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## Efficient TMG catalyzed synthesis of 1,2,3-triazoles

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## ARTICLE INFO

## Article history:

Received 3 March 2013

Accepted after revision 13 May 2013

Available online 5 July 2013

## Keywords:

Azide

Triazole

Tetramethylguanidine

CH-acid

## ABSTRACT

A practical and efficient method for the synthesis of 1,2,3-triazoles via the cycloaddition reaction of azides and CH-acids in the presence of 1,1,3,3-tetramethylguanidine (TMG) in ethanol at 30 °C has been reported. The simple experimental procedure, short reaction times, and good yields are the advantages of the present method.

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## 1. Introduction

1,2,3-Triazoles are very interesting compounds and have received considerable attention as a result of their therapeutic value as cytostatic [1], antiproliferative agents [2], and GABA-antagonists [3]. They are key intermediates in the synthesis of antibiotic [4], antihistaminic agents [5], muscarinic agonists for the treatment of Alzheimer's disease [6], and polyheterocycles with neuroleptic activity [7]. Additionally, triazole derivatives have been widely employed in industry [8–11]. Therefore, numerous methods have been reported for the preparation of 1,2,3-triazoles, including the cyclization of triazenes [12,13], the synthesis of triazoles by Wolff [14], and the cyclization of  $\alpha$ -diazoamides [15]. However, most of these protocols have some disadvantages and require multistep synthetic methods. Thermal Huisgen 1,3-dipolar cycloadditions of azides and alkynes, because of the high activation energy [16,17], are usually very slow and are likely to generate mixtures of regioisomers. Recently, Sharpless [18] and Meldal [19] reported copper(I)-catalyzed Huisgen 1,3-dipolar cycloadditions of azides and alkynes (CuAAC)

under mild conditions for the highly regioselective preparation of 1,4-disubstituted 1,2,3-triazoles in good yields. Notably, the reactions are only suited for terminal alkynes, and this limitation largely restricts the diverse application of this strategy in the preparation of 1,2,3-triazoles. The azide/alkyne [3+2] strategy has shown a broad variety of application prospects in polymeric materials science [20–22]. Very recently, catalytic reaction of azides and active or unactive methylene compounds has proven to be a powerful strategy for the synthesis of a variety of monocyclic and bicyclic 1,2,3-triazole derivatives with different substituents. This triazole formation approach is less developed and only a limited number of catalysts have been reported [23–27]. Thus, the development of a convenient and safe process using new catalysts with high catalytic activity for the preparation of 1,2,3-triazoles is an interesting target for investigation.

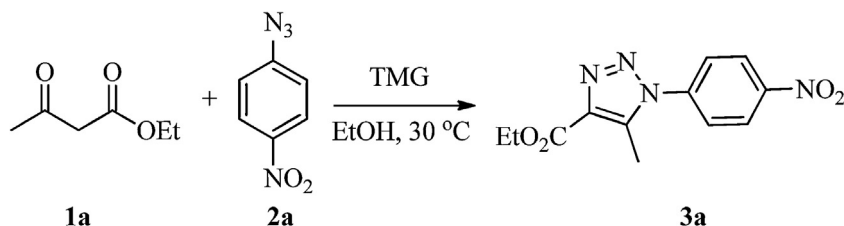
Herein, we would like to report a facile, and practical process for synthesis of 1,2,3-triazoles catalyzed by TMG via a cycloaddition reaction of CH-acids and azides.

## 2. Results and discussion

Our initial experiments were focused on the reaction of ethyl acetoacetate **1a** (1 mmol) and 1-azido-4-nitrobenzene **2a** (1 mmol) as a model reaction in the presence of

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Scheme 1. Synthesis of ethyl 5-methyl-1-(4-nitrophenyl)-riazole-4-carboxylate.

TMG in EtOH at 30 °C (Scheme 1). To study the effect of the amount of catalyst, the reactions were carried out with different amounts of TMG ranging from 10 to 20 mol%. It was found that when increasing the amount of the TMG from 10 to 15, and 20 mol %, the yields increased from 73 to 81 and 82%, respectively. It was found that 15 mol % TMG in EtOH is sufficient to push this reaction forward. More amounts of TMG did not improve the yields. When this reaction was carried out without TMG, the yield of the expected product was trace. To search for the optimal reaction solvent, various solvents, such as EtOH, MeOH, H<sub>2</sub>O, CHCl<sub>3</sub>, and MeCN were screened in the model reaction at 30 °C. It was found that the reaction using EtOH resulted in higher yield after 50 min (Scheme 1).

