# A Simple and Efficient Synthesis of Novel *N,N'*-Bis (1*H*-pyrrol-1-yl)-1-[2-(2-aryl-5-methyl-3-oxo-2,4-dihydro-*3H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides



Prashant R. Latthe, Vinay A. Sunagar and Bharati V. Badami*

Post Graduate Department of Studies in Chemistry,
Karnatak University, Dharwad – 580 003, INDIA.
bbadami@rediffmail.com

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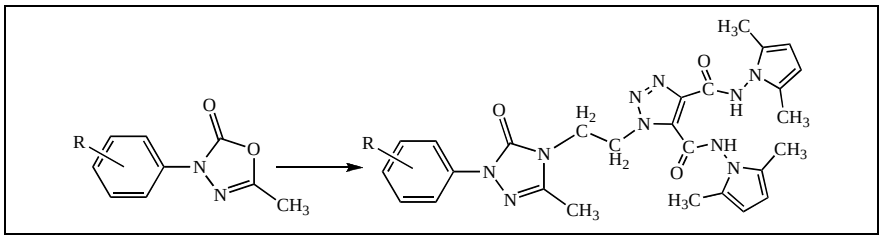

One-pot reaction of 3-aryl-5-methyl-1,3,4-oxadiazolin-2-ones **1a-g** with ethanolamine yielded the 4-(2-hydroxyethyl)-2-aryl-5-methyl-2,4-dihydro-3*H*-1,2,4-triazolin-3-ones **2a-g** which were converted to the azido compounds **6a-g**. These azides on 1,3-dipolar cycloaddition with DMAD afforded the dimethyl-1-[2-(2-aryl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylates **7a-g** which on conversion to bishydrazides **8a-g** and further cyclisation with 2,5-hexanedione afforded the title compounds **9a-g**. This new short route for the so far unkown bis-(triazolinone-triazole)ethanes involves mild and convergent 1,3-dipolar cycloaddition reaction yielding overall good yields of the products.

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## INTRODUCTION

Triazoles have been of continuing interest to organic chemists because of their use in the medicinal and agricultural fields. 1,2,4-Triazole derivatives have been widely used as antifungal [1], insecticidal & ascaricidal [2], analgesic [3], vasodilatory [3], anti-inflammatory [3], diuretic [3] and antibacterial [4] agents. The 1,2,3-triazole moiety is a substructure of a number of biologically active compounds [5] and a number of its derivatives have found diverse uses in synthetic [6a], analytical [6a], medicinal [6a] chemistry, as agrochemicals [6a], dyestuffs [6a], fluorescent whiteners [6b] and photosensitizers [6b]. Although a significant number of triazoles are prepared and stored, expensive starting materials or sensitive intermediates appear to have hindered their industrial synthesis. Most of the reported methods are multistep procedures [2,7-9], starting from compounds that are themselves obtained with difficulty. Though a large number of triazoles are known there are very few examples of the corresponding triazolinones [9a]. In view of the importance of these triazoles we aimed to synthesize some new heterocyclic systems containing these isomeric triazoles through ethylene spacers and to study their structure-activity relationship properties. Our attempt [10] to simplify the synthesis of 1,2,4-triazolin-ones has led to a facile and simple preparative method starting from 3-aryl-5-methyl-[1,3,4]- oxadiazolin-2-ones [11] (obtained in excellent yield, by one-pot ring trans-formation of 3-arylsydnones [11a]) and hydrazine hydrate.

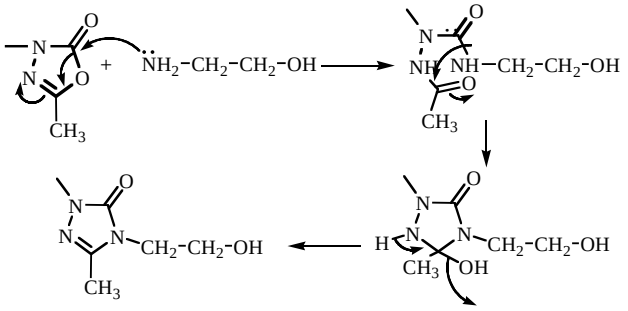
In continuation of this work, we thought of exploring the synthetic scope and reactivity of these oxadiazolin-ones **1a-g** towards other nitrogen nucleophiles like phenylhydrazine and primary amines to obtain some new substituted 1,2,4-triazolinone derivatives. However, the oxadiazolinones were found to be unreactive towards phenylhydrazine and aromatic amines. It appears that the high basicity of the amines determines the ring opening of the oxadiazolinone, because the carbonyl is not of a lactone type but it is a lactam-lactone carbonyl which reduces the susceptibility towards less basic aromatic amines. Hence, we thought of using the more reactive and basic aliphatic primary amines, amongst which we selected the bifunctional ethanolamine for the preparation of 4-(2-hydroxyethyl)-2-aryl-5-methyl-2,4-dihydro-3*H*-1,2,4-triazolin-3- ones **2a-g**.

## RESULTS AND DISCUSSION

In this paper we report a simple one-pot ring conversion of the oxadiazolinones **1a-g** into the so far unknown 4-(2-hydroxyethyl)-2-aryl-5-methyl-2,4-dihydro-*3H*-1,2,4-triazolin-3-ones **2a-g** by reaction with ethanolamine, in ~ 80-85% yield. The mechanism of this one-pot ring reaction may be proposed as follows (Scheme 1). The initial step is the attack of the nucleophile on the carbonyl carbon leading to the ring fission that subsequently undergoes cyclization to the triazolinone ring. The

reaction progress was monitored by TLC and there was no indication of the existence of the intermediate, suggesting a tandem ring fission- recyclization reaction.

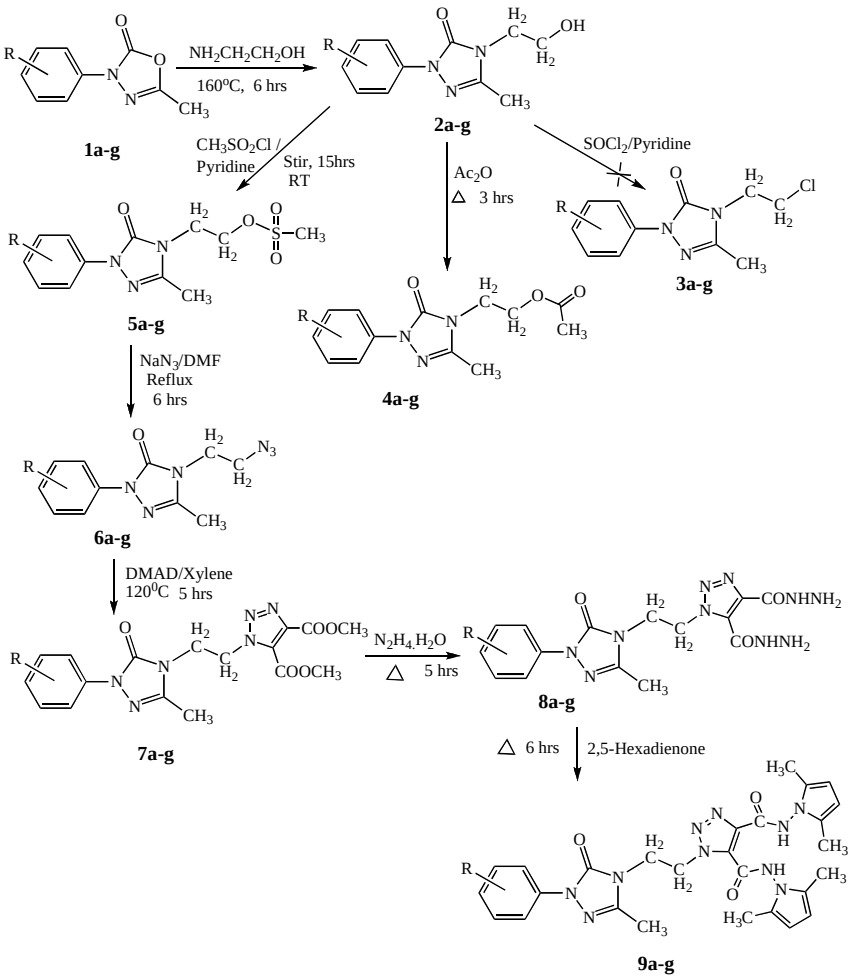
**Scheme 1**



Our purpose in preparing these hydroxyethyl derivatives was to utilize them as precursors to introduce various heterocycles through the hydroxy group. Our attempts to convert the hydroxyethyl compounds **2a-g** to the corresponding chloro derivatives **3a-g** were unsuccessful (Scheme 2). However, these hydroxyethyl triazolinones are of great interest as they contain a free aliphatic -OH group, which could be utilized for a variety of other reactions. Literature has many examples where more potent activity has been exhibited by the acetyl compounds, so in view of this, we converted the hydroxyethyl compounds **2a-g** to the corresponding *O*-acetyl derivatives **4a-g**.

