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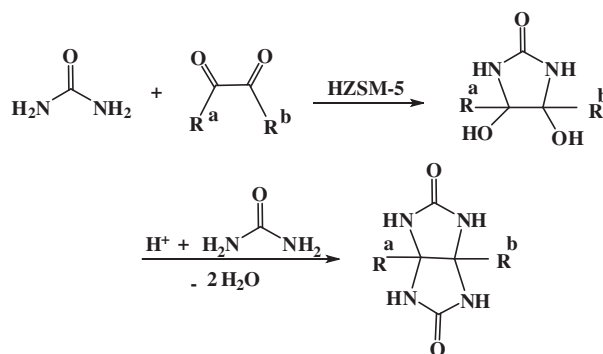
## Synthesis of the glycoluril derivatives by the HZSM-5 nanozeolite as a catalyst

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In this work, we used nano-sized protonated Zeolite Socony Mobil-5 (HZSM-5) zeolite as a mild and efficient catalyst for the synthesis of tetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)dione (=glycoluril) (**1**) and its derivatives (**2–6**) through reaction between urea and dicarbonyl compound. The yield of the reactions and products were determined and discussed. The Zeolite Socony Mobil-5 (ZSM-5) nanozeolite has more reactivity in its H form. HZSM-5 was prepared by ion exchange of ZSM-5 nanozeolite with NH<sub>4</sub>Cl, followed by drying and calcination.



**Keywords:** glycoluril; nanozeolite; HZSM-5; ion exchange

### 1. Introduction

The glycolurils have been received a great deal of attention due to their practical applications, such as fertilizers (*1*), polymer cross-linking (*2, 3*), explosives (*4*), stabilizers of organic compounds against photo-degradation (*5*), combinatorial chemistry (*6*), radio iodination agents for biomolecules, sychotropic agents, catalysts, bleaching activators (*7*), and the monomer in supramolecular chemistry (*8*). The synthesis of glycolurils *via* condensation of benzils with urea catalyzed by classical acid, such as H<sub>2</sub>SO<sub>4</sub>, HCl, and CF<sub>3</sub>COOH, has been reported (*9–11*). However, these reported methods suffer from drawbacks such as longer reaction times, harsh conditions, and corruption. Heterogeneous catalysts dominate the industrial outlook mainly due to the facility of recovery and reusability. Nanocrystalline zeolites have been used as heterogeneous catalysts (*12*). Zeolite Socony Mobil-5 (ZSM-5) has firstly been prepared by Argauer and Landolt in 1972

(*13*). ZSM-5 has a medium pore channel (5.5 Å) with three-dimensional channels defined by 10-membered rings. ZSM-5 has been used as an effective catalyst due to its unique channel structure, thermal stability, acidity, and shape-selective property (*14–16*). The nano-sized zeolite has been prepared according to a modified hydrothermal procedure which reported previously by Miller for micro-sized ZSM-5 zeolite (*17*).

As a continuous of our work on glycoluril derivatives (*18*), and because the particular attention has been turned to cucurbiturils (*19*) (CB[n]) which are intriguing macrocyclic compounds, whose skeleton is constituted by glycolurils ring moieties (*20–24*), we report a novel method to increase the yield of glycoluril (**1**) and its derivatives (**2–6**) (Figure 1 and Table 1). These reactions are carried out in a higher yield, shorter reaction time, and mild conditions in the presence of nanozeolites as a catalyst. It is shown that protonated Zeolite Socony Mobil-5 (HZSM-5) affords a significant improvement for the synthesis of these compounds.

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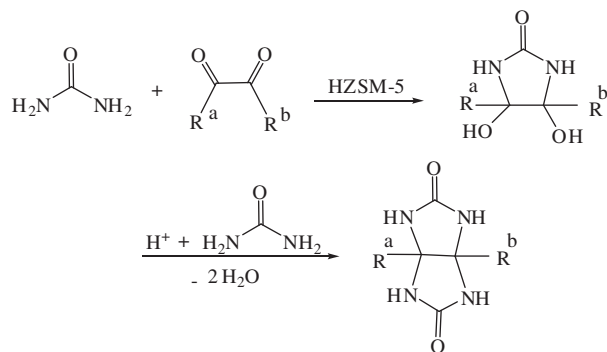


Figure 1. Reaction of the preparation of the glycoluril and derivatives, **1–4** by using HZSM-5.

