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Authors: Pavel S. Silaichev, Tetyana Beryozkina, Mikhail S. Novikov, Wim Dehaen, and Vasiliy A. Bakulev

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A Base-controlled Reaction of 2-Cyanoacetamidines (3,3-Diaminoacrylonitriles) with Sulfonyl Azides as a Route to Nonaromatic 4-Methylene-1,2,3-triazole-5-imines

Pavel S. Silaichev,[a,b] Tetyana V. Beryozkina,*[a] Mikhail S. Novikov,[c] Wim Dehaen,*[d] and Vasiliy A. Bakulev[a]

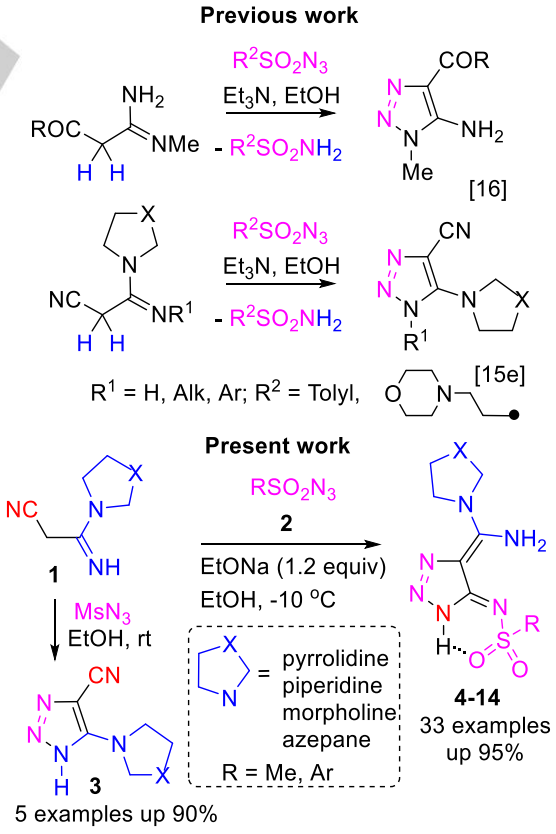
[a] Dr. P. S. Silaichev, Dr. T. V. Beryozkina, Prof. Dr. V. A. Bakulev
Ural Federal University named after the first President of Russia B. N. Yeltsin
19 Mira st. Yekaterinburg 620002, Russia
E-mail: t.v.berezkina@urfu.ru
[b] Dr. P. S. Silaichev
Department of Chemistry, Perm State University
15 Bukireva st., Perm 614990, Russia
[c] Prof. Dr. M. S. Novikov
St. Petersburg State University, Institute of Chemistry
7/9 Universitetskaya nab., St. Petersburg 199034, Russia
[d] Prof. Dr. W. Dehaen
Molecular Design and Synthesis, Department of Chemistry, KU Leuven
Celestijnenlaan 200F, B-3001 Leuven, Belgium
E-mail: wim.dehaen@chem.kuleuven.be

Supporting information for this article is given via a link at the end of the document.

Abstract: Reactions of 2-cyanoacetamidines with sulfonyl azides were shown to take place via two different pathways to form a mixture of 1-substituted 5-amino-1,2,3-triazoles **3** and novel 4-methylene-1*H*-1,2,3-triazole-5(4*H*)-imine derivatives **4-14**. In the absence of a base, 5-amino-1,2,3-triazoles **3** are formed as the only products. The presence of 1.2 equiv of sodium ethoxide or DBU switches the reaction outcome while involving the cyano group, resulting (after a 1,5-protic shift) in triazoles **4-14** as the only products. The methods were elaborated for the selective and efficient synthesis of triazoles **3** and 4-methylene-1,2,3-triazole-5-imines **4-14** including one-pot synthesis from sodium azide and sulfonyl chlorides. The unusual structure of **4-14** compounds was confirmed by X-ray data and 2D $^{1}H–^{15}N$ and $^{1}H–^{13}C$ NMR spectra. The formation of the products was explained by the presence of two strong hydrogen bonds N···H and O···H in these molecules.

Introduction

Since the beginning of this millennium, 1,2,3-triazoles have become very fashionable and rather available compounds due to the landmark discovery of copper catalyzed alkyne azide cycloaddition (CuAAC)[1] giving access to various types of 1,2,3-triazoles and facilitating their use in medicinal chemistry,[2] in organic synthesis as building blocks,[3] in chemical biology,[4] and in material chemistry.[5] Apart from the CuAAC reaction, the transformation of functionalized hydrazones,[6] the reactions of azides with enamines,[7] and carbonyl active methylene compounds,[6,8] reactions of NH-1,2,3-triazoles with electrophiles,[6,9] intra-[10] and intermolecular reactions of diazo compounds with aldimines,[6] and transformations of other heterocyclic compounds[11] are the main synthetic methods towards 1,2,3-triazoles of various structures. However, these methods are not applicable to the synthesis of 1,2,3-triazoles bearing both sulfonylamido and amidino groups which are of interest for medicinal chemistry.[12] Hence, the search of new effective methods for the synthesis of variously substituted 1,2,3-triazoles remains a subject worthy of investigation. Because a few 5-amino-1,2,3-triazole derivatives were synthesized from the reaction of 2-ethoxycarbonylacetamidines[10] and from malonodinitrile with benzenesulfonyl azide[13] we turned our attention to the reactivity of 2-cyanoacetamidines towards sulfonyl azides to prepare derivatives of 5-amino-1,2,3-triazole-4-carbimidamides (Scheme 1).



Scheme 1. Reactions of methylene active amidines with sulfonyl azides.

It is worth noting that in contrast to the well-studied 2-cyanothioacetamides,[11a,14] the chemistry of their aza analogs, 2-cyanoacetamidines is poorly described in the literature[15] and their reactions with azides presented in only one report.[15e] It was shown there that the formation of intermediate diazo compounds took place as a result of diazo group transfer (Regitz reaction), which then cyclized to 5-amino-1,2,3-triazole-4-carbonitriles (Scheme 1). The generally accepted opinion on the single diazo group transfer direction of methylene active amidines with sulfonyl azides has been held for the long time.[16,20]

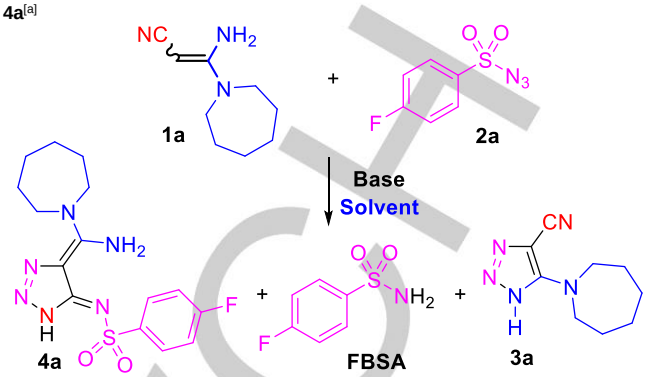
Combined experimental and theoretical studies of the reaction of amidines **1** with azides **2** have now demonstrated two different pathways for this reaction, leading to 5-amino-4-cyano-1,2,3-triazoles **3** and novel 5-sulfonylimido-4-methylene-1,2,3-triazoles **4-14** (Scheme 1). Depending on the presence and amount of base used, the direction of the reaction can be switched in favor of either compound. Thus, proper conditions were found and methods were elaborated for the selective and efficient synthesis of 4-cyano-5-cycloamino-1,2,3-triazoles **3** and 4-methylene-1,2,3-triazole-5-imines **4-14** (Scheme 1). The pathway to triazoles **4-14** represents a novel method of the synthesis of 1,2,3-triazoles based on tandem heterocyclization of 2-cyanoacetamidines and sulfonyl azides to 1-sulfonyl-1,2,3-triazoles and their subsequent rearrangement followed by a 1,5-protic shift to form the final products.

Results and Discussion

Usually, reactions of active methylene compounds with azides take place in the presence of various bases.[11a,17,18] In this work, we have found that 2-cyanoacetamidines **1** can react with mesyl azide even in the absence of an external base to form 4-cyanotriazoles **3** confirming the Regitz diazo-group-transfer course for this reaction.[18] The use of mesyl azide allows to easily separate the triazoles **3** from the by-product, mesyl amide by washing out the latter with water. It should be noted that mesyl azide is potentially explosive, and all reactions should be carried out behind blast shields. At the more available and considerable less expensive than 2-morpholinoethylsulfonyl azide which has been used previously[15e] to prepare compounds **3**. Furthermore the LCMS analysis of the sample **3a** showed, next to same time, mesyl azide is the major products **3a** the presence of a very small impurity of triazole **4a**.

