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Synthesis of some novel Schiff bases containing 1,2,4-triazole ring

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ABSTRACT

4-Allyl-5-piridine-4-yl-4H-1,2,4-triazole-3-thiol was prepared under facile condition via the formation of 2-isonicotinoyl-*N*-allylhydrazinecarbothioamide. In addition, ethyl[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetate was synthesized via the reaction of 4-allyl-5-piridine-4-yl-4H-1,2,4-triazole-3-thiol with ethyl chloroacetate. 2-[(4-Allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide obtained by using ethyl[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetate as a precursor by two steps, was converted to Schiff base derivatives, 6a-j. All synthesized compounds were characterized by elemental analyses, IR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy. The *cis*/*trans* conformers of *E* isomer were present in DMSO solution of compounds 6a-j.

1. Introduction

The chemistry of 1,2,4-triazoles and their fused heterocyclic derivatives have received considerable attention owing to their synthetic and effective biological importance. For example, a large number of 1,2,4-triazoles have been incorporated into a wide variety of therapeutically interesting drug candidates including anti-inflammatory [1,2], antiviral [3], analgesic [4], antimicrobial [5-7], anticonvulsant [8] and antidepressant activities [9]. The hybrid molecules composed of the combination of a heterocyclic ring and a Schiff base may exert potentially biological activities. Some Schiff bases bearing triazoles have been reported to be used as drugs with considerable biological activities [10-16].

In view of this report and also due to the connections of our studies on the synthesis of substituted triazoles [17,18], we turned our attention to synthesis of some new 1,2,4-triazole derivatives and their related Schiff bases obtained from the reaction of 2-(4-allyl-5-(pyridine-4-yl)-4H-1,2,4-triazol-3-ylthio)acetohydrazide, **5**, with various aldehydes (Scheme 1).

2. Experimental

2.1. Instrumentation

Purity of the compounds were checked by thin layer chromatography (TLC) using C_2H_5OH:*n*-hexane (1:1) as an eluent. IR spectra were prepared on the Mattson Galaxy series FT-IR 5000 spectrophotometer using KBr discs. NMR spectra were recorded on Bruker spectrophotometer (300 MHz) in DMSO-d_6 or $CDCl_3$ using TMS as an internal standard. Microanalyses were performed by the Elemental Analyzer (Vario EL III) at the Arak University.

2.2. Synthesis of 2-isonicotinoyl-N-allylhydrazinecarbothio amide, 2

A mixture of isonicotinic acid hydrazide, **1,** (0.01 mol, 1.3700 g) and allyl isothiocyanate (0.01 mol, 0.9900 g) was refluxed in ethanol (30 mL) for 2 h. After cooling, the formed product was collected by filtration and recrystallized from ethanol to give thiosemicarbazide, **2**. Yield: 95% (2.2420 g), M.p.: 227-230 °C. IR (KBr, ν, cm^{-1}): 3070 (aromatic CH stretch.), 3200, 3259 (NH), 2928 (C-H), 1678 (C=O), 1554, 1440 (C=C ring stretch.), 1352 (C=S). ^{1}H NMR (DMSO-d_6, δ, ppm): 10.68 (s, 1H, N*H*), 9.49 (s, 1H, N*H*), 8.75-8.77 (d, 2H, *J*=4.6 Hz, Ar*H*), 8.39 (s, 1H, N*H*), 7.81-7.89 (d, 2H, *J*=4.7 Hz, Ar*H*), 5.76-5.88 (m, 1H, C=C*H*-C), 5.03-5.16 (m, 2H, CH_2=C-C), 4.11 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6, δ, ppm): 46.4, 115.7, 122.1, 135.4, 140.0, 150.6, 164.9, 182.2.