According to the optimized conditions, a variety of CH-acids **1** and azides **2** were employed under similar circumstances to evaluate the substrate scope of the reaction and 1,2,3-triazoles **3** were obtained in good isolated yields (Table 1). We have shown that these reactions preceded very cleanly under mild reaction conditions at 30 °C and the use of a wide diversity of CH-acids and aryl azides in this reaction makes possible the synthesis of libraries under similar circumstances. However, when this methodology was investigated by the reaction of CH-acids with benzyl azide, the TLC and <sup>1</sup>H NMR spectra of the reactions mixture showed a combination of starting

Table 2

Comparison of efficiency of various catalysts in synthesis of triazoles<sup>a</sup>.

Catalyst	TMG	Proline	Et <sub>3</sub> N	Et <sub>2</sub> NH
Yield (%)	81	< 20	41	35

<sup>a</sup> Ethyl acetoacetate **1a** (1 mmol), 1-azido-4-nitrobenzene **2a** (1 mmol) and catalyst (15 mol%) in EtOH at 30 °C for 50 min.

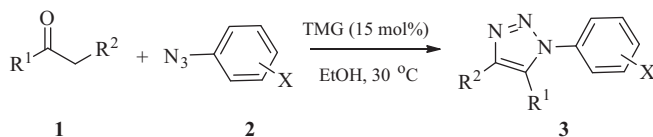
materials and numerous products, the expected product was obtained in only trace amounts.

Table 2 compares the efficiency of TMG with that of other reported catalysts in the synthesis of 1,2,3-triazoles via the reaction of ethyl acetoacetate **1a** and 1-azido-4-nitrobenzene **2a**. It is clear from Table 2 that our method is more efficient for the synthesis of 1,2,3-triazoles derivatives.

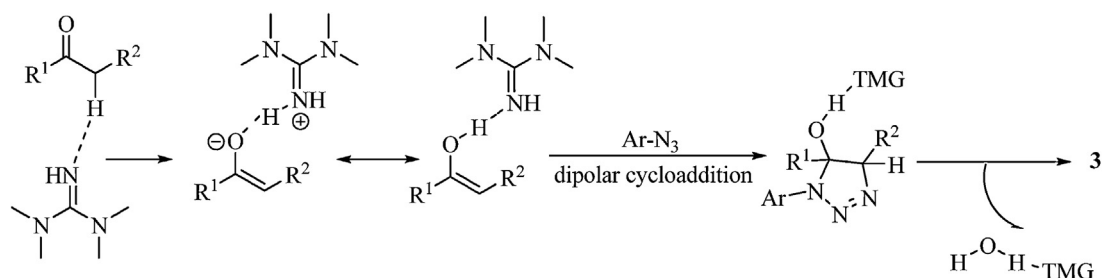
We have not established an exact mechanism for the formation of **3**; however, a reasonable possibility is shown in Scheme 2 [27].

Finally, to further explore the potential of the reaction, we investigated the reaction of cyclic 1,3-diketones **4** with azides **2** and obtained bicyclic or tricyclic triazoles **5** in good isolated yields (Scheme 3).

In conclusion, we have developed a simple and efficient protocol for the synthesis of 1,2,3-triazoles using TMG as an organocatalyst under mild reaction conditions.

Table 1  
Synthesis of 1,2,3-triazoles **3**.

