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The Dimroth rearrangement of 5-amino-1-aryl-1,2,3-triazole-4-carbothioamides

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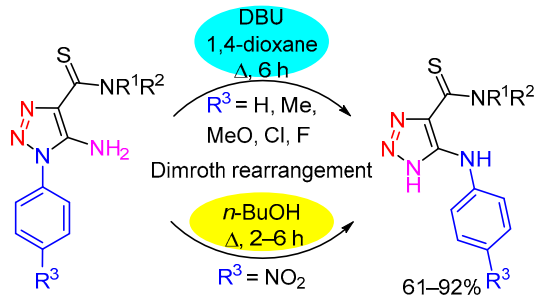


The rearrangement of 5-amino-1-aryl-1,2,3-triazole-4-carbothioamides was investigated. The process was optimized by varying the solvent, temperature, and the type of base. The optimal reaction conditions were found, and new 1-unsubstituted 5-arylamino-1,2,3-triazole-4-carbothioamides were synthesized. It has been shown that 1-aryl-1,2,3-triazoles containing a nitro group in the *para* position undergo rearrangement upon heating under reflux in *n*-butanol in the absence of a base. The rearrangement of compounds containing halogen, hydrogen, methyl, or methoxy groups in the aryl moiety requires the use of a base. The structure of the obtained compounds was confirmed by the data of NMR spectroscopy and mass spectrometry.

Keywords: azides, thioamides, 1,2,3-triazoles, Dimroth rearrangement.

The ability of 1,2,3-triazoles to undergo various transformations and rearrangements of the ring has always attracted numerous researchers.[1] Among 1,2,3-triazole derivatives, many compounds exhibit various biological activities, stimulating interest in the synthesis of novel derivatives of this heterocycle. The 1,2,3-triazole ring creates a structural basis for the manifestation of antibacterial, anti-inflammatory, neuroleptic, antiviral, and pesticidal activity by triazole derivatives.[2] On the other hand, thioamides are of interest as unique reagents[3] used in organic synthesis and possessing anticancer activity.[4] We assume that the combination of the NH fragment[5] and the thioamide group in the 1,2,3-triazole molecule can lead to the manifestation of new chemical properties, to the use of such 1,2,3-triazoles as ligands for the preparation of highly active palladium catalysts for cross-coupling reactions in aqueous media,[6] and to the emergence of new types of biological activity of synthesized hybrid molecules.[2]

The most common methods for the synthesis of 1,2,3-triazoles include copper-catalyzed cycloaddition of azides to acetylenes,[7] oxidative cyclization of functionalized hydrazones,[8] reactions of azides with enamines[9] and compounds with an active methylene group,[8,10] reactions of *NH*-1,2,3-triazoles with electrophilic reagents,[8,11] inter-[12] and intramolecular reactions of diazo compounds with aldimines,[8] and transformation of other heterocyclic compounds.[13] However, these methods are not applicable to the synthesis of *NH*-1,2,3-triazole-4-carbothioamides.

We turned our attention to the Dimroth rearrangement of 5-amino-1-aryl-1,2,3-triazoles leading to the formation of *NH*-triazoles.[14] The term "Dimroth rearrangement" was introduced in 1963[14b] for the isomerization of 1-substituted 1,2,3-triazoles **A** to 5-amino-substituted 1,2,3-triazoles **C** proceeding *via* the opening of the triazole ring and conversion to diazoacetamidines **B** followed by recyclization *via* the heteroelectrocyclic mechanism[12b,15] with the participation of the nitrogen atom of the amino group of compound **B** (Fig. 1). This rearrangement was first described by O. Dimroth[1a] and was subsequently reflected in many publications, including a series of reviews.[14,16]

It was shown that the introduction of strong electron-withdrawing substituents into positions 1 and 4 of the triazole ring facilitates the rearrangement.[14,16] Until this

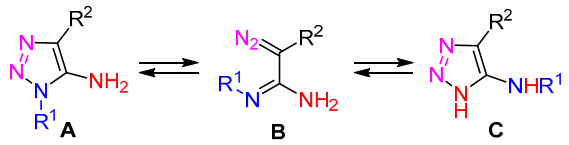
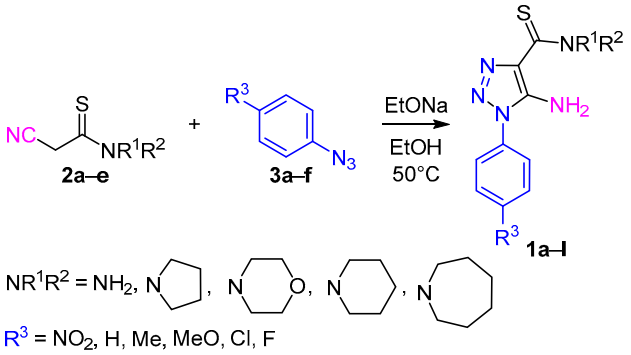


Figure 1. A simplified mechanism of the Dimroth rearrangement in the series of 5-amino-1,2,3-triazoles.

study, there were no data in the literature on the Dimroth rearrangement of 1,2,3-triazole-4-carbothioamides.

