Chemistry of Heterocyclic Compounds **2023**, *59*(9/10), 666–671

Dedicated to the 300th anniversary of Saint Petersburg State University

Rh(II)-catalyzed and non-catalytic synthesis of (*Z*)-ethene-1,2-diamines from 1-tosyl-1,2,3-triazoles and primary anilines

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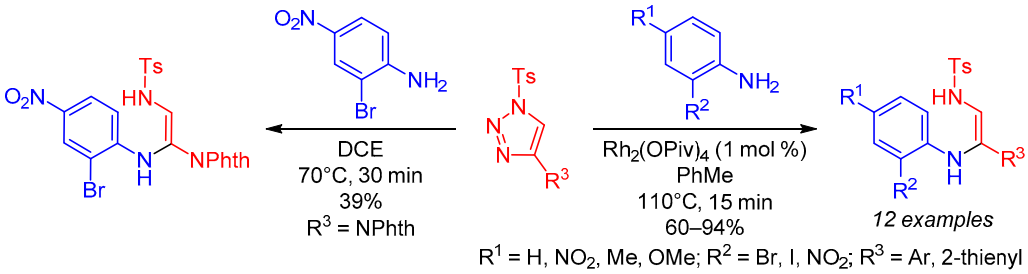
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2023, *59*(9/10), 666–671

Submitted June 10, 2023
Accepted July 13, 2023



The reactions of 4-aryl-1-tosyl-1,2,3-triazoles with substituted primary 2- or 4-nitroanilines, catalyzed by dirhodium tetrapivalate were used to synthesize stable (*Z*)-*N*-aryl-*N'*-tosylethene-1,2-diamines. The analogous reaction of 4-phthalimido-1-tosyl-1*H*-1,2,3-triazole with 2-bromo-4-nitroaniline proceeded upon heating in the absence of catalyst, providing the first example for non-catalytic insertion of a carbene generated from 1-sulfonyl-1,2,3-triazole into an N–H bond. All ethene-1,2-diamines were isolated without resorting to chromatographic purification. The synthesized ethene-1,2-diamines contained two NH groups in a *cis* relationship and present interest as new bidentate ligands, as well as substrates for the synthesis of N,N-heterocycles.

Keywords: anilines, enediamines, carbenes, 1,2,3-triazoles, insertion into N–H bond, metallocatalysis.

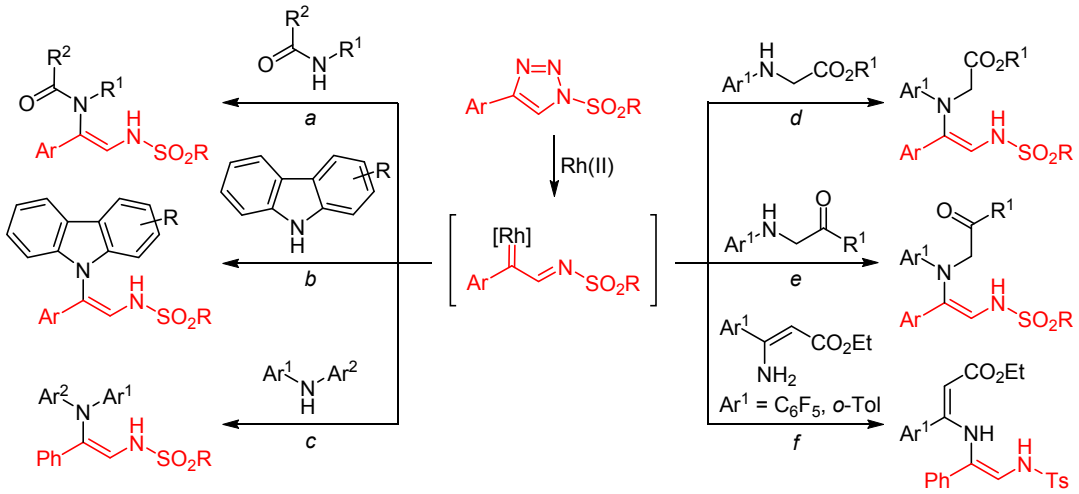
1,2,3-Triazoles are one of the most useful and well-studied types of heterocyclic compounds,[1] found among biologically active molecules,[2] fluorophores,[3] and coating compositions.[4] The concepts of click chemistry[2] and bioorthogonal chemistry[5] are based on formation of 1,2,3-triazoles. A strong impetus for rapid development of 1,2,3-triazole chemistry was provided by the discovery of a simple and effective method for their synthesis *via* copper-catalyzed azide–alkyne cycloaddition (CuAAC) reactions.[6]