In another attempt, reaction of the hydroxyethyl compounds **2a-g** with methane sulphonylchloride afforded the mesylates **5a-g**, which on further reaction with sodium azide in DMF yielded the 2-aryl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ones **6a-g**. These compounds which are the key intermediates in the synthesis of title compounds underwent smooth 1,3-dipolar cycloaddition with dimethyl acetylene dicarboxylate (DMAD) to afford very good yield of the dimethyl-1-[2-(2-aryl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-carboxylates **7a-g**. Reaction of these

**Scheme 2**



(a) R=H; (b) R=4-Br; (c) R =3-Cl; (d) R =4-Cl; (e) R =3-Me; (f) R =4-Me; (g) R =4-OMe.

diesters with hydrazine hydrate gave the bis-(hydrazine-carbonyl)compounds **8a-g** which on cyclisation with 2,5-hexanedione yielded the tetraheterocyclic *N,N'*-bis(1*H*-pyrrol-1-yl)-1-[2-(2-aryl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides **9a-g**.

## CONCLUSION

Such compounds containing two isomeric triazoles - 1,2,4-triazolinone and 1,2,3-triazoles separated by an ethylene group, were not found in the literature and surveying the literature we find that such bistriazole systems would be inaccessible by alternate and routine methods. In the absence of any reported methods for such systems we have here reasoned that they could be obtained by a facile, convenient and an economical method from a simple compound like sydnone (3-arylsydnones are obtained readily from primary amines in fairly good yield [12]). The reaction of the 3-aryl-5-methyl-[1,3,4]-oxadiazo-lin-2-ones **1a-g** with primary amines appears to be the only efficient route for the N-substituted-1,2,4-triazolinones. The title compounds have been prepared by constructing the isomeric triazole rings by two cycloaddition reactions (one with sydnone ring and another with the azide group) which are powerful avenues for convergent synthetic routes for heterocycles accessible with difficulty. 3-Arylsydnones - the 1,3-dipolarophiles, on tandem reaction by reported method [11a] yielded the oxadiazolinones **1a-g** which serve as a precursor for the 1,2,4-triazolinones, while the azides **6a-g** on 1,3-dipolar cycloaddition reaction afforded the isomeric 1,2,3-triazole ring.

**Spectral characterization.** The IR spectra of compounds **2a-g** showed two $\nu_{OH}$ bands at 3450 and 3363 $cm^{-1}$ and a broad band at ~1703 $cm^{-1}$for the $\nu_{C=O}$. These absorption frequencies indicate the hydrogen bonded interactions between the –OH and C=O groups. However, the band for C=O group does not suggest intramolecular hydrogen bonding. The two $\nu_{OH}$ stretching bands suggest two types of intermolecular hydrogen bondings – H-bonding between the two hydroxy groups (Figure 1) and the hydroxy and the carbonyl groups (Figure 2) of the two triazolinone systems.

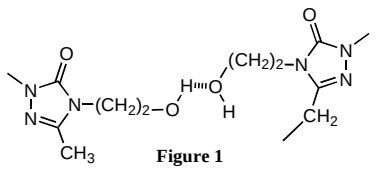


**Figure 1**

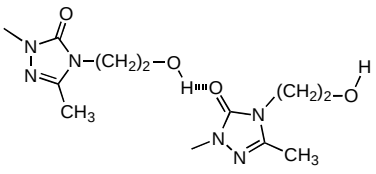


**Figure 2**

$^1$H-NMR (300 MHz) of these compounds showed a singlet at δ 2.36 ppm for the $–CH_3$ protons of triazolinone ring. A broad signal at δ 2.6 ppm (1H, $D_2O$ exchanged) is suggestive of the intermolecular hydrogen bonded –OH group. The two distorted triplets at δ3.85 and 3.95ppm were assigned to the methylene protons $–CH_{2a}$ and the deshielded $–CH_{2b}$ protons respectively (Figure 3) and this pattern is in accordance with literature data [13] of similar type of grouping. The signals at δ7.37 - δ7.95 were assigned to the aromatic protons. This splitting pattern is not clearly of the first order perhaps due to the exchangeable proton on the oxygen, but, two clear triplets appeared on deuteration for these AA'BB' type of protons. The following conformation (Figure 3) was deduced from the $^1$H-NOE difference spectrum of one of the compounds **2e**. Enhancement in the signal of the methylene triplet at δ 3.85 ppm was observed upon irradiation of the triazolinone methyl protons at δ 2.36 ppm, indicating the close proximity of $–CH_{2a}$ and $–CH_3$ in space. This conformation with the C=O and the OH groups far apart rules out intramolecular H-bonding while it can account for two different intermolecular interactions as in Figures 1 and 2. We have also obtained unambiguous evidence for this conformation by Single crystal X-ray study [14].

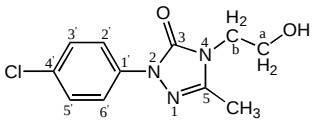


**Figure 3**

The structure of these compounds was further confirmed by its mass spectral analysis. An EIMS of a typical compound **2d** showed the molecular ion peaks at m/z 253 and 255 (3:1, isotopic peak for chlorine), which agrees with the molecular weight of the compound.

The acetyl derivatives **4a-g** were characterized by their IR spectra with the appearance of two $\nu_{C=O}$ bands, one at ~1748 $cm^{-1}$ for the O-acetyl and the other at ~1708 $cm^{-1}$ for the triazolinone ring. The $^1$ H-NMR (300 MHz) spectra of all these compounds showed the singlets at δ 2.0 ppm and δ 2.35 ppm for the $–CH_3$ protons of the O-acetyl and $–CH_3$ protons of the triazolinone ring respectively. The two triplets at δ 3.95 ppm and δ 4.35 ppm corresponded to the $–CH_{2a}$ and the$–CH_{2b}$ protons. The aromatic protons resonated at δ 7.35 - 7.90ppm.

The sulfonate derivatives **5a-g** were characterised by their IR spectra, which displayed bands for the asymmetric and symmetric $\nu_{S=O}$ at 1355 $cm^{-1}$ and 1170 $cm^{-1}$ respectively. The $^1$ H-NMR (300 MHz) spectra of all these compounds showed the singlets at δ 2.34 ppm and δ 3.02 ppm for the $–CH_3$ protons of the triazolinone ring and the methylsufonate respectively. The$–CH_{2a}$ and the$–CH_{2b}$ protons, now highly deshielded due to the sulphonate group resonated downfield as two triplets at δ 4.08 ppm and δ 4.45 ppm. The IR spectra of compounds **6a-g** showed a strong band at

2110 $cm^{-1}$ due to $\nu_{N3,}$ which confirms the formation of azido compounds. These structures were further substantiated by their $^1$ H-NMR (300 MHz) spectra, which showed the absence of methylsulfonate protons at δ 3.02 ppm while the two triplets for the $-CH_{2a}$ and the$-CH_{2b}$ protons appeared upfield at δ 3.73 ppm and δ 3.83 ppm respectively. An EIMS of a typical compound **6d** showed the molecular ion peaks at m/z 188 and 190 (3:1, isotopic peak for chlorine) which agrees with the molecular weight of the compound.

