–212°C; published data [25]: mp 214°C. $^1$H NMR spectrum, δ, ppm: 2.12 s (3H, COMe), 7.83 d (2H, 3-H, 5-H, $J$ = 8.1 Hz), 8.22 d (2H, 2-H, 6-H, $J$ = 8.1 Hz), 10.58 br.s (1H, NH).

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