In order to investigate the possibility of the rearrangement of 1,2,3-triazole-4-carbothioamides and obtaining 5-arylamino-1*H*-1,2,3-triazole-4-carbothioamides not described in the literature, we synthesized a series of thioamides of 1-aryl-1,2,3-triazole-4-carboxylic acid **1**[17,18] from the corresponding thioamides **2** and azides **3** (Scheme 1) and investigated their transformation into isomeric compounds.

Scheme 1. Synthesis of thioamides of 1-aryl-1,2,3-triazole-4-carboxylic acid **1**

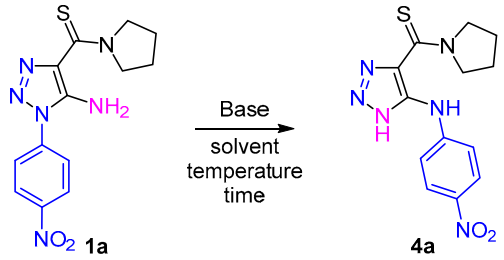


We found that the formation of 5-arylamino-1,2,3-triazole **4a** does not occur by long heating of [5-amino-1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl](pyrrolidin-1-yl)-methanethione (**1a**) in EtOH. The addition of Et_3N changed the situation and led to the formation of triazole **4a** in 49% yield (Table 1, entry 1).

Replacing EtOH with the higher boiling 1,4-dioxane and using DBU (in the amount of 1.0, 3.0, 4.0, and 6.0 mmol) increased the yield of target product **4a** to 90% (Table 1, entries 2–5). Obviously, the use of 6.0 mmol of DBU is optimal, since a further increase in its amount does not lead to an increase in the yield of triazole **4a** (Table 1, entry 6). We also found that the target product **4a** was formed upon heating of 1-aryl-1,2,3-triazole **1a** in DMF, but the product yield was lower and amounted to 50% (Table 1, entry 7). It is interesting to note that the Dimroth rearrangement of 1-aryl-1,2,3-triazole **1a** also occurs when the reaction is carried out in *n*-BuOH at 100°C with an 85% yield of compound **4a** (Table 1, entry 8). A further increase in temperature led to a decrease in the reaction time and an increase in the yield of triazole **4a** to 92% (Table 1, entry 9). Apparently, carrying out the reaction in *n*-BuOH at 118°C for 2 h is optimal for the synthesis of triazole **4a** (Table 1, entry 9). Alternatively, a technique using 1,4-dioxane as a solvent and DBU (6.0 mmol) as a base at 100°C can be recommended (Table 1, entry 5).

We have shown that the procedure for rearranging 1-(4-nitrophenyl)-1,2,3-triazoles **1a**,**f**,**j**,**k** in *n*-BuOH is well suited for all compounds. In these reactions, 5-(4-nitrophenyl)amino-1,2,3-triazoles **4a**,**f**,**j**,**k** were obtained in 71–92% yields (Table 2).

Table 1. Optimization of the conditions of the rearrangement of 1-aryl-1,2,3-triazole **1a*** in 5-arylamino-1,2,3-triazole **4a**

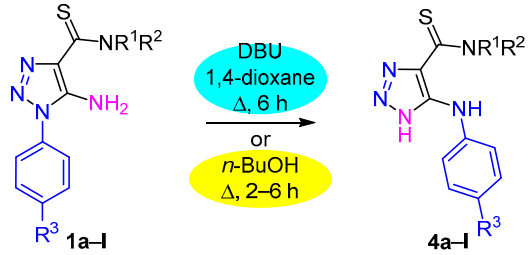


Entry	Base (mmol)	Solvent**	Temperature, °C	Time, h	Isolated yield, %
1	Et_3N	EtOH (95%)	75	10	49
2	DBU (1.0)	1,4-Dioxane	100	6	80
3	DBU (3.0)	1,4-Dioxane	100	6	85
4	DBU (4.0)	1,4-Dioxane	100	6	87
5	**DBU (6.0)**	**1,4-Dioxane**	**100**	**6**	**90**
6	DBU (10.0)	1,4-Dioxane	100	6	90
7	–	DMF	140	–	50
8	**–**	***n*-BuOH**	**100**	**6**	**85**
9	**–**	***n*-BuOH**	**118**	**2**	**92**
10	**–**	***n*-BuOH**	**118**	**6**	**90**

* Amount of compound **1a** – 0.5 mmol.
** Amount of EtOH, 1,4-dioxane, *n*-BuOH – 3 ml; DMF – 1 ml.

