

Synthesis of substituted 1,2,3-triazoles via *N*-sulfonylaziridines

Victor I. Markov* and Evgenij V. Polyakov

**Ukrainian State Chemical-Technological University*

E-mail: markov@email.dp.ua

(received 27 Oct 05; accepted 28 Jan 06; published on the web 28 Feb 06)

Abstract

Nucleophilic ring-opening of *N*-sulfonylaziridines by sodium azide leads to β -azidoamines. The regioselectivity of this reaction and new efficient catalyst for such 1,3-dipolar cycloaddition are reported. Several 1,2,3-triazoles have been synthesized and their structures established by X-ray crystallography, MS, IR and ^1H NMR spectral data.

Keywords: Aziridines, sodium azide, 1,3-dipolar cycloaddition, triazoles

Introduction

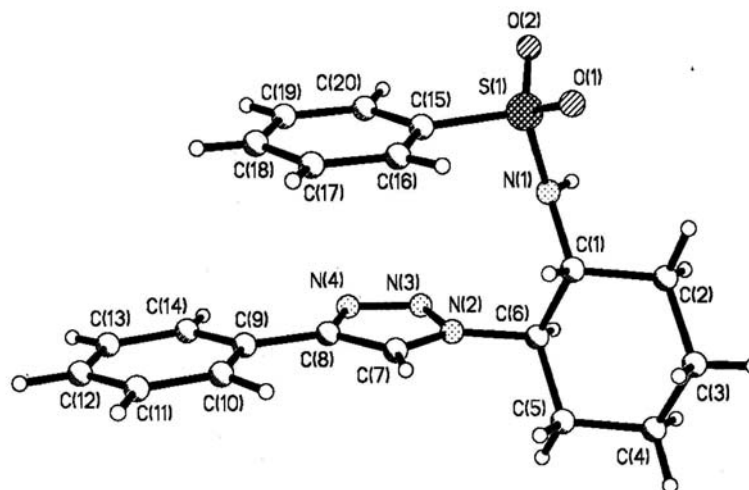
N-Substituted aziridines are versatile intermediates for the synthesis of many biologically active compounds that are valuable for new drugs development. There is a growing interest in ring opening reactions of aziridines with various nucleophiles due to their high reactivity and ease of preparation¹. *N*-Sulfonyl aziridines are well-known alkylating agents and they are used for the synthesis of several types of heterocyclic compounds²⁻⁵.

Antibacterial, antifungal, antiviral, anti-inflammatory and analgesic properties of 1,2,3-triazoles have been extensively studied. Recently some new 1,2,3-triazole derivatives have been reported as inhibiting tumor proliferation, invasion, and metastasis.⁶

We now report a new method for the synthesis of 1,2,3-triazole derivatives containing aminoethyl groups from *N*-sulfonylaziridines. The process can be carried out stepwise, or as multicomponent ("one-pot") synthesis. Nucleophilic ring-opening of aziridines by sodium azide was studied as a synthetic route to the substituted β -azidoamines. Regioselective azidolysis of aziridines with NaN_3 in the presence of Oxone in aqueous acetonitrile, or CeCl_3 was recently reported.²⁻³ However, we have established that azidolysis can be performed without catalyst in DMF in the presence of weak acids, that allowed us to develop a one-pot synthesis of 1,2,3-triazoles **3** by the reaction of aziridines **1** with NaN_3 , acetylenes and catalytic amounts of Cu_2Cl_2 in aqueous acetonitrile under reflux for 2–3 h in good to excellent yields.