2.3. Synthesis of 4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-thiol, 3

A solution of thiosemicarbazide, **2,** (0.005 mol, 1.1800 g) in 2N NaOH (10 mL) was refluxed for 3 h. The resulting solution was cooled to room temperature and acidified (pH=3) with 2N HCl. The precipitate was filtered and washed with water. The compound obtained was dried and crystallized from DMF:C_2H_5OH (1:2) to give compound **3**. Yield (0.9920 g) 91%. M.p.: 219-221 °C. IR (KBr, ν, cm^{-1}): 3070 (aromatic CH stretch.), 2733 (SH), 1568, 1438 (C=C ring stretch). ^{1}H NMR (DMSO-d_6, δ, ppm): 14.27 (s, 1H, S*H*), 8.76 (d, 2H, *J*= 4.8 Hz, Ar*H*), 7.71 (d, 2H, *J*= 4.8 Hz, Ar*H*), 5.80-5.92 (m, 1H, C=C*H*-C), 5.12-5.16 (m, 1H, CH_2=C-C), 4.81-4.89 (m, 1H, CH_2=C-C), 4.79 (br, 2H, CH_2). Anal. Calcd. for $C_{10}H_{10}N_4S$: C, 55.02; H, 4.69; N, 25.67; S, 14.69. Found: C, 54.82; H, 4.51; N, 25.44; S, 14.44 %.

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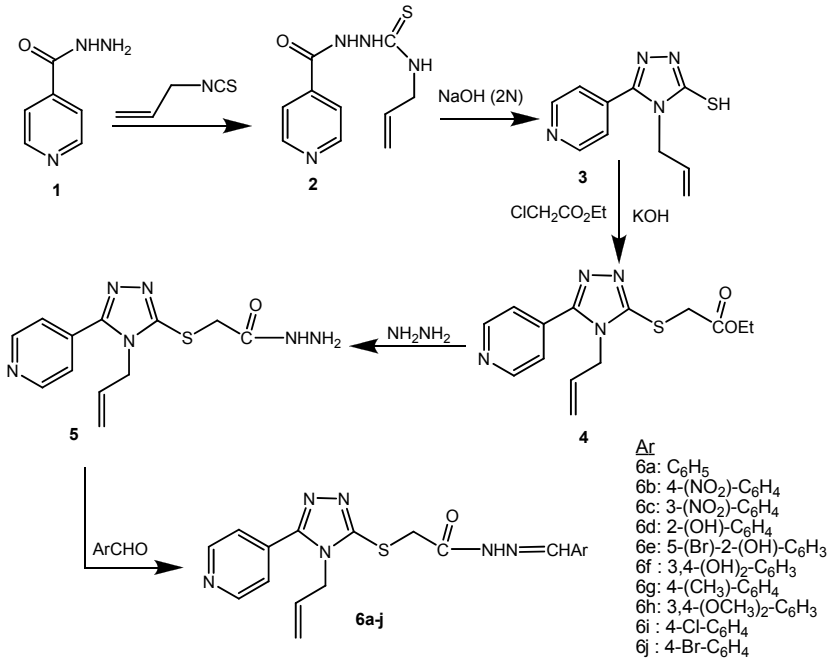


Scheme 1. Synthetic pathway for preparation of Schiff bases **6a-j**.

2.4. Synthesis ethyl[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetate, 4

To a solution of compound **3** (0.003 mol, 0.6500 g) in absolute ethanol (20 mL), ethyl chloroacetate (0.006 mol, 0.7320 g) was added. The mixture was refluxed under stirring for 30 min in the presence of KOH (0.003 mol, 0.1680 g). Then, the solvent was removed under reduced pressure to give the solid product. The crude product was recrystallized from H_2O:C_2H_5OH (1:1) to give compound **4**. Yield (0.6617 g) 73%. M.p.: 143-145 °C. IR (KBr, ν, cm^{-1}): 3069 (aromatic CH stretch.), 2968 (C-H), 1732 (C=O), 1602 (C=N), 1199 (C-O). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.78 (d, 2H, *J*=4.8 Hz, Ar*H*), 7.68 (d, 2H, *J*=4.8 Hz, Ar*H*), 5.88-6.12 (m, 1H, C=C*H*-C), (m, 1H, CH_2), 5.39-5.43 (m, 1H, CH_2=C-C), 5.01-5.07 (m, 1H, CH_2=C-C), 4.72 (br, 2H, C=C-CH_2), 4.22 (q, 2H, *J*=7.1 Hz, CH_2), 4.14 (s, 2H, SCH_2), 1.30 (t, 3H, *J*=7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.0, 35.2, 47.0, 62.0, 18.4, 122.0, 131.0, 134.4, 150.3, 152.0, 153.5, 168.0. Anal. Calcd. for $C_{14}H_{16}N_4O_2S$: C, 55.25; H, 5.30; N, 18.41; S, 10.53. Found: C, 55.02; H, 5.22; N, 18.20; S, 10.34 %.

