ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 12, pp. 1536–1543. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.I. Vas'kevich, N.M. Tsyzoryk, V.I. Staninets, E.B. Rusanov, M.V. Vovk, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 12, pp. 1565–1572.

Intramolecular Electrophilic Cyclization of Functional Derivatives of Unsaturated Compounds: III.* Reaction of *N*,4-Diarylbut-3-enamides with Arenesulfenyl Chlorides. Synthesis of 5-Aryl-4-arylsulfanyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-ones

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Received April 20, 2012

Abstract—*N*-Aryl-4-phenylbut-3-enamides reacted with arenesulfenyl chlorides in chloroform to give *N*,4-diaryl-3-arylsulfanyl-4-chlorobutanamides, whereas in acetic acid in the presence of lithium perchlorate *N*-[4-arylsulfanyl-5-phenyltetrahydrofuran-2-ylidene]arenaminium perchlorates were obtained. Reactions of arenesulfenyl chlorides with *N*,4-diarylbut-3-enamides having strong electron-donating groups in positions *3* and *4* of the *N*-aryl substituent afforded 5-aryl-4-arylsulfanyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-ones.

DOI: 10.1134/S107042801212007X

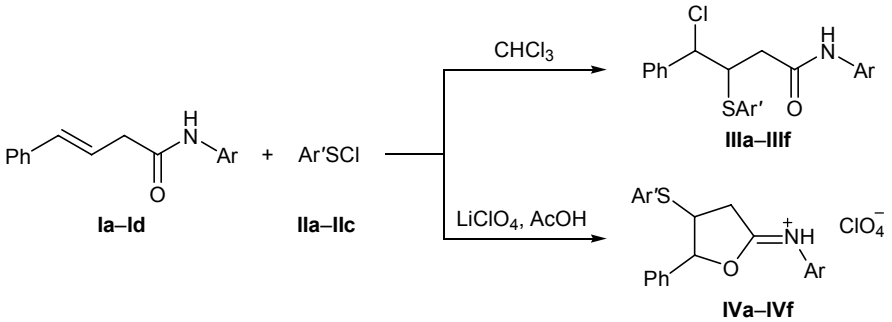
Unsaturated carboxylic acid amides possess two competitive nucleophilic centers and are therefore convenient models for studying the effect of structural factors on chemo- and regioselectivity of electrophilic intramolecular cyclizations [2]. We previously studied cyclization of allyl- and cinnamylacetamides with arenesulfenyl chlorides [1, 3] and found that the size of the resulting heteroring and the formation of iminolactones or lactams are determined by the position and degree of substitution of the double bond in the initial amide, as well as by the nature of the substituent on the nitrogen atom. In particular, allylacetamides gave rise to 2-iminotetrahydrofuran derivatives, whereas six-membered lactams or lactones were formed from cinnamylacetamides, depending on the steric parameters of the amide fragment.

In the present work we selected as substrates *N*-aryl-substituted styrylacetamides **Ia**–**Ig** in which the *N*-aryl groups were characterized by different electron-donor powers. The double C=C bond in **Ia**–**Ig** is separated from the carboxamide fragment by one methylene group, and (as in cinnamylacetamides) the carbon chain terminates with an aromatic substituent. It might be expected that such structural specificity of amides **Ia**–**Ig** should affect the cyclization path and product structure.

As we showed in [1, 3], the cyclization requires the use of a strong electrolyte in a highly polar medium owing to reduced electrophilicity of arenesulfenyl chlorides. The same turned out to be also valid for the reactions of *N*-aryl amides **Ia**–**Id** with arenesulfenyl chlorides **IIa**–**IIc**. The reaction in weakly polar chloroform gave 66–78% of *N*,4-diaryl-3-arylsulfanyl-4-chlorobutanamides **IIIa**–**IIIf** as electrophilic addition products at the C=C bond (Scheme 1). When the reaction was carried out in acetic acid in the presence of lithium perchlorate [4, 5], amides **Ic** and **Id** having electron-donating 4-methoxy or 3,4-dimethyl substituents in the *N*-aryl group gave rise to air-stable *N*-[4-arylsulfanyl-5-phenyltetrahydrofuran-2-ylidene]-arenaminium perchlorates **IVa**–**IVf** in 44–78% yield. The cyclization of amides **Ia** and **Ib** containing no activating substituents was less selective, and the reaction mixtures contained the corresponding perchlorates **IV** and open-chain adducts **III** (according to the ^{1}H NMR data); we failed to separate these product mixtures.

* For communication II, see [1].

Scheme 1.