In order to study the use of 2-cyanoacetamidine as a C–C–C–N building block and to involve the CN group in the process leading to 4-methylene-1,2,3-triazole-5-imines from sulfonyl azides, we screened the reaction conditions using 3-(azepane-1-yl)-3-iminopropanenitrile (**1a**) and 4-fluorobenzenesulfonyl azide **2a** as model reagents (Table 1 and Table SI1 of Supporting Info). Our initial optimization studies revealed the fact that depending on the presence and amount of base used, the direction of the reaction can be switched in favor of either product. In the absence of a base or in the presence of weak bases triazole **3a** is formed as major product. As it is seen from the Table 1 the use of strong bases, low temperature favor the formation of triazole **4a**. The optimal conditions for the synthesis of the target compound **4a** include the use of ethanol as a solvent, 1.2 equiv of a sodium ethoxide, and a temperature of -10 °C. The use of DBU in either 1,4-dioxane or benzene gives a slightly less yield of **4a** and can be considered an alternative protocol of the synthesis of compounds **4** (Table 1, Supporting Info, Table S1).

Table 1. Optimization of the Reaction Conditions for the Synthesis of Triazole **4a**[a]



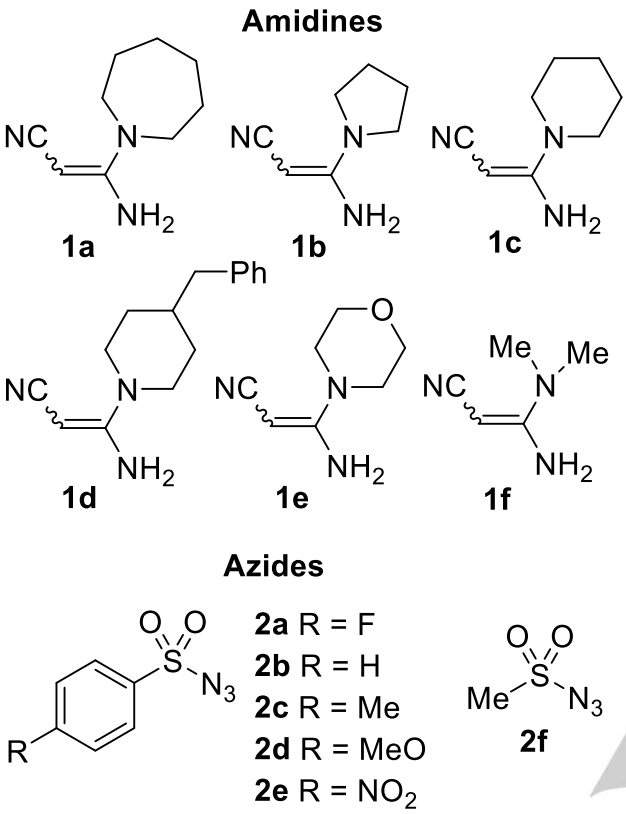
Entry	T, °C	Solvent	Base	Time (min)	Ratio **4a/3a**	Isolated yield, **4a** (%)
1	rt	EtOH (95%)	–	30	2/98	–
2	rt	EtOH (95%)	Et_3N	30	17/83	–
3	rt	EtOH (95%)	DBU	30	69/31	–
4	rt	EtOH (anh.)	EtONa[e]	30	92/8	87[f]
5[c]	rt	EtOH (anh.)	EtONa[e]	30	95/5	89[f]
6	rt	*i*-PrOH (anh.)	*i*-PrONa[e]	30	94/6	89[f]
7	rt	1,4-dioxane	DBU	30	95/5	90[f]
8[b]	**-10**	**EtOH (anh.)**	**EtONa[e]**	**30**	**99/1**	**93[f]**
9[d]	rt	1,4-dioxane	DBU	30	–	91[f]

[a]Unless noted, **1a** (0.1 mmol), **2a** (0.1 mmol), base (100 mol %) in the solvent (0.4 mL) at the indicated temperature for the time given. Ratio **4/3** in mixtures estimated by ^{19}F NMR spectra for compound **4a** and FBSA (concentration of **4a** and FBSA are always equal). [b]Base (120 mol %). [c]Base (200 mol %). [d]**1a** (1.0 mmol), **2a** (1.0 mmol) in the solvent (4 mL). [e]Was used as freshly prepared solution from sodium and anhydrous alcohol. [f]Isolated yield after crystallization from ethanol.

Encouraged by these results, we used these optimized reaction conditions for the reactions of tertiary 2-cyanoacetamidines **1a-f** with sulfonyl azides **2a-f**. Their structures are shown in Scheme 2. We have shown that all amidines **1** smoothly react with azides **2** to form a series of 33 compounds **4-14** (Scheme 3).

The reaction tolerates different tertiary amine moieties in amidine group of compounds **1** and 4-substituents in the aryl of the arylsulfonyl azides **2**. However, in contrast to other compounds, the yields of 1,2,3-triazoles **4e-8e** bearing a 4-nitrobenzenesulfonyl group are only moderate (31–38%). Fortunately, the use of DBU in 1,4-dioxane allowed us to obtain these compounds in high yields. Triazoles **14a-c** bearing methylsulfonimido group were also prepared by alternative protocol. The formation of triazoles **4** took place with retention of all the reagent atoms and therefore can be referred to as an atom economic process, to be used for the design of a new green chemistry process. Thus, we have elaborated a general method for the synthesis of novel 5-sulfonylimino-1*H*-1,2,3-triazole-4(5*H*)-ylidene)methanediamine derivatives **4-14** bearing

various tertiary methylenediamine moieties and sulfonylimino groups in good to excellent yields (mainly 80–95%) (Scheme 3).

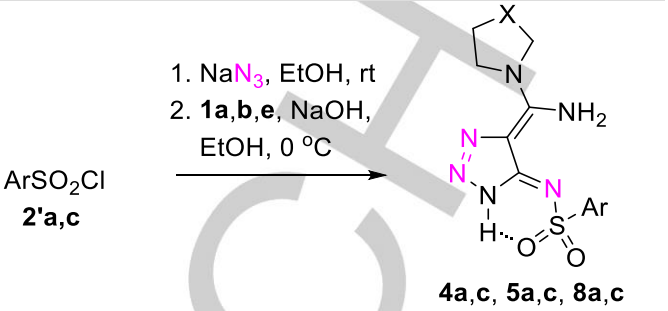


Scheme 2. The structures of starting reagents used in this study.

Based on our knowledge that the reaction of sulfonyl azides **2** with 2-cyanoacetamidines **1** is leading to selective formation of triazoles **4-14**, to show the practical convenience of the developed method we tried to synthesize these compounds in a one-pot protocol starting from arylsulfonyl chlorides **2'a,c**, sodium azide and 2-cyanoacetamidines **1a,b,e** (Table 2). Sulfonyl chlorides **2'** in EtOH were converted with sodium azide to the sulfonyl azides, which were then treated with an ethanol-alkali mixture of the corresponding amidine **1**. After workup with water and acetic acid pure triazoles **4a,c, 5a,c** and **8a,c** could be filtered off in 80–88% yield (Table 2). Table 2 demonstrates that the yields of triazoles **4,5,8** using the one-pot procedure are higher compared to the protocol involving the isolation of sulfonyl azides **2**. Thus, a convenient effective one-pot protocol for the synthesis of triazoles **4,5,8** from readily available starting reagents was elaborated. The method also allows to avoid isolating the potentially explosive sulfonyl azides, increasing the safety.

NMR and HRMS of compounds **4-14** are consistent with the proposed structure. Similar to other NH-triazoles, the ^{1}H NMR spectra of these compounds contain the signals of the NH proton downfield in the range of 13.85–14.29 ppm. Based on the ^{1}H–^{13}C 2D NMR spectra of **11** we identified the signals of C^{4} and C^{5} of 1,2,3-triazole ring at 117–119.5 and 146.1–147.7 ppm, respectively. They are different from those for aromatic 5-sulfonamido-1,2,3-triazole which contain both signals in a narrow range of 131.6–139 ppm,[14c] allowing to exclude the tautomer form **A** from consideration.

Table 2. The yields of triazoles **4a,c, 5a,c, 8a,c** according to the one-pot protocol[a] compared to the yields involving isolation of azides.