Among the variety of known 1,2,3-triazoles, there has been a particular synthetic role to 1-sulfonyl-1,2,3-triazoles, which have been employed as convenient precursors for generating α-iminocarbenoids (metallo-complexes of azavinylcarbenes). These reactive intermediates have been actively used for the preparation of various carbo- and heterocycles, as well as unique acyclic nitrogen-containing compounds, as summarized in a recent review article by Anbarasan and coworkers.[7]

α-Iminocarbenoids are formed from 1-sulfonyl-1,2,3-triazoles upon heating in the presence of transition metal compounds, among which rhodium(II) carboxylates are used the most often. For example, there are quite thorough studies about the insertion reactions of rhodium azavinylcarbenes into the N–H bond of various substrates (Scheme 1): primary and secondary amides[8] (*a*), carbazoles[9] (*b*), diarylamines[10] (*c*), *N*-arylglycinates[10] (*d*), and secondary α-amino ketones[11] (*e*). The products of these reactions are ethene-1,2-diamines (1,2-diaminoethylenes), which in some cases have been converted into heterocyclic structures.[11] The reaction of rhodium azavinylcarbenes with 3-aminoacrylates gave more complicated results, where the primary products arising from insertion into the N–H bond could be obtained only for two substituents (*f*).[12] In the rest of the cases, these products were cyclized to imidazolines.

It should be noted that the only aromatic derivatives studied in the aforementioned insertion reactions into the N–H bond were secondary amines. No information has been published on rhodium(II)-catalyzed reactions of 1-sulfonyl-1,2,3-triazoles with anilines lacking additional substituents at the nitrogen atom. Obviously, these reactions must proceed in a complex way due to the presence of aniline NH group in the product arising from insertion into the first N–H bond, and this NH group is susceptible to secondary reactions.

Scheme 1



Besides the reactions based on using 1-sulfonyl-1,2,3-triazoles, there are several more previously known methods for the synthesis of ethene-1,2-diamines.[13] However, none of them allows to obtain ethene-1,2-diamines containing two NH groups. At the same time, known natural compounds – the cyclic peptides callyaerin[14] and viomycin[15] characterized by antituberculosis activity contain exactly such (*Z*)-1,2-enediamine moiety.

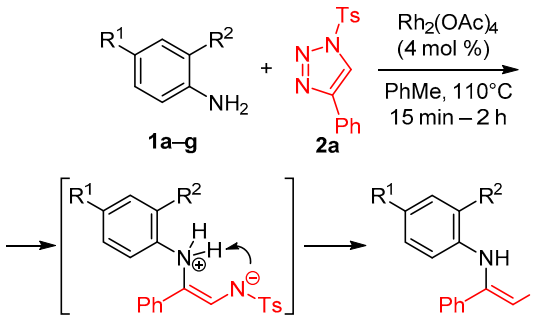
In the context of our efforts to develop new methods for the synthesis and functionalization of nitrogen heterocycles through catalytic reactions of 1-sulfonyl-1,2,3-triazoles,[16] in this work we report for the first time a simple and effective synthesis of *N*-aryl-*N*′-tosylethene-1,2-diamines through the insertion reactions of azavinylcarbene and its rhodium complexes into the N–H bond of primary anilines.

The starting 4-aryl-1-sulfonyl-1,2,3-triazoles **2a**,**b**,**d**–**f**,**h**,[17a] **2c**,**i**,[17b] **2g**[17c] and 4-phthalimido-1-tosyl-1,2,3-triazole **2j**[18] were prepared according to published procedures from the respective sulfonylazides and alkynes in toluene in the presence of copper(I) thiophene-2-carboxylate as catalyst. The synthesis of 2-halo-substituted anilines **1d**–**g** was achieved by oxidative halogenation of anilines with a H_2O_2–Na_2SO_4–NaCl system in acetic acid medium, using KI or KBr as the halogen source.[19] Anilines **1a**–**c**,**h**–**j** were used as commercially available reagents.

The study was started by testing a series of primary anilines with various substitution patterns in reactions with 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**2a**) in toluene at 110°C in the presence of dirhodium tetraacetate (4 mol %). According to ^{1}H NMR data and TLC analysis, the reactions that started from anilines **1a**–**e** gave complex mixtures of products, containing among other components also insignificant amounts of the desired products resulting from insertion into the N–H bond – compounds **3a**–**e** (Scheme 2). However, separation by silica gel chromatography failed to provide enediamines **3a**–**e**, which are probably unstable under acidic conditions. Different results were obtained from the reactions with 2,4-disubstituted anilines **1f**,**g** containing a nitro group at position 4: the products of insertion into the N–H bond – compounds **3f**,**g** – crystallized from the reaction mixtures already during the reactions and were obtained in good yields.

