Synthesis and structure of novel 1,2,4-triazole derivatives containing the 2,4-dinitrophenylthio group

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Some novel 1,2,4-triazole derivatives containing the 2,4-dinitrophenylthio group have been synthesised in high yields by means of the reactions of 3-substituted-4-amino -1*H*-1,2,4-triazole-5(4*H*)-thiones or (*E*)-3-aryl-4-(benzylideneamino)-1*H*-1,2,4-triazole-5(4*H*)-thiones with 1-chloro-2,4-dinitrobenzene. The (*E*)-3-aryl-4-(benzylideneamino)-1*H*-1,2,4-triazole-5(4*H*)-thiones were prepared by the reaction of 4-amino-3-aryl-2*H*-1,2,4-triazole-3(4*H*)-thiones and diverse aromatic aldehydes. The 2, 4-dinitrophenyl group linked to the S atom, not to the N atom, was confirmed by the crystal structures. The structures of all the compounds were determined by elemental analysis, IR, MS, ^{1}H NMR and ^{13}C NMR.

Keywords: 1,2,4-triazole, 1-chloro-2,4-dinitrobenzene, Schiff base, aromatic aldehydes, thioether

Various 1,2,4-triazole derivatives have been reported to possess diverse types of biological properties such as antibacterial,[1] antifungal,[2,3] anti-inflammatory,[4] antihypertensive,[5] antiviral,[6] antileishmanial[7] and antimigraine activities.[8] They can be used as plant-growth inhibitors,[9] paints and surface active agents,[10] inhibitors of malignant cellular proliferation[11] *etc.* So the development of new compounds containing 1,2,4-triazole rings is of much importance. On the other hand, 1,2,4-triazole derivatives containing 2,4-dinitrophenylthio group have been reported only by a few papers up to now and all of the reported compounds are confined to 4-aryl or 4-alkyl 1,2,4-triazoles.[22-24]

Several years ago Tang *et al.*[25] made 2*H*-1,2,4-triazol-3(4*H*)-one react with 1-fluoro-2,4-dinitrobenzene, then they obtained 2-(2,4-dinitrophenyl)-2*H*-1,2,4-triazol-3(4*H*)-one (Scheme 1) in which the 2,4-dinitrophenyl group was linked to the N atom, but not to the O atom. There are also some papers which have reported that the substituted groups linked to the N atom of 3-substituted-4-amino-1*H*-1,2,4-triazol-5(4*H*)-ones or (*E*)-4-(benzylideneamino)-5-aryl-1*H*-1,2,4-triazol-5(4*H*)-ones, not to the O atom.[26-32] As the substituted groups linked to the O atom have not yet been reported, we believed that when we made the sulfur analogues 3-substituted-4-amino-1*H*-1,2,4-triazol-5(4*H*)-thiones or (*E*)-3-aryl-4-(benzylideneamino)-1*H*-1,2,4-triazole-5(4*H*)-thiones they would react with 1-chloro-2,4-dinitrobenzene in the same way, the 2,4-dinitrophenyl group would be linked to the N atom, not to the S atom in the products. But when we obtained the crystal structures of **2e** (Fig. 1) and **3b** (Fig. 2), we were surprised to find that the 2,4-dinitrophenyl group is linked to the S atom, not to the N atom (Scheme 2). Also to our surprise, Sarva *et al.* made 4-amino-3-(4-propoxyphenyl)-

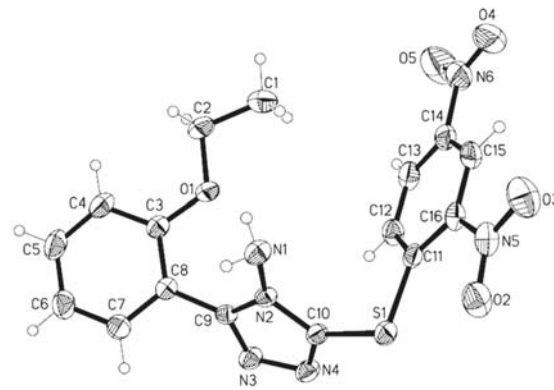
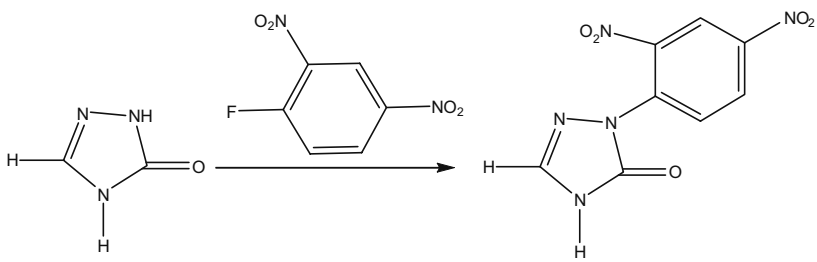


Fig. 1

1*H*-1,2,4-triazole-5(4*H*)-thione react with 1-(2-chloroethyl)-4-(2-methoxyphenyl)piperazine in the solution of EtOH added KOH and KI, when they got two products[33](Scheme 5), and Nasser also obtained two compounds when he made 4-amino-3-(pyridin-2-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione react with (2*S*,3*R*,4*R*,5*R*,6*R*)-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl triacetate[34] (Scheme 6). Tang *et al.* made the reaction in the alkalescent solution of $NaHCO_3$ and EtOH, while our reactions were carried out in the mixed solution of Et_3N and EtOH, which is also alkalescent, so we considered that the conditions of the two methods were generally the same. There are also thioethers obtained in several papers in which 1,2,4-triazoles react with halohydrocarbons.[24,35-37]