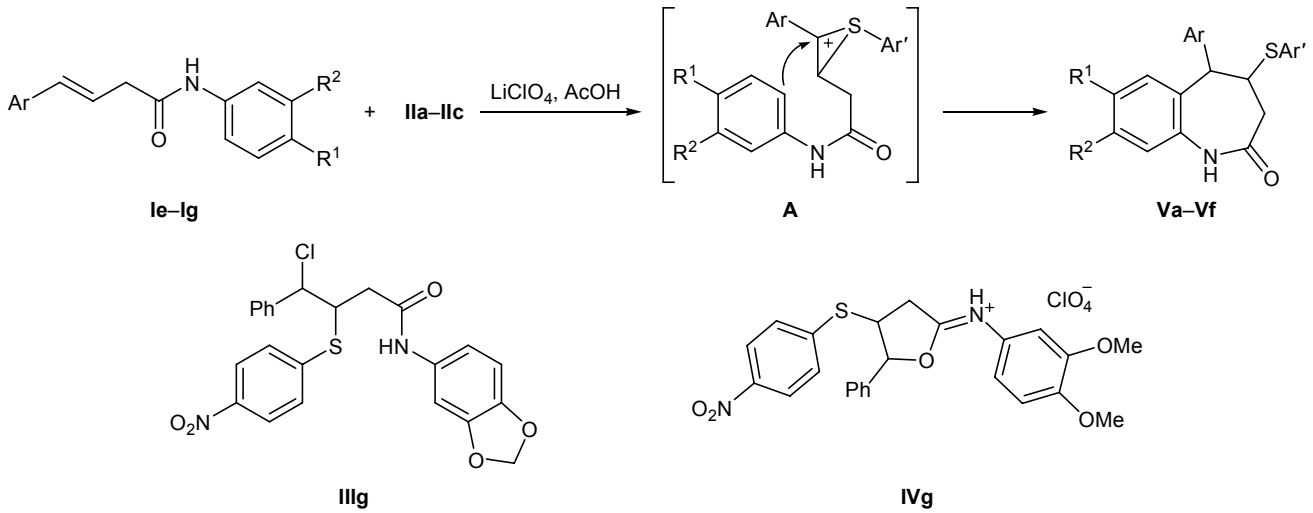
I, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 3,4-$Me_2C_6H_3$ (**d**); **II**, Ar′ = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**); **III**, Ar = Ph, Ar′ = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**); Ar = 4-ClC_6H_4, Ar′ = 4-MeC_6H_4 (**d**), 4-$O_2NC_6H_4$ (**e**); Ar = 4-$MeOC_6H_4$, Ar′ = 4-$O_2NC_6H_4$ (**f**); **IV**, Ar = 4-$MeOC_6H_4$, Ar′ = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**); Ar = 3,4-$Me_2C_6H_3$, Ar′ = Ph (**d**), 4-MeC_6H_4 (**e**), 4-$O_2NC_6H_4$ (**f**).

The site of the addition of arenesulfenyl chlorides to amides **Ia**–**Id** follows from the structure of compounds **IIIa**–**IIIf** which displayed in the ^{1}H NMR spectra a multiplet signal at δ 4.06– 4.35 ppm due to 3-H and a doublet at δ 5.11–5.13 ppm (J = 7–8.8 Hz) due to 4-H. Thus the reaction is highly regioselective. The ^{1}H NMR spectra of iminium salts **IVa**–**IVf** contained a multiplet at δ 4.14–4.61 ppm due to 4-H and a doublet at δ 5.87–6.03 ppm (J = 6.4–9.6 Hz) due to 5-H, indicating *trans* orientation of the phenyl and arylsulfanyl substituents in the tetrahydrofuran ring. Unlike analogous salts obtained from allylacetamides [1], the hydrolysis of **IVa**–**IVf** in the presence of sodium acetate or ethoxide was not selective, and we failed to isolate the corresponding γ-lactones.

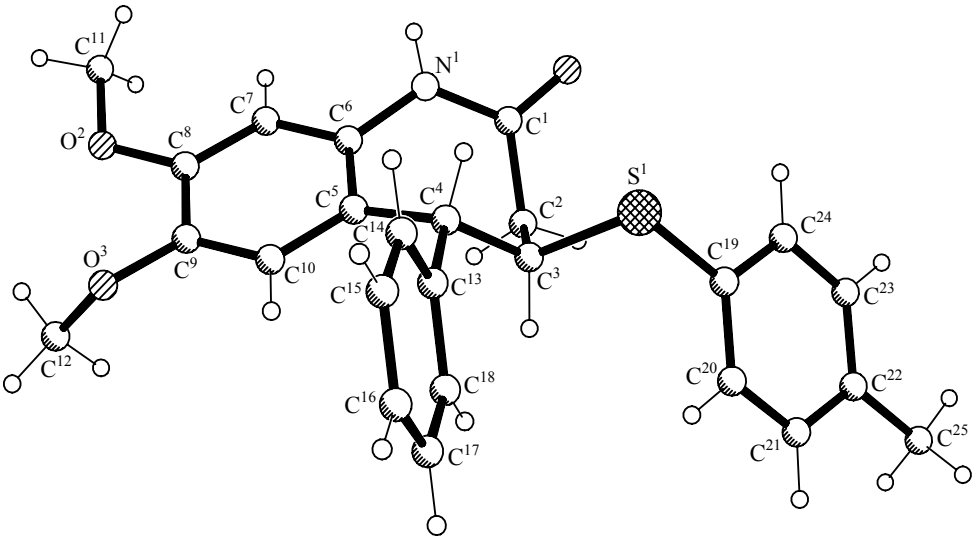
The results of reactions of arenesulfenyl chlorides with *N*-aryl amides **Ie**–**Ig** having strong electron-donating substituents in positions *3* and *4* of the *N*-phenyl ring were quite surprising. Compounds **Ie**–**Ig** reacted with sulfenyl chlorides **IIa** and **IIb** in acetic acid in the presence of lithium perchlorate to give 5-aryl-4-arylsulfanyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-ones **Va**–**Vf** (Scheme 2) which were isolated in 31–82% yield. Analysis of the reaction mixtures by ^{1}H NMR also revealed the presence of perchlorates **IV** and adducts **III**. The major products of the reactions of 4-nitrobenzenesulfenyl chloride (**IIc**) with amides **Ie** and **If** were perchlorate **IVg** and 3-arylsulfanyl-4-chlorobutanamide **IIIg**, respectively; the amounts of the corresponding benzazepinones **V** were so small that they cannot be isolated and characterized.

Presumably, compounds **Va**–**Vf** are formed as a result of electrophilic intramolecular cyclization where the nucleophilic center is the *ortho* position in

Scheme 2.



I, Ar = Ph, $R^1 = R^2$ = MeO (**e**), R^1R^2 = OCH_2O (**f**); Ar = 4-FC_6H_4, $R^1 = R^2$ = MeO (**g**); **V**, Ar = Ph, $R^1 = R^2$ = OMe, Ar′ = Ph (**a**), 4-MeC_6H_4 (**b**); Ar = Ph, R^1R^2 = OCH_2O, Ar′ = Ph (**c**), 4-MeC_6H_4 (**d**); Ar = 4-FC_6H_4, $R^1 = R^2$ = OMe, Ar′ = Ph (**e**), 4-MeC_6H_4 (**f**).