The IR spectra of dimethyl-1-[2-(2-aryl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylates **7a-g** showed three $\nu_{C=O}$ bands at 1740, 1720, and 1700 $cm^{-1}$ due to the diester carbonyls and triazolinone carbonyl respectively. The structures were further evidenced by their $^1$ H-NMR (300 MHz) spectra, which showed two singlets at δ 3.92 and δ 3.99 ppm due to diester methyl protons while the triazolinone methyl protons and the $-CH_{2a}$ and the$-CH_{2b}$ protons appeared as a singlet and two triplets at δ 2.30, δ 4.22 and δ 5.00 respectively. The IR spectra of compounds **8a-g** showed a broad band in the region 3270-3391 $cm^{-1}$ due to $\nu_{NH}$ vibrations of the hydrazide groups and another broad band at 1667 $cm^{-1}$ for the $\nu_{C=O}$ vibrations. The $^1$H-NMR (300 MHz) spectra showed a singlet at δ 2.46 for the triazolinone ring methyl protons and two triplets at δ 4.23 and 5.08, corresponding to $-CH_{2a}$ and the$-CH_{2b}$ protons. A broad signal at δ 12.82 was assigned to two NH protons of the hydrazide groups, which disappeared on $D_2O$ exchange. The IR spectra of compounds **9a-g** showed a broad band at 3213 $cm^{-1}$ due to $\nu_{NH}$ of amide groups and another broad band at 1666 $cm^{-1}$ corresponding to amide $\nu_{C=O}$. The triazolinone $\nu_{C=O}$ appeared at 1710 $cm^{-1}$. The $^1$H-NMR (300 MHz) spectra showed two singlets in the region δ 2.08-2.18 for the four methyl protons (6H each) on the pyrrole rings, whereas another singlet was observed at δ 2.43 for triazolinone methyl protons. The $-CH_{2a}$ and the $-CH_{2b}$ resonated as two triplets at δ 4.18 ppm and δ 5.08 ppm. The two singlets at δ 5.72 and δ 5.76 corresponded to pyrrole ring protons (2H each). The two NH protons resonated as two singlets at δ 11.29 and δ 12.80 (different H-bonding interactions) and disappeared on $D_2O$ exchange. The aromatic protons in all these compounds resonated in δ 7.21 – 7.90 region.

**Biological evaluation.** All these newly synthesized compounds were evaluated for their antimicrobial activities against *Escherichia coli*, *Micrococcus luteus* bacteria and *Aspergillus flavus* and *Penicillium notatum* fungi, with Norfloxacin and Griseofulvin as the reference drugs respectively, at a dose of 50$\mu$gm/0.1ml in DMF(control solvent). The halogen derivatives of all the series of these new compounds were found to be more active than the reference drugs and also the other derivatives in the order 4-Br > 4-Cl > 3-Cl. The compounds **2b** and **2d** (4-Br and 4-Cl) were found to exhibit slightly enhanced activity against only *M. luteus* while the antifungal activity of **2a, 2b, 2c** and **2d** (H, 4-Br, 3-Cl and 4-Cl) was found to be considerably higher than the reference drug, selectively against *A. niger*. The acetylation of these compounds proved fruitful as most of them were active against both the fungi in the order 4-Br > 4-Cl & 4-Me > 4-H > 4-OMe. Compounds **6a-g** (except 4-$OCH_3$ which was active against *M. luteus*) were moderately active against all these microbes inspite of the presence of a potent azido group as a pharmacophore while their cycloaddition products-the bis triazoles - **7a, 7b, 7c, 7d** and **7e** (H, 4-Br, 3-Cl, 4-Cl & 4-Me) were considerably more active than the reference drugs against *M. luteus* and *A. niger*. The bis triazolopyrroles - **9e** (3-Me) showed growth inhibition higher than the reference drug against *A. niger* while **9b, 9c** and **9d** (4-Br, 3-Cl and 4-Cl) were active only against *P. notatum*. The remaining compounds exhibited weak to moderate activity against these microbes. The antimicrobial activities have been compared in Table 1.

**Table 1**

Antimicrobial Activity

| Compd | Antibacterial Zone of Iinhibition(mm) | | Antifungal Zone of inhibition(mm) | |
|---|---|---|---|---|
| | E.coli | M.luteus | P.notatum | A.niger |
| Norfloxacin | 25 | 15 | 18 | 12 |
| Griseofulvin | | | | |
| **2a** | - | - | - | 16 |
| **2b** | - | 14 | 19 | 18 |
| **2c** | - | - | - | 17 |
| **2d** | - | 14 | | 16 |
| **4a** | - | - | 20 | 18 |
| **4b** | - | - | 22 | 22 |
| **4c** | - | - | 22 | 20 |
| **4d** | - | - | 20 | 20 |
| **4e** | - | - | 22 | 18 |
| **4f** | - | - | 22 | 20 |
| **4g** | - | - | 18 | 15 |
| **5b** | - | - | 18 | 16 |
| **6g** | - | 18 | - | - |
| **7a** | - | 18 | - | 16 |
| **7b** | - | 17 | - | 17 |
| **7c** | - | 18 | - | 18 |
| **7d** | - | 17 | - | 16 |
| **7e** | - | 17 | - | 17 |
| **8a** | - | 18 | - | - |
| **8b** | - | 18 | - | - |
| **9b** | - | - | - | 19 |
| **9c** | - | - | - | 18 |
| **9d** | - | - | - | 18 |
| **9e** | - | - | - | 18 |

## EXPERIMENTAL

The IR spectra were recorded on a NICOLET-IMPACT-410FT-IR spectrophotometer as KBr pellets. $^1$H-NMR spectra were recorded on a Bruker AC-300 F, 300 MHz spectrometer in $CDCl_3$/DMSO-$d_6$ with TMS as internal standard. The mass

spectra were recorded on MIver 14 UIC 002002 spectrometer. Elemental analysis was obtained on Heraus C,H,N rapid analyzer.

**General Procedures. 4-(2-Hydroxyethyl)-2-aryl-5-methyl-2,4-dihydro-3*H*-1,2,4 -triazol-3-ones (2a-g).** 3-Aryl-5-methyl-*3H*-[1,3,4]-oxadiazolin-2-ones **1a-g** (0.001 mol) in excess of ethanolamine were heated in an oil-bath at 155-160 °C for 5-6 hrs. The reaction mixture was then poured into ice cold water. The resultant solid was collected by filtered, washed with water and crystallised from ethanol.

**4-(2-Hydroxyethyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-[1,2,4]-triazolin-3-one (2a).** Yield 80%; mp. 116-118°C; ir 3456-3363 ($\nu_{OH}$), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.35 (s, 3H, $CH_3$), δ2.59 (s, 1H, OH, $D_2O$ exchanged), δ3.82 (t, 2H, $CH_2$ J=5Hz), δ3.92 (t, 2H, $CH_2$, J=5Hz), δ7.4-δ7.9 (m, 5H, Ar-H). *Anal.* Calcd. for $C_{11}H_{13}N_3O_2$ (219.09): C, 60.30; H, 6.02; N, 19.20 %; Found: C, 60.01; H, 5.85; N, 18.75%.

**4-(2-Hydroxyethyl)-5-methyl-2-(4-bromo)phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2b).** Yield 80%. mp.114-116°C; ir 3455-3363 ($\nu_{OH}$), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.36 (s, 3H, $CH_3$) δ2.55(s, 1H, OH, $D_2O$ exchanged), δ3.85 (t, 2H, $CH_2$, J=5Hz), δ3.95 (t, 2H, $CH_2$ J=5Hz), δ7.37 (d, 2H, Ar-H *J*= 8.2Hz). δ7.95 (d, 2H, Ar-H *J*= 8.2Hz). *Anal.* Calcd. for $C_{11}H_{12}BrN_3O_2$ (298.09): C, 44.36; H, 4.12; N, 14.14%; Found: C, 44.01; H, 3.87; N, 13.75%.

**4-(2-Hydroxyethyl)-5-methyl-2-(4-chloro)phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2c).** Yield 82%. mp.118-120°C; ir 3460-3362 ($\nu_{OH}$), 1707 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$):δ 2.30 (s, 3H, $CH_3$) δ2.47 (s, 1H, OH, $D_2O$ exchanged), δ3.80 (t, 2H, $CH_2$, J=5Hz), δ3.92 (t, 2H, $CH_2$, J=5Hz), δ7.35 -δ 7.77 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{11}H_{12}ClN_3O_2$ (253.54): C, 52.15; H, 4.82; N, 16.92%; Found: C, 51.88, H, 4.50, N, 16.56%.