Table 1. Nucleophilic addition of NaN_3 to *N*-arylsulfonylaziridines **1**

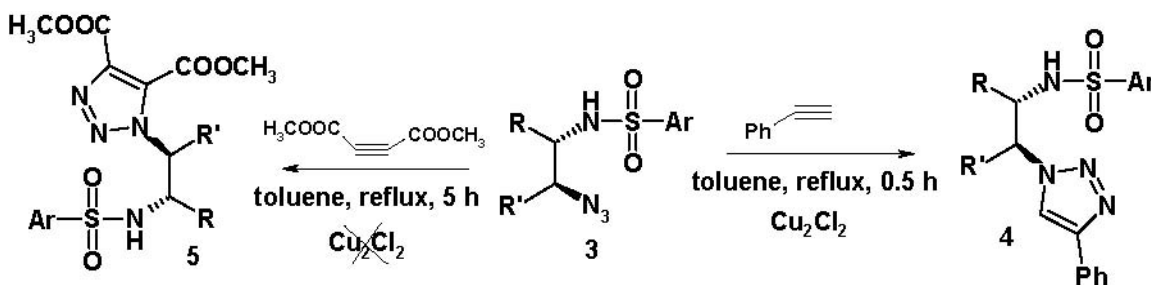
Entry	Aziridine 1	Product 3	Yield (%)
a			97
b			91
c			95
d			91
e			98
f			97
g			99
h			96
i			90

**Figure 1**

The cyclohexane ring is in the chair conformation (Figure 1). The 4-phenyltriazole substituent is in an equatorial position of the cyclohexane ring (torsion angle N(2)-C(6)-C(5)-C(4) 180.0(2)°). The phenyl ring C(9)...C(14) and triazole are essentially coplanar (torsion angle C(7)-C(8)-C(9)-C(10) 4.4(3)°).

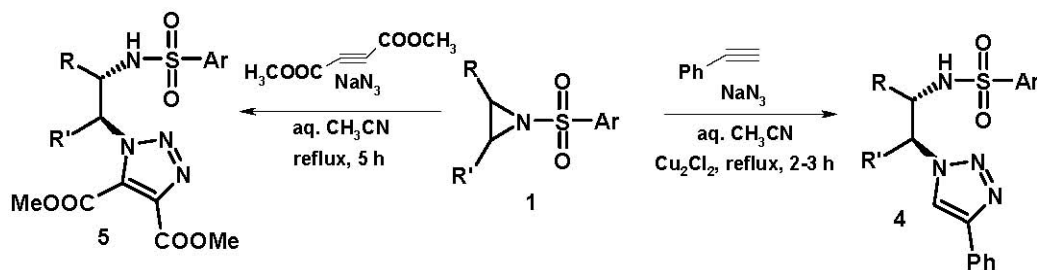
The crystals (Figure 1) form stacks along a crystallographic direction (0 1 0) bound by weak intermolecular hydrogen bonds N(1)-H(1N)...N(4) (2-x, -y, l-z) H...N 2.20 Å and N-H...N 137.5°.

Dimethyl acetylenedicarboxylate also reacted with alkyl azides to produce substituted 1,2,3-triazoles. However, in this case catalysis by Cu(I) was not observed possibly because of the absence of a terminal hydrogen atom in the acetylene, which makes complex formation impossible. Products of type **5** were also observed but required a long reaction time to form.

**Scheme 2**

We modified the reported two-step sequence, i.e. aziridine ring-opening followed by a cycloaddition, to provide a "one-pot" synthesis of 1,2,3-triazoles **4**, **5**. This was successfully achieved by using *N*-sulfonylaziridines, NaN₃, phenylacetylene and catalytic amounts of Cu₂Cl₂ in aqueous acetonitrile (Scheme 3). The advantage of this method is that it produces substantial amounts of 1,2,3-triazoles in a short time, avoiding purification of the intermediated azides. The

use of a "one-pot" method did not decrease yield of the 1,2,3-triazoles **4** (Table 2).