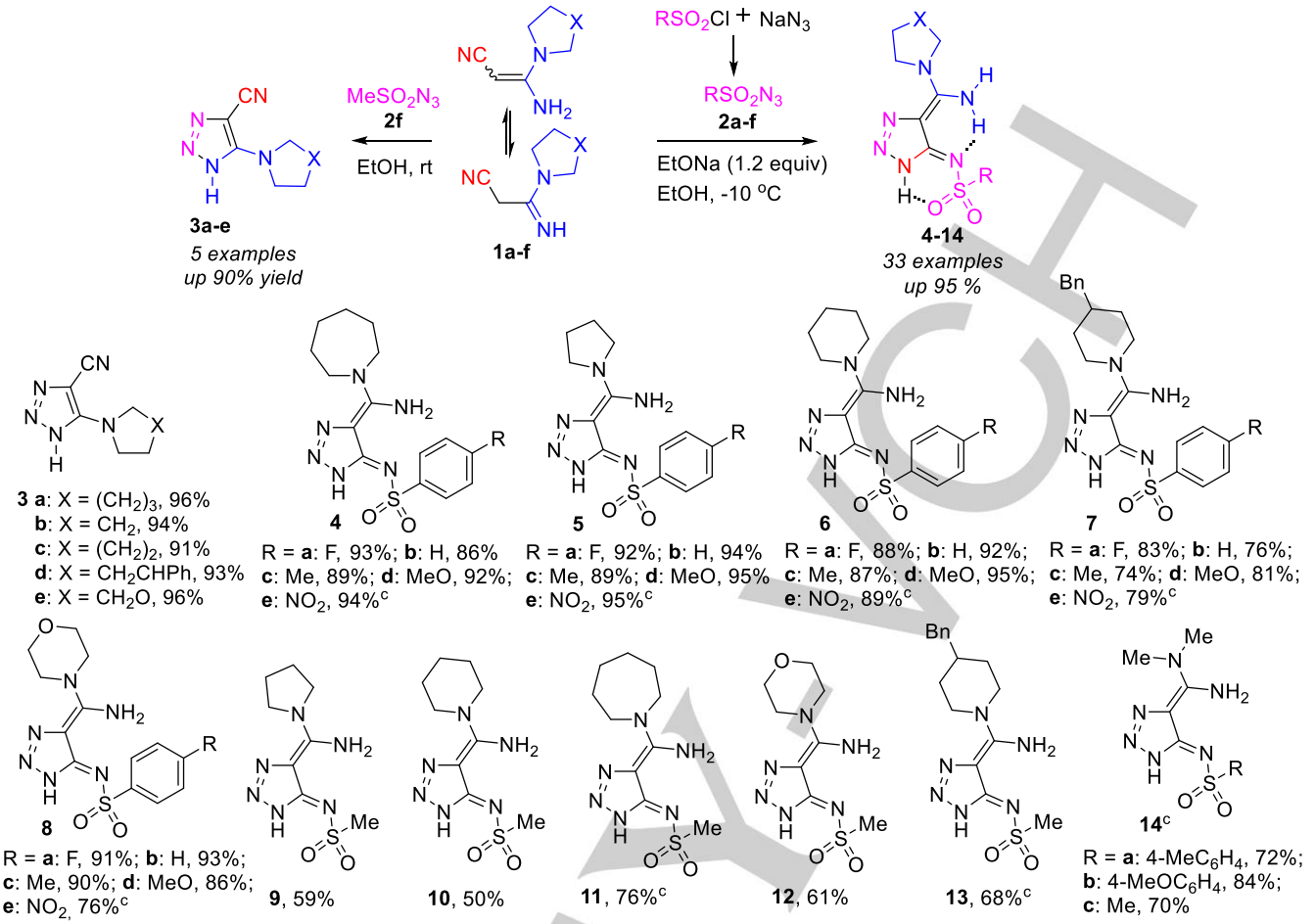
Entry	$ArSO_2Cl$ **2'**	Amidine **1**	Product	Yields of triazoles, %	
	Ar			one-pot synthesis	with isolation of azide **2**
1	4-FC_6H_4 (**2'a**)	**1a**	**4a**	80	79
2	4-FC_6H_4 (**2'a**)	**1b**	**5a**	88	81
3	4-FC_6H_4 (**2'a**)	**1e**	**8a**	85	81
4	Tolyl (**2'c**)	**1a**	**4c**	88	80
5	Tolyl (**2'c**)	**1b**	**5c**	87	81
6	Tolyl (**2'c**)	**1e**	**8c**	88	80

[a]1) **2'** (1.00 mmol), NaN_3 (1.05 mmol), EtOH (2 mL), rt, 24 h. 2) **1** (0.90 mmol), Na (1.08 mmol), EtOH (2 mL), 0 °C, 0.5 h.

The final prove of structure of **4-14** in the solid state was made based on X-ray analysis for monocrystals of triazoles **4c**, **5b**, **7c** (Figs. S1-S3 of Supporting Info), and in the solution the confirmation came from HSQC and HMBC ^{1}H–^{15}N 2D NMR spectra of **5c** where there are cross peaks of the signals of both protons of the NH_2 group with the signal of ^{15}N (Supporting Info). The quantum chemical evaluation (DFT wB97XD/ccpvtz) of the relative thermodynamic stability and bond lengths of all possible tautomeric forms of compound **5b** are shown in Figure 1.

The calculated bond lengths are close to those determined by X-ray analysis for the **5b** tautomer. Data of calculated energies showed that tautomer **5b** with the exocyclic C=C bond is more stable than all other tautomers by more than 5 kcal/mol (Fig. 1).

The unexpectedly high thermodynamic stability of the non-aromatic isomer **5b** compared to its aromatic tautomers is due to two very strong hydrogen bonds, N···H (1.854 Å) and O···H (2.059 Å). A tentative mechanism for the formation of compounds **3-14** is depicted in Scheme 4. We propose that the triazenyl anion **I1** generated by the addition of sulfonyl azide **2** to the carbanion formed after deprotonation of **1** is a common intermediate of the pathways leading to products **3-14**. The cyclization of anion **I1** onto the cyano group leading to triazolidine **I2** (route *a*), and 1,4-prototropic shift in **I1** leading to diazo compound **I6** (route *b*)[14] are competitive reactions. Cyclization of diazoimines **I6** via heteroelectrocyclic ^{19} ring closure occurs to give final triazoles **3**.



[a]Reaction condition: amidine **1** (1.0 mmol), sodium (28 mg, 1.2 mmol), anhydrous ethanol (4 mL), +10 °C, 5–10 min → azide **2** (1.0 mmol), -10 °C, 1 h. [b]Isolated yields. [c]With DBU (1.0 mmol) as the base, 1,4-dioxane (4 mL) as the solvent at room temperature for 10 min.

Scheme 3. Synthesis of triazole-4-carbonitriles **3** and triazoles **4-14**.[a,b]

Alternatively addition of sulfonamide anion onto cyano group and protonation of the latter by reaction by protic medium affords 1,2,3-triazoline **I2**. We propose that triazoline **I2** easily transforms in basic solution to aromatic triazole **I3**, and this is in agreement with the isolation of stable 5-amino-1-aryl-1,2,3-triazole-4-carbonitriles in reactions of malonodinitrile with arylazides.[17] Then rearrangement of triazole **I3**, bearing strong withdrawing sulfonyl group destabilizing the ring,[20] can undergoes by either Dimroth type or double Cornforth type resulting triazole **I5** which are well known in the 1,2,3-triazole series.[18]. An alternative for the transformation of **I3** to **I5** would be intra- or intermolecular sulfonyl transfer similar to the report of Watanabe *et al.*[21] The final step includes unprecedented 1,5-protropic shift for 1-sulfonylamino-3-iminopropenes leading to products **4-14**.

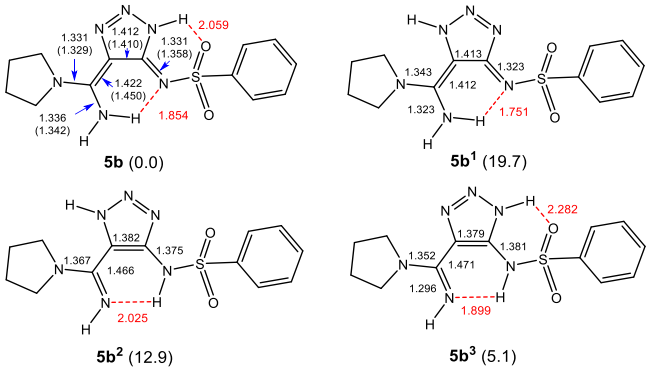
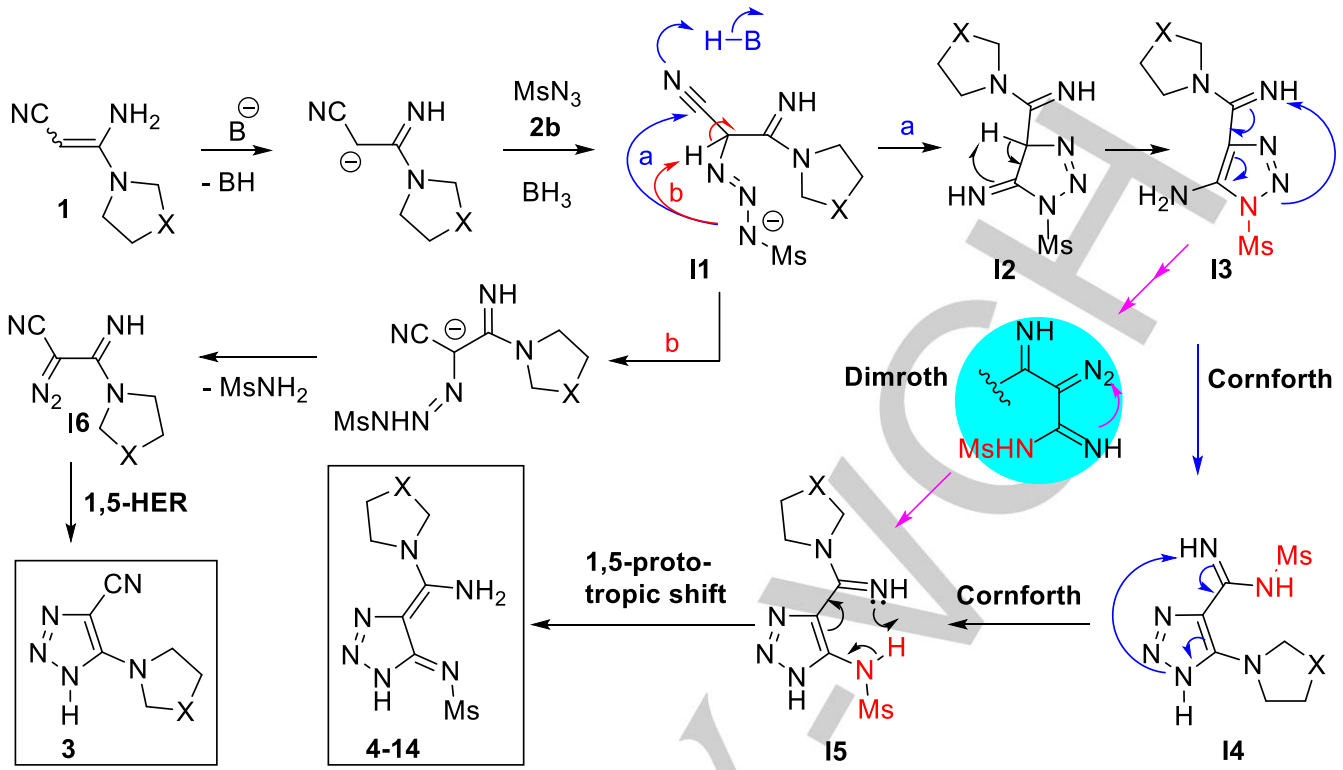