Structure of the molecule of 7,8-dimethoxy-4-(4-methylphenylsulfanyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (**Vb**) according to the X-ray diffraction data. Selected bond lengths and bond angles: C^6–N^1 1.417(2), C^1–N^1 1.350(2), C^1–C^2 1.499(3), C^2–C^3 1.531(3), C^3–C^4 1.542(3), C^4–C^5 1.525(3), C^5–C^6 1.397(3), C^1–O^1 1.234(2), C^3–S^1 1.832(2), C^{19}–S^1 1.768(2) Å; $N^1C^1C^2$ 116.61(17), $C^1C^2C^3$ 113.77(16), $C^2C^3C^4$ 114.11(15), $C^5C^4C^3$ 113.88(15), $C^6C^5C^4$ 119.99(17), $C^5C^6N^1$ 121.54(18), $C^{19}S^1C^3$ 101.73(9)°.

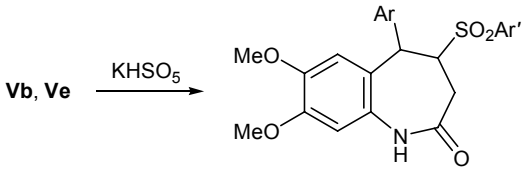
the *N*-phenyl group activated by strong electron-donating substituents (OCH_3 or OCH_2O) rather than the amide oxygen or nitrogen atom. Azepine ring closure is likely to involve initial generation of cation **A** stabilized by perchlorate ion and subsequent 7-*endo*-*trig* cyclization.

The assumed structure of benzazepinones **Va**–**Vf** is consistent with their NMR and mass spectra. In the ^{1}H NMR spectra, the most informative were singlets from 6-H and 9-H in the benzene ring at δ 6.20–6.38 and 6.54–6.68 ppm, a doublet from 5-H (δ 4.03–4.28 ppm, J = 9.5–10.5 Hz), and multiplets from 3-H (δ 2.21–2.62 and 2.51–2.74 ppm) and 4-H (δ 4.18–4.53 ppm). The ^{13}C NMR spectra contained signals from C^2 at δ_C 170–172 ppm and C^3–C^5 at δ_C 38–39, 50–51, and 53–54 ppm, respectively.

The structure of benzazepinones **V** was unambiguously proved by the X-ray diffraction data obtained for compound **Vb** (see figure). The central seven-membered ring in molecule **Vb** is not planar. The $C^4C^5C^6N^1$ fragment is almost planar (deviations of atoms from the mean-square plane do not exceed 0.0204 Å). The $N^1C^1C^3C^4$ plane (deviation of atoms from the mean-square plane is 0.0886 Å) with the $C^4C^5C^6N^1$ fragment forms a dihedral angle of 48.9(1)°, while the $C^1C^2C^3$ and $N^1C^1C^3C^4$ planes form a dihedral angle of 51.0(2)°. The N^1–C^1 bond is considerably shortened [1.350(2)] relative to standard single C–N bond due to conjugation between the lone electron pair on the nitrogen atom and carbonyl π-bond; this is also reflected in flattened configuration of the N^1 atom [the sum of bond angles at N^1 is 358.9(2)°]. The C^1–C^3 and C^1–C^{19} bonds are nonequivalent [1.832(2) and 1.768(2) Å, respectively] due to different orbital structure of the carbon atoms attached to sulfur. Molecules **Vb** in crystal are linked to centrosymmetric dimers by hydrogen bonds $N^1H\cdots O^{1a}$ [N–H 0.83(2), $N^1\cdots O^{1a}$ 2.871(2) Å, ∠NHO 172(2)°]; the O^{1a} atom is related to the base molecule by the symmetry operation –*x*, 2–*y*, –*z*.

It is known that polysubstituted partly hydrogenated benzazepin-2-ones exhibit diverse and often very important pharmacological properties [6–11]. Methods for their synthesis generally include a number of steps and are based on transformations of difficultly accessible anthranilic acid derivatives. In this article we described an efficient procedure for the synthesis of benzazepines containing a readily modifiable arylsulfanyl substituent in position *4* of the azepine ring. For example, compounds **Vb** and **Ve** were readily oxidized to derivatives **VIa** and **VIb** possessing a biophoric sulfonyl group (Scheme 3).

Scheme 3.



VIa, **VIb**

Ar = Ph, Ar′ = 4-MeC_6H_4 (**a**); Ar= 4-FC_6H_4, Ar′ = Ph (**b**).

EXPERIMENTAL

The IR spectra were recorded from KBr pellets or CH_2Cl_2 solutions on a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance DRX-500 spectrometer at 500.13 and 125.75 MHz, respectively, using tetramethylsilane as internal reference. The mass spectra were obtained on an Agilent 110\DAD\HSD\VLG 119562 instrument.