2.5. Synthesis of 2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 5

80% hydrazine hydrate (0.003 mol, 0.15 g) was added to **4** (0.002 mol, 0.6080 g) in ethanol (10 mL) in drops and refluxed for 2 h. The solvent was then removed under reduced pressure and a solid was obtained. Next, the precipitate was filtered and recrystallized from CCl_4 to give the pure acetohydrazide **5**. Yield (0.4930 g) 85%. M.p.: 143-145 °C. IR (KBr, ν, cm^{-1}): 3286 3196 (NH_2), 3234, (NH), 3024 (aromatic CH stretch.), 1672 (C=O), 1604 (C=N), 1547, 1456 (C=C ring stretch.). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.78-8.80 (d, d, 2H, *J*=4.5 Hz, 1.4 Hz, Ar*H*), 7.58-7.60 (d, d, 2H, *J*=4.5 Hz, 1.5 Hz, Ar*H*), 5.92-6.01 (m, 1H, C=C*H*-C), 5.40-5.44 (m, 1H, CH_2=C-C), 5.04-5.10 (m, 1H, CH_2=C-C), 4.62 (br, 2H, CH_2), 3.96 (s, 2H, SCH_2). Anal. Calcd. for $C_{12}H_{14}N_6O_2S$: C, 49.64; H, 4.86; N, 28.95; S, 11.04. Found: C, 49.49; H, 4.75; N, 28.74; S, 10.81 %.

2.6. General procedure for the synthesis of compounds 6a-j

A solution of acetohydrazide, **5,** (0.0006 mol, 0.1740 g) in ethanol (7 mL), the appropriate aldehyde (0.0006 mol) and 4-5 drops of glacial acetic acid (as a catalyst) was refluxed for a predetermined time frame (Table 1). The resultant was allowed to cool and poured into cold water (15-20 mL). The solid was collected by filtration and recrystallized from ethanol to give the pure acetohydrazide **6a-j**.

***N'*-benzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6a**: IR (KBr, ν, cm^{-1}): 3203 (NH), 3051 (aromatic CH stretch.), 1689 (C=O), 1608 (C=N), 1577, 1456 (C=C ring stretch.), 761 (C-S-C). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.82 and 11.71 (s, 1H, N*H*, *trans/cis* conformers), 8.72-8.76 (m, 2H, Ar*H*), 8.19 and 8.02 (s, 1H, N=C*H*, *trans/cis* conformers), 7.61-7.70 (m, 4H, Ar*H*), 7.40-7.42 (m, 3H, Ar*H*), 5.97-6.03 (m, 1H, C=C*H*-C), 5.23-5.27 (m, 1H, CH_2=C-C), 4.83-4.89 (m, 1H, CH_2=C-C), 4.77 (d, 2H, *J*=1.8 Hz, CH_2), 4.53 and 4.15 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{18}N_6OS$: C, 60.30; H, 4.79; N, 22.21; S, 8.47. Found: C, 60.11; H, 4.71; N, 22.09; S, 8.38 %.