Figure 1. Relative free energies (kcal/mol) and the bond lengths (Å) of triazoles **5b**,**5b**^{1},**5b**^{2},**5b**^{3} (bond lengths according RSA are in parentheses).



Scheme 4. A plausible mechanism for the formation of compounds **3-14**.

Conclusion

In conclusion, an effective and flexible approach to functionalized 1,2,3-triazoles from 2-cyanoacetamidines and sulfonyl azides is described. The variation of the type of a solvent and base allowed using the 2-cyanoacetamidines either as C–C–N or C−C building blocks to form NH-1,2,3-triazoles **3** and **4-14**, respectively, from the same reagents. The use of 1.2 equiv of sodium ethoxide in ethanol or in other alcohols and use of DBU in either 1,4-dioxane of benzene changes the direction of the reaction, allowing the construction of novel 5-sulfonylimido-4-methylene-1,2,3-triazoles **4-14** as the only products. This dramatic redirection of the reaction course is explained by a plausible mechanism: a common intermediate triazenide-anion resulting from cyanoacetamidine and sulfonyl azides undergoes either 1,4-prototropic shift followed by 1,5-cyclization or cyclization of azide involving the cyano group to form triazoles **3** or **4-14**, respectively. The unusual structure of compounds **4-14** is rationalized by the presence of two hydrogen bonds N···H and O···H in these molecules.

Experimental Section

General

Starting materials and reagents were purchased from commercial sources and used without further purification. Ethanol was dried and distilled over CaO and magnesium shavings correspondingly prior to use. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with $SiMe_4$ as internal reference in DMSO-d_6, the chemical shifts (δ) were expressed in ppm, and J values were given in Hz. High-resolution mass spectra (HRMS) were obtained via electrospray ionization source (ESI). The IR spectra were recorded with a FT-IR ATR (attenuated total reflection, ZnSe) spectrometer in the 4000−500 cm^{-1} region. The reactions were monitored by analytical TLC on Sorbfil UV-254 aluminum foil plates with 0.2 mm silica gel with a fluorescent indicator visualized under UV light. Melting points were determined on Stuart SMP10 melting point apparatus and are uncorrected.

Preparation of Amidines. Amidines **1b-f** were synthesized from ethyl 2-cyanoacetimidate and corresponding amines according to the literature procedures.[22,15e]

Preparation of Sulfonyl Azides. Sulfonyl azides **2a-f** were prepared from the corresponding sulfonyl chlorides[23] following the literature procedures. Warning! Sulfonyl azides are potentially explosive, and all reactions should be carried out behind blast shields. We recommend the use of plastic spatulas for the handling of solid material.

(*E*)-3-Amino-3-(azepane-1-yl)acrylonitrile (1a).[24] A solution of ethyl 2-cyanoacetimidate (6.08 g, 54.3 mmol) and azepane (5.37 g, 54.3 mmol) in anhydrous EtOH (54 mL) was stirred at ambient temperature for 24 h. Then the solution was kept in a cold place for 3 h. The formed precipitate was filtered off and washed with dry Et_2O to give **1a** as a colorless solid; mp 109–110 °C (lit.[22] 108–109 °C (PhH)). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.44–1.50 (m, 4H), 1.62 (br. s, 4H), 2.87 (s, 1H), 3.26–3.29 (m, 4H), 5.45 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.2 (2C), 27.3 (2C), 37.3 (2C), 48.1, 124.3, 161.8.

General Procedure for the Synthesis of Triazole-4-carbonitriles 3

Mesyl azide (**2f**) (121 mg, 1.0 mmol) was added to the solution of amidine **1** (1.0 mmol) in ethanol (4–8 mL) and the resulting mixture was

stirred at room temperature (at 50 ºC for **3d**) for 30 min. Then the solvent was removed under reduced pressure and water (4 mL) was added to the residue. The resulting suspension was heated at reflux for 1 min and then cooled to room temperature. The precipitate was filtered off, washed with water, dried and crystallized from ethanol or DCM.

5-(Azepane-1-yl)-1*H*-1,2,3-triazole-4-carbonitrile (3a).[15e] Compound **3a** was obtained in 96% yield (366 mg) according to the general procedure (amidine **1a**: 330 mg, 2.0 mmol; azide **2f**: 252 mg, 2.0 mmol; ethanol (8 mL)) as a colorless solid; mp 175–176 °C (DCM) (lit.[15e] 174–175 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.44–1.54 (m, 4H, 2CH$_2$), 1.66–1.76 (m, 4H, 2CH$_2$), 3.43–3.54 (m, 4H, 2CH$_2$), 14.78 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.4 (CH$_2$), 27.4 (CH$_2$), 49.7 (CH$_2$), 99.6 (C^4), 115.2 (CN), 151.0 (C^5).

5-(Pyrrolidin-1-yl)-1*H*-1,2,3-triazole-4-carbonitrile (3b).[15e] Compound **3b** was obtained in 94% yield (153 mg) according to the general procedure (amidine **1b**: 137 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 217–219 °C (ethanol) (lit.[15e] 219–220 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.94 (br. s, 4H, 2CH$_2$), 3.40 (br. s, 4H, 2CH$_2$), 14.81 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.0 (CH$_2$), 48.7 (CH$_2$), 100.0 (C^4), 115.1 (CN), 149.6 (C^5).

5-(Piperidin-1-yl)-1H-1,2,3-triazole-4-carbonitrile (3c).[15e] Compound **3c** was obtained in 91% yield (161 mg) according to the general procedure (amidine **1c**: 151 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 180–183 °C (DCM) (lit.[15e] 180–181 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.57–1.62 (m, 6H, 3CH$_2$), 3.34–3.41 (m, 4H, 2CH$_2$), 15.03 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.1 (CH$_2$), 24.3 (2CH$_2$), 48.5 (2CH$_2$), 102.4 (C^4), 114.6 (CN), 153.4 (C^5).

5-(4-Benzylpiperidin-1-yl)-1*H*-1,2,3-triazole-4-carbonitrile (3d).[15e] Compound **3d** was obtained in 93% yield (247 mg) according to the general procedure (amidine **1d**: 241 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL) as a colorless solid; mp 172–174 °C (DCM) (lit.[15e] 173–174 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.23-1.33 (m, 2H, CH$_2$), 1.64–1.67 (m, 2H, CH$_2$), 1.70–1.80 (m, 1H, CH), 2.51-2.58 (m, 2H, CH$_2$), 2.94–2.99 (m, 2H, CH$_2$), 3.80 (d, *J* = 12.0 Hz, 2H, C<u>H</u>$_2$Ph), 7.16–7.20 (m, 3H, Ph), 7.26–7.30 (m, 2H, Ph), 15.00 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.2 (CH$_2$), 36.2 (CH), 41.7 (<u>C</u>H$_2$Ph), 47.8 (CH$_2$), 102.7 (C^4), 114.3 (CN), 125.6 (C^{p-}), 127.9 (C^{o-}), 128.8 (C^{m-}), 139.7 (C^{i-}), 153.5 (C^5).

5-Morpholino-1*H*-1,2,3-triazole-4-carbonitrile (3e).[15e] Compound **3e** was obtained in 96% yield (171 mg) according to the general procedure (amidine **3e**: 153 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 206–207 °C (DCM) (lit.[15e] 207–208 °C). ^{1}H NM**R** (400 MHz, DMSO-d$_6$): δ 3.30–3.39 (m, 4H, 2CH$_2$), 3.68–3.79 (m, 4H, 2CH$_2$), 15.14 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 47.5 (CH$_2$), 65.2 (CH$_2$), 103.4 (C^4), 114.3 (CN), 154.6 (C^5).