We found that 1-aryl-1,2,3-triazoles **1b**–**e**,**g**–**i**,**l** containing either electron-donating substituents or H, Cl, and F in the *para* position of the aryl moiety do not rearrange to isomeric triazoles by heating under reflux in

Table 2. Yields of 5-arylamino-1,2,3-triazoles **4a**–**l** as a result of the rearrangement of 1-aryl-1,2,3-triazoles **1a**–**l**



Compound	NR^1R^2	R^3	Yield, %
4a	Pyrrolidin-1-yl	NO_2	92
4b	Pyrrolidin-1-yl	H	71
4c	Pyrrolidin-1-yl	Me	91
4d	Pyrrolidin-1-yl	OMe	83
4e	Pyrrolidin-1-yl	Cl	90
4f	Morpholin-4-yl	NO_2	85
4g	Morpholin-4-yl	H	87
4h	Morpholin-4-yl	Me	93
4i	Morpholin-4-yl	F	95
4j	Piperidin-1-yl	NO_2	61
4k	Azepan-1-yl	NO_2	88
4l	NH_2	H	88

n-BuOH. Therefore, to obtain triazoles **4b**–**e**,**g**–**i**,**l**, we used an alternative procedure for the rearrangement of 1-aryl-1,2,3-triazoles **4b**–**e**,**g**–**i**,**l** in 1,4-dioxane in the presence of 6.0 mmol of DBU (Table 2). The reaction is fully completed in 6 h and leads to the formation of triazoles **4b**–**e**,**g**–**i**,**l** in high yields. Presumably, the addition of DBU stabilizes the final product, which has a higher acidity than the starting 1-substituted triazole, which favors an easier rearrangement and higher yields of triazoles **4b**–**e**,**g**–**i**,**l**.

The structure of compounds **4a**–**l** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. EI mass spectra of all compounds contain a molecular ion peak. The molecular formula of compound **4e** was confirmed by the high-resolution mass spectrum. The ^{1}H NMR spectra of all compounds **4a**–**l** contain signals of NH protons downfield at 11.18–15.07 ppm, which is typical for the spectra of *NH*-1,2,3-triazoles[18] and signals of the NH protons of arylamino groups at 8.76–10.11 ppm which are absent in the spectra of isomeric triazoles **1a**–**l**. Analysis of the ^{13}C NMR spectrum of compound **4i** made it possible to identify the signals of the carbon atoms of the aryl substituent and the signals at 130.3 and 147.3 ppm corresponding to the C-4 and C-5 atoms of the 1,2,3-triazole ring.

To conclude, as a result of the study of the Dimroth rearrangement of 1-aryl-1,2,3-triazoles to 5-arylamino-1,2,3-triazoles, it was shown that in the case of 1-(4-nitrophenyl)-1,2,3-triazoles, the reaction proceeds by heating under reflux in *n*-butanol. The transformation of 1-phenyl-1,2,3-triazole, as well as 1-aryl-1,2,3-triazoles with electron-donating substituents and halogens at position 4, requires heating under reflux in 1,4-dioxane in the presence of DBU.

Experimental

IR spectra were registered on a Bruker Alpha Fourier transform spectrometer (ATR, ZnSe) in 4000–500 cm^{-1} range. ^{1}H and ^{13}C NMR spectra were acquired on Bruker Avance II 400 (400 and 100 MHz, respectively) and Bruker Avance Neo (600 and 150 MHz, respectively) spectrometers in DMSO-d_6 and $CDCl_3$. Chemical shifts were determined relative to the residual signals of the corresponding solvent (DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 40.1 ppm for ^{13}C nuclei; $CDCl_3$: 7.26 ppm for ^{1}H nuclei, 77.1 ppm for ^{13}C nuclei). Mass spectra were recorded on a GCMS-QP 2010 Ultra mass spectrometer (EI ionization, 70 eV). High-resolution mass spectra were recorded on an Orbitrap Elite spectrometer (Thermo Fisher Scientific) with electrospray ionization. Elemental analysis was performed on a PerkinElmer Series II 2400 CHN-analyzer. Melting points were determined on a Stuart SMP10 apparatus. Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC on Sorbfil UV-254 plates, visualization under UV light.

5-Amino-1-aryl-1,2,3-triazole-4-carbothioamides **1a**,**f**,**i**–**l** were obtained and characterized by us earlier.[19]

Synthesis of 5-amino-1-aryl-1,2,3-triazole-4-carbothioamides 1b–e,g,h (General method). The corresponding thioamide **2a**,**b** (1.00 g, 5.87–6.48 mmol) was added to a freshly prepared solution of EtONa (150 mg Na and 20 ml EtOH), and the resulting mixture was stirred at room temperature for 10 min. Then, the corresponding aryl azide **3b**–**e** (5.87–6.48 mmol) was added. The reaction mixture was kept at 50°C for 2 h, then cooled. The formed precipitate was filtered off, washed with cooled EtOH until the filtrate decolorized, or crystallized from EtOH (compounds **1b**,**c**,**h**). The resulting product was dried in an oven at 80°C.