Product <b>3</b>	R <sup>1</sup>	R <sup>2</sup>	X	Time (min)	Yield (%)
<b>a</b>	Me	CO <sub>2</sub> Et	4-NO <sub>2</sub>	50	81
<b>b</b>	Me	CO <sub>2</sub> Me	4-NO <sub>2</sub>	45	77
<b>c</b>	Ph	CN	4-NO <sub>2</sub>	50	70
<b>d</b>	Ph	CO <sub>2</sub> Et	4-NO <sub>2</sub>	120	73
<b>e</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	4-NO <sub>2</sub>	45	77
<b>f</b>	Me	CO <sub>2</sub> Et	3-NO <sub>2</sub>	90	81
<b>g</b>	Me	CO <sub>2</sub> Me	3-NO <sub>2</sub>	90	75
<b>h</b>	Ph	CN	3-NO <sub>2</sub>	90	71
<b>i</b>	Ph	CO <sub>2</sub> Et	3-NO <sub>2</sub>	160	71
<b>j</b>	Me	CO <sub>2</sub> Et	4-Cl	60	80
<b>k</b>	Me	CO <sub>2</sub> Me	4-Cl	70	76
<b>l</b>	Me	CO <sub>2</sub> Et	4-Me	180	80
<b>m</b>	Me	CO <sub>2</sub> Me	4-Me	140	72
<b>n</b>	Me	CO <sub>2</sub> Et	4-MeO	180	68



Scheme 2. Proposed mechanism.

### 3. Experimental

#### 3.1. Materials and techniques

The melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with solutions in  $\text{DMSO}-d_6$ . IR spectra were recorded using a Bomem MB-Series device. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer. The chemicals used in this work were obtained from Fluka and Merck and were used without purification.

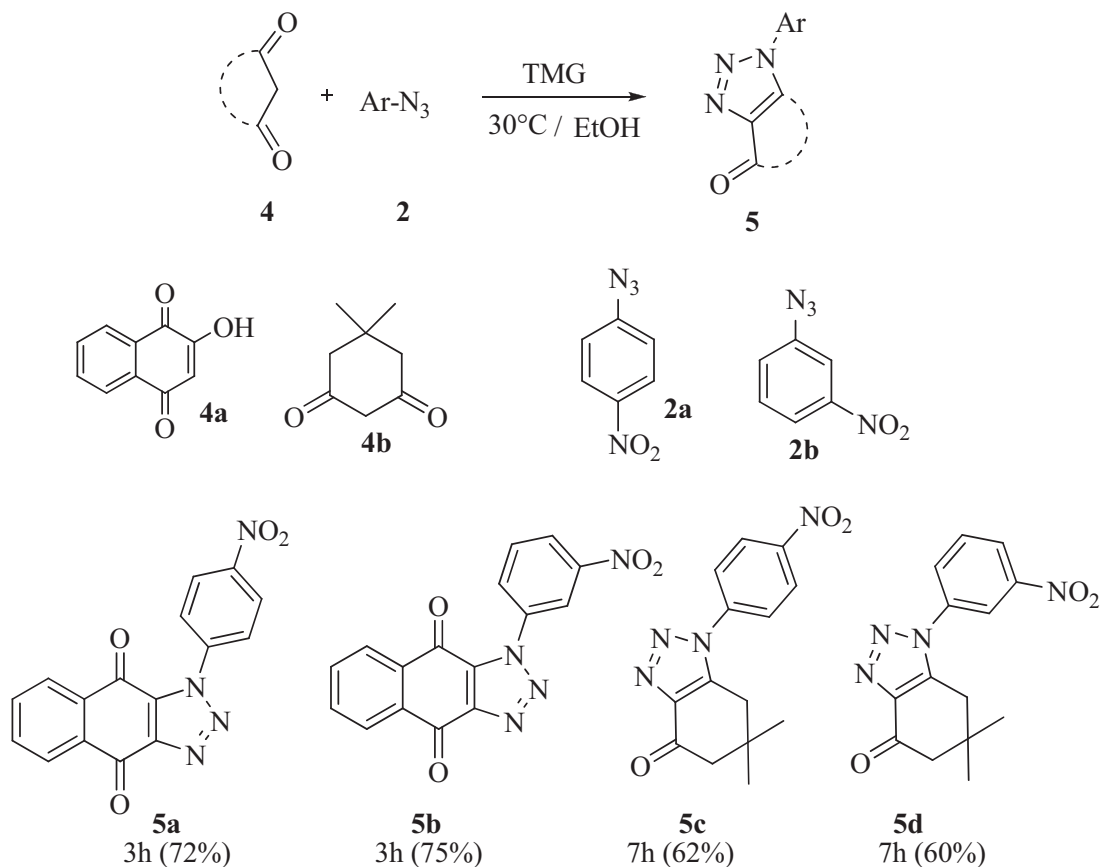
#### 3.2. Typical procedure for the preparation of 1,2,3-triazoles

A mixture of CH-acid (1 mmol), azide (1 mmol) and TMG (15 mol%) in EtOH (5 ml) was stirred for an appropriate time at  $30^\circ\text{C}$ . After completion (TLC), the solvent was removed under reduced pressure. The residue was washed with ether (5 mL) and recrystallized from  $\text{CHCl}_3/n$ -hexane (1:3) to afford the pure product.