X-Ray analysis of compound Vb. The X-ray diffraction data were acquired from a 0.16×0.23×0.33-mm single crystal of **Vb** at room temperature on a Bruker Smart Apex II diffractometer (λMoK_α irradiation, graphite monochromator, θ_{max} = 26.39°, spherical segment $-46 \le h \le 48$, $-6 \le k \le 6$, $-32 \le l \le 31$). Monoclinic crystal system, space group $C2/c$; unit cell parameters: a = 38.8665(9), b = 5.2029(1), c = 25.7886(6) Å; β = 122.457(1)°; V = 4400.33(17) Å^3; Z = 8; d_{calc} = 1.267 g/cm^3; μ = 0.173 mm^{-1}; $F(000)$ = 1776. Total of 20352 reflections were measured, 4506 of which were independent (averaging R-factor 0.0398). A correction for absorption was introduced by the multiscan method using SADABS program (T_{min}/T_{max} = 0.745412). The structure was solved by the direct method and was refined by the least-squares procedure using SHELXTL software package [12]. The positions of all non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms (except for the NH hydrogen atom whose position was refined in isotropic approximation) were placed into positions calculated on the basis of geometry considerations and were refined according to the riding model (along with the positions and thermal parameters of the corresponding carbon atoms). The refinement procedure involved 3320 reflections with $I > 2\sigma(I)$; number of refined parameters 277, 12 reflections per parameters; the weight scheme $\omega = 1/[\sigma^2(Fo^2) + (0.07R)^2 + 2.9P]$, where $P = (Fo^2 + 2Fc^2)/3$, was used; the ratio of the maximal (average) deviation to the error in the last iteration was 0.014 (0.001). The final divergence factors were $R_1(F)$ = 0.0431, $wR_2(F^2)$ = 0.1146 for reflections with $I > 2\sigma(I)$ and $R_1(F)$ = 0.0655, $wR_2(F^2)$ = 0.1370 for all reflections; goodness of fit 1.052. The residual electron density from the Fourier difference series after the last iteration was 0.30 and –0.26 e/Å^3. The set of crystallographic data for compound **Vb** was deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 873693).

Compounds IIIa–IIIf (*general procedure*). A solution of 2 mmol of arenesulfenyl chloride **IIa**–**IIc** in 5 ml of chloroform was added dropwise under stirring at 15°C to a solution of 2 mmol of amide **Ia**–**Ic** in 10 ml of chloroform. The mixture was stirred for 4 h at room temperature and evaporated under reduced pressure, the residue was treated with 5 ml of diethyl ether, and the precipitate was filtered off and dried in air.

4-Chloro-*N*,4-diphenyl-3-phenylsulfanylbutanamide (IIIa). Yield 75%, mp 101–102°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.61–2.70 m (1H, CH), 3.11–3.18 m (1H, CH), 4.08–4.15 (1H, CH), 5.10 d (1H, CH, J = 7.6 Hz), 7.14–7.34 m (13H, H_{arom}), 7.49 d (2H, H_{arom}, J = 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.24 (C^2), 53.92 (C^3), 66.32 (C^4); 120.02, 124.48, 127.77, 127.84, 128.33, 128.48, 128.94, 129.01, 133.06, 133.90, 137.67, 138.70 (C_{arom}); 168.08 (C^1). Found, %: C 69.07; H 5.22; Cl 9.16; N 3.58. $C_{22}H_{20}ClNOS$. Calculated, %: C 69.19; H 5.28; Cl 9.28; N 3.67.

4-Chloro-3-(4-methylphenylsulfanyl)-*N*,4-diphenylbutanamide (IIIb). Yield 68%, mp 106–107°C. IR spectrum, ν, cm^{-1}: 1650, 1595, 1540, 1495. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 2.66–2.73 m (1H, CH), 3.10–3.17 m (1H, CH), 4.06–4.12 m (1H, CH), 5.13 d (1H, CH, J = 7 Hz), 7.01 d (2H, H_{arom}, J = 7.5 Hz), 7.11–7.36 m (10H, H_{arom}), 7.54 d (2H, H_{arom}, J = 7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.12 (Me), 40.04 (C^2), 54.05 (C^3), 66.31 (C^4); 120.05, 124.41, 127.83, 128.37, 128.43, 128.97, 129.76, 129.98, 133.57, 137.78, 138.13, 138.81 (C_{arom}); 168.26 (C^1). Found, %: C 69.71; H 5.52; Cl 8.79; N 3.59. $C_{23}H_{22}ClNOS$. Calculated, %: C 69.77; H 5.60; Cl 8.95; N 3.54.

4-Chloro-3-(4-nitrophenylsulfanyl)-*N*,4-diphenylbutanamide (IIIc). Yield 78%, mp 134–135°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68–2.77 m (1H, CH), 3.29–3.36 m (1H, CH), 4.28–4.35 m (1H, CH), 5.11 d (1H, CH, J = 8.4 Hz), 7.11–7.52 m (12H, H_{arom}), 7.94 d (2H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.57 (C^2), 53.63 (C^3), 65.98 (C^4); 120.10, 123.63, 124.83, 127.94, 128.34, 128.78, 129.08, 130.99, 137.39, 138.22, 144.19, 146.34 (C_{arom}); 167.74 (C^1). Found, %: C 61.78; H 4.42; Cl 8.21; N 6.54. $C_{22}H_{19}ClN_2O_3S$. Calculated, %: C 61.89; H 4.49; Cl 8.30; N 6.56.

4-Chloro-*N*-(4-chlorophenyl)-3-(4-methylphenylsulfanyl)-4-phenylbutanamide (IIId). Yield 66%, mp 114–115°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (3H, CH_3), 2.61–2.69 m (1H, CH), 3.08–3.15 m (1H, CH), 4.01–4.08 m (1H, CH), 5.10 d (1H, CH, J = 7.2 Hz), 6.99 d (2H, H_{arom}, J = 7.6 Hz), 7.15 d (2H, H_{arom}, J = 7.2 Hz), 7.22–7.32 m (6H, H_{arom}), 7.43–

7.49 m (3H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.09 (Me), 39.98 (C^2), 53.95 (C^3), 66.24 (C^4); 121.20, 127.79, 128.41, 128.51, 128.98, 129.45, 129.78, 133.53, 133.73, 136.26, 138.24, 138.69 (C_{arom}); 168.11 (C^1). Found, %: C 64.09; H 4.87; Cl 16.38; N 3.31. $C_{23}H_{21}Cl_2NOS$. Calculated, %: C 64.19; H 4.92; Cl 16.47; N 3.25.