The present work deals with the preparation and characterization of nano-sized zeolite ZSM-5 and uses the ZSM-5 nano-zeolite in the synthesis of glycoluril derivatives, **1–6**.

## 2. Results and discussion

The glycoluril and several substituted derivatives were already used as starting materials for the preparation of molecular clip based on glycoluril. The first step of the synthetic route is the cyclization reaction of urea and glyoxal or diketones in acidic solution. [Table 1](#)

summarizes the chemical structures and indices of the synthesized glycoluril derivatives. The glycolurils carry the aliphatic groups  $R_a$  and  $R_b$  and are accessible in good yields at room temperature by increasing the reaction time to values above 24 h. The bulky substituents such as  $R_a$  and  $R_b$  cause higher steric effects and increase the activation energies for the cyclocondensation. Thus, the diphenyl glycoluril **3** and dimethoxyphenyl glycoluril, **4**, can be synthesized only by heating the mixture and collecting the reaction water in Dean and Stark trap to shift the equilibrium to the product side.

The glycoluril and its derivatives (**1–6**) were synthesized in the presence of nanozeolite ZSM-5 as a catalyst. Different amounts of nanozeolite were used in the synthesis of **1–6** because they increase the yields of the reactions. The products were obtained without any further purification with a quantitative yield. The products were crystallized in a mixture of ethanol and water. The structures of the products were deduced from their infrared (IR),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analyses. For example, the  $^1\text{H}$  NMR spectrum of **4** exhibited distinct signals arising from  $\text{CH}_3\text{O}$  ( $\delta_{\text{H}} = 3.61$ ),  $-\text{NH}$  ( $\delta_{\text{H}} = 5.65$ ), and aromatic  $-\text{CH}$  ( $\delta_{\text{H}} = 7.05\text{--}7.67$ ). The  $^{13}\text{C}$  NMR spectrum of **4** indicated several distinct resonances arising  $\text{CH}_3\text{O}$  ( $\delta_{\text{C}} = 55.7$ ),  $\text{CNH}$  ( $\delta_{\text{C}} = 71.14$ ) aromatic carbons

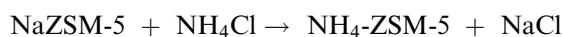
Table 1. The molecular structures of glycoluril **1** and its derivatives, **2–6**.

Substance No.	$R^a$	$R^b$
<b>1</b>	H	H
<b>2</b>	$^{11}\text{H}_3\text{C}$	$^9\text{CH}_2\text{CH}_3$
<b>3</b>		
<b>4</b>		
<b>5</b>	$\text{CH}_3$	$\text{CH}_3$
<b>6</b>	$\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_3$

Table 2. The yields of **1** and **2** during reaction according to the used catalyst.

Entry number	Used catalyst	Amount of used catalyst	Yield of <b>1</b> (%)	Yield of <b>2</b> (%)
1	HCl&HZSM-5	0.04 mL to 0.1 g	65	76
2	HCl	0.04 mL	50	60
3	HZSM-5	0.1 g	30	36
4	HCl&HX	0.04 mL to 0.5 g	25	30
5	HX	0.5 g	10	10

( $\delta_C = 111.81\text{--}125.19$ ), and CO of amide ( $\delta_C = 151.69$ ). The ZSM-5 nanozeolite has more reactivity in its H form. HZSM-5 was prepared by ZSM-5 nanozeolite ion exchange with  $\text{NH}_4\text{Cl}$ , followed by drying and calcinations.  $\text{Na}^+$  in ZSM-5 was replaced with  $\text{NH}_4^+$  by impregnating NaZSM-5 in the solution of  $\text{NH}_4\text{Cl}$  solution:



The syntheses of **1–6** were carried out by using the zeolites ZSM-5, HZSM-5, and nanozeolite ZSM-5 with HCl. The yields of catalysts are presented in Tables 2 and 3 which indicate the effect of reaction time and a type of catalyst. We conclude that the yield of the reaction increases when the time of the reaction reaches 72 h. The yield of the reaction also increases when a zeolite was used. However, the yield of the reaction is the largest when the nanozeolite ZSM-5 was applied. Moreover, the yield of the reaction is larger by using HZSM-5 with respect to ZSM-5. It is seemed that these reactions were occurred in the surface of the nanozeolite or zeolite which increased the yield of these reactions. It can be seen that the ease of work-up and the efficiency of catalyst make

Table 3. The yields of **1** and **2** accordance to the used catalyst and time of reaction.