General Procedure for the Synthesis of Triazoles 4-14

Method A

Amidine **1** (1.0 mmol) was added into a solution of sodium ethoxide, cooled to +10 °C, freshly prepared from sodium (28 mg, 1.2 mmol) and anhydrous ethanol (4 mL), and the resulting mixture was stirred at +10 °C for a further 5–10 min. Then the reaction mixture was cooled to -10 °C and the corresponding azide **2** (1.0 mmol) was added to the reaction mixture and the resulting mixture were stirred at -10 °C for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in water (4 mL) and acetic acid was added (72 mg, 1.2 mmol). The formed precipitate was filtered off, washed with water, purified by crystallization from ethanol and dried in a desiccator over P_4O_{10}.

Method B

DBU (152 mg, 1.0 mmol) was added to the solution of amidine **1** (1.0 mmol) in 1,4-dioxane (4 mL) at room temperature was stirred for 5 min and then azide **2** (1.0 mmol) was added. The reaction mixture was stirred for 10 min at room temperature, then glacial acetic acid (0.6–0.8 mL) was added and the resulting solution was stirred for 15 min more. Then water (15 mL) was added to the reaction mixture, formed precipitate was filtered off, washed with water and dried in a desiccator over P_4O_{10}.

Method C

A mixture of sulfonyl chloride **2'** (1.00 mmol) and NaN_3 (68.25 mg, 1.05 mmol) was stirred in ethanol (2 mL) for 24 h at room temperature. Ethanol-alkali mixture of corresponding amidine **1**, prepared from ethanol (2 mL), Na (25 mg, 1.08 mmol) and amidine **1** (0.9 mmol) was added to the reaction mixture at 0° C, and the resulting suspension was stirred at 0 °C for 30 min. Then water (10 mL) and glacial acid (0.8 mL) were added to the reaction mixture. Formed precipitate was filtered off, washed with water and dried in a desiccator over P_4O_{10}.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)fluorobenzenesulfonamide (4a)**. Compound **4a** was obtained in 93% yield (340 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2a**: 201 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 185–186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (br. s, 4H), 1.77 (br. s, 4H), 3.61 (br. s, 2H), 4.21 (br. s, 2H), 7.27 (t, *J* = 9.0 Hz, 2H), 7.88 (dd, *J* = 9.0, 5.4 Hz, 2H), 8.19 (br. s, 1H), 8.54 (br. s, 1H), 14.18 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.1, 25.8, 25.9, 28.2, 50.0, 51.8, 115.4 (d, *J* = 22 Hz), 118.6, 128.4 (d, *J* = 9 Hz), 141.1 (d, *J* = 3 Hz), 146.9, 155.2, 163.2 (d, *J* = 248 Hz). IR (ATR, ZnSe, cm^{-1}): *v* 3313, 3171, 3110, 2935, 2857, 1650, 1587, 1550, 1368, 1219, 1043, 935. HRMS (ESI-TOF) *m/z calcd*. for $C_{15}H_{20}FN_6O_2S$ [M+H]$^+$: 367.1347, found 367.1356.

Compound **4a** was obtained in 80% yield (263.5 mg) according to the **general procedure C** (4-fluorobenzenesulfonyl chloride (**2'a**): 194 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1a**: 148.5 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 185–186 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)benzenesulfonamide (4b)**. Compound **4b** was obtained in 86% yield (299 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2b**: 183 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 198–199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (br. s, 4H), 1.76 (br. s, 4H), 3.60 (m, 2H), 4.22 (br. s, 2H), 7.41–7.48 (m, 3H), 7.81–7.86 (m, 2H), 8.17 (br. s, 1H), 9.60 (br. s, 1H), 14.17 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.0, 25.7, 25.9, 28.2, 50.0, 51.7, 118.3, 125.5, 128.4, 130.7, 144.7, 147.0, 155.2. IR (ATR, ZnSe, cm^{-1}): *v* 3301, 3110, 2922, 2853, 1652, 1591, 1554, 1124, 1084, 994. HRMS (ESI-TOF) *m/z calcd*. for $C_{15}H_{21}N_6O_2S$ [M+H]$^+$: 349.1441, found 349.1443.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methylbenzenesulfonamide (4c).** Compound **4c** was obtained in 89% yield (322 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 231–232 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.53 (br. s, 4H), 1.77 (br. s, 4H), 2.31 (s, 3H), 3.60 (br. s, 2H), 4.23 (br. s, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 8.15 (br. s, 1H), 9.63 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 25.1, 25.7, 25.9, 28.2, 50.0, 51.7, 118.1, 125.6, 128.8, 140.6, 141.8, 147.0, 155.1. IR (ATR, ZnSe, cm^{-1}): *v* 3272, 3147, 2930, 1658, 1594, 1542, 1134, 1084, 930. HRMS (ESI-TOF) *m/z calcd*. for $C_{16}H_{23}N_6O_2S$: [M+H]$^+$: 363.1598, found 363.1602.

Compound **4c** was obtained in 88% yield (287 mg) according to the **general procedure C** (4-methylbenzenesulfonyl chloride (**2'c**): 190 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1a**: 148.5 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 229–230 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methoxybenzenesulfonamide (4d).** Compound **4d** was obtained in 92% yield (345 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 190–191 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.52 (br. s, 4H), 1.77 (br. s, 4H), 3.60 (br. s, 2H), 3.77 (s, 3H), 4.24 (br. s, 2H), 6.97 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 8.14 (br. s, 1H), 9.66 (br. s, 1H), 14.11 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.1, 25.8, 25.9, 28.2, 50.0, 51.7, 55.3, 113.6, 118.0, 127.5, 136.7, 147.0, 155.1, 161.0. IR (ATR, ZnSe, cm^{-1}): v 3257, 3150, 3075, 2940, 1594, 1567, 1496, 1244, 1083, 1031, 908. HRMS (ESI-TOF) *m/z calcd*. for: $[M+H]^+$: $C_{16}H_{23}N_6O_3S$ 379.1547, found 379.1557.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)nitrobenzenesulfonamide (4e)**. Compound **4e** was obtained in 38% yield (149 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; ethanol (4 mL)) as a light yellow solid; mp 258–259 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.45–1.60 (m, 4H), 1.66–1.86 (m, 4H), 3.50–3.73 (m, 2H), 4.00–4.22 (m, 2H), 8.04 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 9.0 Hz, 3H), 9.33 (br. s, 1H), 14.37 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.0, 25.6, 26.0, 28.1, 49.9, 51.7, 119.5, 123.9, 127.0, 146.0, 148.5, 150.6, 155.5. IR (ATR, ZnSe, cm^{-1}): v 3211, 3160, 2944, 1662, 1605, 1558, 1520, 1342, 1088, 958. HRMS (ESI-TOF) *m/z calcd*. for $C_{15}H_{20}N_7O_4S$ $[M+H]^+$: 394.1292, found 394.1302.

Compound **4e** was obtained in 94% yield (370 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; 1,4-dioxane (4 mL)) as a light yellow solid; mp 258–259 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)fluorobenzenesulfonamide (5a)**. Compound **5a** was obtained in 92% yield (311 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2a**: 201 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 236–237 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.94–1.97 (m, 4H), 3.48–3.52 (m, 2H), 4.06–4.18 (m, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.86–7.90 (m, 2H), 8.06 (br. s, 1H), 8.26 (br. s, 1H), 14.20 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.5, 25.5, 48.8, 52.1, 115.4 (d, J = 22 Hz), 118.8, 128.3 (d, J = 9 Hz), 141.1 (d, J = 3 Hz), 146.8, 153.1, 163.2 (d, J = 248 Hz). IR (ATR, ZnSe, cm^{-1}): v 3393, 3160, 3078, 2926, 1647, 1602, 1494, 1266, 1215, 1119, 1073, 947. HRMS (ESI-TOF) *m/z calcd*. for $C_{13}H_{16}FN_6O_2S$ $[M+H]^+$: 339.1034, found 339.1044.

Compound **5a** was obtained in 88% yield (267.5 mg) according to the **general procedure C** (4-fluorobenzenesulfonyl chloride (**2'a**): 194 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1b**: 123 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 235–237 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)benzenesulfonamide (5b)**. Compound **5b** was obtained in 94% yield (301 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2b**: 183 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 267–268 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.95 (t, J = 8.0 Hz, 4H), 3.48–3.51 (m, 2H), 4.06–4.09 (m, 2H), 7.42–7.48 (m, 3H), 7.82–7.84 (m, 2H), 8.04 (br. s, 1H), 9.32 (br. s, 1H), 14.17 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.4, 25.4, 48.7, 52.0, 118.6, 125.5, 128.4, 130.7, 144.7, 146.9, 153.1. IR (ATR, ZnSe, cm^{-1}): v 3452, 3277, 3171, 2966, 1634, 1605, 1219, 1078, 938. HRMS (ESI-TOF) *m/z calcd*. for $C_{13}H_{17}N_6O_2S$ $[M+H]^+$: 321.1128, found 321.1133.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methylbenzenesulfonamide (5c)**. Compound **5c** was obtained in 89% yield (279 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 238–239 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.91–1.99 (m, 4H), 2.30 (s, 3H), 3.46–3.53 (m, 2H), 4.04-4.11 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 8.02 (br. s, 1H), 9.33 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 23.4, 25.4, 48.7, 52.0, 118.5, 125.6, 128.9, 140.6, 141.9, 147.0, 153.1. IR (ATR, ZnSe, cm^{-1}): v 3387, 3220, 3103, 3085, 1605, 1550, 1496, 1359, 1266, 1129, 1078, 927. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{19}N_6O_2S$ $[M+H]^+$: 335.1285, found 335.1291.