***N'*-4-Nitrobenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6b:** IR (KBr, ν, cm^{-1}): 3080 (aromatic CH stretch.), 1679 (C=O), 1601 (C=N), 1450, 1516 (C=C ring stretch.), 1342, 1500 (NO_2). ^{1}H NMR (DMSO-d_6, δ, ppm): 12.01 (br, 1H, N*H*), 8.71-8.76 (m, 2H, Ar*H*), 8.25-8.31 (m, 2H, Ar*H*), 8.10 (s, 1H, N=C*H*), 7.92-7.99 (m, 2H, Ar*H*), 7.60-7.67 (m, 2H, Ar*H*), 5.96-6.08 (m, 1H, C=C*H*-C), 5.24-5.28 (m, 1H, CH_2=C-C), 4.79-4.80 (m, 1H, CH_2=C-C), 4.79 (br, 2H, CH_2), 4.55 and 4.17 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{17}N_7O_3S$: C, 53.89; H, 4.05; N, 23.15; S, 7.57. Found: C, 53.61; H, 3.97; N, 22.97; S, 7.41 %.

***N'*-3-Nitrobenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6c:** IR (KBr, ν, cm^{-1}): 3212 (NH), 3074 (aromatic CH stretch.), 1689 (C=O), 1608 (C=N), 1352-1529 (N=O). ^{1}H NMR (DMSO-d_6, δ, ppm): 12.06 and 11.93 (s, 1H, N*H*, *trans/cis* conformers), 8.72-8.76 (m, 2H, Ar*H*), 8.53 and 8.47 (s, 1H, N=C*H*, *trans/cis* conformers), 8.12-8.33(m, 3H, Ar*H*), 7.60-7.75 (m, 3H, Ar*H*), 6.00 (br, 1H, C=C*H*-C), 5.25-5.28 (m, 1H, CH_2=C-C), 4.83-4.89 (m, 1H, CH_2=C-C), 4.79 (br, 2H, CH_2), 4.55 and 4.17 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{17}N_7O_3S$: C, 53.89; H, 4.05; N, 23.15; S, 7.57. Found: C, 53.57; H, 3.93; N, 23.01; S, 7.38 %.

***N'*-2-Hydroxybenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6d:** IR (KBr, ν, cm^{-1}): 3435 (O-H), 3213 (NH), 3047 (aromatic CH stretch.), 2982 (C-H), 1685 (C=O), 1608 (C=N); ^{1}H NMR (DMSO-d_6, δ, ppm): 12.98 and 11.62 (s, 1H, N*H*, *trans/cis* conformers), 10.95 and 10.06 (s, 1H, O*H*, *trans/cis* conformers), 8.73-8.76 (d, d, 2H, *J*=4.3 Hz, 1.5 Hz, Ar*H*), 8.32 and 8.42 (s, 1H, N=C*H*, *trans/cis* conformers), 7.21-7.32 (m, 1H, Ar*H*), 7.54-7.67 (m, 3H, Ar*H*), 6.85-6.92 (m, 2H, Ar*H*), 5.98-6.09 (m, 1H, C=C*H*-C), 5.24-5.30 (m, 1H, CH_2=C-C), 4.84-4.90 (d, d, 1H, *J*=17.3 Hz, 3.4 Hz, CH_2=C-C), 4.77 (br, 2H, CH_2), 4.51 and 4.14 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{18}N_6O_2S$: C, 57.85; H, 4.60; N, 21.31; S, 8.13. Found: C, 57.54; H, 4.51; N, 21.10; S, 7.95 %.

***N'*-5-Bromo-2-hydroxybenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6e:** IR (KBr, ν, cm^{-1}): 3431 (O-H), 3175 (N-H), 2978 (C-H), 1674 (C=O), 1606 (C=N). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.54 and 11.47 (s, 1H, N*H*, *trans/cis* conformers), 9.29 (s, 1H, O*H*), 9.43 (s, 1H, O*H*), 8.74 (br, 2H, Ar*H*), 7.88 and 7.83 (s, 1H, N=C*H*, *trans/cis* conformers), 7.62-7.67 (m, 2H, Ar*H*), 7.15 (br, 1H, Ar*H*), 6.87-6.92 (m, 1H, Ar*H*), 6.76 (br, 1H, Ar*H*), 5.96-6.06 (m, 1H, C=C*H*-C), 5.23-5.27 (m, 1H, CH_2=C-C), 4.83-4.89 (m, 1H, CH_2=C-C), 4.77 (br, 2H, CH_2), 4.50 and 4.09 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{18}N_6BrO_2S$: C, 48.21; H, 3.62; N, 17.75; S, 6.77. Found: C, 47.96; H, 3.55; N, 17.41; S, 6.59 %.