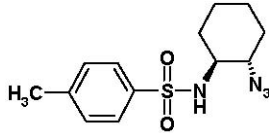
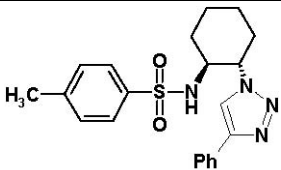
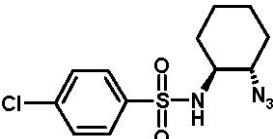
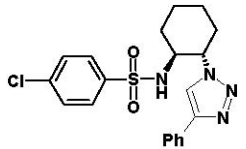
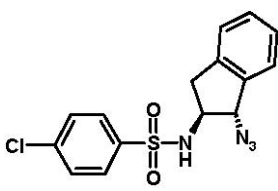
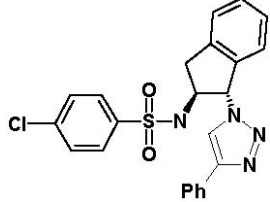
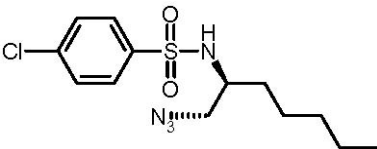
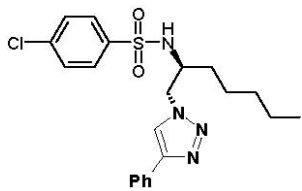
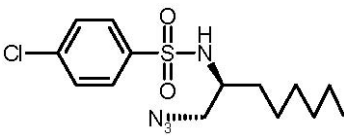
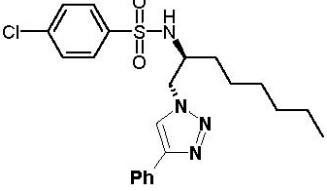
Scheme 3

All 1,2,3-triazole derivatives obtained are white solids with high-melting points. Interestingly, melting points of substituted 1,2,3-triazoles do not dramatically decrease with length of the alkyl chain.

Table 2. 1,3-Dipolar cycloaddition of β -azidoamines to acetylenes

Entry	Azide	1,2,3-Triazole	Yield % / (%) ^a
a			89
b			79
c			96 / (97)
d			74 / (78)
e			84 / (86)

Table 2. Continued

f			78 / (80)
g			90 / (90)
h			95 / (94)
i			68
j			72

^a Yields in parenthesis are given for "one-pot" synthesis of **4** and **5** from **1** as described in the Experimental Section.

Experimental Section

General Procedures. NMR spectra were recorded on a Bruker DRX200 spectrometer in CDCl₃ or DMSO-d₆ and chemical shifts (δ_{H}) are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Mass spectra were obtained with a Varian 1200L(-70eV) instrument with straight penetration by an electronic impact, and Infrared spectra were recorded as KBr pellets or in CHCl₃ solution on an Impact 400 ("NICOLET") spectrometer. Melting points were taken in open capillary tubes and are uncorrected.

The single-crystal X-ray study was performed on a Siemens P3/PC diffractometer. Compound **4e**, (C₂₀H₂₂N₄O₂S) (20 °C), crystallized in the space group P2₁/n, monoclinic, from DMF as colorless rectangular prisms, $a = 14.661(5)$, $b = 8.641(2)$, $c = 15.450(5)$ Å, $\beta^\circ =$

104.18(3), $V = 897.8(1) \text{ \AA}^3$, $M_r = 382.48$.

Lattice constants were determined from least squares refinement on diffractometer angles for 24 automatically centered reflections; $\rho = 1.339 \text{ Mg/m}^3$, $Z = 4$, $\mu = 0.194 \text{ mm}^{-1}$, $F(000) = 808$. Data collection: monitoring of check reflexion showed no signs of decay. A total of 3748 reflections were measured, (3352 were independent, $R_{\text{int}} = 0.050$).

(F^2 : $wR_2 = 0.1046$, 3337 reflections ($R_1 = 0.039$, 2250 reflections with $F > 4\sigma(F)$, $S = 1.002$). All calculations were carried out using the SHELX 97 program package.⁷⁻⁹

(For final atom's coordinates see **general information**)

General procedure of nucleophilic ring opening of *N*-sulfonylaziridines with sodium azide

To a solution of *N*-sulfonylaziridine (0.02 mol) in DMF (50 mL) was added sodium azide (0.022 mol) and water (10 mL). After dissolving the sodium azide, carbon dioxide was bubbled into mixture. The reaction was completed when pH of the solution became constant. The reaction mixture was diluted with cold water and the product was extracted with ethyl acetate (3 x 50 mL). The extracts were separated, dried over sodium sulfate and solvent removed under vacuum to give (**3b–f**) either as white crystals or a colorless liquid.