#### 3.3. Spectral data

##### 3.3.1. Ethyl 5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (3a)

White powder; yield: 223.76 mg (81%); Mp  $181\text{--}184^\circ\text{C}$ . IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1725, 1592, 1531, 1434.  $^1\text{H}$  NMR



Scheme 3. Reaction of cyclic 1,3-diketones 4 with azides 2.

(300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.43 (3H, t,  $^3J_{\text{HH}}$  = 7.1 Hz, CH<sub>3</sub>), 2.68 (3H, s, CH<sub>3</sub>), 4.45 (2H, q,  $^3J_{\text{HH}}$  = 7.1 Hz, OCH<sub>2</sub>), 7.74 (2H, d,  $^3J_{\text{HH}}$  = 8.9 Hz, H-Ar), 8.45 (2H, d,  $^3J_{\text{HH}}$  = 8.9 Hz, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.2, 14.3, 61.3, 125.2, 125.9, 137.4, 138.8, 140.2, 148.1, 161.3. Anal. calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C, 52.17; H, 4.38; N, 20.28%. Found: C, 52.10; H, 4.32; N, 20.21.

### 3.3.2. Methyl 5-methyl-1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (3b)

White powder; yield: 201.90 mg (77%); Mp 172–175 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1732, 1617, 1527, 1501, 1450. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.70 (3H, s, CH<sub>3</sub>), 4.01 (3H, s, OCH<sub>3</sub>), 7.75 (2H, d,  $^3J_{\text{HH}}$  = 8.0 Hz, H-Ar), 8.47 (2H, d,  $^3J_{\text{HH}}$  = 8.0 Hz, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.2, 52.5, 125.2, 125.8, 137.2, 138.9, 140.1, 148.2, 161.7. Anal. calcd for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>: C, 50.38; H, 3.84; N, 21.37%. Found: C, 50.29; H, 3.89; N, 21.29.

### 3.3.3. 1-(4-Nitrophenyl)-5-phenyl-1H-1,2,3-triazole-4-carbonitrile (3c)

White powder; yield: 203.88 mg (70%); Mp 162–165 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 2238, 1597, 1533, 1495. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 7.35–7.48 (2H, m, H-Ar), 7.49–7.61 (4H, m, H-Ar), 8.33–8.36 (2H, d,  $^3J_{\text{HH}}$  = 8.8 Hz, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 111.4, 121.3, 122.5, 125.2, 125.7, 128.9, 129.8, 131.7, 139.8, 143.4, 148.2. Anal. calcd for C<sub>15</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 61.85; H, 3.11; N, 24.04%. Found: C, 61.95; H, 3.19; N, 23.98.

### 3.3.4. Ethyl 1-(4-nitrophenyl)-5-phenyl-1H-1,2,3-triazole-4-carboxylate (3d)

White powder; yield: 246.97 mg (73%); Mp 130–133 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1712, 1528, 1347, 1224, 1105. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.58 (3H, bs, CH<sub>3</sub>), 5.41 (2H, bs, OCH<sub>2</sub>), 7.37–7.50 (5H, m, H-Ar), 7.98 (2H, d,  $^3J_{\text{HH}}$  = 8.2 Hz, H-Ar), 8.48 (2H, d,  $^3J_{\text{HH}}$  = 8.2 Hz, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.3, 66.5, 125.5, 127.0, 128.7, 128.8, 129.0, 136.2, 136.4, 140.3, 140.6, 148.3, 161.2. Anal. calcd for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.35; H, 4.17; N, 16.56%. Found: 60.28; H, 4.12; N, 16.49.