***N'*-3,4-Dihydroxybenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6f:** IR (KBr, ν, cm^{-1}): 3429 (OH), 3178 (NH), 3033 (aromatic CH stretch.), 1674 (C=O), 1605 (C=N). 729 (C-S-C), ^{1}H NMR (DMSO-d_6, δ, ppm): 12.06 and 11.68 (s, 1H, N*H*, *trans/cis* conformers), 8.73-8.76 (m, 2H, Ar*H*), 11.03 and 10.40 (s, 1H, O*H*, *trans/cis* conformers), 8.38 and 8.24 (s, 1H, N=C*H*, *trans/cis* conformers), 7.77 (br, 1H, Ar*H*), 7.60-7.66 (m, 2H, Ar*H*), 7.37-7.43 (m, 1H, Ar*H*), 6.84-6.90 (m, 1H, Ar*H*), 5.98-6.05 (m, 1H, C=C*H*-C), 5.24-5.28 (m, 1H, CH_2=C-C), 4.85-4.90 (m, 1H, CH_2=C-C), 4.78 (br, 2H, CH_2), 4.50 and 4.13 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{18}N_6O_3S$: C, 55.60; H, 4.42; N, 20.48; S, 7.81. Found: C, 55.31; H, 4.34; N, 20.32; S, 7.56 %.

***N'*-4-Methylbenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6g:** IR (KBr, ν, cm^{-1}): 3205 (NH), 3047 (aromatic CH stretch.), 2931 (C-H), 1697 (C=O), 1606 (C=N), 1375, 1450 (CH_3). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.73 and 11.63 (s, 1H, N*H*, *trans/cis*, conformers), 8.75 (d, 2H, *J*=4.8 Hz, Ar*H*), 7.97 and 8.15 (s, 1H, N=C*H*, *trans/cis* conformers), 7.54-7.67 (m, 4H, Ar*H*), 7.22-7.27 (m, 2H, Ar*H*), 5.97-6.07 (m, 1H, C=C*H*-C), 5.23-5.27 (m, 1H, CH_2=C-C), 4.77-4.88 (m, 1H, CH_2=C-C), 4.55 (br, 2H, CH_2), 4.12 and 4.50 (s, 2H, SCH_2, *trans/cis* conformers), 2.32 (s, 3H, CH_3). Anal. Calcd. for $C_{20}H_{20}N_6OS$: C, 61.20; H, 5.14; N, 21.41; S, 8.17. Found: C, 61.00; H, 5.30; N, 21.11; S, 8.32 %.

***N'*-3,4-Dimethoxylbenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6h**

IR (KBr, ν, cm^{-1}): 3205 (NH), 3050 (aromatic CH stretch.), 2962 (C-H), 1680 (C=O), 1602 (C=N), 1512, 1438 (C=C ring stretch.). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.95 and 11.59 (s, 1H, N*H*, *trans/cis* conformers), 8.72-8.76 (br, 2H, Ar*H*), 8.11 and 7.93 (s, 1H, N=C*H*, *trans/cis* conformers), 7.59 (s, 1H, Ar*H*), 7.19 (t, 1H, *J*=8.5 Hz, Ar*H*), 6.99 (t, 1H, *J*=8.5 Hz, Ar*H*), 5.97-6.06 (m, 1H, C=CH-C), 5.24 (d, 1H, *J*=10.5 Hz, CH_2=C-C), 4.82-4.90 (m, 1H, CH_2=C-C), 4.77 (br, 2H, CH_2), 4.48 and 4.11 (s, 2H, SCH_2, *trans/cis* conformers), 3.79 (s, 6H, 2OCH_3). Anal. Calcd. for $C_{21}H_{22}N_6O_3S$: C, 57.52; H, 5.06; N, 19.17; S, 7.31. Found: C, 57.82; H, 5.03; N, 19.00; S, 7.61 %.