(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)(pyrrolidin-1-yl)methanethione (1b) was obtained from 3-(pyrrolidin-1-yl)-3-thioxopropionitrile (**2a**) (1.00 g, 6.48 mmol) and phenyl azide (**3b**) (772 mg, 6.48 mmol). Yield 1.27 g (72%), colorless powder, mp 154–156°C. IR spectrum, ν, cm^{-1}: 3364, 3229, 3178, 2969, 2938, 1597, 1378, 1340, 1288, 1254, 1151, 1018, 973, 916, 825, 730. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.90–2.00 (2H, m, CH_2); 2.02–2.05 (2H, m, CH_2); 3.87 (2H, t, *J* = 8.0, CH_2); 4.21 (2H, t, *J* = 8.0, CH_2); 7.37 (2H, s, NH_2); 7.55–7.77 (5H, m, H Ph). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 23.3; 26.5; 53.8; 54.9; 124.6 (2C); 126.1; 129.3; 129.8 (2C); 134.7; 146.6; 180.2. Mass spectrum, *m*/*z* (I_{rel}, %): 273 [M]$^+$ (97), 244 (26), 176 (100), 175 (54), 132 (41), 119 (52), 99 (19), 77 (81). Found, %: C 57.03; H 5.62; N 25.36. $C_{13}H_{15}N_5S$. Calculated, %: C 57.12; H 5.53; N 25.62.

[5-Amino-1-(4-methylphenyl)-1*H*-1,2,3-triazol-4-yl]-(pyrrolidin-1-yl)methanethione (1c) was obtained from 3-(pyrrolidin-1-yl)-3-thioxopropionitrile (**2a**) (1.00 g, 6.48 mmol) and 4-methylphenyl azide (**3c**) (863 mg, 6.48 mmol). Yield 1.38 g (74%), colorless powder, mp 153–155°C. IR spectrum, ν, cm^{-1}: 3408, 3224, 3035, 2967, 2912, 2849, 1600, 1580, 1513, 1488, 1435, 1373, 1320, 1224, 1206, 1155, 1110, 1015, 974, 943, 813. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.90–2.05 (4H, m, 2CH_2); 3.86 (2H, t, *J* = 8.0, CH_2); 4.21 (2H, t, *J* = 8.0, CH_2); 7.29 (2H, s, NH_2); 7.42–7.47 (4H, m, H Ph). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 20.7; 23.2; 26.5; 53.8; 54.9; 124.6 (2C); 126.2; 130.3 (2C); 132.2; 139.0; 146.6; 180.6. Mass spectrum, *m*/*z* (I_{rel}, %): 287 [M]$^+$ (69), 258 (29), 190 (100), 146 (25), 133 (45), 91 (70). Found, %: C 58.20; H 5.62; N 24.68. $C_{14}H_{17}N_5S$. Calculated, %: C 58.51; H 5.96; N 24.37.

[5-Amino-1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl]-(pyrrolidin-1-yl)methanethione (1d) was obtained from 3-(pyrrolidin-1-yl)-3-thioxopropionitrile (**2a**) (1.00 g, 6.48 mmol) and 4-methoxyphenyl azide (**3d**) (966 mg, 6.48 mmol). Yield 1.81 g (92%), colorless powder, mp 170–172°C, R_f 0.88 (EtOAc – petroleum ether, 2:1). IR spectrum, ν, cm^{-1}: 3374, 3252, 2971, 1660, 1585, 1521, 1379, 1340, 1301, 1251, 1152, 1027, 1016, 980, 829. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.97–2.11 (4H, m, 2CH_2); 3.87 (3H, s, OCH_3); 4.03 (2H, t, *J* = 6.0, CH_2); 4.36 (2H, t, *J* = 6.0, CH_2); 6.33 (2H, s, NH_2); 7.06 (2H, d, *J* = 9.0, H Ar); 7.42 (2H, d, *J* = 9.0, H Ar). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 23.9; 27.1; 54.3; 55.3; 55.8; 115.4; 126.4; 127.5; 127.6; 146.7; 160.7; 181.4. Mass spectrum, *m*/*z* (I_{rel}, %): 303 [M]$^+$ (22), 275 (33), 274 (41), 260 (33), 206 (100), 191 (57), 149 (55), 77 (52), 70 (53). Found, %: C 55.73; H 5.57; N 23.33. $C_{14}H_{17}N_5OS$. Calculated, %: C 55.43; H 5.65; N 23.08.