Reaction time (h)	Used catalyst	Yield of <b>1</b> (%)	Yield of <b>2</b> (%)
24	HCl&HZSM-5	40	50
24	HZSM-5	10	25
48	HCl&HZSM-5	60	76
48	HZSM-5	18	30
72	HCl&HZSM-5	65	76
72	HZSM-5	30	36
96	HCl&HZSM-5	65	76
96	HZSM-5	30	36

HZSM-5 a catalyst in this synthetic reaction. In our mind, it could be attributed to the well proton delivering of HZSM-5 in comparison with the other used catalysts in this work.

### 3. Experimental

#### 3.1. Materials and methods

All solvents were distilled using the standard procedures. All chemicals were commercial materials used without further purification.

##### 3.1.1. Synthesis of ZSM-5

Nano-sized zeolite ZSM-5 was prepared according to a modified hydrothermal procedure which reported previously by Miller for micro-sized zeolite ZSM-5 (17). Kaolin was heated at  $600^\circ\text{C}$  by which the dehydrated kaolin was obtained. To synthesize ZSM-5, 5 g of silicic acid was added to different amounts (1.0, 0.5, and 0.25 g) of *meta*-kaolin (70.05%  $\text{SiO}_2$  and 18.44%  $\text{Al}_2\text{O}_3$ ). Then, 1.6 ml of tetra-*n*-propylammonium hydroxide (TPAOH) and 20-ml distilled water were mixed for 1 h in a mixer. A solution of 0.42 g  $\text{H}_3\text{BO}_3$  in 2.5-ml water was then added to the above mixture along with a NaOH solution (0.33 g in 2.5-ml water). The mixture was placed in a stainless steel reactor with internal Teflon vessel and heated at autogenous pressure at different temperatures. Finally, it was calcined in air at  $500^\circ\text{C}$  for 8 h (yield 76%).

##### 3.1.2. ZSM-5 characterization

The X-ray diffraction (XRD) patterns were obtained through D 500 Siemens X-ray diffractometer using monochromatic Cu  $\text{K}\alpha$  radiation (30–40 kV and 40–50 mA), and the relative crystallinity of ZSM-5 was calculated based on the intensity of the peaks of  $2\theta = 22\text{--}25$ . Figure 2 shows the XRD patterns of the series ZSM-5 nanozeolite. The XRD pattern in Figure 2 confirms its highly crystallized for ZSM-5 nanozeolite.

The morphology and crystalline size of the samples were determined under a transmission electron microscope (TEM) Philips CM 200 FEG (Field

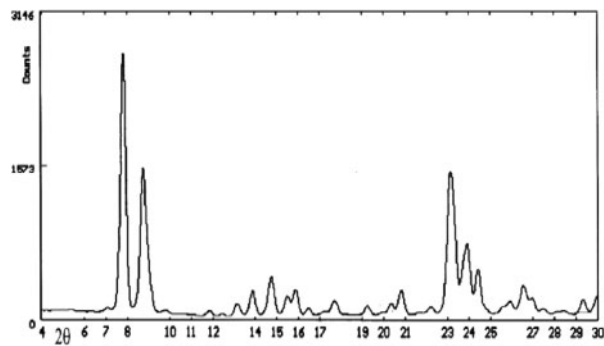


Figure 2. The XRD pattern of ZSM-5 nanozeolite.

Emission gun) and scanning electron microscope (SEM, LEO 440i) using samples coated with Au film. Elemental analysis was carried out using link, ISIS-300, and Oxford EDS (energy dispersion spectroscopy) detector (Figures 3 and 4a and b). TEM images (Figure 3a and b) clearly exhibit that the obtained ZSM-5 nanozeolites are aggregates of primary units. Significantly, it is interesting that all of the crystal plane strings go throughout the whole particles, suggesting the high orientation and intergrowth of adjacent primary units. This fact can also be observed in the crystallinity of other zeolites. SEM image of the resulting ZSM-5 nanozeolite is shown in Figure 4. It can be seen that it possesses a uniform nanosize.