### 3.3.5. Ethyl 1,5-bis(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (3e)

White powder; yield: 295.15 mg (77%); Mp 159–162 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1724, 1525, 1347, 1222, 1075. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.16 (3H, t,  $^3J_{\text{HH}}$  = 6.9 Hz, CH<sub>3</sub>), 4.24 (2H, q,  $^3J_{\text{HH}}$  = 6.9 Hz, OCH<sub>2</sub>), 7.69 (2H, d,  $^3J_{\text{HH}}$  = 8.5 Hz, H-Ar), 7.75 (2H, d,  $^3J_{\text{HH}}$  = 8.2 Hz, H-Ar), 8.28 (2H, d,  $^3J_{\text{HH}}$  = 8.2 Hz, H-Ar), 8.34 (2H, d,  $^3J_{\text{HH}}$  = 8.5 Hz, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 14.2, 61.4, 123.7, 125.4, 127.5, 132.4, 132.6, 137.5, 139.9, 140.1, 148.2, 148.7, 160.3. Anal. calcd for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>6</sub>: 53.27; H, 3.42; N, 18.27%. Found: C, 53.14; H, 3.50; N, 18.35.

### 3.3.6. Ethyl 5-methyl-1-(3-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (3f)

White powder; yield: 218.23 mg (81%); Mp 144–146 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1724, 1537, 1425. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.34 (3H, t,  $^3J_{\text{HH}}$  = 7.4 Hz, CH<sub>3</sub>), 2.56 (3H, s, CH<sub>3</sub>), 4.37 (2H, q,  $^3J_{\text{HH}}$  = 7.4 Hz, OCH<sub>2</sub>), 7.95 (1H, t,

$^3J_{\text{HH}}$  = 7.5 Hz, H-Ar), 8.13 (1H, d,  $^3J_{\text{HH}}$  = 7.9 Hz, H-Ar), 8.46–8.52 (2H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.1, 14.6, 61.0, 112.4, 124.3, 126.8, 137.6, 138.4, 138.8, 140.6, 147.7, 162.1. Anal. calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C, 52.17; H, 4.38; N, 20.28%. Found: C, 52.27; H, 4.31; N, 20.34.

### 3.3.7. Methyl 5-methyl-1-(3-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (3g)

White powder; yield: 196.55 mg (75%); Mp 134–135 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1725, 1537, 1527, 1434. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.55 (3H, s, CH<sub>3</sub>), 4.35 (3H, s, OCH<sub>3</sub>), 7.94 (1H, t,  $^3J_{\text{HH}}$  = 7.3 Hz, H-Ar), 8.11 (1H, d,  $^3J_{\text{HH}}$  = 7.7 Hz, H-Ar), 8.46–8.52 (2H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 9.9, 52.3, 112.7, 124.0, 126.8, 137.9, 138.1, 138.7, 140.9, 147.8, 161.8. Anal. calcd for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>: C, 50.38; H, 3.84; N, 21.37%. Found: C, 50.26; H, 3.75; N, 21.44.

### 3.3.8. 1-(3-Nitrophenyl)-5-phenyl-1H-1,2,3-triazole-4-carbonitrile (3h)

White powder; yield: 206.61 mg (71%); Mp 150–152 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 2235, 1604, 1535, 1499. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 7.46–7.57 (5H, m, H-Ar), 7.81–7.94 (2H, m, H-Ar), 8.42–8.44 (2H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 110.9, 121.7, 122.3, 125.2, 126.1, 126.4, 128.1, 130.2, 130.4, 131.8, 139.5, 143.8, 148.0. Anal. calcd for C<sub>15</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 61.85; H, 3.11; N, 24.04%. Found: C, 61.28; H, 3.06; N, 24.10.

### 3.3.9. Ethyl 1-(3-nitrophenyl)-5-phenyl-1H-1,2,3-triazole-4-carboxylate (3i)

White powder; yield: 239.98 mg (71%); Mp 160–162 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1729, 1527, 1347, 1217, 1069. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.16 (3H, t,  $^3J_{\text{HH}}$  = 6.9 Hz, CH<sub>3</sub>), 4.24 (2H, q,  $^3J_{\text{HH}}$  = 6.9 Hz, OCH<sub>2</sub>), 7.75–7.85 (5H, m, H-Ar), 8.25–8.28 (2H, m, H-Ar), 8.35–8.39 (2H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 14.2, 61.4, 121.6, 123.6, 125.4, 130.2, 131.6, 132.4, 132.6, 136.0, 137.3, 140.1, 148.3, 148.6, 160.3. Anal. calcd for C<sub>17</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.35; H, 4.17; N, 16.56%. Found: C, 60.26; H, 4.12; N, 16.49.