**4-(2-Hydroxyethyl)-5-methyl-2-(3-chlorophenyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2d).** Yield 81%. mp.120-122°C; ir 3458-3363 ($\nu_{OH}$), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$):δ 2.36 (s, 3H, $CH_3$ Triazolinone) δ2.60 (s, 1H, OH, $D_2O$ exchanged), δ3.85 (t, 2H, $CH_2$, J=5Hz), δ3.95 (t, 2H, $CH_2$, J=5Hz), δ7.37 (d, 2H, Ar-H *J*= 8.2Hz). δ7.95 (d, 2H, Ar-H *J*= 8.2Hz). ms: m/z 253 (M+1), 209,127. *Anal.* Calcd. for $C_{11}H_{12}ClN_3O_2$ (253.54): C, 52.15; H, 4.82; N, 16.92%; Found: C, 51.78; H, 4.47; N, 16.66%.

**4-(2-Hydroxyethyl)-5-methyl-2-(3-methyl)phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2e).** Yield 75%. mp.106-108°C; ir 3450-3362 ($\nu_{OH}$), 1701 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.27 (s, 3H, $CH_3$), δ 2.34 (s, 3H, $CH_3$ Triazolinone) δ2.60 (s, 1H, OH, $D_2O$ exchanged), δ3.48 (t, 2H, $CH_2$, J=5Hz), δ3.90 (t, 2H, $CH_2$, J=5Hz), δ7.28 -δ 7.83 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{12}H_{15}N_3O_2$ (233.10): C, 61.85; H, 6.55; N, 18.10%; Found: C, 61.59; H, 6.18; N, 17.75%.

**4-(2-Hydroxyethyl)-5-methyl-2-(4-methyl)phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2f).** Yield 78%. mp. 110-112°C; ir 3450-3362 ($\nu_{OH}$), 1704 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.25 (s, 3H, $CH_3$), δ 2.31 (s,3H, $CH_3$ Triazolinone) δ2.63 (s, 1H, OH, $D_2O$ exchanged), δ3.42 (t, 2H, $CH_2$, J=5Hz), δ3.82 (t, 2H, $CH_2$, J=5Hz), δ 7.28 (d, 2H, Ar-H *J*= 8.2Hz), δ 7.92 (d, 2H, Ar-H *J*= 8.2Hz). *Anal.* Calcd. for $C_{12}H_{15}N_3O_2$ (233.10): C, 61.85; H, 6.55; N, 18.10%; Found: C, 61.46; H, 6.20; N, 17.77%.

**4-(2-Hydroxyethyl)-5-methyl-2-(4-methoxy)phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one one (2g).** Yield 81%. mp.118-120°C; ir 3460-3362 ($\nu_{OH}$), 1707 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.36 (3H, s, $CH_3$) δ2.58 (s, 1H, OH, $D_2O$ exchanged), δ 3.72 (s, 3H, $OCH_3$), δ3.85 (t, 2H, $CH_2$, J=5Hz), δ3.95 (t, 2H, $CH_2$, J=5Hz), δ7.25 (d, 2H, Ar-H *J*= 8.4 Hz). δ 7.55 (d, 2H, Ar-H *J*= 8.4 Hz). *Anal.* Calcd. for $C_{12}H_{15}N_3O_3$ (249.09): C, 57.86; H, 6.10; N, 16.90%; Found: C, 57.56; H, 5.87; N, 16.46%.

**4-(2-Aryl-5-methyl-3-oxo-2,4-dihydro-*3H*-1,2,4-triazol-4-yl)ethyl acetates (4a-g).** The 4-(2-hydroxyethyl)-1,2,4-triazolin-3-ones **2a-g** (0.001 mol) in excess of acetic anhydride were heated on a water- bath for 2-3 hrs. The reaction mixture was then poured into ice-cold water. The resultant solid filtered, washed with water and crystallised from ethanol.

**4-(2-Phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl acetate (4a).** Yield 75%; mp. 90-92°C; ir 1748 ($\nu_{C=O}$ Acetyl), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.08 (s, 3H, $CH_3$ O-Acetyl), δ2 .34 (s, 1H, $CH_3$), δ3.82 (t, 2H, $CH_2$, J=4.6Hz), δ3.98 (t, 2H, $CH_2$, J=4.6Hz), δ7.36-δ7.95 (m, 5H, Ar-H). *Anal.* Calcd. for $C_{13}H_{15}N_3O_3$ (261.10): C, 59.80; H, 5.85; N, 16.15%; Found: C, 59.46; H, 549; N, 15.80%.

**4-[2-(4-Bromo)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate (4b).** Yield 85%. mp.118-120°C; ir 1745 ($\nu_{C=O}$ Acetyl), 1705 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.11 (3H, s, $CH_3$, O-Acetyl), δ 2 .34 (1H, s, $CH_3$), δ 3.95 (2H, t, $CH_2$, J=4.6Hz), δ 4.32 (2H, t, $CH_2$, J=4.6Hz), δ 7.29 (2H, d, Ar-H *J*= 8.4 Hz). δ 7.69 (2H, d, Ar-H *J*= 8.4 Hz). *Anal.* Calcd. for $C_{13}H_{14}BrN_3O_3$ (340.10): C, 46.96; H, 4.20; N, 12.42%; Found: C, 46.50; H, 3.85; N, 12.15%.

**4-[2-(3-Chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate (4c).** Yield 80% mp.102-104°C; ir 1748 ($\nu_{C=O}$ Acetyl), 1700 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.09 (3H, s, $CH_3$, O-Acetyl), δ 2 .29 (1H, s, $CH_3$), δ 3.89 (2H, t, $CH_2$, J=4.6Hz), δ 4.02 (2H, t, $CH_2$, J=4.6Hz), δ 7.43 - 7.89 (4H, m, Ar-H). *Anal.* Calcd. for $C_{13}H_{14}ClN_3O_3$ (295.55): C, 52.85; H, 4.82; N, 14.26%; Found: C, 52.55; H, 4.80; N, 13.88%.

**4-[2-(4-Chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate (4d).** Yield 85% mp.110-112°C; ir 1748 ($\nu_{C=O}$ Acetyl), 1708 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.08 (3H, s, $CH_3$, O-Acetyl), δ 2 .34 (1H, s, $CH_3$), δ 3.95 (2H, t, $CH_2$, J=4.6Hz), δ 4.32 (2H, t, $CH_2$, J=4.6Hz), δ 7.36 (2H, d, Ar-H *J*= 8.2 Hz). δ 7.89 (2H, d, Ar-H *J*= 8.2 Hz). *Anal.* Calcd. for $C_{13}H_{14}ClN_3O_3$ (295.55): C, 52.85; H, 4.82; N, 14.26%; Found: C, 52.44; H, 4.50; N, 13.75%.

**4-[2-(3-Methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate (4e).** Yield 78%. mp.100-102°C; ir 1744 ($\nu_{C=O}$ Acetyl), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.13 (3H, s, $CH_3$, O-Acetyl), δ 2 .29 (1H, s, $CH_3$), δ 3.88 (2H, t, $CH_2$, J=4.6Hz), δ 4.01 (2H, t, $CH_2$, J=4.6Hz), δ7.30-δ7.67 (5H, m, Ar-H). *Anal.* Calcd. for $C_{14}H_{17}N_3O_3$ (275.11): C, 61.15; H, 6.26; N, 15.26%; Found: C, 60.78; H, 5.88; N, 14.75%.

**4-[2-(4-Methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate (4f).** Yield 78%. mp.100-102°C; ir 1744 ($\nu_{C=O}$ Acetyl), 1702 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.10 (3H, s, $CH_3$ O-Acetyl), δ 2 .35 (1H, s, $CH_3$), δ 3.92 (2H, t, $CH_2$, J=4.6Hz), δ 4.06 (2H, t, $CH_2$, J=4.6Hz), δ 7.37 (2H, d, Ar-H *J*= 8.2Hz). δ 7.95 (2H, d, Ar-H *J*= 8.2Hz). *Anal.* Calcd. for $C_{14}H_{17}N_3O_3$ (275.11): C, 61.15; H, 6.26; N, 15.26%; Found: C, 59.80; H, 5.80; N, 14.95%.

**4-[2-(4-Methoxy)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethyl acetate ones (4g).** Yield 70%. mp.88-90°C; ir 1740 ($\nu_{C=O}$ Acetyl), 1705 ($\nu_{C=O}$); $^1$H-NMR ($CDCl_3$): δ 2.15 (3H, s, $CH_3$ O-Acetyl), δ 2 .35 (1H, s, $CH_3$), δ 3 .75 (3H, s, $OCH_3$), δ 3.83 (2H, t, $CH_2$, J=4.6Hz), δ 3.97 (2H, t, $CH_2$, J=4.6Hz), δ 7.44 (2H, d, Ar-H *J*= 8.4Hz). δ 7.69 (2H, d, Ar-H *J*= 8.4Hz). *Anal.* Calcd. for $C_{14}H_{17}N_3O_4$ (291.10): C, 57.80; H, 5.94; N, 14.48%; Found: C, 57.42; H, 5.48; N, 14.12%.