The structures of compounds **3f**,**g** were established on the basis of ^{1}H and ^{13}C NMR spectra, as well as two-dimensional ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC experiments (for compound **3f**), while elemental composition was confirmed by high-resolution mass spectral data. The features of ^{1}H NMR spectra acquired in DMSO-d_6 for compounds **3f**,**g** included the signals of NHTs proton (10.38 ppm, J = 10.3–10.4 Hz), alkenyl proton (6.92–6.96 ppm, J = 10.3–10.4 Hz), as well as the aniline NH group and the aromatic ring protons. The signals of two alkenyl carbon atoms in ^{13}C NMR spectra were observed in the range of 118.5–121.4 ppm.

Scheme 2



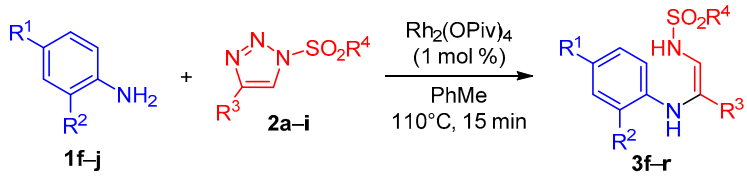
3a–e (0%), **f** (86%), **g** (84%)

1, **3** **a** R^1 = Br, R^2 = H; **b** R^1 = H, R^2 = Br; **c** R^1 = NO_2, R^2 = H; **d** R^1 = Me, R^2 = Br; **e** R^1 = Cl, R^2 = I; **f** R^1 = NO_2, R^2 = Br; **g** R^1 = NO_2, R^2 = I

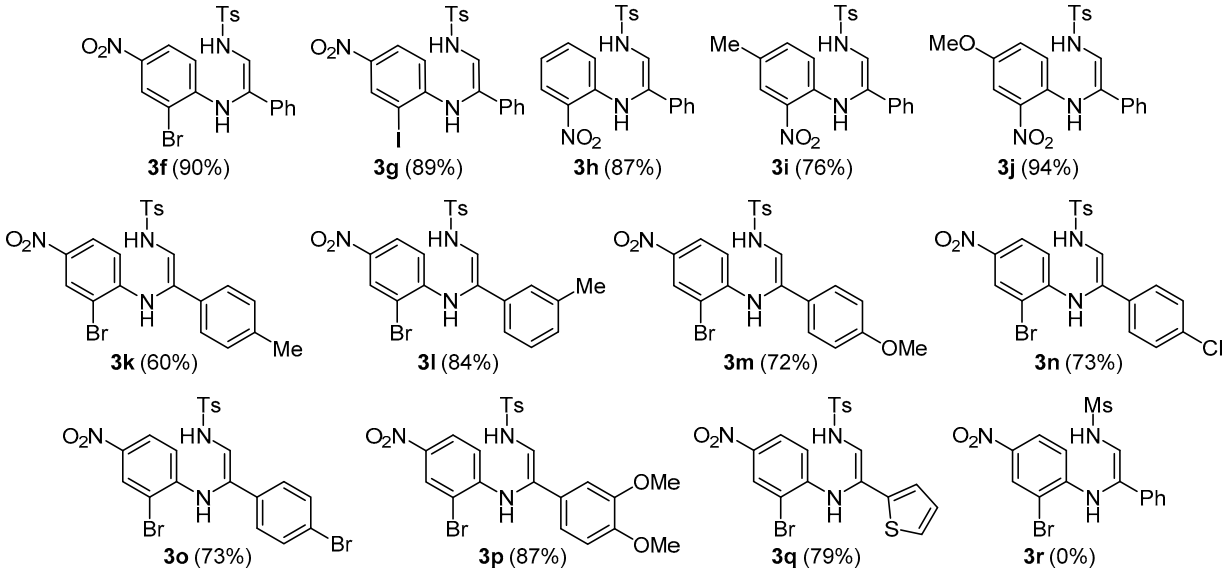
Remarkably, enediamines **3f**,**g** were isolated as individual stereoisomers with *Z*-configuration of the C=C bond, which was confirmed by two-dimensional NOESY experiments: the spectra contained cross peaks between the alkenyl proton and the phenyl ring protons. The high stereoselectivity of the reaction probably can be explained by the formation of an ammonium ylide intermediate, followed by intramolecular prototropic 1,4-shift.