1-(4-Methyl-benzenesulfonamide)-2-phenyl-2-azidoethane (3b). Colorless liquid; IR: 2150, 3275 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): $\delta = 2.45$ (s, 3H, ArCH_3), 2.95–3.10 (m, 1H, CHNH), 3.10–3.30 (m, 1H, CHNH), 4.55–4.65 (dd, $J = 7.7, 5.0 \text{ Hz}$, 1H, CHN_3), 5.30–5.50 (m, 1H, NH), 7.05–7.40 (m, 7H, ArH), 7.75 (d, $J = 8.0 \text{ Hz}$, 2H, ArH). MS (EI): $m/z = 274$ ($M - \text{N}_3$)⁺.

1-(4-Chloro-benzenesulfonamide)-2-phenyl-2-azidoethane (3c). White microcrystals, mp 83–85 °C; IR (cm^{-1}) 3050, 3028, 2133, 1320, 1150, 1028, 540; ^1H NMR (200 MHz, CDCl_3): $\delta = 3.10$ –3.20 (m, 2H, CH_2NH), 4.50–4.70 (t, $J = 7.2, 4.9 \text{ Hz}$, 1H, CHN_3), 5.0–5.1 (t, 1H, NH), 7.05–7.40 (m, 5H, ArH), 7.6 (d, $J = 8.0 \text{ Hz}$, 2 H, ArH), 7.75 (d, $J = 8.0 \text{ Hz}$, 2H, ArH).

1-(4-Methyl-benzenesulfonamide)-2-azido-cyclohexane (3e). Colorless liquid; IR (neat): 2100, 3320 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.20$ –1.40 (m, 4H), 1.60–1.75 (m, 2H), 2.00–2.15 (m, 2H), 2.45 (s, 3H, ArCH_3), 2.85–2.95 (m, 1H, CHN_3), 3.00–3.10 (m, 1H, CHNH), 4.80 (d, $J = 5.4 \text{ Hz}$, 1H, NH), 7.30 (d, $J = 8.1 \text{ Hz}$, 2H, ArH), 7.80 (d, $J = 8.1 \text{ Hz}$, 2H, ArH). MS (EI): $m/z = 294$ (M)⁺.

1-(4-Chloro-benzenesulfonamide)-2-azido-cyclohexane (3f). White microcrystals, mp 88–90 °C; ^1H NMR (200 MHz, $\text{DMSO}-d_6$): $\delta = 1.0$ –1.3 (m, 4H, cyclohexyl), 1.5 (m, 3H, cyclohexyl), 1.9 (m, 1H, cyclohexyl), 2.9–3.05 (m, 1H, cyclohexyl $\text{CH}-\text{N}_3$), 3.1–3.15 (m, 1H, cyclohexyl $\text{CH}-\text{NH}$), 7.9 (d, $J = 8.0 \text{ Hz}$, 1H, NH), 7.60 (d, $J = 8.1 \text{ Hz}$, 2H, ArH), 7.75 (d, $J = 8.1 \text{ Hz}$, 2H, ArH).

General procedure of synthesis of 1,2,3-triazoles (4, 5)

A. Using β -azidoamines. To a solution of β -azidoamines (0.01 mol) in 40 mL of toluene was added phenylacetylene (0.011 mol) and catalytic amount of Cu_2Cl_2 . The resulting mixture was refluxed for 30 min. Then triazole contaminated with copper sulfide was filtered off and subsequently purified by bubbling of H_2S through the solution in DMF. The filtrate was cooled down and the precipitate was filtrated to give pure triazole.

B. "One-pot" synthesis 1,2,3-triazoles (4) from *N*-sulfonylaziridines (1). *N*-sulfonylaziridine (10.0 mmol), sodium azide (11.0 mmol), phenylacetylene (11.0 mol) and catalytic amount of Cu_2Cl_2 (0.55 mmol) were added to a mixture of water (2 mL) and acetonitrile (20 mL). The reaction mixture was refluxed for 2–3 h. A small amount of product precipitated out during the reflux. The reaction mixture was cooled down, the solid was filtered off, and further purification was done according to the procedure A.