[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-yl]-(pyrrolidin-1-yl)methanethione (1e) was obtained from

3-(pyrrolidin-1-yl)-3-thioxopropionitrile (**2a**) (1.00 g, 6.48 mmol) and 4-chlorophenyl azide (**3e**) (995 mg, 6.48 mmol). Yield 1.70 g (85%), colorless powder, mp 182–184°C, R_f 0.49 (EtOAc – petroleum ether, 1:4). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.90–2.05 (4H, m, $2CH_2$); 3.86 (2H, t, *J* = 6.7, CH_2); 4.20 (2H, t, *J* = 6.7, CH_2); 7.42 (2H, s, NH_2), 7.63 (2H, d, *J* = 8.7, H Ar); 7.70 (2H, d, *J* = 8.7, H Ar). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 23.2; 26.5; 53.8; 54.9; 126.1; 126.6 (2C); 129.8 (2C); 133.5; 133.8; 146.7; 180.1. Found, *m*/*z*: 308.0738 $[M+H]^+$. $C_{13}H_{14}ClN_5S$. Calculated, *m*/*z*: 308.0731.

(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)(morpholin-4-yl)methanethione (1g) was obtained from 3-(morpholin-4-yl)-3-thioxopropionitrile (**2b**) (1.00 g, 5.87 mmol) and phenyl azide (**3b**) (700 mg, 5.87 mmol). Yield 1.28 g (75%), colorless powder, mp 155–157°C. IR spectrum, ν, cm^{-1}: 3366, 3221, 2863, 1602, 1505, 1433, 1272, 1234, 1113, 1018, 970, 868, 766. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 3.70–3.80 (4H, m, $2CH_2$); 4.24–4.47 (4H, m, $2CH_2$); 7.02 (2H, br. s, NH_2); 7.56–7.66 (5H, m, H Ph). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 49.4; 53.3; 66.0; 66.2; 124.5 (2C); 125.6; 129.2; 129.6 (2C); 134.4; 146.4; 184.1. Mass spectrum, *m*/*z* (I_{rel}, %): 289 $[M]^+$ (80), 176 (100), 132 (38), 119 (66), 77 (83). Found, %: C 53.95; H 5.53; N 24.29. $C_{13}H_{15}N_5OS$. Calculated, %: C 53.96; H 5.23; N 24.20.

[5-Amino-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl](morpholin-4-yl)methanethione (1h) was obtained from 3-(morpholin-4-yl)-3-thioxopropionitrile (**2b**) (1.00 g, 5.87 mmol) and 4-methylphenyl azide (**3c**) (782 mg, 5.87 mmol). Yield 1.26 g (71%), colorless powder, mp 166–168°C. IR spectrum, ν, cm^{-1}: 3381, 3265, 3002, 2913, 2858, 1602, 1519, 1472, 1429, 1380, 1235, 1168, 1104, 1023, 936, 820. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.42 (3H, s, CH_3); 3.70–3.83 (4H, m, $2CH_2$); 4.32–4.39 (4H, m, $2CH_2$); 6.97 (2H, s, NH_2); 7.42–7.48 (4H, m, H Ar). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 20.7; 49.3; 53.6; 66.4 (2C); 124.6 (2C); 125.7; 130.2 (2C); 132.1; 139.2; 146.6; 184.3. Mass spectrum, *m*/*z* (I_{rel}, %): 303 $[M]^+$ (53), 190 (100), 146 (22), 133 (58), 91 (73). Found, %: C 55.12; H 5.34; N 23.43. $C_{14}H_{17}N_5OS$. Calculated, %: C 55.43; H 5.65; N 23.08.

Synthesis of 5-arylamino-1,2,3-triazoles 4a,f,j,k (General method). A solution of 5-amino-1-aryl-1,2,3-triazole **1a,f,j,k** (2.00 mmol) in *n*-BuOH (10 ml) was heated under reflux for 2–6 h. The solvent was evaporated under reduced pressure, the residue was crystallized from EtOH. The formed precipitate was filtered off and dried in an oven at 80°C.

Synthesis of 5-arylamino-1,2,3-triazoles 4b–e,g–i,l (General method). DBU (913 mg, 6.00 mmol) was added to a solution of the corresponding 5-amino-1-aryl-1,2,3-triazole **1b–e,g–i,l** (2.00 mmol) in anhydrous 1,4-dioxane (12 ml), and the mixture was heated under reflux for 6 h. The solvent was evaporated under reduced pressure, AcOH (2–4 ml) was added to the residue, and the mixture was kept stirring at room temperature for 1 h. The product was extracted with EtOAc, washed with aqueous $NaHCO_3$, H_2O, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, the residue was triturated with H_2O, filtered off, and dried in an oven at 80°C.