In our opinion, the successful synthesis of enediamines **3f**,**g** can be explained by three reasons. First, nitroanilines are relatively poor nucleophiles, retarding the repeated reaction of iminocarbenoid at the aniline nitrogen atom of enediamine. Second, by precipitating from the reaction

Scheme 3



1 **f** R^1 = NO_2, R^2 = Br; **g** R^1 = NO_2, R^2 = I; **h** R^1 = H, R^2 = NO_2; **i** R^1 = Me, R^2 = NO_2; **j** R^1 = MeO, R^2 = NO_2
2 **a** R^3 = Ph, R^4 = *p*-Tol; **b** R^3 = *p*-Tol, R^4 = *p*-Tol; **c** R^3 = *m*-Tol, R^4 = *p*-Tol; **d** R^3 = 4-$MeOC_6H_4$, R^4 = *p*-Tol; **e** R^3 = 4-ClC_6H_4, R^4 = *p*-Tol; **f** R^3 = 4-BrC_6H_4, R^4 = *p*-Tol; **g** R^3 = 3,4-$(MeO)_2C_6H_3$, R^4 = *p*-Tol; **h** R^3 = 2-thienyl, R^4 = *p*-Tol; **i** R^3 = Ph, R^4 = Me

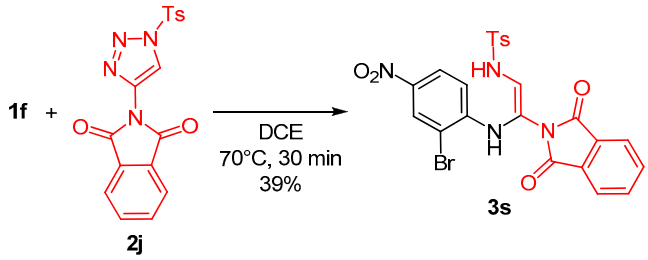


mixture the product is removed from the reaction and cannot subsequently interact with carbenoid, which would have led to the formation of byproducts. Third, the crystallization of these products from the reaction mixtures allowed to avoid laborious chromatographic purification on silica gel: the products were isolated by filtration and were purified by washing with hexane.

Other rhodium(II) carboxylates besides $Rh_2(OAc)_4$ were tested as catalysts for these reactions in further experiments. When using 1 mol % of dirhodium tetrapivalate ($Rh_2(OPiv)_4$), the yields of enediamines **3f**,**g** increased to 90% (Scheme 3). Besides that, the replacement of sparingly soluble $Rh_2(OAc)_4$ with the much more soluble $Rh_2(OPiv)_4$ allowed to completely remove the catalyst from the product during the purification step. Enediamines could be obtained not only from 4-nitro-, but also from 2-nitroanilines, and the yields were good (products **3h**–**j**). In the case of 2-bromo-4-nitroaniline (**1f**), we tested a series of 1,2,3-triazoles **2a**–**i**. The substituents in the aryl ring at the triazole C-4 atom generally had little effect on the yields of products **3k**–**q** (60–87%). This reaction allowed to successfully obtain enediamine **3q** containing a 2-thienyl substituent. Unfortunately, the replacement of tosyl substituent with a mesyl in the triazole ring did not allow to obtain enediamine **3r**.

In an attempt to extend the range of accessible enediamines **3**, 4-phthalimido-1-tosyl-1*H*-1,2,3-triazole (**2j**) was selected as a starting material for these reactions. It is known that such 4-phthalimido-1-sulfonyl-1,2,3-triazoles are able to generate azavinylcarbenes upon simple heating in the absence of catalyst, which can further participate in cyclopropanation,[20] insertion into C–H bond, and [3+2] cycloaddition reactions.[18] We demonstrated that the reaction of triazole **2j** with 2-bromo-4-nitroaniline (**1f**) proceeded upon heating in 1,2-dichloroethane (DCE) at 70°C in the absence of rhodium catalyst and led to the formation of compound **3s**, resulting from insertion into the N–H bond, in a satisfactory yield (Scheme 4).

Scheme 4



Thus, in the current work, we have for the first time synthesized (*Z*)-ethene-1,2-diamines containing two NH groups, by starting from 1-tosyl-1,2,3-triazoles, as well as primary 2- and 4-nitroanilines. The reactions of 4-aryl-1-tosyl-1,2,3-triazoles occurred in the presence of dirhodium tetrapivalate catalyst, while the reaction of 4-phthalimido-1-tosyl-1*H*-1,2,3-triazole – upon heating in the absence of rhodium catalyst. All ethene-1,2-diamines were isolated without resorting to chromatographic purification and were stable under normal conditions. The

synthesized ethene-1,2-diamines may find applications as new bidentate ligands and intermediates for the synthesis of N,N-heterocycles.