Scheme 1

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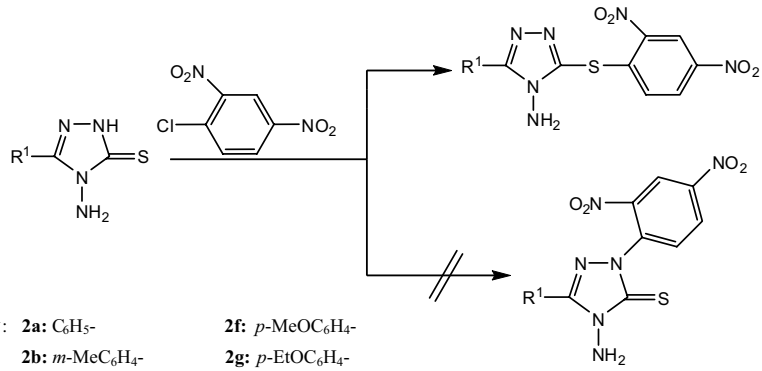
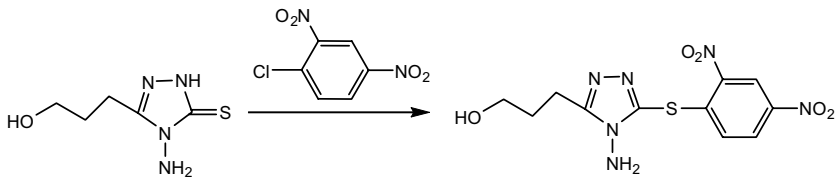


R[1]: **2a:** C_6H_5- **2f:** *p*-$MeOC_6H_4$-
2b: *m*-MeC_6H_4- **2g:** *p*-$EtOC_6H_4$-
2c: *p*-ClC_6H_4- **2h:** $C_6H_5OCH_2$-
2d: *p*-MeC_6H_4- **2i:** *o*-OHC_6H_4-
2e: *o*-$EtOC_6H_4$- **2j:** *p*-OHC_6H_4-

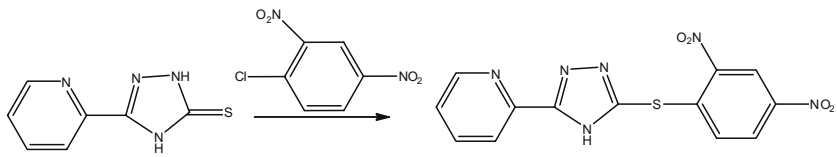
Scheme 2



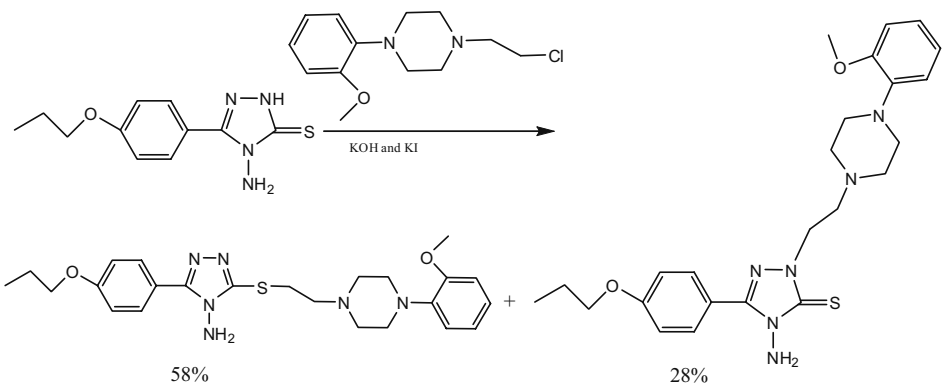
2k

Scheme 3

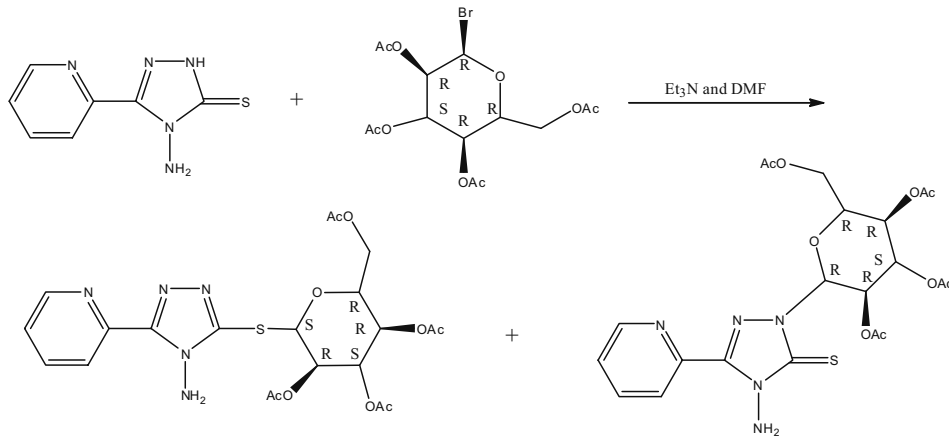
Kulish *et al.* obtained 2-(5-(2,4-dinitrophenylthio)-4*H*-1,2,4-triazol-3-yl)pyridine by the reaction of 3-(pyridin-2-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione and 1-chloro-2,4-dinitrobenzene at the temperature of 2°C in alcohol (Scheme 4).[24] That was very interesting. Generally speaking, the nucleophilicity of mercapto group is stronger than that of NH, so substituted groups would be linked to the S rather than to N atom. At the same time there are still many abnormal cases.[33,34,38-41] As all of these points puzzled us, we decided to investigate the mechanisms of these reactions. We now report the synthesis of the title compounds. This is the first report of the 2,4-dinitrophenyl group linking to the S atom of 3-substituted-4-amino-1*H*-1,2,4-triazole-5(4*H*)-thiones and (*E*)-3-aryl-4-(benzylideneamino)-1*H*-1,2,4-triazole-5(4*H*)-thiones.