C. Synthesis of 1,2,3-triazole (5) from acetylenedicarboxylic acid ester and azide (3). Acetylenedicarboxylic ester (0.011 mol) was added to a solution of alkyl azide **3** (0.01 mol) in 40 mL of toluene. Reaction mixture was refluxed for 5 h. A small amount of product precipitated during the reflux. The reaction mixture was cooled down, the solid was filtered off and 1,2,3-triazole obtained was recrystallized from aqueous DMF.

D. "One-pot" synthesis of 1,2,3-triazoles (5) using acetylenedicarboxylic acid ester. Synthesis was carried out in $\text{H}_2\text{O}:\text{MeCN}$ (1:10). To the solution of *N*-sulfonylaziridine (0.01 mol) were added sodium azide (0.011 mol), acetylenedicarboxylic ester (0.011 mol) all at once. Reaction mixture was refluxed for 5 h. Resulting solution was cooled down, solid was filtered off and obtained 1,2,3-triazoles were recrystallized from aqueous DMF.

***N*-[2-Phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl] benzenesulfonamide (4a).** General procedure A. White powder, mp 190–192 °C. ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ = 2.6–2.8 (m, 2H, $\text{CH}_2\text{-NH}$), 4.5 (m, 1H, CH-N(Tr)), 7.9 (m, 1H, NH), 8.5 (s, 1H, (CH(Tr))), 7.1–7.8 (m, 15 H, ArH). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$: C, 65.33; H, 4.98; N, 13.85. Found: C, 65.43; H, 4.94; N, 13.65.

Benzenesulfonamide, 4-methyl-*N*-[2-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl] (4b). General procedures A. White solid, mp 201–203 °C. ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ = 2.55 (s, 3H, ArCH_3), 3.5–3.6 (m, 1H, CH-NH), 3.8–3.9 (m, 1H, CH-NH), 5.8 (dd, 1H, CH-N(Tr)), 8.1 (m, 1H, NH), 9.05 (s, 1H, (CH(Tr))), 7.35–7.95 (m, 14H, ArH). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$: C, 66.01; H, 5.30; N, 13.39. Found: C, 66.18; H, 5.36; N, 13.08.

Benzenesulfonamide, 4-chloro-*N*-[2-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl] (4c). General procedures A, B. White powder, mp 214–216 °C. IR (cm^{-1}) 3250, 3032, 1350, 1150, 1070, 640. ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ = 3.5 (m, 1H, CH-NH), 3.9 (m, 1H, CH-NH), 5.8 (dd, 1H, CH-N(Tr)), 8.2 (m, 1H, NH), 8.6 (s, 1H, (CH(Tr))), 7.2–7.9 (m, 14H, ArH). MS (EI): m/z = 438 (5) (M^+), 294 (9), 235 (49.2), 175 (22.4), 145 ($\text{Ph-Tr(M}^+)$) (6.8), 116 (100) 111 ($p\text{-Cl-Ph(M}^+)$) (37.3), 104 (42.0). Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_4\text{O}_2\text{S}$: C, 60.20; H, 4.36; N, 12.76. Found: C, 60.29; H, 4.31; N, 12.16.

1*H*-1,2,3-Triazole-4,5-dicarboxylic acid, 1-[2-[(4-chlorophenyl)sulfonyl]amino]-1-phenylethyl]-, dimethyl ester (5d). General procedure C, D. White solid, mp 160–162 °C. ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ = 3.3 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 4.1 (dd, 2H, $\text{CH}_2\text{-NH}$), 5.05 (m, 1H, CH-N(Tr)), 8.8 (m, 1H, NH), 9.2 (s, 1H, (CH(Tr))), 7.9 (d, J = 8.0 Hz, 1H, NH), 7.70 (d, J = 8.0 Hz, 2H, ArH), 7.2–7.5 (m, 5H, ArH). Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{O}_6\text{S}$: C, 50.16; H, 4.00; N, 11.70. Found: C, 50.11; H, 4.14; N, 12.31.