Experimental

^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance 400 instrument (400 and 100 MHz, respectively) in DMSO-d_6, using residual solvent signals as internal standards (2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei). Two-dimensional NMR spectra (^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC) were acquired on a Bruker Avance 500 instrument for samples in DMSO-d_6 solutions. Mass spectra were recorded on a Bruker maXis mass spectrometer with electrospray ionization. Melting points were determined on a Stuart SMP30 melting point apparatus. The reaction progress was controlled with TLC using Alugram SIL G UV 254 plates.

Synthesis of enediamines 3f–q (General method). A test tube with air-tight screw cap was charged with the appropriate nitroaniline **1f–j** (0.3 mmol), the appropriate 1-tosyl-1*H*-1,2,3-triazole **2a–h** (0.3 mmol), and anhydrous toluene (0.5 ml). The solution was flushed with argon, then $Rh_2(OPiv)_4$ (1.8 mg, 1 mol %) was added, the screw cap was tightly closed, and the magnetically stirred mixture was heated at 110°C until precipitate appeared (approximately 15 min). The completion of the reaction was controlled by TLC (eluent hexane–EtOAc, 5:1). The precipitate was filtered off and washed with cold toluene (3 ml), followed by hexane (2×10 ml).

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-phenylvinyl}-4-methylbenzenesulfonamide (3f). Yield 132 mg (90%), yellow crystals, mp 198–199°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.38 (1H, d, *J* = 10.4, TsNH); 8.31 (1H, d, *J* = 2.6, H Ar); 7.80–7.69 (4H, m, H Ar, NH); 7.40 (2H, d, *J* = 8.0, H Ar); 7.31–7.26 (4H, m, H Ph); 7.24–7.19 (1H, m, H Ph); 6.96 (1H, d, *J* = 10.4, NHC<u>H</u>=); 6.12 (1H, d, *J* = 9.2, H Ar); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.2 (C-1 Ar); 143.4 (C Tol); 137.8 (C Tol); 137.4 (C-4 Ar); 135.7 (C Ph); 129.8 (2CH Tol); 128.7 (2CH Ph); 128.4 (3-CH Ar); 127.1 (4-CH Ph); 126.4 (2CH Tol); 124.6 (5-CH Ar); 124.3 (2CH Ph); 121.4 (NHCH=); 118.5 (NHC=); 111.9 (6-CH Ar); 107.8 (C-2 Ar); 21.0 (CH_3). Found, *m*/*z*: 510.0092 $[M+Na]^+$. $C_{21}H_{18}BrN_3NaO_4S$. Calculated, *m*/*z*: 510.0094.

(*Z*)-*N*-{2-[(2-Iodo-4-nitrophenyl)amino]-2-phenylvinyl}-4-methylbenzenesulfonamide (3g). Yield 143 mg (89%), yellow crystals, mp 211–213°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.38 (1H, d, *J* = 10.3, TsNH); 8.49 (1H, s, H Ar); 7.78 (2H, d, *J* = 7.9, H Ar); 7.74 (1H, d, *J* = 9.1, H Ar); 7.41 (2H, d, *J* = 7.9, H Ar); 7.35–7.24 (5H, m, H Ph, NH); 7.23–7.18 (1H, m, H Ph); 6.92 (1H, d, *J* = 10.3, NHC<u>H</u>=); 6.03 (1H, d, *J* = 9.1, H Ar); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 151.5; 143.4; 138.1; 137.8; 135.7; 134.7; 129.8; 128.7; 127.2; 126.4; 125.0; 124.4; 120.9; 119.4; 111.4; 83.4; 21.0. Found, *m*/*z*: 533.9995 $[M-H]^-$. $C_{21}H_{17}IN_3O_4S$. Calculated, *m*/*z*: 533.9990.

(*Z*)-4-Methyl-*N*-{2-[(2-nitrophenyl)amino]-2-phenylvinyl}benzenesulfonamide (3h). Yield 107 mg (87%), yellow-orange crystals, mp 184–185°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.34 (1H, d, *J* = 10.6, TsNH); 8.71 (1H, s, NH); 8.10 (1H, dd, *J* = 8.5, *J* = 1.6, H Ar); 7.75 (2H, d, *J* = 8.2, H Ar); 7.43–7.35 (4H, m, H Ar); 7.30 (2H, t, *J* = 7.7, H Ar); 7.26–7.17 (2H, m, H Ar); 6.94 (1H, d, *J* = 10.6, NHC<u>H</u>=); 6.79–6.67 (1H, m, H Ar); 6.40–6.35 (1H, m, H Ar); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 143.4; 143.0; 137.8; 135.9; 135.8; 133.0; 129.8; 128.8; 127.2; 126.3; 125.9; 124.2; 121.0; 118.3; 116.6; 115.8; 21.0. Found, *m*/*z*: 408.1033 $[M-H]^-$. $C_{21}H_{18}N_3O_4S$. Calculated, *m*/*z*: 408.1024.