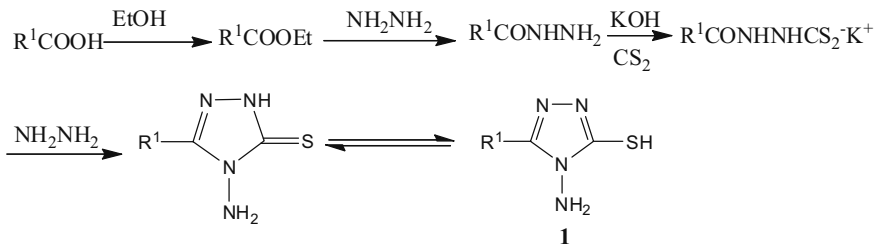
Scheme 4



Scheme 5



Scheme 6



Scheme 7

4-Amino-3-aryl-1*H*-1,2,4-triazole-5(4*H*)-thiones, whose tautomers are 4-amino-3-aryl-5-mercapto-1,2,4-triazoles, are generally prepared from aromatic acids (Scheme 7), following the procedure of Zhang *et al.* [42]

We made **1** react with 1-chloro-2,4-dinitrobenzene in the mixed solution of Et_3N and EtOH at the temperature of 120 °C, refluxing for only about 10 min. In this way, we obtained 3-(2,4-dinitrophenylthio)-5-aryl-4*H*-1,2,4-triazol-4-amines readily (Scheme 2). We also used 4-amino-5-(3-hydroxypropyl)-2*H*-1,2,4-triazole-3(4*H*)-thione which was prepared following the procedure of Zhang *et al.* [43] (Scheme 8) to react with 1-chloro-2,4-dinitrobenzene in the same conditions as mentioned above. We obtained 3-(4-amino-5-(2,4-dinitrophenylthio)-4*H*-1,2,4-triazol-3-yl)propan-1-ol successfully (Scheme 3).

Meanwhile, we used (*E*)-3-aryl-4-(benzylideneamino)-1*H*-1,2,4-triazole-5(4*H*)-thiones (**2**) that were prepared by the reaction of 4-amino-3-aryl-1*H*-1,2,4-triazole-5(4*H*)-thiones and diverse aromatic aldehydes to react with 1-chloro-2,4-dinitrobenzene in the same condition as mentioned above. In this way, we successfully obtained (*E*)-*N*-benzylidene-3-(2,4-dinitrophenylthio)-5-aryl-4*H*-1,2,4-triazol-4-amines (**3**, Scheme 9) and the crystal structure of **3b** is shown in Fig. 2.

Experimental

Carbon, hydrogen and nitrogen analyses were determined on a Flash-1112 series elemental analyser. IR spectra were recorded on a

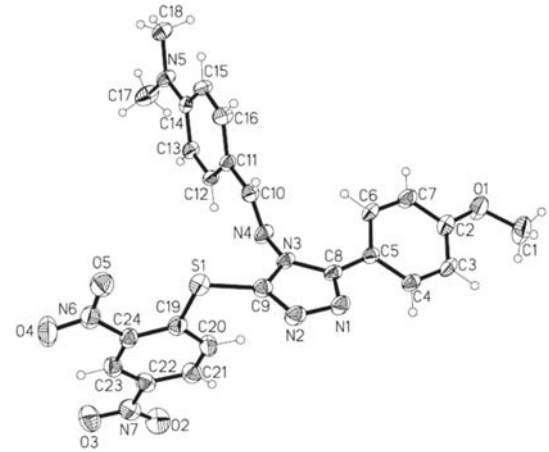
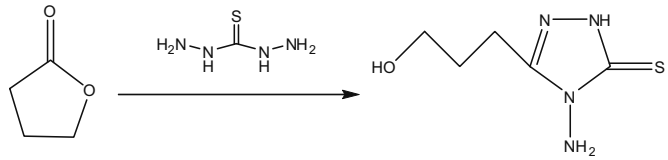
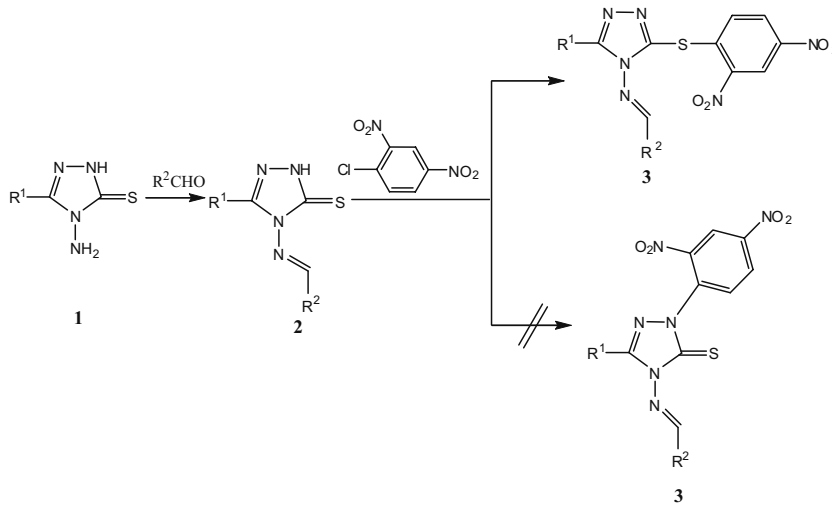