**2-(2-Aryl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethylmethane sulfonates (5a-g).** To an ice cold solution of methanesulphonyl chloride (0.02m) in pyridine was added 4-(2-hydroxyethyl)-2-aryl-5-methyl-2,4-dihydro-3*H*-[1,2,4]-triazolin-3-ones **2a-g** (0.01 mol) in small portions. The solution was stirred at room temperature for 15 hrs and then poured onto ice. The separated solid was collected by filtration, washed with water and crystallized from ethanol.

**2-(2-Phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethylmethane sulfonate (5a).** Yield 72%; mp. 84-86°C; ir 1700 ($\nu_{C=O}$) 1354; $^1$H-NMR ($CDCl_3$): δ 2.34 (s, 3H, $CH_3$, Triazolinone), δ 3.01 (s, 1H, $CH_3$), δ4.03 (t, 2H, $CH_2$, J=4.4Hz), δ 4.51 (t, 2H, $CH_2$, J=4.4Hz), δ7.29-δ7.81 (m, 5H, Ar-H). *Anal.* Calcd. for $C_{12}H_{15}N_3O_4S$ (2914): C, 54.33; H, 5.66; N, 15.84%; Found: C, 54.03; H, 5.20; N, 15.48%.

**2-[2-(4-Bromo)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5b).** Yield 75%. mp. 96-98°C; ir 1700 ($\nu_{C=O}$) 1354; $^1$H-NMR ($CDCl_3$): δ 2.34 (s, 3H, $CH_3$), δ3.21 (s, 1H, $CH_3$), δ 4.10 (t, 2H, $CH_2$, J=4.4Hz), δ 4.58 (t, 2H, $CH_2$, J=4.4Hz), δ7.33 (d, 2H, Ar-H *J*= 8.4 Hz). δ7.68 (d, 2H, Ar-H *J*= 8.4 Hz). *Anal.* Calcd. for $C_{12}H_{14}BrN_3O_4S$ (376.14): C, 38.29; H, 3.72; N, 11.17%; Found: C, 37.85; H, 3.37; N, 10.78%.

**2-[2-(3-Chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5c).** Yield 68%. mp.101-103°C; ir 1700 ($\nu_{C=O}$) 1354; $^1$H-NMR ($CDCl_3$): δ 2.36 (s, 3H, $CH_3$, Triazolinone), δ 3.19 (s, 1H, $CH_3$), δ 4.01 (t, 2H, $CH_2$, J=4.4Hz), δ 4.39 (t, 2H, $CH_2$, J=4.4Hz), δ7.23 -7.81 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{12}H_{14}ClN_3O_4S$ (332.59): C, 43.37; H, 4.21; N, 12.65%; Found: C, 43.01; H, 3.80; N, 12.20%.

**2-[2-(4-Chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5d).** Yield 68% mp.110-112°C; ir 1708 ($\nu_{C=O}$) 1350; $^1$H-NMR ($CDCl_3$): δ 2.34 (s, 3H, $CH_3$,Triazolinone), δ3.07 (s, 1H, $CH_3$), δ 4.11 (t, 2H, $CH_2$, J=4.4Hz), δ 4.55 (t, 2H, $CH_2$, J=4.4Hz), δ7.33 (d, 2H, Ar-H *J*= 8.2 Hz). δ7.86 (d, 2H, Ar-H *J*= 8.2 Hz). *Anal.* Calcd. for $C_{12}H_{14}ClN_3O_4S$ (332.59): C, 43.37; H, 4.21; N, 12.65%; Found: C, 43.02; H, 3.76; N, 12.26%.

**2-[2-(3-Methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5e).** Yield 68%. mp.118-120°C; ir 1700 ($\nu_{C=O}$) 1354,; $^1$H-NMR ($CDCl_3$): δ 2.34 (s, 3H, $CH_3$), δ 2.36 (s, 3H, $CH_3$,Triazolinone), δ3.07 (s, 1H, $CH_3$), δ 4.08 (t, 2H, $CH_2$, J=4.4Hz), δ 4.45 (t, 2H, $CH_2$, J=4.4Hz), δ7.39-δ7.71 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{13}H_{17}N_3O_4S$ (311.15): C, 50.16; H, 5.46; N, 13.50%; Found: C, 49.82; H, 5.10; N, 13.18%.

**2-[2-(4-Methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5f).** Yield 75%. mp.96-98°C; ir 1706 ($\nu_{C=O}$) 1359,; $^1$H-NMR($CDCl_3$): δ 2.34 (s, 3H, $CH_3$), δ 2.36 (s, 3H, $CH_3$,Triazolinone), δ3.07 (s, 1H, $CH_3$), δ 4.08 (t, 2H, $CH_2$, J=4.4Hz), δ 4.45 (t, 2H, $CH_2$, J=4.4Hz), δ7.23(d, 2H, Ar-H *J*= 8.4 Hz). δ7.81 (d, 2H, Ar-H *J*= 8.4 Hz). *Anal.* Calcd. for $C_{13}H_{17}N_3O_4S$ (311.15): C, 50.16; H, 5.46%; N, 13.50; Found: C, 49.75; H, 5.11; N, 13.05%.

**2-[2-(4-Methoxy)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl]ethylmethane sulfonate (5g).** Yield 71%. mp.112-114°C; ir 1703 ($\nu_{C=O}$) 1354; $^1$H-NMR ($CDCl_3$): δ 2.29 (s, 3H, $CH_3$), δ3.07 (s, 1H, $CH_3$,Triazolinone), δ3.71 (s, 1H, $OCH_3$), δ 3.96 (t, 2H, $CH_2$, J=4.4Hz), δ 4.32 (t, 2H, $CH_2$, J=4.4Hz), δ7.44 (d, 2H, Ar-H *J*= 8.1 Hz). δ7.99 (d, 2H, Ar-H *J*= 8.1 Hz). *Anal.* Calcd. for $C_{13}H_{17}N_3O_5S$ (327.14): C, 47.70; H, 5.19; N, 12.84%; Found: C, 47.35; H, 4.81; N, 12.50%.

**2-Aryl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ones (6a-g).** To the solution of compounds **4a-g** (0.005 mol) in dimethylformamide was added sodium azide (0.33 g, 0.005 mol) in water. The mixture was refluxed for 6 hrs and then poured into ice water. The solid separated was collected by filtration, dried and recrystallised from ethanol.

**2-Phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6a).** Yield 74%; mp. 112-114°C; ir 2115($\nu_{N3}$) 1711 ($\nu_{C=O}$) 1601,; $^1$H-NMR ($CDCl_3$): δ 2.37 (s, 3H, $CH_3$), δ 3.73(t, 2H, $CH_2$, J=4.5Hz), δ 3.83 (t, 2H, $CH_2$, J=4.5Hz), δ7.21-δ7.80 (m, 5H, Ar-H). *Anal.* Calcd. for $C_{11}H_{12}N_6O$ (244.10): C, 54.09; H, 4.91; N, 34.42%; Found: C, 53.65; H, 4.45; N, 34.06%.

**2-(4-Bromo)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6b).** Yield 72%. mp. 126-128°c; ir 2107($\nu_{N3}$) 1710 ($\nu_{C=O}$) 1600,; $^1$H-NMR ($CDCl_3$): δ 2.31 (s, 3H, $CH_3$), δ 3.78(t, 2H, $CH_2$, J=4.5Hz), δ 3.92 (t, 2H, $CH_2$, J=4.5Hz), δ7.41 (d ,2H, Ar-H, *J*= 8.2 Hz). δ7.73 (d, 2H, Ar-H, *J*= 8.2 Hz). *Anal.* Calcd. for $C_{11}H_{11}BrN_6O$ (323.10): C, 40.99; H, 3.41; N, 26.08%; Found: C, 39.70; H, 3.16; N, 25.65%.