Benzenesulfonamide, *N*-[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexyl] (4e). General procedures A, B. White solid, mp 245–246 °C. ¹H NMR (200 MHz, DMSO-*d*₆): δ = 0.9–1.2 (m, 3H, cyclohexyl), 1.5–2.1 (m, 5H, cyclohexyl), 3.5 (m, 1H, cyclohexyl CH-NH), 4.3 (dt, 1H, cyclohexyl CH-N(Tr)), 7.85 (m, 1H, NH), 8.4 (s, 1H, (CH(Tr))), 7.0–7.7 (m, 10H, ArH). Anal. Calcd for C₂₀H₂₂N₄O₂S: C, 62.81; H, 5.80; N, 14.65. Found: C, 62.88; H, 5.72; N, 15.30.

Benzenesulfonamide, 4-methyl-*N*-[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexyl] (4f). General procedures A, B. White solid, mp 230–231 °C. ¹H NMR (200 MHz, DMSO-*d*₆): δ = 1.1–2.0 (m, 8H, cyclohexyl), 2.05 (s, 3H, ArCH₃), 3.45 (m, 1H, cyclohexyl CH-NH), 4.6 (m, 1H, cyclohexyl CH-N(Tr)), 8.4 (m, 1H, NH), 8.6 (s, 1H, (CH(Tr))), 7.2–7.7 (m, 9H, ArH). Anal. Calcd for C₂₁H₂₄N₄O₂S: C, 63.61; H, 6.10; N, 14.13. Found: C, 63.67; H, 6.21; N, 13.50.

Benzenesulfonamide, 4-chloro-*N*-[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexyl] (4g). General procedures A, B. White solid, mp 250–251 °C. ¹H NMR (200 MHz, DMSO-*d*₆): δ = 1.1–1.45 (m, 3H, cyclohexyl), 1.5–2.0 (m, 5H, cyclohexyl), 3.65 (m, 1H, cyclohexyl CH-NH), 4.4 (dt, 1H, cyclohexyl CH-N(Tr)), 8.1 (d, *J* = 8.0 Hz, 1H, NH), 8.45 (s, 1H, (CH(Tr))), 7.70 (d, *J* = 8.0 Hz, 2H, ArH), 7.5 (d, *J* = 8.0 Hz, 2H, ArH), 7.2–7.5 (m, 5H, ArH). MS (EI): *m/z* = 416 (M⁺) (8.1), 272 (29.5), 213 (76.2), 175 (47.2), 145 (Ph-Tr(M⁺)) (7.8), 111 (*p*-Cl-Ph(M⁺)) (79.0), 81(cyclohexene (M⁺)) (100). Anal. Calcd for C₂₀H₂₁ClN₄O₂S: C, 57.62; H, 5.08; N, 13.44. Found: C, 57.34; H, 5.00; N, 13.47.

Benzenesulfonamide, 4-chloro-*N*-[2,3-dihydro-1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1*H*-inden-2-yl] (4h). General procedures A, B. White solid, mp 295–297 °C. ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.5–3.0 (m, 2H, -CH₂-), 4.5 (s, 1H, CH-N(Tr)), 6.0 (m, 1H, CH-NH), 8.8 (s, 1H, NH), 8.5 (s, 1H, (CH(Tr))), 6.70–8.0 (m, 13H, ArH). MS (EI): *m/z* = 307(³⁷Cl, M⁺) (1.6), 305(³⁵Cl, M⁺), (12.5), 279 (1.3), 212 (1.2), 178 (2.2), 111 (*p*-Cl-Ph(M⁺)) (26.2), 103 (100). Anal. Calcd for C₂₃H₁₉ClN₄O₂S: C, 61.26; H, 4.25; N, 12.42. Found: C, 61.01; H, 4.21; N, 12.30.