Fig. 2



Scheme 8



3a: R^1 = *p*-$EtOC_6H_4$- R^2 = *p*-FC_6H_4-
3b: R^1 = *p*-$MeOC_6H_4$- R^2 = *p*-$(CH_3)_2NC_6H_4$-
3c: R^1 = *o*-EtOC6H4- R^2 = *p*-MeC_6H_4-
3d: R^1 = *o*-HOC_6H_4- R^2 = *o*-FC_6H_4-
3e: R^1 = *p*-ClC_6H_4- R^2 = *p*-$MeOC_6H_4$-
3f: R^1 = *p*-$MeOC_6H_4$- R^2 = *p*-BrC_6H_4-
3g: R^1 = *p*-HOC_6H_4- R^2 = *m*-$NO_2C_6H_4$-
3h: R^1 = C_6H_5- R^2 = *p*-HOC_6H_4-
3i: R^1 = C_6H_5- R^2 = *o*-HOC_6H_4-

Scheme 9

Nicolet 670FT-IR using the smart OMNI-Sampler in the range 4000–400 cm^{-1}. MS spectra were recorded on an Agilent 1100 LC/MS. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300 NMR Spectrometer in DMSO-d_6 solution using TMS as an internal reference. Melting points were determined on an XT-4 melting point apparatus and were uncorrected. The crystal structures were measured on Bruker APEX area-detector diffractometer. All chemicals and solvents used were of AR grade.

Synthesis of 3-(2,4-dinitrophenylthio)-5-substituted-4H-1,2,4-triazol-4-amine (**2a–k**): *general procedure*
A mixture of 4-amino-3-substituted-1*H*-1,2,4-triazole-5(4*H*)-thione (0.02 mol, **1**), and 1-chloro-2,4-dinitrobenzene (0.02 mol) were added EtOH (10 mL) and Et_3N (30 mL), refluxed at the temperature of 120 °C (on the oil-bath) for only about 10 min. After concentration under reduced pressure, the crude products were recrystallised from alcohol to afford the compounds (**2a–k**).

Synthesis of (E)-3-(2,4-dinitrophenylthio)-N-(4-benzylidene)-5-aryl-4H-1,2,4-triazol-4-amines (**3a–i**): *general procedure*
Aromatic aldehydes (0.02 mol, distilled under reduced pressure before use) were added to a solution of 4-amino-3-substituted-1*H*-1,2,4-triazole-5-thione (0.02 mol) in absolute ethanol (30 mL). The pH value then was adjusted to 5–6 with dilute HCl. The mixture was stirred and refluxed for about 2 h. The crude products were recrystallised from ethanol and gave the pure (*E*)-3-aryl-4-(benzylidene-amino)-1*H*-1,2,4-triazole-5(4*H*)-thiones (**2**). Then to a solution of 2 (0.02 mol) dissolved in EtOH (10 mL) and Et_3N (30 mL) was added 1-chloro-2,4-dinitrobenzene (0.02 mol). The mixture was refluxed for only about 10 minutes under stirring at the temperature of 120 °C (on the oil-bath). After concentration under reduced pressure, the crude products were recrystallised from alcohol to afford the compounds **(3a–i)**.

3-(2,4-Dinitrophenylthio)-5-phenyl-4H-1,2,4-triazol-4-amine (**2a**): M.p. 246–248 °C; yield: 92.6%; IR (cm^{-1}): 3104 (ArH), 1598 (C=N), 1463 (aryl skeleton), 703 (C–S–C); MS-ESI (*m/z*): 359.4 ($M^+ + 1$); ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.95 (d, *J* = 2.5 Hz, 1H, ArH), 8.44–8.40 (m, 1H, ArH), 8.16–8.13 (m, 2H, ArH), 7.62–7.56 (m, 3H, ArH), 7.18 (d, *J* = 8.9 Hz, 1H, ArH), 6.31 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6) δ (ppm) = 155.24, 146.87, 145.22, 144.63, 141.44, 130.16, 129.87, 128.44, 128.26, 128.09, 126.49, 121.14; Elemental anal. Calcd for $C_{14}H_{10}N_6O_4S$: C 46.93,H 2.81, N 23.45. Found: C 46.72, H 2.86, N 23.56%.

3-(2,4-Dinitrophenylthio)-5-m-tolyl-4H-1,2,4-triazol-4-amine (**2b**): M.p. 88–90 °C; yield: 91.3%; IR (cm^{-1}): 3100 (ArH), 1598 (C=N), 1469 (aryl skeleton), 702 (C–S–C); MS-ESI (*m/z*): 373.6 ($M^+ + 1$); ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.93 (d, *J* = 2.6 Hz, 1H, ArH), 8.44–8.40 (m, 1H, ArH), 7.92–7.83 (m, 2H, ArH), 7.47–7.42 (m, 2H, ArH), 7.17 (d, *J* = 8.9 Hz, 1H, ArH), 6.25 (s, 2H, NH_2), 2.38 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 156.37, 147.25, 146.03, 141.96, 138.34, 137.71, 129.76, 128.80, 128.62, 128.41, 127.65, 126.90, 125.30, 123.54, 20.68; Elemental anal. Calcd for $C_{15}H_{12}N_6O_4S$: C 48.38, H 3.25, N 22.57. Found: C 48.56, H 3.30, N 22.38%.

3-(4-Chlorophenyl)-5-(2,4-dinitrophenylthio)-4H-1,2,4-triazol-4-amine (**2c**): M.p. 90–92 °C; yield: 92.4%; IR (cm^{-1}): 3086 (ArH), 1586 (C=N), 1475 (aryl skeleton), 698 (C–S–C); MS-ESI (*m/z*): 393.3 ($M^+ + 1$); ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.94 (d, *J* = 2.6 Hz, 1H, ArH), 7.78 (dd, J_1 = 3.6 Hz, J_2 = 8.5 Hz, 2H, ArH), 7.57 (dd, J_1 = 1.8 Hz, J_2 = 7.5 Hz, 1H, ArH), 7.18 (dd, J_1 = 2.3 Hz, J_2 = 7.6 Hz, 1H, ArH), 6.35 (d, *J* = 8.5 Hz, 2H, ArH), 6.13 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6) δ (ppm) = 154.28, 148.68, 147.18, 145.24, 135.20, 137.14, 129.77, 129.58, 128.86, 128.23, 127.90, 125.34; Elemental anal. Calcd for $C_{14}H_9ClN_6O_4S$: C 42.81, H 2.31, N 21.40. Found: C 42.98, H 2.36, N 21.22%.