{5-[(4-Nitrophenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(pyrrolidin-1-yl)methanethione (4a). Yield 585 mg (92%), yellow powder, mp 224–225°C, R_f 0.53 (EtOAc – petroleum ether, 2:1). IR spectrum, ν, cm^{-1}: 3296, 2981, 2954, 2924, 2905, 1596, 1577, 1538, 1442, 1287, 1168, 1106. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 2.05–2.14 (4H, m, $2CH_2$); 4.02–4.05 (2H, m, CH_2); 4.14–4.20 (2H, m, CH_2); 7.63 (2H, d, *J* = 8.8, H Ar); 8.21 (2H, d, *J* = 8.8, H Ar); 10.72 (1H, s, NH); 11.18 (1H, br. s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 23.8; 26.9; 54.7; 55.2; 116.1 (2C); 125.7 (2C); 131.6; 140.9; 146.5; 149.4; 180.9. Mass spectrum, *m*/*z* (I_{rel}, %): 318 $[M]^+$ (43), 289 (6), 285 (7), 202 (6), 70 $[C_4H_8N]^+$ (100). Found, %: C 48.85; H 4.55; N 26.45. $C_{13}H_{14}N_6O_2S$. Calculated, %: C 49.05; H 4.43; N 26.40.

[5-(Phenylamino)-1*H*-1,2,3-triazol-4-yl](pyrrolidin-1-yl)methanethione (4b). Yield 384 mg (71%), yellow crystals, mp 164–166°C (EtOAc), R_f 0.78 (EtOAc – petroleum ether, 2:1).). IR spectrum, ν, cm^{-1}: 3163, 3081, 2965, 2873, 1591, 1562, 1529, 1380, 1248, 1010, 971, 739, 686. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.95–1.99 (4H, m, $2CH_2$); 3.85–3.88 (2H, m, CH_2); 4.03–4.05 (2H, m, CH_2); 6.87–6.91 (1H, m, H Ar); 7.27–7.31 (2H, m, H Ar); 7.46–7.48 (2H, m, H Ar); 9.85 (1H, s, NH); 14.85 (1H, s, NH). ^{1}H NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 23.4; 26.3; 54.1; 54.8; 116.2 (2C); 120.3; 129.1 (2C); 129.8; 141.0; 149.2; 180.7. Mass spectrum, *m*/*z* (I_{rel}, %): 273 $[M]^+$ (100), 203 (13), 104 (13), 77 (27). Found, %: C 57.35; H 5.57; N 25.93. $C_{13}H_{15}N_5S$. Calculated, %: C 57.12; H 5.53; N 25.62.

{5-[(4-Methylphenyl)amino]-1*H*-1,2,3-triazol-4-yl)}-(pyrrolidin-1-yl)methanethione (4c). Yield 552 mg (91%), yellow powder, mp 164–166°C, R_f 0.77 (EtOAc – petroleum ether, 1:2). ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.91–2.00 (4H, m, $2CH_2$); 2.24 (3H, s, CH_3); 3.84–3.87 (2H, m, CH_2); 4.05 (2H, br. s, CH_2); 7.10 (2H, d, *J* = 8.5, H Ar); 7.35 (2H, d, *J* = 8.5, H Ar); 9.79 (1H, br. s, NH); 14.77 (1H, br. s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 20.0; 23.1; 26.1; 53.9; 54.5; 116.3 (2C); 128.9; 129.3 (2C); 129.6; 138.5; 149.5; 180.8. Mass spectrum, *m*/*z* (I_{rel}, %): 287 $[M]^+$ (100), 190 (39), 91 (42). Found, %: C 58.17; H 5.82; N 24.37. $C_{14}H_{17}N_5S$. Calculated, %: C 58.51; H 5.96; N 24.37.

{5-[(4-Methoxyphenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(pyrrolidin-1-yl)methanethione (4d). Yield 503 mg (83%), yellow crystals, mp 163–165°C (EtOAc), R_f 0.61 (EtOAc – petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3279, 3207, 2956, 1598, 1562, 1511, 1489, 1442, 1231, 1290, 1130, 1024, 822, 692. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.94–2.01 (4H, m, $2CH_2$); 3.71 (3H, s, OCH_3); 3.84–3.87 (2H, m, CH_2); 4.04–4.06 (2H, m, CH_2); 6.89 (2H, d, *J* = 12.0, H Ar); 7.40 (2H, d, *J* = 12.0, H Ar); 9.69 (1H, s, NH); 14.70 (1H, s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 23.3; 26.3; 54.1; 54.8; 55.2; 114.4 (2C); 118.0 (2C); 129.2; 134.4; 149.6; 153.6; 180.6. Mass spectrum, *m*/*z* (I_{rel}, %): 303 $[M]^+$ (70), 274 (47), 260 (36), 206 (100). Found, %: C 55.25; H 5.67;

N 23.35. $C_{14}H_{17}N_5OS$. Calculated, %: C 55.43; H 5.65; N 23.08.