**2-(3-Chloro)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6c).** Yield 73%. mp. 109-111°C; ir 2110($\nu_{N3}$) 1700 ($\nu_{C=O}$) 1604,; $^1$H-NMR ($CDCl_3$): δ 2.35 (s, 3H, $CH_3$), δ 3.70 (t, 2H, $CH_2$, J=4.5Hz), δ 3.90 (t, 2H, $CH_2$, J=4.5Hz), δ7.24 -7.80 (d, 2H, Ar-H). *Anal.* Calcd. for $C_{11}H_{11}ClN_6O$ (278.5): C, 47.48; H, 3.95; N, 30.21%; Found: C, 47.03; H, 3.60; N, 29.78%.

**2-(4-Chloro)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6d).** Yield 75%. mp. 115-117°C; ir 2107($\nu_{N3}$) 1710 ($\nu_{C=O}$) 1600,; $^1$H-NMR ($CDCl_3$): δ 2.31 (s,3H, $CH_3$), δ 3.78(t,2H, $CH_2$, J=4.5Hz), δ 3.92 (t,2H, $CH_2$, J=4.5Hz), δ7.24 (d,2H, Ar-H, *J*= 8.3 Hz). δ 7.80 (d, 2H, Ar-H, *J*= 8.3 Hz). ms: m/z 278 (M+1), 250,209, 125. *Anal.* Calcd. for $C_{11}H_{11}ClN_6O$ (278.5): C, 47.48; H, 3.95; N, 30.21%; Found: C, 47.11; H, 3.59; N, 29.70%.

**2-(3-Methyl)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6e).** Yield 75% mp. 127-129°C; ir 2101($\nu_{N3}$) 1710 ($\nu_{C=O}$) 1604,; $^1$H-NMR ($CDCl_3$):δ 2.27 (s,3H, $CH_3$),δ 2.31 (s,3H, $CH_3$), δ 3.78 (t,2H, $CH_2$, J=4.5Hz), δ 3.97 (t,2H, $CH_2$, J=4.5Hz), δ 7.33-δ7.79(m,4H, Ar-H). *Anal.* Calcd. for $C_{12}H_{14}N_6O$ (258.11): C, 55.81; H, 5.42; N, 32.55%; Found: C, 55.47; H, 5.17; N, 32.15%.

**2-(4-Methyl)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6f).** Yield 75%. mp. 127-129°C; ir 2110($\nu_{N3}$) 1710 ($\nu_{C=O}$) 1600,; $^1$H-NMR ($CDCl_3$): δ 2.37 (s,6H, $CH_3$), δ 3.70(t,2H, $CH_2$, J=4.5Hz), δ 3.87 (t,2H, $CH_2$, J=4.5Hz), δ7.21 (d,2H, Ar-H, *J*= 8.3 Hz). δ7.82 (d,2H, Ar-H, *J*= 8.3 Hz). *Anal.* Calcd. for $C_{12}H_{14}N_6O$ (258.11): C, 55.81; H, 5.42; N, 32.55%; Found: C, 55.36; H, 5.01; N, 32.10%.

**2-(4-Methoxy)phenyl-4-(2-azidoethyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6g).** Yield 70%. mp. 131-133°C; ir 2110($\nu_{N3}$) 1710 ($\nu_{C=O}$) 1600,; $^1$H-NMR ($CDCl_3$): δ 2.37 (s,3H, $CH_3$), δ 3.71 (s,3H, $OCH_3$), δ 3.82(t,2H, $CH_2$, J=4.5Hz), δ 3.94 (t,2H, $CH_2$, J=4.5Hz), δ 7.37 (d,2H, Ar-H, *J*= 8.2 Hz). δ 7.78 (d,2H, Ar-H, *J*= 8.2 Hz). *Anal.* Calcd. for $C_{12}H_{14}N_6O_2$ (274.10): C, 52.55; H, 5.10; N, 30.65%; Found: C, 52.10; H, 4.75; N, 29.65%.

**Dimethyl-1-[2-(2-aryl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylates (7a-g).** To the solution of azido compounds **6a-g** (0.001 mol) in dry acetone (25 ml) was added dimethylacetylenedicarboxylate DMAD (0.15 g, 0.001 mol) and the mixture was heated at

reflux for 5 hr. The solvent was removed under reduced pressure and the residue obtained was recrystallised from ethanol.

**Dimethyl-1-[2-(2-phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7a).** Yield 81%; mp. 155-157°C; ir 1738 ($\nu_{C=O}$ ester), 1720 ($\nu_{C=O}$), 1701 ($\nu_{C=O}$ triazole); $^1$H-NMR ($CDCl_3$): δ 2.36 (s, 3H, $CH_3$), δ 3.85 (s, 3H, $OCH_3$), δ 3.97 (s, 3H, $OCH_3$), δ 4.22(t, 2H, $CH_2$, J=4.5Hz), δ 4.98 (t, 2H, $CH_2$, J=4.5Hz), δ7.20-δ7.77 (m, 5H, Ar-H). *Anal.* Calcd. for $C_{17}H_{18}N_6O_5$ (386.12): C, 52.84; H, 4.66; N, 21.76%; Found: C, 52.48; H, 4.16; N, 21.42%.

**Dimethyl-1-[2-(2-(4-bromo)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7b).** Yield 85%. mp. 149-151°C; ir 1744(br, $\nu_{C=O}$ ester), 1700 ($\nu_{C=O}$ triazole); $^1$H-NMR($CDCl_3$): δ 2.25(s, 3H, $CH_3$), δ 3.84 (s, 3H, $OCH_3$), δ 3.93(s, 3H, $OCH_3$), δ 4.20(t, 2H, $CH_2$, J=4.5Hz), δ 4.89 (t, 2H, $CH_2$, J=4.5Hz), δ7.29 (d, 2H, Ar-H, *J*= 8.4 Hz). δ7.82 (d, 2H, Ar-H, *J*= 8.4 Hz). *Anal.* Calcd. for $C_{17}H_{17}BrN_6O_5$ (465.12): C, 43.96; H, 3.66; N, 18.10%; Found: C, 43.49; H, 3.3; N, 17.77%.

**Dimethyl-1-[2-(2-(3-chloro)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7c).** Yield 73%. mp. 126-128°C; ir 1740 (br, $\nu_{C=O}$ ester), 1707 ($\nu_{C=O}$ triazole); $^1$H-NMR($CDCl_3$): δ 2.31(s 3H, , $CH_3$), δ 3.88 (s, 3H, $OCH_3$), δ 3.97(s, 3H, $OCH_3$), δ 4.22(t, 2H, $CH_2$, J=4.5Hz), δ 4.79 (t, 2H, $CH_2$, J=4.5Hz), δ7.39 - 7.76 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{17}H_{17}ClN_6O_5$ (420.57): C, 48.57; H, 4.04; N, 20.00%; Found: C, 48.22; H, 3.67; N, 19.74%.

**Dimethyl-1-[2-(2-(4-chloro)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7d).** Yield 80%. mp. 138-140°C; ir 1744(br, $\nu_{C=O}$ ester), 1700 ($\nu_{C=O}$ triazole); $^1$H-NMR ($CDCl_3$):δ 2.25(s, 3H, $CH_3$,Triazolinone,), δ 3.82 (s, 3H, $OCH_3$), δ 3.93(s, 3H, $OCH_3$), δ 4.18(t, 2H, $CH_2$, J=4.5Hz), δ 4.89 (t, 2H, $CH_2$, J=4.5Hz), δ7.19 (d, 2H, Ar-H, *J*= 8.4 Hz). δ7.80 (d, 2H, Ar-H, *J*= 8.4 Hz). *Anal.* Calcd. for $C_{17}H_{17}ClN_6O_5$ (420.57): C, 48.57; H, 4.04; N, 20.00%; Found: C, 48.20; H, 3.75; N, 19.74%.

**Dimethyl-1-[2-(2-(3-methyl)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7e).** Yield 76% mp. 133-135°C; ir 1740 ($\nu_{C=O}$ ester), 1718 ($\nu_{C=O}$), 1700 ($\nu_{C=O}$ triazole); $^1$H-NMR ($CDCl_3$): δ 1.91 (s, 3H, $CH_3$), δ 2.30 (s, 3H, $CH_3$,Triazolinone,), δ 3.92 (s, 3H, $OCH_3$), δ 4.03(s, 3H, $OCH_3$), δ 4.22(t, 2H, $CH_2$, J=4.5Hz), δ 5.00 (t, 2H, $CH_2$, J=4.5Hz), δ7.31- δ7.69 (m, 4H, Ar-H). *Anal.* Calcd. for $C_{18}H_{20}N_6O_5$ (400.13): C, 54.00; H, 5.00; N, 21.00%; Found: C, 53.93; H, 4.95; N, 20.94%.