The Fourier transform infrared (FT-IR) spectra were recorded using Bruker Model Tensor 27 equipment. Calculation of the degree of the crystallinity was carried out using the IR data as follows: degree of % crystallinity = peak area at 542/peak area at 450  $\text{cm}^{-1}$  (Figure 5). As shown in Figure 5, the bands in the region of 450  $\text{cm}^{-1}$  are characteristic bands of MFI structure, which derive from the bending vibrations of 4-, 5-, and 6-membered rings in the zeolite. The bands at

780 and 1100  $\text{cm}^{-1}$  can be assigned to symmetric and asymmetric stretching vibrations of Si–O–Si bonds in ZSM-5, respectively.

### 3.1.3. HZSM-5 preparation

HZSM-5 was prepared by ion exchange of NaZSM-5 with  $\text{NH}_4\text{Cl}$ .  $\text{Na}^+$  in NaZSM-5 was replaced with  $\text{NH}_4^+$  by impregnating NaZSM-5 in the solution of 1 mol/l  $\text{NH}_4\text{Cl}$  solution at 363 K for 2 h. The exchange procedure was repeated for three times using fresh  $\text{NH}_4\text{Cl}$  solution to ensure a complete exchange of  $\text{Na}^+$  cations. Then, it was washed by distilled water, dried at 393 K, and calcined at 773 K for 5 h to decompose  $\text{NH}_4^+$  to  $\text{H}^+$  and to form the acidic HZSM-5 zeolite.

### 3.1.4. Glycolurils synthesis

Glyoxal (40% in water), 2,3-pentanedione (tech. 97%), ammonium chloride, urea, benzil, 4,4'-dimethoxybenzyl were all purchased from Fluka Chemie AG, Buchs, Switzerland and were used without further purification. Hydrochloric acid (puriss. 32%), trifluoroacetic acid (purum >98%), toluene (puriss.), ethanol (puriss.), and dimethylsulphoxide (DMSO, purum) were all used from Fluka. Hexadeuterodimethylsulphoxide (puriss. >99.5%) from Fluka was used as a solvent for the recording of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The resonances of hexadeuterodimethylsulphoxide were used as lock signals.  $^1\text{H}$  and  $^{13}\text{C}$  resonance experiments were carried out using Bruker Avance DRX 500 (Bruker Analytik, Rheinstetten, Germany). The elemental analyses were performed with a CHNS 932 elemental analyser (Leco Instrumente GmbH, Mönchengladbach, Germany). The thin layer chromatography (TLC) and NMR methods were used to monitor the reactions process. The TLC and NMR technique indicated that there were no side products.

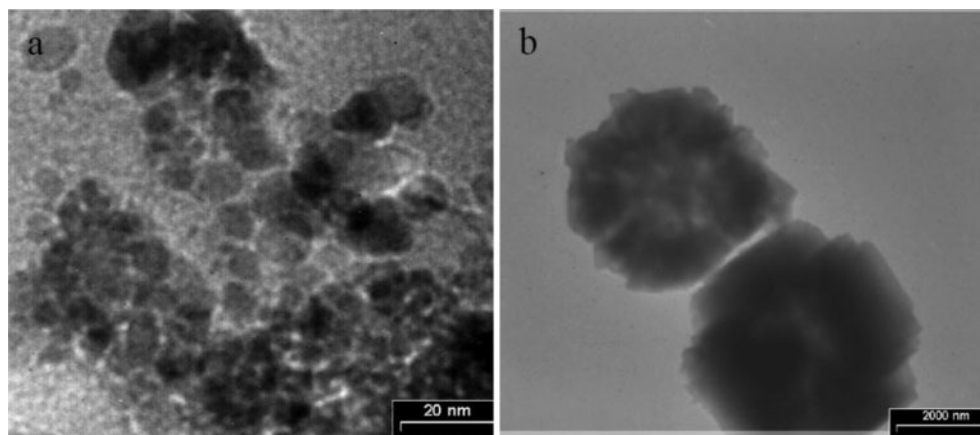


Figure 3. (a) The TEM image of ZSM-5 zeolite and (b) the TEM image of some well-grown ZSM-5 crystals.