{5-[(4-Chlorophenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(pyrrolidin-1-yl)methanethione (4e). Yield 558 mg (90%), light-yellow crystals, mp 166–168°C (EtOH), R_f 0.49 (EtOAc – petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3357, 3189, 2938, 1597, 1564, 1489, 1438, 1406, 1313, 1112, 1009, 837, 747, 682. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.94–2.00 (4H, m, $2CH_2$); 3.85 (2H, t, *J* = 6.4, CH_2); 4.03 (2H, t, *J* = 6.5, CH_2); 7.31 (2H, d, *J* = 8.4, H Ar); 7.51 (2H, d, *J* = 8.3, H Ar); 9.90 (1H, s, NH); 14.88 (1H, s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 23.4; 26.2; 53.8; 54.9; 117.7 (2C); 123.6; 128.8 (2C); 130.1; 140.0; 148.7; 180.6. Found, *m/z*: 308.0734 $[M+H]^+$. $C_{13}H_{14}ClN_5S$. Calculated, *m/z*: 308.0731.

(Morpholin-4-yl){5-[(4-nitrophenyl)amino]-1*H*-1,2,3-triazol-4-yl}methanethione (4f). Yield 568 mg (85%), yellow powder, mp 249–250°C, R_f 0.28 (EtOAc – petroleum ether, 2:1). IR spectrum, ν, cm^{-1}: 3184, 3115, 2898, 2859, 1600, 1573, 1529, 1486, 1634, 1432, 1296, 1259, 1102. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 3.58–3.68 (2H, m, CH_2); 3.72–3.77 (2H, m, CH_2); 3.84–3.90 (2H, m, CH_2); 4.25–4.34 (2H, m, CH_2); 7.50 (2H, d, *J* = 8.4, H Ar); 8.15 (2H, d, *J* = 8.4, H Ar); 9.45 (1H, s, NH); 15.07 (1H, br. s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm: 49.1; 52.6; 65.7; 66.2; 114.9 (2C); 125.6 (2C); 133.5; 139.1; 144.2; 148.4; 185.1. Mass spectrum, *m/z* (I_{rel}, %): 334 $[M]^+$ (68), 289 (10), 264 (13), 248 (12), 202 (18), 86 $[C_4H_8NO]^+$ (100). Found, %: C 46.78; H 4.01; N 25.25. $C_{13}H_{14}N_6O_3S$. Calculated, %: C 46.70; H 4.22; N 25.14.

(Morpholin-4-yl)[5-(phenylamino)-1*H*-1,2,3-triazol-4-yl]-methanethione (4g). Yield 498 mg (87%), yellow powder, mp 163–165°C, R_f 0.53 (EtOAc – petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3279, 2980, 2848, 1594, 1561, 1494, 1433, 1382, 1296, 1232, 1115, 999, 752. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm: 3.66–3.77 (4H, m, $2CH_2$); 4.00 (2H, br. s, CH_2); 4.31 (2H, br. s, CH_2); 6.86 (1H, br. s, H Ar); 7.25–7.27 (3H, m, H Ar); 7.43 (1H, br. s, H Ar); 8.77 (1H, br. s, NH); 14.76 (1H, br. s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 49.2; 52.8; 65.7; 65.9; 115.9 (2C); 119.9; 128.7 (2C); 130.8; 141.4; 147.8; 185.3. Found, %: C 53.96; H 4.88; N 23.89. $C_{13}H_{15}N_5OS$. Calculated, %: C 53.96; H 5.23; N 24.20.

{5-[(4-Methylphenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(morpholin-4-yl)methanethione (4h). Yield 503 mg (93%), yellow powder, mp 142–144°C, R_f0.51 (EtOAc – petroleum ether, 1:2). ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.23 (3H, s, CH_3); 3.62–3.71 (4H, m, $2CH_2$); 3.99–4.38 (4H, m, $2CH_2$); 7.07 (2H, d, *J* = 12.0, H Ar); 7.32 (2H, d, *J* = 12.0, H Ar); 8.79 (1H, s, NH); 14.68 (1H, br. s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 20.2; 49.3; 52.9; 66.1 (2C); 116.2 (2C); 128.7; 129.4 (2C); 130.0; 139.1; 147.8; 185.2. Mass spectrum, *m/z* (I_{rel}, %): 303 $[M]^+$ (100), 190 (36), 133 (20), 91 (36), 81 (36). Found, %: C 55.77; H 5.63; N 23.04. $C_{14}H_{17}N_5OS$. Calculated, %: C 55.43; H 5.65; N 23.08.