Benzenesulfonamide, 4-chloro-*N*-[1-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]hexyl] (4i). Phenylacetylene (0.011 mol) and catalytic amount of Cu₂Cl₂ were added to the solution of β-azidoamine (0.01 mol) in 40 mL of toluene. Resulting mixture was refluxed for 30 min. Precipitation of yellow crude 1,2,3-triazole were observed. After that, the mixture was filtered, and filtrate was cooled. Precipitate was filtered and filtrate was extra diluted with hexane. Obtained crude 1,2,3-triazole was purified by recrystallization from DMF. White solid, mp 165–167 °C; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 0.8–0.9 (m, 3H), 1.0–1.15 (m, 6H), 1.5–1.4 (m, 2H), 3.7 (dd, 1H, CH-N(Tr)), 4.3–4.45 (m, 2H, CH₂NH), 7.9 (d, *J* = 8.0 Hz, 1H, NH), 8.3 (s, 1H, (CH(Tr))), 7.70 (d, *J* = 8.0 Hz, 2H, ArH), 7.5 (d, *J* = 8.0 Hz, 2H, ArH), 7.1–7.5 (m, 5H, ArH). MS (EI): *m/z* = 432 (M⁺) (12.5), 274 (7.2), 230 (8.3), 229 (58.1), 145 (Ph-Tr(M⁺)) (5.2), 111 (*p*-Cl-Ph(M⁺)) (100). Anal. Calcd for C₂₁H₂₅ClN₄O₂S: C, 58.26; H, 5.82; N, 12.94. Found: C, 57.99; H, 5.94; N, 12.90.

Benzenesulfonamide, 4-chloro-*N*-[1-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]heptyl] (4j). Obtained according to 4i. White solid, mp 165–167 °C; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 0.6–0.7 (m, 3H), 0.85–1.05 (m, 8H), 1.5–1.4 (m, 2H), 3.5 (dd, 1H, CH-N(Tr)), 4.25–4.4 (m, 2H, CH₂NH), 8.0 (d, *J* = 8.0 Hz, 1H, NH), 8.4 (s, 1H, (CH(Tr))), 7.70 (d, *J* = 8.0 Hz, 2H, ArH), 7.5

(d, $J = 8.0$ Hz, 2H, ArH), 7.2–7.5 (m, 5H, ArH). MS (EI): $m/z = 446$ (M⁺) (16.6%), 302 (7.5%), 290 (3.2%), 243(100%), 145 (Ph-Tr(M⁺)) (8.3%), 111 (*p*-Cl-Ph(M⁺))(89%). Anal. Calcd for C₂₂H₂₇ClN₄O₂S: C, 59.11; H, 6.09; N, 12.53. Found: C, 58.82; H, 6.11; N, 12.14.

[Supplementary Material is Available](#)

Acknowledgments

The authors thank Scientific and Technological Corporation "Institute for Single Crystals" (Dr. O. Shishkin, Dr. V. Chebanov, Dr. E. Gladkov, Dr. R. Zubatuk) for their support in characterization of obtained compounds.

Financial support by the state-grant 0103U001186.

References

1. Markov, V. I.; Burmistrov, S. I.; Danilei`ko, D. A.; Doroshenko, V. A.; Gella, I. M. *Rus. J. Org. Chem. (Russ. Ed.)* **1971**, 7, 602; *Chem. Abstr.* **1971**, 75, 5588.
2. Hu, X. E. *Tetrahedron* **2004**, 60, 2701.
3. Sabitha, G.; Babu, R. S.; Rajkumar, M.; Yadav, J. S. *Synthesis* **2002**, 15, 2254.
4. Sabitha, G.; Babu, R. S.; Rajkumar, M.; Yadav, J. S. *Org. Lett.* **2002**, 4, 343.
5. Abu-Orabi, S. T. *Molecules* **2002**, 7, 302.
6. Heng, S. D.; Kun, W. I.; Qing, L. W.; Bin, Q.; Zhang, Z. Y. *J. Chinese Chem. Soc.* **2000**, 47, 343.
7. Zefirov, N. S.; Palyulin, V. A.; Dashevskaya, E. E. *J. Phys. Org. Chem. (Russ. Ed.)* **1990**, 3, 147.
8. Zefirov, Y. V.; Zorkiy, P. M. *Russ. Chem. Rev. (Russ. Ed.)* **1989**, 5, 713.
9. Sheldrick, G.M. *SHELX97. PC Version. A system of computer programs for the crystal structure solution and refinement*. Rev.2, 1998.