3-(2,4-Dinitrophenylthio)-5-p-tolyl-4H-1,2,4-triazol-4-amine (**2d**): M.p. 266–268 °C; yield: 89.2%; IR (cm^{-1}): 3093 (ArH), 1564 (C=N), 1465 (aryl skeleton), 701 (C–S–C); MS-ESI (*m/z*): 373.4 ($M^+ + 1$); ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.93 (d, *J* = 2.3 Hz, 1H, ArH), 8.44 (dd, J_1 = 2.6 Hz, J_2 = 8.3 Hz, 2H, ArH), 7.68 (dd, J_1 = 1.9 Hz, J_2 = 7.9 Hz, 1H, ArH), 7.12 (dd, J_1 = 2.2 Hz, J_2 = 8.9 Hz, 1H, ArH), 6.67 (d, *J* = 8.5 Hz, 2H, ArH), 6.17 (s, 2H, NH_2), 2.35 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 155.79, 150.55, 145.43, 145.12, 144.52, 142.01, 129.75, 129.10, 128.19, 121.11, 113.45, 113.20, 21.2; Elemental anal. Calcd for $C_{15}H_{12}N_6O_4S$: C 48.38, H 3.25, N 22.57. Found: C 48.17, H 3.31, N 22.76%.

3-(2,4-Dinitrophenylthio)-5-(2-ethoxyphenyl)-4H-1,2,4-triazol-4-amine (**2e**): M.p. 168–170 °C; yield: 90.8%; IR (cm^{-1}): 3099 (ArH), 1595 (C=N), 1462 (aryl skeleton), 917 (C–S–C); MS-ESI (*m/z*): 403.2 ($M^+ + 1$); ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.97 (d, *J* = 2.3 Hz, 1H, ArH), 8.47–8.43 (m, 1H, ArH), 7.61–7.51 (m, 2H, ArH), 7.23–7.01 (m, 3H, ArH), 5.85 (s, 2H, NH_2), 4.12 (q, *J* = 6.8 Hz, 2H, CH_2), 1.25 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 156.38, 156.07, 145.90, 145.30, 144.55, 142.13, 132.58, 131.64, 129.34, 128.53, 121.68, 120.69, 115.53, 112.61, 64.08, 14.54; Elemental anal. Calcd for $C_{16}H_{14}N_6O_5S$: C 47.76, H 3.51, N 20.89. Found: C 47.98, H 3.45, N 20.62%.

3-(2,4-Dinitrophenylthio)-5-(4-methoxyphenyl)-4H-1,2,4-triazol-4-amine (**2f**): M.p. 248–250 °C; yield: 91.2%; IR (cm^{-1}): 3096 (ArH), 1598 (C=N), 1461 (aryl skeleton), 684 (C–S–C); MS-ESI (*m/z*):

389.6 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.94 (d, J = 2.4 Hz, 1H, ArH), 8.44–8.40 (m, 1H, ArH), 7.86 (dd, J_1 = 2.3 Hz, J_2 = 8.5 Hz, 2H, ArH), 7.12 (d, J = 8.9 Hz, 1H, ArH), 6.66 (dd, J_1 = 3.6 Hz, J = 7.8 Hz, 2H, ArH), 6.15 (s, 2H, NH_2), 3.73 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 160.54, 155.78, 150.63, 145.41, 145.10, 144.50, 142.05, 129.74, 129.09, 128.22, 121.15, 113.12, 55.8; Elemental anal. Calcd for $C_{15}H_{12}N_6O_5S$: C 46.39, H 3.11, N 21.64. Found: C 46.15, H 3.15, N 21.84%.

3-(2,4-Dinitrophenylthio)-5-(4-ethoxyphenyl)-4H-1,2,4-triazol-4-amine (**2g**): M.p. 121–123 °C; yield: 88.9%; IR (cm^{-1}): 3093 (ArH), 1588 (C=N), 1477 (aryl skeleton), 699 (C–S–C); MS-ESI (*m/z*): 403.4 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.94 (d, J = 2.3 Hz, 1H, ArH), 8.43–8.37 (m, 1H, ArH), 8.08 (dd, J_1 = 2.0 Hz, J_2 = 7.9 Hz, 2H, ArH), 7.91 (d, J = 8.6 Hz, 1H, ArH), 7.10 (dd, J_1 = 3.2 Hz, J = 8.9 Hz, 2H, ArH), 6.25 (s, 2H, NH_2), 4.10 (q, J = 7.6 Hz, 2H, CH_2), 1.34 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 160.02, 155.08, 146.28, 145.20, 144.62, 141.64, 129.86, 128.45, 121.12, 118.76, 114.84, 114.44, 63.31, 14.43; Elemental anal. Calcd for $C_{16}H_{14}N_6O_5S$: C 47.76, H 3.51, N 20.89. Found: C 47.98, H 3.44, N 20.65%.