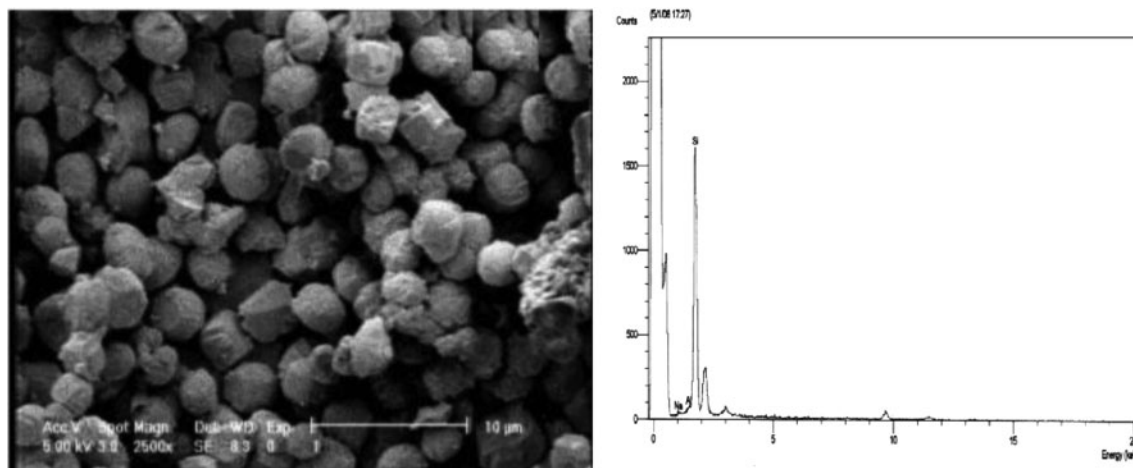


Figure 4. (a) The SEM image of ZSM-5 nano zeolite and (b) the EDX pattern of ZSM-5 nanozeolite.

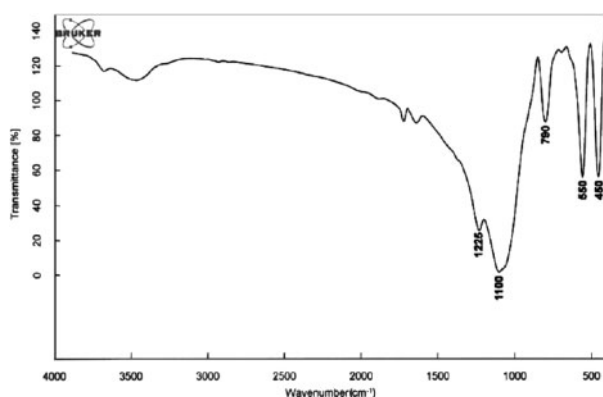


Figure 5. FT-IR spectra of ZSM-5 nanozeolite.

The melting points were measured on Electrothermal 9100 apparatus and were uncorrected. IR spectra were measured on Perkin-Elmer RXI FT-IR spectrometer. The chemical structures of the glycoluril derivatives and their atom indices and substituents  $R_a$  and  $R_b$  are given in Table 1.

### 3.1.5. Reusability of the catalyst

The recycling potential of HZSM-5 nanozeolite catalyst was studied by coupling urea and glyoxal in five consecutive cycles. The HZSM-5 nanozeolite could be recycled and reused by separation from the mixture through centrifugation, frequent washing with EtOH, and then drying under vacuum. The results show that the yield of relative product was only slightly reduced after five runs (Table 4).

**3.1.5.1. Tetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)dione (= glycoluril) (1).** Urea (0.5 mol), 0.15 mol of glyoxal, and 150 ml of water were mixed at 20°C.

Table 4. Development of the yield after several recycling cycles of the catalyst.

Recycle times	Yield (%)
1	56
2	54
3	52
4	50
5	50

HZSM-5 (0.2 g) was added. The solution was stirred for 72 h at room temperature. The precipitate was filtered, washed three times with 20 ml of water and twice with 20 ml of ethanol, dried in vacuum, and recrystallized from water.

Yield: 56%. M.p 337 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1684, 3201.