(*Z*)-4-Methyl-*N*-{2-[(4-methyl-2-nitrophenyl)amino]-2-phenylvinyl}benzenesulfonamide (3i). Yield 97 mg (76%), orange crystals, mp 191–192°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.30 (1H, d, *J* = 10.4, TsNH); 8.58 (1H, s, NH); 7.90 (1H, s, H Ar); 7.74 (2H, d, *J* = 8.1, H Ar); 7.40 (2H, d, *J* = 8.1, H Ar); 7.37–7.17 (5H, m, H Ph); 7.02 (1H, dd, *J* = 8.8, *J* = 2.1, H Ar); 6.89 (1H, d, *J* = 10.4, NHC<u>H</u>=); 6.27 (1H, d, *J* = 8.7, H Ar); 2.40 (3H, s, CH_3); 2.20 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 143.3; 141.1; 137.8; 137.0; 136.0; 132.6; 129.8; 128.7; 127.2; 126.3; 125.9; 125.0; 124.3; 120.6; 118.7; 116.0; 21.0; 19.4. Found, *m*/*z*: 446.1155 $[M+Na]^+$. $C_{22}H_{21}N_3NaO_4S$. Calculated, *m*/*z*: 446.1145.

(*Z*)-*N*-{2-[(4-Methoxy-2-nitrophenyl)amino]-2-phenylvinyl}-4-methylbenzenesulfonamide (3j). Yield 124 mg (94%), red crystals, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.30 (1H, d, *J* = 10.5, TsNH); 8.55 (1H, s, NH); 7.75 (2H, d, *J* = 8.3, H Ar); 7.54 (1H, d, *J* = 3.0, H Ar); 7.40 (2H, d, *J* = 8.0, H Ar); 7.39–7.32 (2H, m, H Ph); 7.29 (2H, t, *J* = 7.6, H Ph); 7.25–7.18 (1H, m, H Ph); 6.93 (1H, dd, *J* = 9.3, *J* = 3.0, H Ar); 6.87 (1H, d, *J* = 10.5, NHC<u>H</u>=); 6.33 (1H, d, *J* = 9.3, H Ar); 3.73 (3H, s, OCH_3); 2.39 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 150.0; 143.4; 138.2; 137.8; 136.0; 132.3; 129.8; 128.8; 127.2; 126.3; 125.6; 124.4; 120.4; 119.1; 117.6; 107.0; 55.7; 21.0. Found, *m*/*z*: 438.1139 $[M-H]^-$. $C_{22}H_{20}N_3O_5S$. Calculated, *m*/*z*: 438.1129.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(4-methylphenyl)vinyl}-4-methylbenzenesulfonamide (3k). Yield 90 mg (60%), yellow crystals, mp 194–195°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.31 (1H, d, *J* = 10.4, TsNH); 8.31 (1H, d, *J* = 2.7, H Ar); 7.79–7.69 (4H, m, H Ar, NH); 7.40 (2H, d, *J* = 8.0, H Ar); 7.18 (2H, d, *J* = 7.9, H Ar); 7.10 (2H, d, *J* = 7.9, H Ar); 6.88 (1H, d, *J* = 10.4, NHC<u>H</u>=); 6.09 (1H, d, *J* = 9.2, H Ar); 2.39 (3H, s, CH_3); 2.25 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.2; 143.4; 137.8; 137.4; 136.5; 132.8; 129.8; 129.3; 128.3; 126.4; 124.5; 124.3; 120.4; 118.9; 112.1; 107.9; 21.0; 20.6. Found, *m*/*z*: 500.0272 $[M-H]^-$. $C_{22}H_{19}BrN_3O_4S$. Calculated, *m*/*z*: 500.0285.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(3-methylphenyl)vinyl}-4-methylbenzenesulfonamide (3l). Yield 127 mg (84%), pale-yellow crystals, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.35 (1H, d, *J* = 10.4, TsNH); 8.31 (1H, d, *J* = 2.6, H Ar); 7.75–7.69 (4H, m, H Ar, NH); 7.40 (2H, d, *J* = 8.3, H Ar); 7.20–7.12 (2H, m, H Ar); 7.07–7.00 (2H, m, H Ar); 6.94 (1H, d, *J* = 10.4, NHC<u>H</u>=); 6.12 (1H, d, *J* = 9.2, H Ar); 2.40 (3H, s, CH_3); 2.26 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.2;