Compound **5c** was obtained in 87% yield (261 mg) according to the **general procedure C** (4-methylbenzenesulfonyl chloride (**2'c**): 190 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1b**: 123 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 238–240 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methoxybenzenesulfonamide (5d)**. Compound **5d** was obtained in 95% yield (333 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 182–183 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.94–1.97 (m, 4H), 3.48–3.51 (m, 2H), 3.77 (s, 3H), 4.06–4.09 (m, 2H), 6.96 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 8.02 (br. s, 1H), 9.35 (br. s, 1H), 14.10 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.4, 25.4, 48.7, 52.0, 55.3, 113.6, 118.4, 127.5, 136.7, 147.0, 153.1, 170.0. IR (ATR, ZnSe, cm^{-1}): v 3243, 3157, 3134, 1644, 1598, 1369, 1231, 1123, 1088, 944. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{19}N_6O_3S$ $[M+H]^+$: 351.1234, found 351.1242.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)nitrobenzenesulfonamide (5e)**. Compound **5e** was obtained in 31% yield (113 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; ethanol (4 mL)) as a light yellow solid; mp 225–226 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.92–2.01 (m, 4H), 3.46–3.51 (m, 2H), 4.01–4.11 (m, 2H), 8.05 (d, J = 9.0 Hz, 2H), 8.13 (br. s, 1H), 8.28 (d, J = 9.0 Hz, 2H), 9.11 (br. s, 1H), 14.37 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.5, 25.4, 48.8, 52.1, 119.4, 123.9, 127.0, 146.2, 148.6, 150.4, 153.1. IR (ATR, ZnSe, cm^{-1}): v 3268, 3132, 2949, 1659, 1609, 1564, 1521, 1345, 1263, 1141, 1090, 966. HRMS (ESI-TOF) *m/z calcd* for $C_{13}H_{16}N_7O_4S$ $[M+H]^+$: 366.0979, found 366.0989.

Compound **5e** was obtained in 95% yield (348 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; 1,4-dioxane (4 mL)) as a light yellow solid; mp 224–226 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-fluorobenzenesulfonamide (6a)**. Compound **6a** was obtained in 88% yield (310 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2a**: 201 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 194–195 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.56–1.71 (m, 6H), 3.65–3.98 (m, 4H), 7.26 (t, J = 8.9 Hz, 2H), 7.86 (dd, J = 8.9, 5.4 Hz, 2H), 8.39 (br. s, 1H), 9.28 (br. s, 1H), 14.14 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.6, 23.1, 25.4, 48.9, 59.6, 115.3 (d, J = 22 Hz), 118.9, 128.3 (d, J = 9 Hz), 141.3 (d, J = 3 Hz), 146.5, 154.8, 163.1 (d, J = 248 Hz). IR (ATR, ZnSe, cm^{-1}): v 3329, 3250, 3178, 2972, 1652, 1603, 1554, 1294, 1189, 1131, 1083, 1083, 946. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{18}FN_6O_2S$ $[M+H]^+$: 353.1190, found 353.1200.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)benzenesulfonamide (6b)**. Compound **6b** was obtained in 92% yield (274 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2b**: 183 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 197–198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.57–1.69 (m, 6H), 3.66–4.08 (m, 4H), 7.41–7.47 (m, 3H), 7.81–7.83 (m, 2H), 8.37 (br. s, 1H), 9.35 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.1, 25.4, 48.7, 118.7, 125.5, 128.4, 130.6, 144.8, 146.7, 154.8. IR (ATR, ZnSe, cm^{-1}): *v* 3269, 3111, 2943, 1655, 1605, 1552, 1495, 1443, 1365, 1127, 1084, 939. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{19}N_6O_2S$ $[M+H]^+$: 335.1285, found 335.1288.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methylbenzenesulfonamide (6c)**. Compound **6c** was obtained in 87% yield (303 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 217–218 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.58–1.69 (m, 6H), 2.31 (s, 3H), 3.63–4.09 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.35 (br. s, 1H), 9.39 (br. s, 1H), 14.06 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 23.1, 25.4, 48.8, 118.5, 125.6, 128.8, 140.5, 142.0, 146.9, 154.8. IR (ATR, ZnSe, cm^{-1}): *v* 3363, 3224, 3048, 2943, 2854, 1662, 1605, 1556, 1487, 1371, 1119, 1084, 948. HRMS (ESI-TOF) *m/z calcd*. for $C_{15}H_{21}N_6O_2S$ $[M+H]^+$: 349.1441, found 349.1447.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methoxybenzenesulfonamide (6d)**. Compound **6d** was obtained in 95% yield (346 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 185–186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.59–1.70 (m, 6H), 3.75–4.05 (m, 4H), 3.78 (s, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 8.34 (br. s, 1H), 9.40 (br. s, 1H), 14.06 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.1, 25.4, 48.7, 55.3, 113.5, 118.3, 127.5, 136.8, 146.9, 154.7, 160.9. HRMS (ESI-TOF) *m/z calcd*. for $C_{15}H_{21}N_6O_3S$ $[M+H]^+$: 365.1390, found 365.1398.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-nitrobenzenesulfonamide (6e)**. Compound **6e** was obtained in 38% yield (144 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; ethanol (4 mL)) as a light yellow solid; mp 241–242 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.54–1.73 (m, 6H), 3.50–4.10 (m, 4H), 8.02 (d, *J* = 8.9 Hz, 2H), 8.27 (d, *J* = 8.9 Hz, 2H), 8.46 (br. s, 1H), 9.09 (br. s, 1H), 14.29 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.1, 25.4, 49.4, 119.9, 123.9, 127.0, 145.9, 148.5, 150.9, 155.2. IR (ATR, ZnSe, cm^{-1}): *v* 3208, 3099, 3049, 2933, 2853, 1668, 1603, 1559, 1522, 1454, 1344, 1265, 1188, 998. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{18}N_7O_4S$ $[M+H]^+$: 380.1135, found 380.1146.

Compound **6e** was obtained in 89% yield (338 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; 1,4-dioxane (4 mL)) as a light yellow solid; mp 241–243 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)fluorobenzenesulfonamide (7a)**. Compound **7a** was obtained in 83% yield (368 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1d**: 241 mg, 1.0 mmol; azide **2a**: 201 mg, 1.0 mmol; ethanol (8 mL)) as a colorless solid, mp 175–176 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.20–1.35 (m, 2H), 1.60–1.74 (m, 2H), 1.89 (m, 1H), 2.50–2.57 (m, 2H), 3.10–3.26 (m, 2H), 4.02 (br. s, 1H), 4.90 (br. s, 1H), 7.13–7.22 (m, 3H), 7.22–7.32 (m, 4H), 7.87 (dd, *J* = 8.4, 5.7 Hz, 2H), 8.45 (br. s, 1H), 9.29 (br. s, 1H), 14.21 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 31.4, 36.5, 41.6, 46.5, 49.5, 115.4 (d, *J* = 22 Hz), 118.9, 125.9, 128.2, 128.4 (d, *J* = 9 Hz), 129.0, 139.8, 141.3 (d, *J* = 3 Hz), 146.5, 154.9, 163.2 (d, *J* = 248 Hz). IR (ATR, ZnSe, cm^{-1}): *v* 3356, 3160, 3059, 2926, 1651, 1594, 1556, 1494, 1133, 1087, 953. HRMS (ESI-TOF) *m/z calcd*. for $C_{21}H_{24}FN_6O_2S$ $[M+H]^+$: 443.1660, found 443.1673.

***N*-((4*Z*,5*Z*)-5-(Amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)benzenesulfonamide (7b)**. Compound **7b** was obtained in 76% yield (323 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1d**: 241 mg, 1.0 mmol; azide **2b**: 183 mg, 1.0 mmol; ethanol (8 mL)) as a colorless solid; mp 128–129 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.24–1.34 (m, 2H), 1.67–1.70 (m, 2H), 1.83–1.98 (m, 1H), 2.53–2.54 (m, 2H), 3.19 (t, *J* = 12 Hz, 2H), 4.44 (br. s, 2H), 7.16–7.20 (m, 3H), 7.27–7.30 (m, 2H), 7.43–7.45 (m, 3H), 7.82–7.84 (m, 2H), 8.38 (br. s, 1H), 9.37 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 31.3, 36.4, 41.5, 48.0, 118.6, 125.5, 125.8, 128.1, 128.4, 128.9, 130.6, 139.7, 144.8, 146.9, 154.8. IR (ATR, ZnSe, cm^{-1}): *v* 3247, 3169, 2913, 1653, 1601, 1556, 1138, 1087, 945. HRMS (ESI-TOF) *m/z calcd*. for $C_{22}H_{27}N_6O_2S$ $[M+H]^+$: 439.1911, found 439.1917.