***N'*-4-Chlorobenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6i:** IR (KBr, ν, cm^{-1}): 3205 (NH), 3040 (aromatic CH stretch.), 1697 (C=O), 1606 (C=N), 1547, 1440 (C=C ring stretch.), 827 (C-Cl). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.86 and 11.75 (s, 1H, N*H*, *trans/cis* conformers), 8.73-8.76 (br, 2H, Ar*H*), 8.19 and 8.00 (s, 1H, N=C*H*, *trans/cis* conformers), 7.60-7.74 (m, 4H, Ar*H*), 7.47-7.52 (m, 2H, Ar*H*), 5.98-6.07 (m, 1H, C=C*H*-C), 5.24-5.27 (m, 1H, CH_2=C-C), 4.83-4.88 (m, 1H, CH_2=C-C), 4.77 (br, 2H, CH_2), 4.53 and 4.13 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{17}ClN_6OS$: C, 55.27; H, 4.15; N, 20.35; S, 7.77. Found: C, 54.95; H, 4.31; N, 20.00; S, 7.40 %.

***N'*-4-Bromobenzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, 6j:** IR (KBr, ν, cm^{-1}): 3207 (NH), 3033 (aromatic CH stretch.), 1686 (C=O), 1606 (C=N). ^{1}H NMR (DMSO-d_6, δ, ppm): 11.85 and 11.74 (s, 1H, N*H*, *trans/cis* conformers), 8.75 (d, 2H, *J*=5.2 Hz, Ar*H*), 8.17 and 7.98 (s, 1H, N=C*H*, *trans/cis* conformers), 7.60-7.67 (m, 6H, Ar*H*), 6.01-6.07 (m, 1H, C=C*H*-C), 5.24-5.27 (m, 1H, CH_2=C-C), 4.77-4.89 (m, 1H, CH_2=C-C), 4.77 (br, 2H, CH_2), 4.51 and 4.13 (s, 2H, SCH_2, *trans/cis* conformers). Anal. Calcd. for $C_{19}H_{17}BrN_6OS$: C, 49.90; H, 3.75; N, 17.47; S, 7.01. Found: C, 49.70; H, 3.66; N, 17.31; S, 6.82 %.