143.4; 137.9; 137.8; 137.4; 135.7; 129.8; 128.6; 128.3; 127.9; 126.4; 124.7; 124.6; 121.5; 121.2; 118.6; 111.9; 107.8; 21.1; 20.9. Found, *m*/*z*: 500.0295 $[M-H]^-$. $C_{22}H_{19}BrN_3O_4S$. Calculated, *m*/*z*: 500.0285.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(4-methoxyphenyl)vinyl}-4-methylbenzenesulfonamide (3m). Yield 112 mg (72%), yellow crystals, mp 171–172°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.23 (1H, d, *J* = 10.3, TsNH); 8.31 (1H, d, *J* = 2.6, H Ar); 7.76 (2H, d, *J* = 8.2, H Ar); 7.73 (1H, dd, *J* = 9.2, *J* = 2.6, H Ar); 7.68 (1H, s, NH); 7.39 (2H, d, *J* = 8.2, H Ar); 7.22 (2H, d, *J* = 8.8, H Ar); 6.87 (2H, d, *J* = 8.8, H Ar); 6.78 (1H, d, *J* = 10.3, NHC<u>H</u>=); 6.10 (1H, d, *J* = 9.2, H Ar); 3.72 (3H, s, OCH_3); 2.39 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 158.7; 149.2; 143.3; 137.8; 137.4; 129.8; 128.3; 127.9; 126.4; 125.8; 124.5; 119.4; 119.1; 114.2; 112.2; 107.9; 55.1; 21.0. Found, *m*/*z*: 516.0239 $[M-H]^-$. $C_{22}H_{19}BrN_3O_5S$. Calculated, *m*/*z*: 516.0234.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(4-chlorophenyl)vinyl}-4-methylbenzenesulfonamide (3n). Yield 115 mg (73%), pale-green crystals, mp 208–209°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.45 (1H, d, *J* = 10.5, TsNH); 8.32 (1H, d, *J* = 2.6, H Ar); 7.83–7.70 (4H, m, H Ar, NH); 7.40 (2H, d, *J* = 8.0, H Ar); 7.36–7.29 (4H, m, H Ar); 7.04 (1H, d, *J* = 10.5, NHC<u>H</u>=); 6.12 (1H, d, *J* = 9.2, H Ar); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.1; 143.4; 137.8; 137.5; 134.8; 131.4; 129.8; 128.6; 128.4; 126.4; 126.0; 124.6; 122.3; 117.2; 111.8; 107.9; 21.0. Found, *m*/*z*: 519.9733 $[M-H]^-$. $C_{21}H_{16}BrClN_3O_4S$. Calculated, *m*/*z*: 519.9739.

***N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(4-bromophenyl)vinyl}-4-methylbenzenesulfonamide (3o)**, a mixture of *Z*- and *E*-isomers in 6:1 ratio. Yield 124 mg (73%), beige crystals, mp 202–204°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.46 (0.9H, d, *J* = 10.6, TsNH); 10.37 (0.15H, d, *J* = 10.6, TsNH); 8.31 (0.8H, d, *J* = 2.6, H Ar); 8.30 (0.15H, d, *J* = 2.6, H Ar); 7.81–7.73 (4H, m, H Ar, NH); 7.47 (2H, d, *J* = 8.6, H Ar); 7.40 (2H, d, *J* = 8.0, H Ar); 7.25 (2H, d, *J* = 8.6, H Ar); 7.05 (0.9H, d, *J* = 10.6, NHC<u>H</u>=); 6.94 (0.15H, d, *J* = 10.5, NHC<u>H</u>=); 6.12 (0.9H, d, *J* = 9.2, H Ar); 6.07 (0.15H, d, *J* = 9.2, H Ar); 2.40 (2.6H, s, CH_3); 2.39 (0.5H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: *Z*-isomer: 149.1; 143.5; 137.8; 137.5; 135.2; 131.5; 129.8; 128.4; 126.4; 126.3; 124.6; 122.4; 119.9; 117.3; 111.8; 107.9; 21.0. Found, *m*/*z*: 563.9236 $[M-H]^-$. $C_{21}H_{16}Br_2N_3O_4S$. Calculated, *m*/*z*: 563.9234.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(3,4-dimethoxyphenyl)vinyl}-4-methylbenzenesulfonamide (3p). Yield 143 mg (87%), yellow-orange crystals, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.20 (1H, d, *J* = 10.3, TsNH); 8.31 (1H, d, *J* = 2.6, H Ar); 7.77 (2H, d, *J* = 7.9, H Ar); 7.72 (1H, dd, *J* = 9.2, *J* = 2.6, H Ar); 7.65 (1H, s, NH); 7.40 (2H, d, *J* = 7.9, H Ar); 6.90 (1H, d, *J* = 2.1, H Ar); 6.88–6.82 (2H, m, H Ar, NHC<u>H</u>=); 6.73 (1H, dd, *J* = 8.4, *J* = 2.1, H Ar); 6.11 (1H, d, *J* = 9.2, H Ar); 3.73 (3H, s, OCH_3); 3.70 (3H, s, OCH_3); 2.39 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.2; 148.8; 148.5; 143.3; 137.9; 137.4; 129.7; 128.3 (2C); 126.4; 124.4; 119.6; 119.3; 117.2; 112.3; 111.9; 108.3; 107.9; 55.5 (2C); 21.0. Found, *m*/*z*: 570.0309 $[M+Na]^+$. $C_{23}H_{22}BrN_3NaO_6S$. Calculated, *m*/*z*: 570.0305.