**Dimethyl-1-[2-(2-(4-methyl)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7f).** Yield 73%. mp. 141-143°C; ir 1740 ($\nu_{C=O}$ ester), 1718 ($\nu_{C=O}$), 1700 ($\nu_{C=O}$ triazole); $^1$H-NMR ($CDCl_3$): δ 1.89 (s, 3H, $CH_3$), δ 2.36 (s, 3H, $CH_3$,Triazolinone), δ 3.88 (s, 3H, $OCH_3$), δ 3.99(s, 3H, $OCH_3$), δ 4.20(t, 2H, $CH_2$, J=4.5Hz), δ 5.02 (t, 2H, $CH_2$, J=4.5Hz), δ7.23 (d, 2H, Ar-H, *J*= 8.4 Hz). δ7.77 (d, 2H, Ar-H, *J*= 8.4 Hz). *Anal.* Calcd. for $C_{18}H_{20}N_6O_5$ (400.13): C, 54.00; H, 5.00; N, 21.00%; Found: C, 53.93; H, 4.95; N, 20.94%.

**Dimethyl-1-[2-(2-(4-methoxy)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarboxylate (7g).** Yield 73%. mp. 120-122°C; ir 1740 ($\nu_{C=O}$ ester), 1718 ($\nu_{C=O}$), 1700 ($\nu_{C=O}$ triazole); $^1$H-NMR ($CDCl_3$): δ 2.32 (s, 3H, $CH_3$,Triazolinone), δ 3.71(s, 3H, $OCH_3$), δ 3.88 (s, 3H, $OCH_3$), δ 3.99(s, 3H, $OCH_3$), δ 4.20(t, 2H, $CH_2$, J=4.5Hz), δ 5.02 (t, 2H, $CH_2$, J=4.5Hz), δ7.23 (d, 2H, Ar-H, *J*= 8.3 Hz). δ7.70 (d, 2H, Ar-H, *J*= 8.3 Hz). *Anal.* Calcd. for $C_{18}H_{20}N_6O_6$ (416.12): C, 51.92; H, 4.80; N, 20.19%; Found: C, 51.86; H, 4.75; N, 20.13%.

**1-[2-(2-aryl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-*1H*-1,2,3-triazol-4,5-dicarbohydrazides (8a-g).** To a solution of compounds (7a-g) (0.001 mol) in 10 ml of ethanol, hydrazine hydrate (99-100%, 0.001 mol) was added and the reaction mixture refluxed for 5 hours. The white solid separated on cooling was filtered, washed with water and recrystallised from ethanol/DMF.

**1-[2-(2-Phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8a).** Yield 61%; mp. 167-169°C; ir 3382, 3289($\nu_{NH}$) 1700 ($\nu_{C=O}$ triazole) 1667 ($\nu_{C=O}$); $^1$H-NMR(DMSO): δ 2.28(s, 3H, $CH_3$), δ 4.18(t, 2H, $CH_2$, J=4.5Hz), δ 5.08 (t, 2H, $CH_2$, J=4.5Hz), δ7.20-δ7.66 (m, 5H, Ar-H), δ 12.10(br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{15}H_{18}N_{10}O_3$ (386.12): C, 46.63; H, 4.66; N, 36.26%; Found: C, 46.27; H, 4.31; N, 35.85%.

**1-[2-(2-(4-Bromo)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-*1H*-1,2,3-triazol-4,5-dicarbohydrazide (8b).** Yield 65%. mp. 184-186°C; ir 3381, 3270 ($\nu_{NH}$) 1701($\nu_{C=O}$ triazole) 1657 ($\nu_{C=O}$); $^1$H-NMR (DMSO): δ 2.20 (s, 3H, $CH_3$), δ 4.20 (t, 2H, $CH_2$, J=4.5Hz), δ 5.08 (t, 2H, $CH_2$, J=4.5Hz), δ 7.12(d, 2H, Ar-H, *J*= 8.2 Hz), δ 7.67 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 12.10 (br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{15}H_{17}BrN_{10}O_3$ (465.12): C, 38.70; H, 3.65; N, 30.10%; Found: C, 38.33; H, 3.29; N, 29.75%.

**1-[2-(2-(3-Chloro)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8c).** Yield 60%. mp. 144-146°C; ir 3391, 3277 ($\nu_{NH}$) 1707 ($\nu_{C=O}$ triazole) 1659 ($\nu_{C=O}$); $^1$ H-NMR (DMSO):δ 2.20(s ,3H, $CH_3$), δ 4.20 (t, 2H, $CH_2$, J=4.5Hz), δ 5.06 (t, 2H, $CH_2$, J=4.5Hz), δ 7.29 -7.67 (m, 4H, Ar-H) δ 12.02 (br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{15}H_{17}ClN_{10}O_3$ (420.57): C, 42.85; H, 4.04; N, 33.33%; Found: C, 42.49; H, 3.68; N, 32.88%.

**1-[2-(2-(4-Chloro)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8d).** Yield 67%. mp. 157-159°C; ir 3391, 3273 ($\nu_{NH}$) 1704($\nu_{C=O}$ triazole) 1667 ($\nu_{C=O}$); $^1$ H-NMR (DMSO): δ 2.22(s, 3H, $CH_3$), δ 4.23 (t, 2H, $CH_2$, J=4.5Hz), δ 5.08 (t, 2H, $CH_2$, J=4.5Hz), δ 7.29 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 7.78 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 12.10 (br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{15}H_{17}ClN_{10}O_3$ (420.57): C, 42.85; H, 4.04; N, 33.33%; Found: C, 42.37; H, 3.69; N, 32.80%.

**1-[2-(2-(3-Methyl)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8e).** Yield 68%. mp. 173-175°C; ir 3383, 3280 ($\nu_{NH}$) 1702 ($\nu_{C=O}$ triazole) 1660 ($\nu_{C=O}$); $^1$ H-NMR (DMSO): δ 2.23(s, 3H, $CH_3$), δ 2.32(s, 3H, $CH_3$), δ 4.11(t, 2H, $CH_2$, J=4.5Hz), δ 4.98 (t, 2H, $CH_2$, J=4.5Hz), δ 7.21 - 7.69 (m, 4H, Ar-H), δ 11.98 (br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{16}H_{20}N_{10}O_3$(400.13): C, 48.00; H, 5.00; N, 35.00%; Found: C, 47.65; H, 4.75; N, 34.70%.

**1-[2-(2-(4-Methyl)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)-ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8f).** Yield 62%. mp. 169-171°C; ir 3389, 3280 ($\nu_{NH}$) 1700 ($\nu_{C=O}$ triazole) 1667 ($\nu_{C=O}$); $^1$ H-NMR (DMSO): δ 2.18(s, 3H, $CH_3$), δ 2.28(s, 3H, $CH_3$), δ 4.18(t, 2H, $CH_2$, J=4.5Hz), δ 5.08 (t, 2H, $CH_2$, J=4.5Hz), δ7.19 (d, 2H, Ar-H, *J*= 8.4 Hz), δ7.80 (d, 2H, Ar-H, *J*= 8.4 Hz), δ 12.02(br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{16}H_{20}N_{10}O_3$ (400.13): C, 48.00; H, 5.00; N, 35.00%; Found: C, 47.64; H, 4.73; N, 34.75%.