4-Chloro-*N*-(4-chlorophenyl)-3-(4-nitrophenylsulfanyl)-4-phenylbutanamide (IIIe). Yield 78%, mp 107–108°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.65–2.76 m (1H, CH), 3.27–3.35 m (1H, CH), 4.24–4.33 m (1H, CH), 5.08 d (1H, CH, J = 7.6 Hz), 7.12–7.36 m (11H, H_{arom}), 7.92 d (2H, H_{arom}, J = 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.50 (C^2), 53.59 (C^3), 66.04 (C^4); 121.36, 123.66, 127.95, 128.38, 128.86, 129.12, 129.87, 130.97, 135.93, 138.14, 144.07, 146.41 (C_{arom}); 167.80 (C^1). Found, %: C 67.15; H 3.85; Cl 15.24; N 6.14. $C_{22}H_{18}Cl_2N_2O_3S$. Calculated, %: C 67.27; H 3.93; Cl 15.37; N 6.07.

4-Chloro-*N*-(4-methoxyphenyl)-3-(4-nitrophenylsulfanyl)-4-phenylbutanamide (IIIf). Yield 73%, mp 136–137°C. IR spectrum, ν, cm^{-1}: 1645, 1345, 1245. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.65–2.73 m (1H, CH), 3.27–3.33 m (1H, CH), 3.79 s (3H, CH_3), 4.27–4.35 m (1H, CH), 5.11 d (1H, CH, J = 8.8 Hz), 6.86 d (2H, H_{arom}, J = 9.2 Hz), 7.13–7.40 m (9H, H_{arom}), 7.94 d (2H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.40 (C^2), 53.64 (C^3), 55.62 (OMe), 65.90 (C^4); 107.36, 114.26, 122.10, 123.63, 127.97, 128.36, 128.80, 130.40, 130.98, 138.25, 144.26, 156.84 (C_{arom}); 167.58 (C^1). Found, %: C 60.32; H 4.56; Cl 7.64; N 6.09. $C_{23}H_{21}ClN_2O_4S$. Calculated, %: C 60.46; H 4.63; Cl 7.76; N 6.13.

Compounds IVa–IVf (*general procedure*). A solution of 2.2 mmol of arenesulfenyl chloride **IIa–IIc** in 5 ml of acetic acid was added dropwise at 15°C to a solution of 2.2 mmol of amide **Ic** or **Id** and 0.23 g (2.2 mmol) of lithium perchlorate in 10 ml of acetic acid. The mixture was stirred for 4 h at room temperature, and the precipitate was filtered off, washed with acetic acid and hexane, and dried in air.

4-Methoxy-*N*-[5-phenyl-4-(phenylsulfanyl)tetrahydrofuran-2-ylidene]anilinium perchlorate (IVa). Yield 55%, mp 124–125°C. IR spectrum, ν, cm^{-1}: 1690 (C=N), 1515, 1265, 1120. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.61–3.79 m (4H, CH_3, CH), 4.14–4.25 m (2H, CH), 5.88 d (1H, CH, J = 6.4 Hz), 6.81 d (2H, H_{arom}, J = 8.8 Hz), 7.21–7.48 m (12H, H_{arom}), 12.02 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.92 (C^3), 48.84 (C^4), 55.44 (OCH_3), 98.02 (C^5); 114.79, 124.28, 126.02, 127.12, 129.24, 129.32, 129.69, 129.75, 130.58, 133.00, 134.24, 159.85 (C_{arom}); 175.64 (C^2). Found, %: C 58.11; H 4.62; N 3.01. $C_{23}H_{22}ClNO_6S$. Calculated, %: C 58.04; H 4.66; N 2.94.

4-Methoxy-*N*-[4-(4-methylphenylsulfanyl)-5-phenyltetrahydrofuran-2-ylidene]anilinium perchlorate (IVb). Yield 70%, mp 127–128°C. IR spectrum, ν, cm^{-1}: 1690 (C=N), 1515, 1260, 1115. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 3.60–3.69 m (1H, CH), 3.76 s (3H, CH_3) 4.07–4.20 m (2H, CH), 5.84 d (1H, CH, J = 7.2 Hz), 6.82 d (2H, H_{arom}, J = 8.8 Hz), 7.12 d (2H, H_{arom}, J = 7.6 Hz), 7.30–7.46 m (9H, H_{arom}), 11.99 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.56 (CH_3), 38.74 (C^3), 49.03 (C^4), 55.51 (OCH_3), 97.88 (C^5); 114.75, 124.21, 125.53, 126.04, 127.00, 129.37, 130.51, 130.57, 133.07, 135.11, 140.06, 159.85 (C_{arom}); 175.61 (C^2). Found, %: C 58.91; H 4.99; N 2.80. $C_{24}H_{24}ClNO_6S$. Calculated, %: C 58.83; H 4.94; N 2.86.

4-Methoxy-*N*-[4-(4-nitrophenylsulfanyl)-5-phenyltetrahydrofuran-2-ylidene]anilinium perchlorate (IVc). Yield 44%, mp 144–145°C. IR spectrum, ν, cm^{-1}: 1685 (C=N), 1515, 1340, 1115. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.66–3.75 m (4H, CH_3, CH), 4.39–4.48 m (1H, CH), 4.52–4.61 m (1H, CH), 5.87 d (1H, CH, J = 9.6 Hz), 6.76 d (2H, H_{arom}, J = 8.8 Hz), 7.18–7.49 m (9H, H_{arom}), 7.92 d (2H, H_{arom}, J = 8.4 Hz), 11.87 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 39.52 (C^3), 47.71 (C^4), 55.33 (OCH_3), 97.61 (C^5); 114.83, 124.08, 124.30, 125.78, 127.49, 129.41, 129.75, 131.02, 132.45, 141.08, 146.63, 159.95 (C_{arom}); 175.64 (C^2). Found, %: 53.09; H 4.11; N 5.31. $C_{23}H_{21}ClN_2O_8S$. Calculated, %: C 53.03; H 4.06; N 5.38.