*3-(2,4-Dinitrophenylthio)-5-(phenoxymethyl)-4H-1,2,4-triazol-4-*amine (**2h**): M.p. 190–192 °C; yield: 92.6%; IR (cm^{-1}): 3096 (ArH), 1594 (C=N), 1481 (aryl skeleton), 702 (C–S–C); MS-ESI (*m/z*): 389.3 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.96 (d, J = 2.5 Hz, 1H, ArH), 8.47–8.43 (m, 1H, ArH), 7.37–7.32 (m, 2H, ArH), 7.12–7.08 (m, 3H, ArH), 7.03–6.99 (m, 1H, ArH), 6.24 (s, 2H, NH_2), 5.31 (s, 2H, CH_2); ^{13}C NMR (DMSO-d_6) δ (ppm) = 158.01, 154.23, 145.41, 141.48, 135.42, 129.85, 129.72, 128.47, 128.20, 121.57, 121.17, 115.09, 59.38; Elemental anal. Calcd for $C_{15}H_{12}N_6O_5S$: C 46.39, H 3.11, N 21.64. Found: C 46.24, H 3.17, N 21.71%.

2-*(4-Amino-5-(2,4-dinitrophenylthio)-4H-1,2,4-triazol-3-yl) phenol* (**2i**): M.p. 257–259 °C; yield: 89.7%; IR (cm^{-1}): 3426 (OH), 3095 (ArH), 1585 (C=N), 1465 (aryl skeleton), 681 (C–S–C); MS-ESI (*m/z*): 375.4 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 10.53 (s, 1H, OH), 8.79 (d, J = 2.3 Hz, 1H, ArH), 8.48–8.45 (m, 1H, ArH), 8.10 (d, J = 2.5 Hz, 1H, ArH), 7.67 (d, J = 8.9 Hz, 1H, ArH), 7.58 (d, J = 7.6 Hz, 1H, ArH), 7.37–7.34 (m, 1H, ArH), 6.96–6.94 (m, 1H, ArH), 6.18 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6) δ (ppm) = 156.51, 155.70, 147.20, 146.09, 133.29, 131.45, 130.99, 130.23, 128.84, 123.05, 121.51, 119.82, 116.77, 112.03; Elemental anal. Calcd for $C_{14}H_{10}N_6O_5S$: C 44.92, H 2.69, N 22.45. Found: C 45.08, H 2.73, N 22.26.

4-(4-Amino-5-(2,4-dinitrophenylthio)-4H-1,2,4-triazol-3-yl) phenol (2j): M.p. 258–260 °C; yield: 92.4%; IR (cm-1): 3426 (OH), 3096 (ArH), 1592 (C=N), 1471 (aryl skeleton), 692 (C–S–C); MS-ESI (m/z): 375.2 (M+ + 1); 1H NMR (300 MHz, DMSO-d6, 25 °C, TMS) δ (ppm) = 10.01 (s, 1H, OH), 8.95 (d, J = 2.3 Hz, 1H, ArH), 8.41 (dd, J1 = 1.8 Hz, J2 = 8.2 Hz, 1H, ArH), 8.01 (dd, J1 = 3.5 Hz, J2 = 8.5 Hz, 1H, ArH), 7.16 (d, J = 8.9 Hz, 2H, ArH), 6.93 (dd, J1 = 2.4 Hz, J2 = 8.4 Hz, 2H, ArH), 6.22 (s, 2H, NH2); 13C NMR (DMSO-d6) δ (ppm) = 159.71, 155.83, 146.56, 145.58, 144.94, 142.37, 131.06, 130.20, 128.82, 120.41, 117.71, 115.76; Elemental anal. Calcd for $C_{14}H_{10}N_6O_5S$: C 44.92, H 2.69, N 22.45. Found: C 44.75, H 2.74, N 22.64%.

3-(4-Amino-5-(2,4-dinitrophenylthio)-4H-1,*2,4-triazol-3-yl) propan-1-ol* (**2k**): M.p. 147–149 °C; yield: 93.6%; IR (cm^{-1}): 3428 (OH), 3094 (ArH), 2950 (CH_2), 1592 (C=N), 1463 (aryl skeleton), 691 (C–S–C); MS-ESI (*m/z*): 341.2 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.90 (d, J = 2.4 Hz, 1H, ArH), 8.39–8.35 (m, 1H, ArH), 6.99 (d, J = 8.9 Hz, 1H, ArH), 5.96 (s, 2H, NH_2), 4.56 (s, 1H, OH), 3.47 (t, J = 7.9 Hz, 2H, CH_2), 2.82 (t, J = 8.9 Hz, 2H, CH_2), 1.91–1.82 (m, 2H, CH_2); ^{13}C NMR (DMSO-d_6) δ (ppm) = 158.65, 145.24, 144.90, 144.51, 142.21, 129.69, 128.45, 121.48, 60.22, 29.58, 21.31; Elemental anal. Calcd for $C_{11}H_{12}N_6O_5S$: C 38.82, H 3.55, N 24.69. Found: C 38.98, H 3.58, N 24.58%.

(E)-3-(2,4-Dinitrophenylthio)-5-(4-ethoxyphenyl)-N-(4-fluoro-benzylidene)-4H-1,2,4-triazol-4-amine (**3a**): M.p. 131–133 °C; yield: 91.8%; IR (cm^{-1}): 3100 (ArH), 1600 (C=N), 1470 (aryl skeleton), 692 (C–S–C); MS-ESI (*m/z*): 509.1 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.98 (s, 1H, ArH), 8.64 (s, 1H, N=CH), 8.44 (d, J = 8.7 Hz, 1H, ArH), 7.95 (dd, J_1 = 3.5 Hz, J_2 = 7.8 Hz, 2H, ArH), 7.42 (dd, J_1 = 2.5 Hz, J_2 = 8.7 Hz, 2H, ArH), 7.36 (dd, J_1 = 1.8 Hz, J_2 = 8.9 Hz, 2H, ArH), 7.33 (d, J = 8.4 Hz, 1H, ArH), 7.03 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 2H, ArH), 4.05 (q, J = 8.6 Hz, 2H, OCH_2), 1.33 (t, J = 8.6 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 165.26, 160.26, 152.14, 148.45, 147.36, 145.47, 143.32, 137.11, 135.18, 133.36, 132.48, 131.14, 129.74,127.90, 120.90, 114.81,113.22, 63.35, 14.39; Elemental anal. Calcd for $C_{23}H_{17}FN_6O_5S$: C 54.33, H 3.37, N 16.53. Found: C 54.15, H 3.33, N 16.70%.