{5-[(4-Fluorophenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(morpholin-4-yl)methanethione (4i). Yield 583 mg (95%), yellow powder, mp 164–166°C, R_f 0.38 (EtOAc – petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3279, 3206, 2956, 1599, 1562, 1511, 1489, 1442, 1290, 1231, 1164, 1024, 972, 822, 692. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 3.61–3.83 (4H, m, $2CH_2$); 3.93–4.07 (2H, m, CH_2); 4.21–4.38 (2H, m, CH_2); 7.07–7.12 (2H, m, H Ar); 7.43–7.46 (2H, m, H Ar); 8.76 (1H, s, NH); 14.74 (1H, br. s, NH). ^{13}C NMR spectrum (100 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 49.1; 52.6; 65.8; 66.1; 115.2 (d, *J* = 22.0); 117.5 (d, *J* = 7.0); 130.3; 137.9 (d, *J* = 2.0); 147.3; 156.3 (d, *J* = 235.0, CF); 185.2. Mass spectrum, *m/z* (I_{rel}, %): 307 $[M]^+$ (100), 221 (14), 160 (16), 122 (19), 95 (24), 86 (66). Found, %: C 51.18; H 4.56; N 22.78. $C_{13}H_{14}FN_5OS$. Calculated, %: C 50.80; H 4.59; N 22.79.

{5-[(4-Nitrophenyl)amino]-1*H*-1,2,3-triazol-4-yl}-(piperidin-1-yl)methanethione (4j). Yield 405 mg (61%), yellow crystals, mp 185–187°C, R_f 0.56 (EtOAc – petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3355, 3188, 2937, 1596, 1564, 1487, 1436, 1405, 1311, 1110, 1007, 836, 746, 682. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.58–1.68 (6H, m, $3CH_2$); 3.73 (2H, br. s, CH_2); 4.26 (2H, br. s, CH_2); 7.48 (2H, d, *J* = 9.0, H Ar); 8.15 (2H, d, *J* = 9.0, H Ar); 9.42 (1H, s, NH); 15.03 (1H, br. s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 23.5; 25.3; 26.6; 49.9; 53.0; 114.8 (2C); 125.7 (2C); 133.8; 139.0; 143.6; 148.7; 184.0. Mass spectrum, *m/z* (I_{rel}, %): 332 $[M]^+$ (39), 271 (18), 84 (100). Found, %: C 50.94; H 4.59; N 25.16. $C_{14}H_{16}N_6O_2S$. Calculated, %: C 50.59; H 4.85; N 25.28.

(Azepan-1-yl){5-[(4-nitrophenyl)amino]-1*H*-1,2,3-triazol-4-yl}methanethione (4k). Yield 609 mg (88%), yellow powder, mp 217–218°C, R_f 0.75 (EtOAc – petroleum ether, 2:1). IR spectrum, ν, cm^{-1}: 3254, 2937, 2917, 2853, 1600, 1567, 1536, 1289, 1109. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.60–1.74 (4H, m, $2CH_2$); 1.88–2.06 (4H, m, $2CH_2$); 4.06–4.09 (2H, m, CH_2); 4.24–4.27 (2H, m, CH_2); 7.57 (2H, d, *J* = 9.0, H Ar); 8.21 (2H, d, *J* = 9.0, H Ar); 9.86 (1H, s, NH); 11.23 (1H, br. s, NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 25.5; 26.5; 27.1; 29.5; 55.1; 55.9; 116.1 (2C); 125.8 (2C); 132.5; 141.1; 146.8; 148.9; 184.9. Mass spectrum, *m/z* (I_{rel}, %): 346 $[M]^+$ (100), 313 (23), 285 (67), 98 (92). Found, %: C 52.02; H 4.88; N 23.90. $C_{15}H_{18}N_6O_2S$. Calculated, %: C 52.01; H 5.24; N 24.26.

5-(Phenylamino)-1*H*-1,2,3-triazole-4-carbothioamide (4l). Yield 387 mg (88%), colorless powder, mp 256–258°C, R_f 0.36 (EtOAc – petroleum ether, 3:1). IR spectrum, ν, cm^{-1}: 3278, 3205, 2956, 1600, 1563, 1514, 1490, 1444, 1291, 1233, 1165, 1025, 973, 830, 699. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.38–7.42 (3H, m, Ph); 7.52 (2H, t, *J* = 7.8, H Ph); 8.48 (1H, s, NH); 10.11 (1H, br. s, NH_2); 11.66 (1H, br. s, NH_2); 14.71 (1H, s, NH). ^{13}C NMR spectrum (150 MHz, DMSO-d_6), δ, ppm: 125.3 (2C); 127.4; 128.2; 129.8 (2C); 134.6; 155.0; 156.0. Mass spectrum, *m/z* (I_{rel}, %): 219 $[M]^+$ (100), 191 (24), 163 (22), 131 (27), 104 (31), 77 (70). Found, %: C 49.44; H 4.08; N 31.73. $C_9H_9N_5S$. Calculated, %: C 49.30; H 4.14; N 31.94.

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