### 3.3.10. Ethyl 1-(4-chlorophenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate (3j)

White powder; yield: 212.0 mg (80%); Mp 155–158 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1715, 1566, 1498, 1421, 1244, 1106. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.36 (3H, t,  $^3J_{\text{HH}}$  = 7.0 Hz, CH<sub>3</sub>), 2.52 (3H, s, CH<sub>3</sub>), 4.38 (2H, q,  $^3J_{\text{HH}}$  = 7.0 Hz, OCH<sub>2</sub>), 7.61–7.70 (4H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.1, 14.6, 60.95, 127.7, 130.2, 134.3, 135.3, 136.3, 139.9, 161.4. Anal. calcd for C<sub>12</sub>H<sub>12</sub>ClN<sub>3</sub>O<sub>2</sub>: C, 54.25; H, 4.55; N, 15.82%. Found: C, 54.34; H, 4.61; N, 15.77.

### 3.3.11. Methyl 1-(4-chlorophenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate (3k)

White powder; yield: 190.76 mg (76%); Mp 171–173 °C. IR (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1724, 1566, 1437, 1248, 1110. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.50 (3H, s, CH<sub>3</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 7.63–7.72 (4H, m, H-Ar). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.1, 52.2, 127.7, 130.2, 134.3, 135.2, 136.1, 140.0, 161.9. Anal. calcd for C<sub>11</sub>H<sub>10</sub>ClN<sub>3</sub>O<sub>2</sub>: C, 52.50; H, 4.01; N, 16.70%. Found: C, 52.56; H, 3.97; N, 16.64.

### 3.3.12. Ethyl 5-methyl-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3l)

White powder; yield: 196.0 mg (80%); Mp 136–138 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1711, 1515, 1429, 1239, 1107.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.33 (3H, t,  $^3J_{\text{HH}}$  = 7.0 Hz, CH<sub>3</sub>), 2.42 (3H, s, CH<sub>3</sub>), 2.50 (3H, s, CH<sub>3</sub>), 4.35 (2H, q,  $^3J_{\text{HH}}$  = 7.0 Hz, OCH<sub>2</sub>), 7.44 (2H, d,  $^3J_{\text{HH}}$  = 8.1 Hz, H-Ar), 7.50 (2H, d,  $^3J_{\text{HH}}$  = 8.1 Hz, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 10.1, 14.6, 21.21, 60.8, 125.7, 130.5, 133.1, 136.1, 139.7, 140.4, 161.5. Anal. calcd for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 63.66; H, 6.16; N, 17.13%. Found: C, 63.60; H, 6.23; N, 17.20.

### 3.3.13. Methyl 5-methyl-1-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3m)

White powder; yield: 166.32 mg (72%); Mp 133–135 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1709, 1523, 1421, 1248.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.40 (3H, s, CH<sub>3</sub>), 2.53 (3H, s, CH<sub>3</sub>), 4.31 (3H, s, OCH<sub>3</sub>), 7.37 (2H, d,  $^3J_{\text{HH}}$  = 7.8 Hz, H-Ar), 7.51 (2H, d,  $^3J_{\text{HH}}$  = 7.8 Hz, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 14.1, 21.30, 61.3, 125.7, 130.2, 133.4, 135.7, 139.6, 140.7, 161.0. Anal. calcd for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 62.33; H, 5.67; N, 18.17%. Found: C, 62.25; H, 5.72; N, 18.11.