$^1\text{H}$  NMR (500 MHz, D6-DMSO)  $\delta$  (ppm): 5.2 (s, 2H,  $\text{H}_{3a,6a}$ ), 7.1 (s, 4 H,  $\text{H}_{1,3,4,6}$ ).  $^{13}\text{C}$  NMR (125 MHz, D6-DMSO)  $\delta$  (ppm): 64.5 ( $\text{C}_{3a,6a}$ ), 161.2 ( $\text{C}_{2,5}$ ). Anal. calc. for  $\text{C}_4\text{H}_6\text{N}_4\text{O}_2$ : C, 33.81; H, 4.26; N, 39.42. Found: C, 34.07; H, 4.25; N, 39.26.

**3.1.5.2. 3a-Ethyl-6a-methyltetrahydroimidazo[4,5-d]imidazole-2,5(1H, 3H)dione (=3a-ethyl-6a-methylglycoluril) (2).** Urea (0.5 mol), 0.15 mol of 2,3-pentanedione, and 150 ml of water were mixed at 20°C and then 0.2 g of HZSM-5 was added. The solution was stirred for 72 h at room temperature. The precipitate was filtered, washed three times with 20 ml of water and twice with 20 ml of ethanol, dried in vacuum, and recrystallized from water.

Yield: 67%, M.p. 331°C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1674, 3255.



$^1\text{H}$  NMR (500 MHz, D<sub>6</sub>-DMSO)  $\pm$  (ppm): 0.9 (t, 3H, J D 7:4 Hz, H<sub>10</sub>), 1.3 (s, 3H, H<sub>11</sub>), 1.6 (q, 2H, J D 7:4 Hz, H<sub>9</sub>), 7.1 (s, 2H, H<sub>1,6</sub>), 7.2 (s, 2H, H<sub>3,4</sub>).  $^{13}\text{C}$  NMR (125 MHz, D<sub>6</sub>-DMSO)  $\pm$  (ppm): 7.7 (C<sub>10</sub>), 21.5 (C<sub>11</sub>), 28.1 (C<sub>9</sub>), 77.8 (C<sub>3a,6a</sub>), 159.7 (C<sub>2,5</sub>). Anal. calc. for C<sub>7</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C, 45.64; H, 6.57; N, 30.42. Found: C, 45.36; H, 6.28; N, 29.97.

**3.1.5.3. 3a,6a-diphenyltetrahydroimidazo[4,5-d]imidazole-2,5(1H, 3H)dione (=3a,6a-diphenyl-glycoluril) (3).** Urea (3.0 g, 50 mol), benzil (5.26 g, 25 mmol), and HZSM-5 (0.2 g) were heated in dry toluene (100 ml) to reflux using Dean and Stark apparatus for 4 h. After cooling, the reaction solution was kept at 0°C overnight. The resulting precipitate was collected by filtration, washed with water and acetone, and then dried under vacuum.

Yield: 71%, M.p. 375–378°C; IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 529, 838, 1182, 1258, 1515, 1687, 3234.

$^1\text{H}$  NMR (500 MHz, D<sub>6</sub>-DMSO)  $\pm$  (ppm): 7.0 (m, 10H, H<sub>10–14,16–20</sub>), 7.8 (s, 4H, H<sub>1,3,4,6</sub>).  $^{13}\text{C}$  NMR (125 MHz, D<sub>6</sub>-DMSO)  $\pm$  (ppm): 81.7 (C<sub>3a,6a</sub>), 126.9 (C<sub>11,13,17,19</sub>), 127.3 (C<sub>9,15</sub>), 127.7 (C<sub>10,14,16,20</sub>), 138.2 (C<sub>18,12</sub>), 160.6 (C<sub>2,5</sub>). Anal. calc. for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 65.30; H, 4.79; N, 19.04. Found: C, 63.81; H, 4.90; N, 18.30.

**3.1.5.4. 3a,6a-dimethoxyphenyltetrahydroimidazo[4,5-d]imidazole-2,5(1H, 3H)dione (=3a,6a-dimethoxyphenyl-glycoluril) (4).** Urea (3.0 g, 50 mol) 4,4'-dimethoxybenzil (6.76 g, 25 mmol), and ZSM-5 nanozeolite (0.2 g) were heated in dry toluene (75 ml) to reflux using Dean and Stark apparatus for 4 h. After cooling, the reaction solution was kept at 0°C overnight. The resulting precipitate was collected by filtration, washed with water and acetone, and then dried under vacuum.