***N*-((4*Z*,5*Z*)-5-(Amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methylbenzenesulfonamide (7c)**. Compound **7c** was obtained in 74% yield (325 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1d**: 241 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; ethanol (8 mL)) as a colorless solid; mp 186–187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.23–1.33 (m, 2H), 1.65–1.68 (m, 2H), 1.82–1.96 (m, 1H), 2.30 (s, 3H), 2.53 (d, *J* = 8.0 Hz, 2H), 3.14–3.20 (m, 2H), 4.03 (br. s, 1H), 4.97 (br. s, 1H), 7.16–7.30 (m, 7H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.40 (br. s, 1H), 9.37 (br. s, 1H), 14.14 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.8, 31.4, 36.6, 41.7, 46.5, 49.6, 118.6, 125.7, 126.0, 128.2, 128.9, 129.0, 139.9, 140.7, 142.0, 146.8, 154.8. IR (ATR, ZnSe, cm^{-1}): *v* 3300, 3261, 3167, 2924, 2852, 1651, 1600, 1555, 1494, 1132, 1084, 941. HRMS (ESI-TOF) *m/z calcd*. for $C_{22}H_{27}N_6O_2S$ $[M+H]^+$: 439.1911, found 439.1917.

***N*-((4*Z*,5*Z*)-5-(Amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methoxybenzenesulfonamide (7d)**. Compound **7d** was obtained in 81% yield (369 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1d**: 241 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; ethanol (8 mL)) as a colorless solid; mp 126–127 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.23–1.32 (m, 2H), 1.66–1.69 (m, 2H), 1.82–1.97 (m, 1H), 2.53 (d, *J* = 8.0 Hz, 2H), 3.10–3.25 (m, 2H), 3.76 (s, 3H), 4.03 (br. s, 1H), 5.01 (br. s, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.16–7.20 (m, 3H), 7.26–7.30 (m, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 8.43 (br. s, 1H), 9.42 (br. s, 1H), 14.14 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 31.5, 36.6, 41.6, 46.8, 49.3, 55.4, 113.6, 118.4, 125.9, 127.6, 128.2, 129.0, 136.8, 139.8, 146.9, 154.8, 161.0. IR (ATR, ZnSe, cm^{-1}): *v* 3302, 3226, 3094, 2921, 2838, 1661, 1595, 1543, 1495, 1171, 1133, 1054, 1024, 938. HRMS (ESI-TOF) *m/z calcd*. for $C_{22}H_{27}N_6O_3S$ $[M+H]^+$: 455.1860, found 455.1871.

***N*-((4*Z*,5*Z*)-5-(amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-nitrobenzenesulfonamide (7e)**. Compound **7e** was obtained in 79% yield (186 mg) according to the **general procedure B** (DBU: 76 mg, 0.5 mmol; amidine **1d**: 120 mg, 0.5 mmol; azide **2e**: 114 mg, 0.5 mmol; 1,4-dioxane (2 mL)) as a light yellow solid, mp 219–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.20–1.35 (m, 2H), 1.62–1.72 (m, 2H), 1.85–1.95 (m, 1H), 2.54–2.58 (m, 2H), 3.1–3.23 (m, 2H), 4.08 (br. s, 1H), 4.57 (br. s, 1H), 7.14–7.22 (m, 3H), 7.25–7.32 (m, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H), 8.48 (br. s, 1H), 9.09 (br. s, 1H), 14.30 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 31.3, 36.3, 41.5, 46.9, 49.5, 119.8, 123.8, 125.8, 126.9, 128.1, 128.9, 139.7, 145.8, 148.4, 150.8, 155.0. IR (ATR, ZnSe, cm^{-1}): *v* 3301, 3156, 2913, 2725, 1659, 1600, 1567, 1518, 1463, 1377, 1346, 1233, 1125, 1090, 1056, 840. HRMS (ESI-TOF) *m/z calcd*. for $C_{21}H_{24}N_7O_4S$ $[M+H]^+$: 470.1605, found 470.1611.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-fluorobenzenesulfonamide (8a)**. Compound **8a** was obtained in 91% yield (322 mg) according to the **general procedure**

A (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2a**: 201 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 224–225 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.73–4.02 (m, 8H), 7.27 (t, J = 8.0 Hz, 2H), 7.88 (dd, J = 8.0, 4.0 Hz, 2H), 8.54 (br. s, 1H), 9.44 (br. s, 1H), 14.19 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 48.0, 65.5, 115.3 (d, J = 22 Hz), 118.6, 128.4 (d, J = 9 Hz), 141.2 (d, J = 3 Hz), 146.8, 155.5, 163.1 (d, J = 248 Hz). IR (ATR, ZnSe, cm^{-1}): v 3301, 3210, 3107, 3049, 2930, 2838, 1657, 1588, 1547, 1489, 1174, 1104, 1082, 831. HRMS (ESI-TOF) *m/z calcd*. for $C_{13}H_{16}FN_6O_3S$ $[M+H]^+$: 355.0983, found 355.0984.

Compound **8a** was obtained in 85% yield (271 mg) according to the **general procedure C** (4-fluorobenzenesulfonyl chloride (**2'a**): 194 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1e**: 137.7 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 223–226 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)benzenesulfonamide (8b)**. Compound **8b** was obtained in 93% (313 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2b**: 183 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid mp 196–197 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.60–4.22 (m, 8H), 7.44–7.46 (m, 3H), 7.82–7.84 (m, 2H), 8.55 (br. s, 1H), 9.49 (br. s, 1H), 14.24 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 47.9, 65.6, 118.5, 125.6, 128.6, 130.8, 144.7, 147.0, 155.5. IR (ATR, ZnSe, cm^{-1}): v 3319, 3164, 2956, 2868, 1651, 1577, 1550, 1175, 1140, 1081, 1007, 949. HRMS (ESI-TOF) *m/z calcd*. for $C_{13}H_{17}N_6O_3S$ $[M+H]^+$: 337.1077, found 337.1080.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methylbenzenesulfonamide (8c)**. Compound **8c** was obtained in 90% yield (315 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 219–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H), 3.69–4.16 (m, 8H), 7.24 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 8.49 (br. s, 1H), 9.53 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 47.9, 65.5, 118.2, 125.6, 128.8, 140.6, 141.9, 147.0, 155.5. IR (ATR, ZnSe, cm^{-1}): v 3304, 3223, 3142, 2913, 2864, 1658, 1592, 1546, 1493, 1232, 1171, 1106, 1086, 938. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{19}N_6O_3S$ $[M+H]^+$: 351.1234, found: 351.1236.

Compound **8c** was obtained in 88% yield (277.5 mg) according to the **general procedure C** (4-methylbenzenesulfonyl chloride (**2'c**): 190 mg, 1.0 mmol; NaN_3: 68.3 mg, 1.05 mmol; amidine **1e**: 137.7 mg, 0.9 mmol; Na: 25 mg, 1.08 mmol, EtOH (4 mL)) as a colorless solid; mp 219–221 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methoxybenzenesulfonamide (8d)**. Compound **8d** was obtained in 86% yield (315 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid; mp 205–206 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.73–3.74 (m, 4H), 3.78 (s, 3H), 3.80–4.15 (m, 4H), 6.97 (d, J = 12.0 Hz, 2H), 7.76 (d, J = 12.0 Hz, 2H), 8.48 (br. s, 1H), 9.56 (br. s, 1H), 14.11 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 48.0, 55.3, 65.6, 113.6, 118.1, 127.5, 136.7, 147.0, 155.4, 161.0. IR (ATR, ZnSe, cm^{-1}): v 3269, 3150, 2964, 2904, 2816, 1653, 1590, 1172, 1107, 1083, 940. HRMS (ESI-TOF) *m/z calcd*. for $C_{14}H_{19}N_6O_4S$ $[M+H]^+$: 367.1183, found 367.1181.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-nitrobenzenesulfonamide (8e)**. Compound **8e** was obtained in 34% yield (129 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; ethanol (4 mL)) as a light yellow solid; mp 252–253 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.74–3.95 (m, 8H), 8.03 (d, J = 9.0 Hz, 2H), 8.27 (d, J = 9.0 Hz, 2H), 8.61 (br. s, 1H), 9.27 (br. s, 1H), 14.34 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 48.0, 65.5, 119.5, 125.9, 127.0, 146.1, 148.5, 150.7, 155.8. IR (ATR, ZnSe, cm^{-1}): v 3316, 3240, 3150, 3034, 1662, 1592, 1566, 1510, 1306, 1228, 1187, 1088, 950, 856. HRMS (ESI-TOF) *m/z calcd*. for $C_{13}H_{16}N_7O_5S$ $[M+H]^+$: 382.0928, found 382.0935.

Compound **8e** was obtained in 76% yield (290 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2e**: 228 mg, 1.0 mmol; 1,4-dioxane (4 mL)) as a light yellow solid; mp 250–253 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(pyrrolidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (9)**. Compound **9** was obtained in 59% yield (152 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1b**: 137 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 256–257 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.91–2.04 (m, 4H), 2.81 (s, 3H), 3.51 (br. s, 2H), 4.11 (br. s, 2H), 8.07 (br. s, 1H), 9.32 (br. s, 1H), 14.16 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.6, 25.6, 40.5, 48.6, 52.1, 117.9, 147.5, 153.2. IR (ATR, ZnSe, cm^{-1}): v 3333, 3254, 3135, 2958, 1633, 1594, 1566, 1325, 1221, 1094, 965. HRMS (ESI-TOF) *m/z calcd*. for $C_8H_{15}N_6O_2S$ $[M+H]^+$: 259.0972, found 259.0979.