3,4-Dimethyl-*N*-[5-phenyl-4-(phenylsulfanyl)-tetrahydrofuran-2-ylidene]anilinium perchlorate (IVd). Yield 78%, mp 129–130°C. IR spectrum, ν, cm^{-1}: 1690 (C=N), 1535, 1120–1125. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 s (3H, CH_3), 2.21 s (3H, CH_3), 3.67–3.74 m (1H, CH), 4.13–4.18 m (1H, CH), 4.20–4.27 m (1H, CH), 5.90 d (1H, CH, J = 7 Hz), 7.07–7.11 m (1H, H_{arom}), 7.23–7.46 m (12H, H_{arom}), 12.12 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.48 (CH_3), 19.73 (CH_3), 39.00 (C^3), 48.99 (C^4), 98.11 (C^5); 120.03, 123.62, 126.81, 129.38, 129.42, 129.69, 129.74, 130.59, 130.75, 133.11, 134.38, 138.44, 138.46 (C_{arom}); 176.20 (C^2). Found, %: C 61.01; H 5.13; N 2.91. $C_{24}H_{24}ClNO_5S$. Calculated, %: C 60.82; H 5.10; N 2.95.

3,4-Dimethyl-*N*-[4-(4-methylphenylsulfanyl)-5-phenyltetrahydrofuran-2-ylidene]anilinium per-

chlorate (IVe). Yield 47%, mp 120–121°C. IR spectrum, ν, cm^{-1}: 1690 (C=N), 1535, 1125. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 d (6H, CH_3, J = 4.8 Hz), 2.30 s (3H, CH_3), 3.64–3.73 m (1H, CH), 4.03–4.11 m (1H, CH), 4.14–4.24 m (1H, CH), 5.88 d (1H, CH, J = 7.2 Hz), 7.07–7.47 m (12H, H_{arom}), 12.05 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.41 (CH_3), 19.79 (CH_3), 21.11 (CH_3), 38.94 (C^3), 48.98 (C^4), 97.98 (C^5); 120.01, 123.60, 125.61, 126.85, 129.29, 130.47, 130.58, 130.77, 133.16, 134.00, 135.09, 138.36, 140.03 (C_{arom}); 176.35 (C^2). Found, %: C 61.60; H 5.31; N 2.90. $C_{25}H_{26}ClNO_5S$. Calculated, %: C 61.53; H 5.37; N 2.87.

3,4-Dimethyl-*N*-[4-(4-nitrophenylsulfanyl)-5-phenyltetrahydrofuran-2-ylidene]anilinium perchlorate (IVf). Yield 64%, mp 149–150°C. IR spectrum, ν, cm^{-1}: 1690 (C=N), 1115. ^1H NMR spectrum (CD_3CN), δ, ppm: 2.26 s (6H, CH_3), 3.57–3.66 m (1H, CH), 4.01–4.10 m (1H, CH), 4.46–4.54 m (1H, CH), 6.03 d (1H, CH, J = 9.2 Hz), 7.20–7.27 m (3H, H_{arom}), 7.38–7.52 m (7H, H_{arom}), 8.02 d (2H, H_{arom}, J = 8.8 Hz), 11.22 s (1H, NH). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 18.58 (CH_3), 18.91 (CH_3), 39.04 (C^3), 47.48 (C^4), 97.66 (C^5); 120.05, 123.35, 130.70, 130.71, 130.73, 130.78, 133.01, 138.83, 138.93, 141.08 (C_{arom}); 177.15 (C^2). Found, %: C 55.61; H 4.52; N 5.36. $C_{24}H_{23}ClN_2O_7S$. Calculated, %: C 55.54; H 4.47; N 5.40.

Compounds Va–Vf, IIIg, and IVg (*general procedure*). A solution of 2 mmol of arenesulfenyl chloride **IIa**–**IIc** in 5 ml of acetic acid was added dropwise at 15°C to a solution of 2 mmol of amide **Ie**–**Ig** and 0.21 g (2 mmol) of lithium perchlorate in 10 ml of acetic acid, and the mixture was stirred for 4 h at room temperature. In the reaction of **Ie** with **IIc**, the precipitate of **IVg** was filtered off and washed with a small amount of acetic acid and then with hexane. In the other cases, the solvent was removed under reduced pressure, the residue was treated with chloroform (10 ml), the undissolved material (inorganic) was filtered off, and the filtrate was evaporated. The residue was treated with a mixture of diethyl ether with ethanol (10:1), and the precipitate was filtered off and washed with diethyl ether.

7,8-Dimethoxy-5-phenyl-4-phenylsulfanyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (Va). Yield 67%, mp 145°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1515, 1265, 1220. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.56–2.62 m (1H, CH), 2.67–2.74 m (1H, CH), 3.64 s (3H, CH_3), 3.84 s (3H, CH_3), 4.22–4.27 m (2H, CH), 6.38 s (1H, H_{arom}), 6.54 s (1H, H_{arom}), 7.23–7.45 m (10H, H_{arom}), 7.63 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.36 (C^3), 51.03 (C^5), 53.54 (C^4), 56.04 (OCH_3), 56.15 (OCH_3), 106.12 (C^6), 113.18 (C^9); 126.71, 127.34, 127.78, 128.45, 128.74, 129.11, 130.05, 133.34, 134.04, 139.98, 146.64, 148.51 (C_{arom}); 171.58 (C^2). Found, %: C 71.02; H 5.70; N 3.42. $C_{24}H_{23}NO_3S$. Calculated, %: C 71.08; H 5.72; N 3.45.