Yield: 70%, M.p. 331–334°C; IR (KBr, cm<sup>-1</sup>): 528, 835, 1179, 1257, 1513, 1685, 3232.  $^1\text{H}$  NMR (500 MHz, D<sub>6</sub>-DMSO)  $\pm$  (ppm): 3.61 (s, 6H, OCH<sub>3</sub>), 5.65 (d, J = 16 Hz, 4H), 7.05 (d, J = 16 Hz, 4H), 7.67 (br-s, 4H);  $^{13}\text{C}$  NMR (126 MHz, D<sub>6</sub>-DMSO)  $\delta$  (ppm): 55.7 (OCH<sub>3</sub>), 71.14 (C<sub>3a,6a</sub>), 111.81–125.19 (C<sub>arom</sub>), 151.69 (C<sub>2,5</sub>), 160.16 (C<sub>arom</sub>-O); Anal. calc. for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 61.01; H, 5.12; N, 15.81%. Found: C, 61.01; H, 5.12; N, 15.81%. Found: C, 61.05; H, 5.15; N, 15.92%.

**3.1.5.5. 3a,6a-dimethyltetrahydroimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (5).** Urea (3.0 g, 50 mol), biacetyl (2.15 g, 25 mmol), and ZSM-5 nanozeolite (0.2 g) were heated in dry toluene (75 ml) to reflux using Dean and Stark apparatus for 4 h. After cooling, the reaction solution was kept at 0°C overnight. The resulting precipitate was collected by

filtration, washed with water and acetone, and then dried under vacuum.

Yield: 67%, M.p. 345–348°C. IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 1672, 3258.

$^1\text{H}$  NMR (D<sub>6</sub>-DMSO)  $\delta$  7.08 (br-s, 4H, NH), 1.32 (s, 6H, CH<sub>3</sub>);  $^{13}\text{C}$  NMR (D<sub>6</sub>-DMSO)  $\delta$  159.4 (C–O), 75.3 (C), 21.9 (CH<sub>3</sub>). Anal. calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 42.35; H, 5.92; N, 32.92%. Found: C, 42.38; H, 5.88; N, 32.91%.

**3.1.5.6. 3a,6a-diethyltetrahydroimidazo[4,5-d]imidazole-2,5(1 H, 3 H)-dione (6).** Urea (3.0 g, 50 mol), 3,4-hexanedione (2.85 g, 25 mmol), and ZSM-5 nanozeolite (0.2 g) were heated in dry toluene (75 ml) to reflux using Dean and Stark apparatus for 4 h. After cooling, the reaction solution was kept at 0°C overnight. The resulting precipitate was collected by filtration, washed with water and acetone, and then dried under vacuum.

Yield: 70%, M.p. 341–343°C. IR (KBr)  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 1674, 3250.

$^1\text{H}$  NMR (D<sub>6</sub>-DMSO)  $\delta$  7.20 (br-s, 4H, NH), 1.60 (q, J = 7.48 Hz, 4H, CH<sub>2</sub>-CH<sub>3</sub>), 0.94 (t, J = 7.48 Hz, 6H, CH<sub>2</sub>=CH<sub>3</sub>);  $^{13}\text{C}$  NMR (D<sub>6</sub>-DMSO)  $\delta$  159.9 (C–O), 78.0 (C), 27.5 (CH<sub>2</sub>-CH<sub>3</sub>), 7.5 (CH<sub>2</sub>-CH<sub>3</sub>). Anal. calc. for C<sub>8</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 47.48; H, 7.12; N, 28.26%. Found: C, 47.47; H, 7.10; N, 28.24%.

## 4. Conclusions

In conclusion, we have developed an efficient route for the one pot synthesis of glycoluril derivatives through reaction between urea and dicarbonyl compound in the presence of nano-sized HZSM-5 zeolite as a mild and efficient catalyst. The ease of work-up and efficiency of catalyst make this procedure a useful addition to modern synthetic methods.