*(E)-N-(4-(Dimethylamino)benzylidene)-3-(2,4-dinitrophenylthio)-5-(4-methoxyphenyl)-4H-1,2,4-triazol-4-amine (**3b**)*: M.p. 223–225 °C; yield: 89.7%; IR (cm^{-1}): 3097 (ArH), 1605 (C=N), 1478 (aryl skeleton), 708 (C–S–C); MS-ESI (*m/z*): 520.2 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.85 (s, 1H, ArH), 8.66 (s, 1H, N=CH), 8.44 (d, J = 8.7 Hz, 2H, ArH), 7.94 (dd, J_1 = 1.6, J_2 = 7.9 Hz, 2H, ArH), 7.55 (dd, J_1 = 3.5 Hz, J_2 = 8.0 Hz, 2H, ArH), 7.09 (dd, J_1 = 2.7, J_2 = 8.4 Hz, 2H, ArH), 6.74 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 2H, ArH), 3.80 (s, 3H, OCH_3), 3.01 (s, 6H, NCH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 170.65, 160.91, 153.88, 152.28, 145.46, 144.29, 141.27, 131.23, 129.90, 129.63, 128.80, 124.30, 121.64, 118.64, 117.74, 114.48, 111.75, 55.51, 40.46; Elemental anal. Calcd for $C_{24}H_{21}N_7O_5S$: C 55.48, H 4.07, N 18.87. Found: C 55.30, H 4.12, N 18.99%.

(E)-3-(2,4-Dinitrophenylthio)-5-(2-ethoxyphenyl)-N-(4-methyl-benzylidene)-4H-1,2,4-triazol-4-amine (**3c**): M.p. 87–89 °C; yield: 92.5%; IR (cm^{-1}): 3093 (ArH), 1608 (C=N), 1481 (aryl skeleton), 702 (C–S–C); MS-ESI (*m/z*): 505.5 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.90 (s, 1H, ArH), 8.56 (s, 1H, N=CH), 8.46 (dd, J_1 = 2.6 Hz, J_2 = 8.8 Hz, 1H, ArH), 7.68 (dd, J_1 = 1.8 Hz, J_2 = 7.3 Hz, 1H, ArH), 7.57-7.52 (m, 1H, ArH), 7.44 (dd, J_1 = 3.8 Hz, J_2 = 7.8 Hz, 2H, ArH), 7.25–7.10 (m, 5H, ArH), 3.86 (q, J = 6.8 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.11 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 167.30, 155.69, 151.25, 145.49, 144.44, 144.09, 141.93, 141.20, 132.98, 132.00, 130.03, 129.52, 128.82, 128.65, 121.73, 120.86, 115.03, 112.53, 63.77, 21.39, 14.47; Elemental anal. Calcd for $C_{24}H_{20}N_6O_5S$: C 57.14, H 4.00, N 16.66. Found: C 57.32, H 4.03, N 16.52%.

(E)-2-(5-(2,4-Dinitrophenylthio)-4-(2-fluorobenzylideneamino)-4H-1,2,4-triazol-3-yl)phenol (**3d**): M.p. 202–204 °C; yield: 89.6%; IR (cm^{-1}): 3431 (OH), 3101 (ArH), 1598 (C=N), 1478 (aryl skeleton), 698 (C–S–C); MS-ESI (*m/z*): 479.4 (M - 1); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 10.03 (s, 1H, OH), 8.90 (d, J = 8.2 Hz, 1H, ArH), 8.60 (s, 1H, N=CH), 8.39 (d, J = 3.7 Hz, 1H, ArH), 7.94 (d, J = 8.4 Hz, 1H, ArH), 7.41 (d, J = 4.7 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH), 7.03–6.90 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6) δ (ppm) = 163.47, 161.80, 160.11, 157.01, 156.33, 148.71, 134.99, 132.58, 131.91, 131.34, 127.37, 125.44, 121.47, 120.01, 119.56, 119.07, 116.71, 116.44, 116.13, 112.94, 112.86; Elemental anal. Calcd for $C_{21}H_{13}FN_6O_5S$: C 52.50, H 2.73, N 17.49. Found: C 52.75, H 2.68, N 17.61%.

(E)-3-(4-Chlorophenyl)-5-(2,4-dinitrophenylthio)-N-(4-methoxy-benzylidene)-4H-1,2,4-triazol-4-amine (**3e**): M.p. 102–104 °C; yield: 91.8%; IR (cm^{-1}): 3096 (ArH), 1622 (C=N), 1483 (aryl skeleton), 708 (C–S–C); MS-ESI (*m/z*): 511.4 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 8.95 (s, 1H, ArH), 8.62 (s, 1H, N=CH), 8.43 (d, J = 8.7 Hz, 1H, ArH), 7.99 (dd, J_1 = 2.4 Hz, J_2 = 8.5 Hz, 2H, ArH), 7.76 (dd, J_1 = 4.2 Hz, J_2 = 8.6 Hz, 2H, ArH), 7.66 (dd, J_1 = 3.6 Hz, J_2 = 8.6 Hz, 2H, ArH),7.59 (d, J = 8.6 Hz, 1H, ArH), 7.06 (dd, J_1 = 1.8 Hz, J_2 = 8.6 Hz, 2H, ArH), 3.85 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 170.84, 163.25, 151.76, 148.65, 145.56, 144.33, 140.63, 135.63, 131.65, 131.05, 129.22, 129.03, 128.20, 124.83, 123.45, 121.62, 114.89; Elemental anal. Calcd for $C_{22}H_{15}ClN_6O_5S$: C 51.72, H 2.96, N 16.45. Found: C 51.56, H 3.00, N 16.54%.