7,8-Dimethoxy-4-(4-methylphenylsulfanyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (Vb). Yield 78%, mp 216–217°C. IR spectrum, ν, cm^{-1}: 1675–1680 (C=O), 1510, 1220. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.26–2.32 m (4H, CH_3, CH), 2.52–2.57 m (1H, CH), 3.50 s (3H, CH_3), 3.71 s (3H, CH_3), 4.08 d (1H, CH, J = 10 Hz), 4.37–4.43 m (1H, CH), 6.34 s (1H, H_{arom}), 6.65 s (1H, H_{arom}), 7.16 d (2H, H_{arom}, J = 8 Hz), 7.31 d (2H, H_{arom}, J = 8 Hz), 7.34–7.40 m (5H, H_{arom}), 9.54 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 20.46 (CH_3), 38.17 (C^3), 50.45 (C^5), 52.31 (C^4), 55.55 (OCH_3), 55.68 (OCH_3), 106.46 (C^6), 113.52 (C^9); 125.61, 126.88, 128.43, 128.45, 129.64, 130.31, 131.34, 132.32, 136.89, 140.34, 145.28, 147.93 (C_{arom}); 169.95 (C^2). Found, %: C 71.64; H 6.09; N 3.39. $C_{25}H_{25}NO_3S$. Calculated, %: C 71.57; H 6.01; N 3.34.

9-Phenyl-8-phenylsulfanyl-6,7,8,9-tetrahydro-5*H*-[1,3]dioxolo[4,5-*h*][1]benzazepin-6-one (Vc). Yield 31%, mp 224–225°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1500, 1475–1480, 1215. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.55–2.61 m (1H, CH), 2.68–2.75 m (1H, CH), 4.18–4.28 m (2H, CH), 5.91 d (2H, CH_2, J = 7.2 Hz), 6.36 s (1H, H_{arom}), 6.55 s (1H, H_{arom}), 7.24–7.45 m (10H, H_{arom}), 7.91 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.23 (C^7), 51.12 (C^9), 53.98 (C^8), 101.58 (C^2), 103.70 (C^4), 109.58 (C^{10}); 127.41, 127.82, 128.46, 128.60, 128.79, 129.06, 131.02, 133.44, 133.99, 139.55, 145.49, 146.97 (C_{arom}); 170.72 (C^6). Found, %: C 71.02; H 4.99; N 3.51. $C_{23}H_{19}NO_3S$. Calculated, %: C 70.93; H 4.92; N 3.60.

8-(4-Methylphenylsulfanyl)-9-phenyl-6,7,8,9-tetrahydro-5*H*-[1,3]dioxolo[4,5-*h*][1]benzazepin-6-one (Vd). Yield 36%, mp 222–223°C. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1500, 1480, 1210. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.21–2.30 m (4H, CH_3, CH), 2.53–2.61 m (1H, CH), 4.03 d (1H, CH, J = 10.4 Hz), 4.38–4.46 m (1H, CH), 5.95 d (2H, CH_2, J = 5.6 Hz), 6.20 s (1H, H_{arom}), 6.61 s (1H, H_{arom}), 7.15 d (2H, H_{arom}, J = 7.6 Hz), 7.28–7.38 m (7H, H_{arom}), 9.51 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm:

21.08 (CH_3), 38.41 (C^7), 51.00 (C^9), 53.19 (C^8), 101.87 (C^2), 103.70 (C^4), 109.12 (C^{10}); 127.59, 127.85, 129.07, 129.18, 130.27, 130.86, 132.75, 132.84, 137.45, 140.42, 144.52, 146.65 (C_{arom}); 170.52 (C^6). Found, %: C 71.51; H 5.20; N 3.35. $C_{24}H_{21}NO_3S$. Calculated, %: C 71.44; H 5.25; N 3.47.

5-(4-Fluorophenyl)-7,8-dimethoxy-4-phenylsulfanyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (Ve). Yield 82%, mp 195°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1515, 1220–1225. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.29–2.35 m (1H, CH), 2.58–2.63 m (1H, CH), 3.53 s (3H, CH_3), 3.73 s (3H, CH_3), 4.13 d (1H, CH, J = 10.5 Hz), 4.49–4.53 m (1H, CH), 6.34 s (1H, H_{arom}), 6.68 s (1H, H_{arom}), 7.20 t (2H, H_{arom}, J = 8.5 Hz), 7.24–7.29 m (1H, H_{arom}), 7.33 t (2H, H_{arom}, J = 7 Hz), 7.39 d (2H, H_{arom}, J = 7 Hz), 7.42–7.46 m (2H, H_{arom}), 9.57 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 38.85 (C^3), 50.38 (C^5), 52.70 (C^4), 56.14 (OCH_3), 56.31 (OCH_3), 107.35 (C^6), 114.10 (C^9); 115.51, 115.80, 126.02, 127.54, 129.61, 130.92, 130.97, 131.95, 134.69, 136.96, 136.98, 145.97, 148.63 (C_{arom}); 161.61 d (CF, J = 243.9 Hz), 170.45 (C^2). Found, %: C 68.11; H 5.27; N 3.37. $C_{24}H_{22}FNO_3S$. Calculated, %: C 68.07; H 5.24; N 3.31.