(*Z*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(thiophen-2-yl)vinyl}-4-methylbenzenesulfonamide (3q). Yield 117 mg (79%), yellow crystals, mp 211–212°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.44 (1H, d, *J* = 10.6, TsNH); 8.31 (1H, d, *J* = 2.6, H Ar); 7.82 (1H, s, NH); 7.79–7.71 (3H, m, H Ar); 7.41 (2H, d, *J* = 8.1, H Ar); 7.32 (1H, dd, *J* = 4.6, *J* = 1.7, H Ar); 6.98–6.93 (2H, m, H Ar); 6.91 (1H, d, *J* = 10.6, NHC<u>H</u>=); 6.21 (1H, d, *J* = 9.2, H Ar); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 149.1; 143.5; 140.8; 137.7; 137.6; 129.8; 128.3; 127.9; 126.3; 124.5; 124.1; 122.5; 120.4; 114.3; 111.8; 107.8; 20.9. Found, *m*/*z*: 491.9704 $[M-H]^-$. $C_{19}H_{15}BrN_3O_4S_2$. Calculated, *m*/*z*: 491.9693.

(*E*)-*N*-{2-[(2-Bromo-4-nitrophenyl)amino]-2-(1,3-dioxoisoindolin-2-yl)vinyl}-4-methylbenzenesulfonamide (3s). A test tube with air-tight screw cap was charged with 2-bromo-4-nitroaniline (**1f**) (28 mg, 0.13 mmol), 4-phthalimido-1-tosyl-1*H*-1,2,3-triazole (**2j**) (40.5 mg, 0.11 mmol), and anhydrous 1,2-dichloroethane (0.3 ml); the solution was flushed with argon, the screw cap was tightly closed and the magnetically stirred mixture was heated at 70°C until precipitate appeared (approximately 30 min). The completion of the reaction was controlled by TLC (eluent hexane–EtOAc, 5:1). The precipitate was filtered off and washed with cold dichloromethane (2×3 ml). Yield 24 mg (39%), yellow crystals, mp 223.5–225.5°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.24 (1H, d, *J* = 10.0, TsNH); 8.30 (1H, d, *J* = 2.6, H Ar); 7.90–7.85 (4H, m, H Ar); 7.82 (1H, dd, *J* = 9.2, *J* = 2.6, H Ar); 7.75 (2H, d, *J* = 7.8, H Ar); 7.61 (1H, s, NH); 7.47 (2H, d, *J* = 7.8, H Ar); 6.72 (1H, d, *J* = 10.0, NHC<u>H</u>=); 6.54 (1H, dd, *J* = 9.2, *J* = 1.9, H Ar); 2.46 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 166.9 (2C=O); 147.3 (C-1 Ar); 143.6 (C Tol); 138.1 (C-4 Ar); 137.8 (C Tol); 134.6 (2CH Phth); 131.5 (2C Phth); 129.8 (2CH Tol); 128.0 (3-CH Ar); 126.4 (2CH Tol); 124.0 (5-CH Ar); 123.3 (2CH Phth); 122.1 (NHCH=); 113.2 (6-CH Ar); 108.3 (C-2 Ar); 107.7 (NHC=); 21.0 (CH_3). Found, *m*/*z*: 554.9987 $[M-H]^-$. $C_{23}H_{16}BrN_4O_6S$. Calculated, *m*/*z*: 554.9979.

Supplementary information file containing NMR spectra of all synthesized compounds is available at the journal website http://link.springer.com/journal/10593.

This work received financial support from the Russian Science Foundation (project No. 19-73-10090).

Analysis of the synthesized compounds was performed at the Saint Petersburg State University Magnetic Resonance Research Center and Chemical Analysis and Materials Research Center.

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