### 3.3.14. Ethyl 1-(4-methoxyphenyl)-5-methyl-1H-1,2,3-triazole-4-carboxylate (3n)

White powder; yield: 177.48 mg (68%); Mp 137–139 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1712, 1513, 1248.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.46 (3H, t,  $^3J_{\text{HH}}$  = 7.2 Hz, CH<sub>3</sub>), 2.56 (3H, s, CH<sub>3</sub>), 3.89 (3H, s, OCH<sub>3</sub>), 4.47 (2H, q,  $^3J_{\text{HH}}$  = 7.2 Hz, OCH<sub>2</sub>), 7.06 (2H, d,  $^3J_{\text{HH}}$  = 7.9 Hz, H-Ar), 7.35 (2H, d,  $^3J_{\text{HH}}$  = 7.9 Hz, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 9.9, 14.7, 54.1, 60.9, 120.4, 129.5, 134.1, 135.6, 140.0, 143.2, 161.1. Anal. calcd for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 59.76; H, 5.79; N, 16.08%. Found: C, 59.69; H, 5.74; N, 16.13.

### 3.3.15. 1-(4-Nitrophenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (5a)

White powder; yield: 230.40 mg (72%); Mp 264–266 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 2917, 1658, 1561, 1507.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 7.94–8.02 (2H, m, H-Ar), 8.15 (2H, d,  $^3J_{\text{HH}}$  = 8.4 Hz, H-Ar), 8.25–8.27 (2H, m, H-Ar), 8.53 (2H, d,  $^3J_{\text{HH}}$  = 8.4 Hz, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 124.7, 125.1, 127.2, 127.4, 127.5, 133.0, 133.7, 135.3, 135.6, 140.2, 145.4, 148.8, 174.4, 177.4. Anal. calcd for C<sub>16</sub>H<sub>8</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.00; H, 2.52; N, 17.49%. Found: C, 59.95; H, 2.47; N, 17.41.

### 3.3.16. 1-(3-Nitrophenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (5b)

Orange powder; yield: 240.0 mg (75%); Mp 238–240 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 2917, 1658, 1561, 1507.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 7.97–8.15 (4H, m, H-Ar), 8.25–8.28 (2H, m, H-Ar), 8.55 (1H, bs, H-Ar), 8.78 (1H, bs, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 121.2, 125.8, 127.4, 127.6, 131.4, 132.3, 132.4, 133.1, 133.4, 135.3, 135.6, 136.2, 147.5, 148.2, 174.5, 177.4. Anal. calcd for C<sub>16</sub>H<sub>8</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.00; H, 2.52; N, 17.49%. Found: C, 59.91; H, 2.59; N, 17.43.

### 3.3.17. 6,6-Dimethyl-1-(4-nitrophenyl)-6,7-dihydro-1H-benzo[d][1,2,3]triazol-4(5H)-one (5c)

Cream powder; yield: 177.32 mg (62%); Mp 267–269 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1694, 1598, 1513.  $^1\text{H}$  NMR

(300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.06 (6H, s, 2 CH<sub>3</sub>), 2.52 (2H, s, CH<sub>2</sub>), 3.10 (2H, s, CH<sub>2</sub>), 8.04 (2H, d,  $^3J_{\text{HH}}$  = 8.5 Hz, H-Ar), 8.49 (2H, d,  $^3J_{\text{HH}}$  = 8.5 Hz, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 28.0, 34.6, 36.0, 52.2, 124.9, 125.8, 140.4, 142.1, 145.6, 147.9, 190.1. Anal. calcd for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 58.73; H, 4.93; N, 19.57%. Found: C, 58.65; H, 4.85; N, 19.52.

### 3.3.18. 6,6-Dimethyl-1-(3-nitrophenyl)-6,7-dihydro-1H-benzo[d][1,2,3]triazol-4(5H)-one (5d)

Cream powder; yield: 171.60 mg (60%); Mp 204–206 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1694, 1598, 1513.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 1.06 (6H, s, 2 CH<sub>3</sub>), 2.50 (2H, overlap with solvent, CH<sub>2</sub>), 3.06 (2H, s, CH<sub>2</sub>), 7.94–7.99 (1H, m, H-Ar), 8.18–8.21 (1H, m, H-Ar), 8.44–8.47 (1H, d, H-Ar), 8.53 (1H, s, H-Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  = 28.1, 34.2, 36.0, 52.3, 119.2, 124.8, 130.4, 132.0, 136.3, 143.3, 145.8, 148.8, 190.2. Anal. calcd for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 58.73; H, 4.93; N, 19.57%. Found: C, 58.83; H, 4.99; N, 19.50.

## Acknowledgements

We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University.

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