(E)-N-(4-Bromobenzylidene)-3-(2,4-dinitrophenylthio)-5-(4-methoxy-phenyl)-4H-1,2,4-triazol-4-amine (**3f**): M.p. 242–244 °C; yield: 93.8%; IR (cm^{-1}): 3092 (ArH), 1614 (C=N), 1465 (aryl skeleton), 693 (C–S–C); MS-ESI (*m/z*): 555.4 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 9.02 (s, 1H, ArH), 8.63 (s, 1H, N=CH), 8.44 (d, J = 8.9 Hz, 2H, ArH), 7.83 (dd, J_1 = 2.8 Hz, J_2 = 7.9 Hz, 1H, ArH), 7.72 (dd, J_1 = 3.6 Hz, J_2 = 8.4 Hz, 3H, ArH), 7.06 (dd, J_1 = 4.2 Hz, J_2 = 8.7 Hz, 4H, ArH), 3.81 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6) δ (ppm) = 161.13, 152.53, 146.83, 144.40, 140.89, 138.79, 132.65, 131.39, 131.07, 130.63, 129.94, 129.88, 128.80, 127.79, 124.40, 120.09, 114.15, 55.53; Elemental anal. Calcd for $C_{22}H_{15}BrN_6O_5S$: C 47.58, H 2.72, N 15.13. Found: C 47.70, H 2.75, N 15.02%.

(E)-4-(5-(2,4-Dinitrophenylthio)-4-(3-nitrobenzylideneamino)-4H-1,2,4-triazol-3-yl)phenol (**3g**): M.p. 238–240 °C; yield: 91.7%; IR (cm^{-1}): 3426 (OH), 3098 (ArH), 1592 (C=N), 1462 (aryl skeleton), 696 (C–S–C); MS-ESI (*m/z*): 508.5 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 10.20 (s, 1H, OH), 8.95 (s, 1H, ArH), 8.63 (s, 1H, N=CH), 8.48–8.43 (m, 4H, ArH), 8.22 (d, J = 7.1 Hz, 1H, ArH), 8.13 (dd, J_1 = 2.7 Hz, J_2 = 8.9 Hz, 1H, ArH), 7.80 (dd, J_1 = 1.9 Hz, J_2 = 7.7 Hz, 1H, ArH), 7.13 (d, J = 9.2 Hz, 1H, ArH), 6.93 (dd, J_1 = 2.8 Hz, J_2 = 7.6 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6) δ (ppm) = 168.79, 159.81, 153.01, 148.33, 145.55, 144.45, 140.91, 135.01, 132.77, 131.30, 130.23, 129.86, 128.85, 127.88, 123.68, 121.61, 120.34, 116.46, 115.91; Elemental anal. Calcd for $C_{21}H_{13}N_7O_7S$: C 49.71, H 2.58, N 19.32. Found: C 49.62, H 2.61, N 19.43%.

(E)-4-((3-(2,4-Dinitrophenylthio)-5-phenyl-4H-1,2,4-triazol-4-ylimino) methyl)phenol (**3h**): M.p. 136–138 °C; yield: 93.8%; IR (cm^{-1}):

3438 (OH), 3102 (ArH), 1596 (C=N), 1454 (aryl skeleton), 698 (C–S–C); MS-ESI (*m/z*): 463.0 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 10.02 (s, 1H, ArOH), 8.86 (d, J = 2.2 Hz, 1H, ArH), 8.68 (s, 1H, N=CH), 8.44–8.41 (m, 1H, ArH), 7.97 (dd, J_1 = 3.5 Hz, J_2 = 8.4 Hz, 2H, ArH), 7.62–7.54 (m, 5H, ArH), 7.19 (d, J = 8.9 Hz, 1H, ArH), 6.86 (dd, J_1 = 2.2 Hz, J_2 = 8.5 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6) δ (ppm) = 171.23, 163.23, 152.74, 145.87, 144.78, 141.99, 141.05, 132.06, 130.93, 130.32, 129.31, 128.61, 128.05, 126.46, 122.40, 121.86, 116.69; Elemental anal. Calcd for $C_{21}H_{14}N_6O_5S$: C 54.54, H 3.05, N 18.17. Found: C 54.42, H 3.08, N 18.25%.

(E)-2-((3-(2,4-Dinitrophenylthio)-5-phenyl-4H-1,2,4-triazol-4-ylimino)methyl)phenol (**3i**):M.p. 98–100 °C; yield: 89.3%; IR (cm^{-1}): 3427 (OH), 3099 (ArH), 1596 (C=N), 1458 (aryl skeleton), 698 (C–S–C); MS-ESI (*m/z*): 463.4 ($M^+ + 1$); ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 10.08 (s, 1H, ArOH), 8.97 (s, 1H, ArH), 8.67 (s, 1H, N=CH), 8.45 (d, J = 2.7 Hz, 1H, ArH), 8.17–8.14 (m, 1H, ArH), 7.98 (d, J = 8.5 Hz, 2H, ArH), 7.79 (d, J = 8.7 Hz, 3H, ArH), 7.31 (d, J = 8.7 Hz, 2H, ArH), 6.88 (d, J = 8.2 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6) δ (ppm) = 166.69, 159.36, 155.74, 152.93, 149.15, 145.61, 137.85, 130.73, 129.29, 128.99, 128.45, 127.56, 126.94, 121.90, 121.72, 121.43, 120.17, 117.86, 117.10; Elemental anal. Calcd for $C_{21}H_{14}N_6O_5S$: C 54.54, H 3.05, N 18.17. Found: C 54. 68, H 3.01, N 18.02%.

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