***N*-((4*Z*,5*Z*)-5-(Amino(piperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (10)**. Compound **10** was obtained in 50% yield (136 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1c**: 151 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 216–217 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.60–1.75 (m, 6H), 2.82 (s, 3H), 3.80–4.10 (m, 4H), 8.33 (br. s, 1H), 9.42 (br. s, 1H), 13.85 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.1, 25.4, 40.6, 48.7, 117.9, 147.4, 154.8. IR (ATR, ZnSe, cm^{-1}): v 3326, 3260, 3148, 3084, 2927, 1656, 1595, 1572, 1243, 1109, 951. HRMS (ESI-TOF) *m/z calcd*. for $C_9H_{17}N_6O_2S$: $[M+H]^+$: 273.1128, found 273.1136.

***N*-((4*Z*,5*Z*)-5-(Amino(azepane-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (11)**. Compound **11** was obtained in 66% yield (189 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 242–243 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.47–1.61 (m, 4H), 1.73–1.87 (m, 4H), 2.83 (s, 3H), 3.55–3.72 (m, 2H), 4.21–4.38 (m, 2H), 8.17 (br. s, 1H), 9.67 (br. s, 1H), 14.12 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.2, 25.8, 26.0, 28.4, 40.5, 50.1, 51.8, 117.6, 147.7, 155.1. IR (ATR, ZnSe, cm^{-1}): v 3311, 3257, 3173, 3093, 2924, 2866, 1650, 1603, 1572, 1109, 974. HRMS (ESI-TOF) *m/z calcd*. for $C_{10}H_{19}N_6O_2S$: $[M+H]^+$: 287.1285, found 287.1294.

Compound **11** was obtained in 76% yield (218 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1a**: 165 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; 1,4-dioxane (4 mL)) as a colorless solid, mp 242–243 °C.

***N*-((4*Z*,5*Z*)-5-(Amino(morpholino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (12)**. Compound **12** was obtained in 61% yield (167 mg) according to the **general procedure A** (sodium: 28 mg, 1.2 mmol; amidine **1e**: 153 mg, 1.0 mmol; azide **2f**: 121 mg, 1.0 mmol; ethanol (4 mL)) as a colorless solid, mp 221–222 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.82 (s, 3H), 3.76-3.79 (m, 4H), 3.87–4.15 (m, 4H), 8.48 (br. s, 1H), 9.55 (br. s, 1H), 13.97 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 40.6, 48.1, 65.6, 117.7, 147.6, 155.4. IR (ATR, ZnSe, cm^{-1}): v 3245, 3028, 2861, 1654, 1566, 1183, 1100, 957. HRMS (ESI-TOF) *m/z calcd*. for $C_8H_{15}N_6O_3S$ $[M+H]^+$: 275.0921, found 275.0926.

***N*-((4*Z*,5*Z*)-5-(amino(4-benzylpiperidin-1-yl)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (13)**. Compound **13** was obtained in 68% yield (123 mg) according to the **general procedure B** (DBU: 76 mg, 0.5 mmol; amidine **1d**: 120 mg, 0.5 mmol; azide **2f**: 67

mg, 0.55 mmol; 1,4-dioxane (2 mL)) as a colorless solid, mp 204–205 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.25–1.38 (m, 2H), 1.69–1.77 (m, 2H), 1.85–2.00 (m, 1H), 2.55–2.57 (m, 2H), 2.81 (s, 3H), 3.21–3.25 (m, 2H), 4.62 (br. s, 2H), 7.16–7.22 (m, 3H), 7.27–7.32 (m, 2H), 8.36 (br. s, 1H), 9.42 (br. s, 1H), 13.95 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 31.5, 36.5, 40.6, 41.6, 47.9, 117.8, 125.8, 128.1, 128.9, 139.7, 147.4, 154.7. IR (ATR, ZnSe, cm^{-1}): *v* 3103, 2920, 2852, 2725, 1661, 1601, 1462, 1377, 1257, 1112, 1017. HRMS (ESI-TOF) *m/z calcd*. for $C_{16}H_{23}N_7O_2S$ [M+H]$^+$: 363.1598, found 363.1605.

***N*-((4*Z*,5*Z*)-5-(Amino(dimethylamino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methylbenzenesulfonamide *(14a)*.** Compound **14a** was obtained in 72% yield (221 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1f**: 111 mg, 1.0 mmol; azide **2c**: 197 mg, 1.0 mmol; 1,4-dioxane (3 mL)) as a colorless solid, mp 232–233 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.30 (s, 3H), 3.15 (br.s, 3H), 3.56 (br. s, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.15 (br. s, 1H), 9.46 (br. s, 1H), 14.10 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 20.7, 39.6 (from HSQC), 42.3, 118.5, 125.6, 128.8, 140.6, 141.9, 146.9, 156.0. IR (ATR, ZnSe, cm^{-1}): *v* 3592, 3455, 3327, 3113, 1659, 1632, 1556, 1496, 1461, 1377, 1254, 1138, 1085, 1062, 1036, 1021. HRMS (ESI-TOF) *m/z calcd*. for $C_{12}H_{16}N_6O_2S$ [M+H]$^+$: 309.1128, found 309.1137.

***N*-((4*Z*,5*Z*)-5-(Amino(dimethylamino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)-4-methoxybenzenesulfonamide (14b)**. Compound **14b** was obtained in 84% yield (272 mg) according to the **general procedure B** (DBU: 152 mg, 1.0 mmol; amidine **1f**: 111 mg, 1.0 mmol; azide **2d**: 213 mg, 1.0 mmol; 1,4-dioxane (3 mL)) as a colorless solid, mp 130–131 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.16 (br.s, 3H), 3.56 (br.s, 3H), 3.78 (s, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 8.15 (br. s, 1H), 9.47 (br. s, 1H), 14.08 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 39.5 (from HSQC), 42.2, 55.3, 113.6, 118.4, 127.5, 136.7, 147.0, 156.0, 160.9. IR (ATR, ZnSe, cm^{-1}): *v* 3571, 3437, 3327, 3259, 3096, 1656, 1631, 1594, 1576, 1557, 1499, 1466, 1437, 1376, 1310, 1254, 1181, 1137, 1089, 1063, 1033, 1016. HRMS (ESI-TOF) *m/z calcd*. for $C_{12}H_{16}N_6O_3S$ [M+H]$^+$: 325.1077, found 325.1085.

***N*-((4*Z*,5*Z*)-5-(Amino(dimethylamino)methylene)-3,5-dihydro-4*H*-1,2,3-triazol-4-ylidene)methanesulfonamide (14c)**. Compound **14c** was obtained in 70% yield (326 mg) according to the **general procedure B** (DBU: 304 mg, 2.0 mmol; amidine **1f**: 222 mg, 2.0 mmol; azide **2f**: 242 mg, 2.0 mmol; 1,4-dioxane (6 mL)) as a colorless solid, mp 235–236 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.81 (s, 3H), 3.24 (br.s, 3H), 3.58 (br.s, 3H), 8.15 (br. s, 1H), 9.46 (br. s, 1H), 14.02 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 39.4 (from HSQC), 40.6, 42.2, 118.0, 147.5, 156.0. IR (ATR, ZnSe, cm^{-1}): *v* 3317, 3244, 3159, 3116, 3028, 1650, 1631, 1571, 1463, 1417, 1377, 1334, 1255, 1234, 1165, 1115, 1062, 1040. HRMS (ESI-TOF) *m/z calcd.* for $C_6H_{12}N_6O_2S$ [M+H]$^+$: 233.0815, found 233.0814.

X-ray structural analysis of compounds 4c, **5b**, and **7c** were performed on an Xcalibur Ruby diffractometer using Mo X-ray source (MoKα 0.71073 Å), scanning at 295(2) K. The structures were solved by the SHELXS software and refined by full-matrix least-squares on all F2 data using SHELXL-97[25] in conjunction with the WinGX graphical user interface.[26] Full crystallographic data are deposited at the Cambridge Crystallographic Data Center (CCDC 1959386 (**4c**), 1959374 (**5b**), 1959375 (**7c**)).

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Keywords: 2-cyanoacetamidines • sulfonyl azides • 1,2,3-triazoles • rearrangement • diazo group transfer

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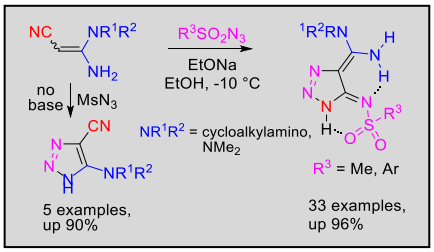

The generally accepted opinion on the single diazo group transfer direction of methylene active amidines with sulfonyl azides has been disproved by this study. Thus two products for reaction of 2-cyanoacetamidines with sulfonyl azides were found to afford different types of 1,2,3-triazoles. Mesyl azide reacts with 2-cyanoacetamidines in the absence of a base to afford 5-amino-4-cyano-1,2,3-triazole. The use of strong base switches the direction of the reaction in favor of nonaromatic 4-methylene-1,2,3-triazole-5-imines.

Key Topic Nonaromatic NH-1,2,3-triazoles