5-(4-Fluorophenyl)-7,8-dimethoxy-4-(4-methylphenylsulfanyl)-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (Vf). Yield 71%, mp 197°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1515, 1225. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.25–2.31 m (4H, CH_3, CH), 2.51–2.57 m (1H, CH), 3.52 s (3H, CH_3), 3.72 s (3H, CH_3), 4.09 d (1H, CH, J = 9.5 Hz), 4.36–4.41 m (1H, CH), 6.33 s (1H, H_{arom}), 6.66 s (1H, H_{arom}), 7.15 d (2H, H_{arom}, J = 8 Hz), 7.19 t (2H, H_{arom}, J = 9 Hz), 7.30 d (2H, H_{arom}, J = 8 Hz), 7.39–7.44 m (2H, H_{arom}), 9.54 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.05 s (CH_3), 38.77 (C^3), 50.44 (C^5), 53.35 (C^4), 56.21 (OCH_3), 56.31 (OCH_3), 107.30 (C^6), 114.18 (C^9); 115.55, 115.72, 126.07, 130.30, 130.81, 130.93, 131.91, 132.97, 137.06, 137.52, 145.94, 148.60 (C_{arom}); 161.59 d (CF, J = 242.7 Hz), 170.48 (C^2). Found, %: C 68.71; H 5.48; N 3.21. $C_{25}H_{24}FNO_3S$. Calculated, %: C 68.63; H 5.53; N 3.20.

***N*-(1,3-Benzodioxol-5-yl)-4-chloro-3-(4-nitrophenylsulfanyl)-4-phenylbutanamide (IIIg).** Yield 76%, mp 128°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.59–2.74 m (1H, CH), 3.22–3.34 m (1H, CH), 4.23–4.34 m (1H, CH), 5.02–5.11 m (1H, CH), 5.87–5.98 m (2H, CH_2), 6.66–6.79 m (2H, H_{arom}), 7.07–7.38 m (8H, H_{arom}), 7.85–7.94 m (2H, H_{arom}). Found, %: C 58.54; H 4.01; Cl 7.62; N 5.89. $C_{23}H_{19}ClN_2O_5S$. Calculated, %: C 58.66; H 4.07; Cl 7.53; N 5.95.

3,4-Dimethoxy-*N*-[4-(4-nitrophenylsulfanyl)-5-phenyltetrahydrofuran-2-ylidene]anilinium perchlorate (IVg). Yield 54%, mp 148–149°C. IR spectrum, ν, cm^{-1}: 1685 (C=N), 1515, 1340, 1115. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.63–3.87 m (7H, CH_3, CH), 4.32–4.47 m (1H, CH), 4.52–4.64 m (1H, CH), 5.84–5.94 m (1H, CH), 6.64–6.73 m (1H, H_{arom}), 7.01–7.52 m (9H, H_{arom}), 7.87–7.96 m (2H, H_{arom}), 11.82 s (1H, NH). Found, %: C 52.21; H 4.16; N 5.14. $C_{24}H_{23}ClN_2O_9S$. Calculated, %: C 52.32; H 4.21; N 5.08.

5-Aryl-4-arylsulfonyl-7,8-dimethoxy-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-ones VIa and VIb (*general procedure*). A solution of 4 mmol of $KHSO_5$ in 5 ml of water was added under stirring to a solution of 1 mmol of benzazepinone **Vb** or **Ve** in 5 ml of methanol. The mixture was stirred for 5 h at 70°C and cooled, the undissolved inorganic material was filtered off, the filtrate was evaporated, and the residue was recrystallized from water.

5-(4-Fluorophenyl)-7,8-dimethoxy-4-phenylsulfonyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (VIa). Yield 95%, mp 190–191°C. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1520, 1240. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.36–2.41 m (1H, CH), 2.64–2.71 m (1H, CH), 3.69 s (3H, CH_3), 3.70 s (3H, CH_3), 4.51–4.55 m (1H, CH), 4.76–4.78 m (1H, CH), 6.54 s (1H, H_{arom}), 6.84 s (1H, H_{arom}), 7.05 t (2H, H_{arom}, J = 8.8 Hz), 7.14 t (2H, H_{arom}, J = 8 Hz), 7.64 t (2H, H_{arom}, J = 8 Hz), 7.76 t (1H, H_{arom}, J = 7.5 Hz), 7.98 d (2H, H_{arom}, J = 7.5 Hz), 9.54 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.79 (C^3), 45.13 (C^5), 55.99 (OCH_3), 56.43 (OCH_3), 67.95 (C^4), 107.66 (C^9), 115.93 (C^6); 115.35, 115.52, 124.39, 129.64, 129.82, 129.88, 129.94, 130.96, 134.77, 137.02, 137.63, 137.65, 146.24, 148.83 (C_{arom}); 169.01 (C^2). Mass spectrum: m/z 456.2 $[M + 1]^+$. Found, %: C 63.37; H 4.81; N 3.05. $C_{24}H_{22}FNO_5S$. Calculated, %: C 63.28; H 4.87; N 3.08. M 455.5.

7,8-Dimethoxy-4-(4-methylphenylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one (VIb). Yield 96%, mp 122°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1525. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.41 s (3H, CH_3), 2.63–2.71 m (1H, CH), 3.70 s (3H, CH_3), 3.71 s (3H, CH_3), 4.38–4.45 m (1H, CH), 4.74–4.76 m (1H, CH), 6.53 s (1H, H_{arom}), 6.84 s (1H, H_{arom}), 7.09–7.26 m (5H, H_{arom}), 7.45 d (2H, H_{arom}, J = 7.6 Hz), 7.88 d (2H, H_{arom}, J = 8 Hz), 9.51 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.57 (CH_3), 33.95 (C^3), 45.93 (C^5), 56.04 (OCH_3), 56.46 (OCH_3),

68.16 (C^4), 107.69 (C^9), 116.16 (C^6); 124.42, 126.96, 127.77, 128.77, 129.72, 130.46, 130.98, 133.94, 141.74, 145.44, 146.28, 148.79 (C_{arom}); 169.00 (C^2). Mass spectrum: m/z 452.2 $[M + 1]^+$. Found, %: C 66.58; H 5.46; N 3.12. $C_{25}H_{25}NO_5S$. Calculated, %: C 66.50; H 5.58; N 3.10. M 451.5.

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