## Acknowledgements

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## References

- (1) Li, J.T.; Liu, X.R.; Sun, M.X. *Ultrason. Sonochem.* **2010**, *17*, 55.
- (2) Parekh, G.G. US Patent, 4105708, **1978**.
- (3) Wang, A.; Bassett, D. US Patent 4310450, 1982.
- (4) Boileau, J.; Carail, M.; Wimmer, E.; Gallo, R.; Pierrot, M. *Propell. Explos. Pyrotech.* **1985**, *10*, 118.
- (5) Krause, A.; Aumueller, A.; Korona, E.; Trauth, H. US Patent. 5670613, **1997**.
- (6) Pryor, K.E.; Rebek, J. *Org. Lett.* **1999**, *1*, 39.

- (7) (a) Sun, S.; Britten, J.F.; Cow, C.N.; Matta, C.F.; Harrison, P.H.M. *Can. J. Chem.* **1998**, *76*, 301; (b) Jacobs, W.; Foster, D.; Sansur, S.; Lees, R.G. *Prog. Org. Coat.* **1996**, *29*, 127; (c) Yinon, J.; Bulusu, S.; Axenrod, T.; Yazdekhasti, H. *Org. Mass Spectrom.* **1994**, *29*, 625.
- (8) Wu, A.X.; Fettingner, J.C.; Isaacs, L. *Tetrahedron.* **2002**, *58*, 9769.
- (9) Slezaka, F.B.; Hirsch, A.; Rosen, I. *J. Org. Chem.* **1960**, *25*, 660.
- (10) (a) Slezak, F.B.; Bluestone, H.; Magee, T.A.; Wotiz, J. H. *J. Org. Chem.* **1962**, *27*, 2181; (b) Burnett, C.A.; Lagona, J.; Wu, A.X.; Shaw, J.A.; Coady, D.; Fettingner, J.C.; Day, A.I.; Isaacs, L. *Tetrahedron.* **2003**, *59*, 1961.
- (11) (a) Murray, B.A.; Whelana, G.S. *Pure Appl. Chem.* **1996**, *68*, 1561; (b) Kang, J.; Meissner, R.S.; Wyler, R.; Mendoza, J.; Rebek, J.R., Jr. *Bull. Korean. Chem. Soc.* **2000**, *21*, 221; (c) OLeary, B.M. Szabo, T.; Svenstrup, N.; Schalley, C.A.; Ltzen, A.; Schfer, M.; Rebek, J. *J. Am. Chem. Soc.* **2001**, *123*, 11519; (d) Moon, K.; Chen, W.Z.; Ren, T.; Kaifer, A.E. *Cryst. Eng. Commun.* **2003**, *5*, 451.
- (12) Hagen, J. *Industrial Catalysis*, Wiley-VCH: New York, 1999.
- (13) Argauer, R.J.; Landolt, G.R. US Patent 3702886, 1972.
- (14) Vitale, G.; Molero, H.; Hernandez, E.; Aquino, S.; Birss, V.; Pereira-Almao, P. *Appl. Catal. A-Gen.* **2013**, *452*, 75.
- (15) Niei, A.; Salari, D.; Hosseini, S.A. *Turk. J. Chem.* **2010**, *34*, 15.
- (16) Takahashi, A.; Xia, W.; Wu, Q.; Furukawa, T.; Nakamura, I.; Shimada, H.; Fujitani, T. *Appl. Catal. A-Gen.* **2013**, *467*, 380.
- (17) Khatamian, M.; Irani, M. *J. Iran. Chem. Soc.* **2009**, *6*, 187.
- (18) Vessally, E.; Hokmabadi, F. *Tetrahedron Lett.* **2012**, *53*, 5645.
- (19) Freeman, W.A.; Mock, W.L.; Shih, N.Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367.
- (20) Isobe, H.; Tomita, N.; Lee, J.W.; Kim, H.-J.; Kim, K.; Nakamura, E. *Angew. Chem. Int. Ed.* **2000**, *39*, 4257.
- (21) Buschmann, H.J.; Gardberg, A.; Schollmeyer, E. *Textilverdlung.* **1991**, *26*, 153.
- (22) Karcher, S.; Kornmuller, A.; Jekel, M. *Water Sci. Technol.* **1999**, *40*, 425.
- (23) Kornmuller, A.; Karcher, S.; Jekel, M. *Water Res.* **2001**, *35*, 3317.
- (24) Micheletti, G.; Delpivo, C.; Baccolini, G. *Green Chem. Lett. Rev.* **2013**, *6*, 135.