**1-[2-(2-(4-Methoxy)phenyl-5-methyl-3-oxo-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazol-4,5-dicarbohydrazide (8g).** Yield

65%. mp. 191-193°C; ir 3389, 3280 ($\nu_{NH}$) 1700 ($\nu_{C=O}$ triazole) 1667 ($\nu_{C=O}$); $^1$H-NMR (DMSO): δ 2.18(s, 3H, $CH_3$), δ 2.28(s, 3H, $CH_3$), δ 4.10(t, 2H, $CH_2$, J=4.5Hz), δ 4.99 (t, 2H, $CH_2$, J=4.5Hz), δ7.31 (d, 2H, Ar-H, *J*= 8.4 Hz), δ7.87 (d, 2H, Ar-H, *J*= 8.4 Hz), δ 11.96(br, 2H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{16}H_{20}N_{10}O_4$ (416.12): C, 46.15; H, 4.80; N, 33.65%; Found: C, 45.80; H, 4.44; N, 33.29%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-aryl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9a-g).** To a suspension of compounds (**8a-g**) (0.001 mol) in ethanol (15 ml) was added acetonyl acetone (0.002 mol) and glacial acetic acid (0.5 ml) and the reaction mixture was heated on a boiling water bath for 6 hrs. The solution was concentrated to half of its volume and poured into crushed ice. The separated solid was collected by filtration, washed with water, dried and crystallized from benzene-pet ether as white compound.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9a).** Yield 69%; mp. 228-230°C; ir 3289 ($\nu_{NH}$) 1705 ($\nu_{C=O}$ triazole) 1672 ($\nu_{C=O}$); $^1$H-NMR (DMSO): δ 2.08 (s, 6H, $CH_3$), 2.15 (s, 6H, $CH_3$), 2.47(s, 3H, $CH_3$, Triazolinone), δ 4.18 (t, 2H, $CH_2$, J=4.4Hz), δ 5.08 (t, 2H, $CH_2$, J=4.4Hz), 5.72 (s, 2H, Pyrrole ring CH), 5.76 (s, 2H, Pyrrole ring CH), δ7.11-δ7.66 (m, 5H, Ar-H), δ 11.26(br, 1H, NH $D_2O$ exchanged) δ 12.80(br, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{27}H_{30}N_{10}O_3$ (542.24): C, 59.77; H, 5.57; N, 25.81%; Found: C, 59.40; H, 5.21; N, 25.44%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(4-bromo)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9b).** Yield 74%. mp. 251-253°C; ir 3270 ($\nu_{NH}$) 1710 ($\nu_{C=O}$ triazole) 1655 ($\nu_{C=O}$); $^1$H-NMR (DMSO):δ 2.13(s, 6H, $CH_3$), 2.21 (s, 6H, $CH_3$), 2.33(s, 3H, $CH_3$, Triazolinone), δ 4.14 (t, 2H, $CH_2$, J=4.4Hz), δ 5.31 (t, 2H, $CH_2$, J=4.4Hz), 5.64 (s, 2H, Pyrrole ring CH), 5.71 (s, 2H, Pyrrole ring CH), δ 7.35 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 7.96(d, 2H, Ar-H, *J*= 8.2 Hz), δ 11.29 (br ,1H, NH $D_2O$ exchanged) δ 12.57(br, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{27}H_{29}BrN_{10}O_3$ (621.24): C, 52.18; H, 4.70; N, 22.54%; Found: C, 51.75; H, 4.33; N, 22.19%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(3-chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9c).** Yield 64%. mp. 222-224°C; ir 3285($\nu_{NH}$) 1701 ($\nu_{C=O}$ triazole) 1670 ($\nu_{C=O}$); $^1$H-NMR (DMSO):δ 2.11 - 2.19 (s, 12H, $CH_3$), 2.35 (s, 3H, $CH_3$, Triazolinone), δ 4.25 (t, 2H, $CH_2$, J=4.4Hz), δ 5.20 (t, 2H, $CH_2$, J=4.4Hz), 5.72 (s, 2H, Pyrrole ring CH), 5.76 (s, 2H, Pyrrole ring CH), δ 7.11 - 7.69(m, 4H, Ar-H), δ 11.33 (br, 1H, NH $D_2O$ exchanged) δ 12.73 (s, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{27}H_{29}ClN_{10}O_3$ (576.69): C, 56.20; H, 5.04; N, 22.28%; Found: C, 55.75; H, 4.65; N, 21.90%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(4-chloro)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9d).** Yield 67%. mp. 236-238°C; ir 3285($\nu_{NH}$) 1701 ($\nu_{C=O}$ triazole) 1670 ($\nu_{C=O}$); $^1$H-NMR (DMSO): δ 2.11(s, 6H, $CH_3$), 2.19 (s, 6H, $CH_3$), 2.37(s, 3H, $CH_3$, Triazolinone), δ 4.19 (t, 2H, $CH_2$, J=4.4Hz), δ 5.22 (t, 2H, $CH_2$, J=4.4Hz), 5.69 (s, 2H, Pyrrole ring CH), 5.75 (s, 2H, Pyrrole ring CH), δ 7.28 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 7.69(d, 2H, Ar-H, *J*= 8.2 Hz), δ 11.33 (br, 1H, NH $D_2O$ exchanged) δ 12.73(s, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{27}H_{29}ClN_{10}O_3$ (576.69): C, 56.20; H, 5.04; N, 22.28%; Found: C, 55.81; H, 4.66; N, 21.90%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(3-methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9e).** Yield 68%. mp. 223-225°C; ir 3284($\nu_{NH}$) 1702 ($\nu_{C=O}$ triazole) 1670($\nu_{C=O}$); $^1$H-NMR (DMSO):δ 2.01-2.09 (s, 12H, $CH_3$), 2.21(s, 3H, $CH_3$), 2.37(s, 3H, $CH_3$, Triazolinone), δ 4.11 (t, 2H, $CH_2$, J=4.4Hz), δ 5.20 (t, 2H, $CH_2$, J=4.4Hz), 5.71 (s, 2H, Pyrrole ring CH), 5.75 (s, 2H, Pyrrole ring CH), δ 7.28 -7.67 (m, 4H, Ar-H), δ 11.35(br, 1H, NH $D_2O$ exchanged) δ 12.59(br, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{28}H_{32}N_{10}O_3$ (556.25): C, 60.42; H, 5.79; N, 25.16%; Found: C, 59.77; H, 5.43; N, 24.85%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(4-methyl)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9f).** Yield 65%. mp. 184-186°C; ir 3280 ($\nu_{NH}$) 1700 ($\nu_{C=O}$ triazole) 1672 ($\nu_{C=O}$); $^1$H-NMR (DMSO): δ 2.01(s, 6H, $CH_3$), 2.10 (s, 6H, $CH_3$), 2.25(s, 3H, $CH_3$), 2.37(s, 3H, $CH_3$, Triazolinone), δ 4.21 (t, 2H, $CH_2$, J=4.4Hz), δ 5.22 (t, 2H, $CH_2$, J=4.4Hz), 5.70 (s, 2H, Pyrrole ring CH), 5.75 (s, 2H, Pyrrole ring CH), δ 7.11 (d, 2H, Ar-H, *J*= 7.8 Hz), δ 7.67 (d, 2H, Ar-H, *J*= 7.8 Hz), δ 11.26(br, 1H, NH $D_2O$ exchanged) δ 12.80(br, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{28}H_{32}N_{10}O_3$ (556.25): C, 60.42; H, 5.79; N, 25.16%; Found: C, 60.14; H, 5.44; N, 24.85%.

***N,N'*-Bis(1*H*-pyrrol-1-yl)-1-[2-(2-(4-methoxy)phenyl-5-methyl-3-oxo-2,4-dihydro-3*H*-1,2,4-triazol-4-yl)ethyl]-1*H*-1,2,3-triazole-4,5-dicarboxamides (9g).** Yield 70%. mp. 211-213°C; ir 3277 ($\nu_{NH}$) 1705 ($\nu_{C=O}$ triazole) 1668 ($\nu_{C=O}$); $^1$H-NMR (DMSO):δ 2.11(s, 6H, $CH_3$), 2.19 (s, 6H, $CH_3$), 2.37(s, 3H, $CH_3$,Triazolinone), 3.73(s, 3H, $OCH_3$), δ 4.19 (t, 2H, $CH_2$, J=4.4Hz), δ 5.22 (t, 2H, $CH_2$, J=4.4Hz), 5.69 (s, 2H, Pyrrole ring CH), 5.75 (s, 2H, Pyrrole ring CH), δ 7.31 (d, 2H, Ar-H, *J*= 8.2 Hz), δ 7.86(d, 2H, Ar-H, *J*= 8.2 Hz), δ 11.20 (br, 1H, NH $D_2O$ exchanged) δ 12.67(br, 1H, NH $D_2O$ exchanged). *Anal.* Calcd. for $C_{28}H_{32}N_{10}O_4$ (572.24): C, 58.74; H, 5.62; N, 24.46%; Found: C, 58.38; H, 5.26; N, 24.10%.

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* Author for correspondence e-mail: bbadami@rediffmail.com

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