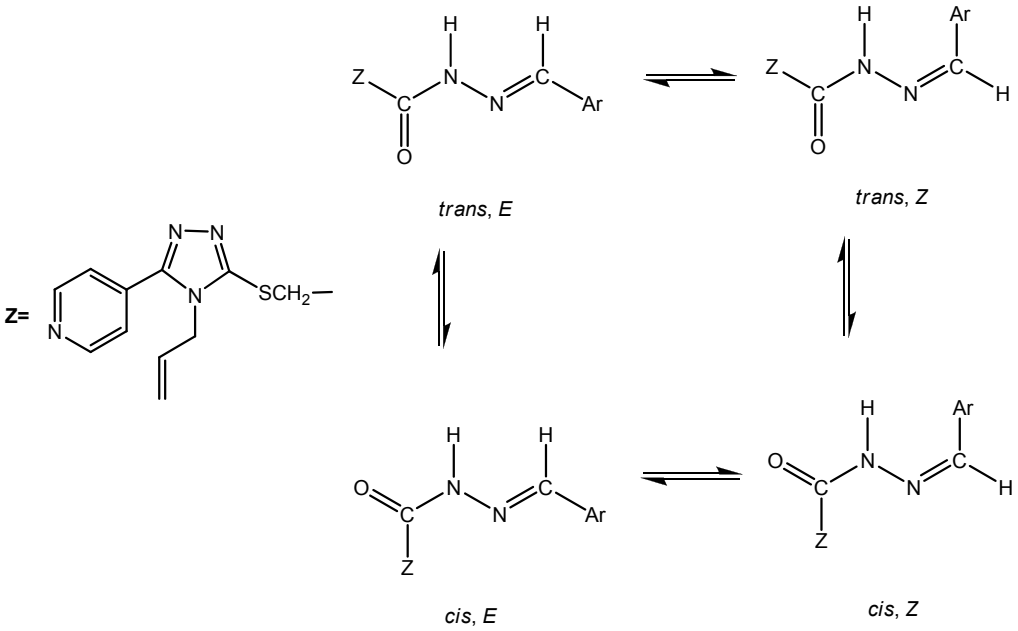
3. Results and Discussion

In continuation of our efforts to develop the synthesis of the new fused heterocyclic and Schiff bases [19-21] we report herein, a simple and efficient method for the synthesis of some novel Schiff bases containing 1,2,4-triazole ring. Our synthetic approaches are depicted in Scheme 1. Initial compound was prepared from available isonicotinic acid hydrazide, **1**. 2-Isonicotinoyl-*N*-allylhydrazinecarbothioamide, **2,** was prepared by reaction of compound **1** with allylisothiocyanate in ethanol. The cyclization of compound **2** in the presence of sodium hydroxide resulted in the formation of 4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-thiol, **3**. The reaction of triazole **3** with ethyl chloroacetate in the presence of potassium hydroxide produced ethyl[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]aceta te **4**, which then converted to 2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, **5,** via the reaction with hydrazine hydrate. The treatment of acetohydrazide **5** with several aldehydes gave *N*'-substitue-benzylidene-2-[(4-allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]acetohydrazide, **6a-j,** (Scheme 1). The results are shown in Table 1. The compounds having aryliden-hydrazid structure may exist as *E*/*Z* geometrical isomers about CH=N double bond and cis/trans amide conformers (Scheme 2) [22-24]. According to the literature [23,24], compounds containing imine bonds are present in higher percentage in dimethyl-d_6 sulfoxide solution in the form of geometrical *E* isomer about C=N double bond. The *Z* isomer can be stabilized in less polar solvent by an intramolecular hydrogen bond. In the present study, the spectral data were obtained in DMSO-d_6 and no signal belonging to the *Z* isomer was observed. On the other hand, the *cis*/*trans* conformers of the *E* isomer were present in DMSO solution of compounds **6a-j**.

Table 1. Synthesized Schiff bases 6a-j.

Compound	Ar*	Time (h)	M.p. (°C)	Yield (%)
6a	C_6H_5	6	102-104	62
6b	4-(NO_2)C_6H_4	8	201-203	55
6c	3-(NO_2)C_6H_4	7	164-165	54
6d	2-(OH)C_6H_4	1	160-161	83
6e	5-(Br),2-(OH)C_6H_3	0.5	213-215	75
6f	3,4-$(OH)_2C_6H_3$	0.5	234-236	73
6g	4-(CH_3)C_6H_4	4	119-122	81
6h	3,4-$(OCH_3)_2C_6H_3$	3	248-251	74
6i	4-(Cl)C_6H_4	3	128-130	77
6j	4-(Br)C_6H_4	2	183-185	68

*Scheme 1.



Scheme 2. *E*/*Z* Geometrical isomers and *cis*/*trans* conformers of **6a-j**.

The structures of the synthesized compounds were determined on the basis of spectral data analysis including IR, ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectrum of compound **2** showed two characteristic absorptions (singlet at δ=9.49 ppm and δ=10.68 ppm) attributed to the NH groups, which were disappeared by the formation of the triazole **3**. In the ^{1}H NMR spectrum of compound **4**, additional signals derived from the ester group were observed at 1.30 (OCH_2CH_3), 4.14 (SCH_2) and 4.22 OCH_2CH_3) ppm. The ^{1}H NMR spectra of **6a-j** displayed additional signals due to the aromatic ring derived from aldehyde moiety at the aromatic region, while the signal belonging to the NH_2 group of hydrazide structure was not appeared. In the ^{1}H NMR spectra of compounds **6a-j** two signals each belonging to the SCH_2, N=CH and NH groups of *cis* and *trans* conformers were observed between 3.98-4.55, 7.97-9.85 and 11.47-12.00 ppm, respectively.

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