



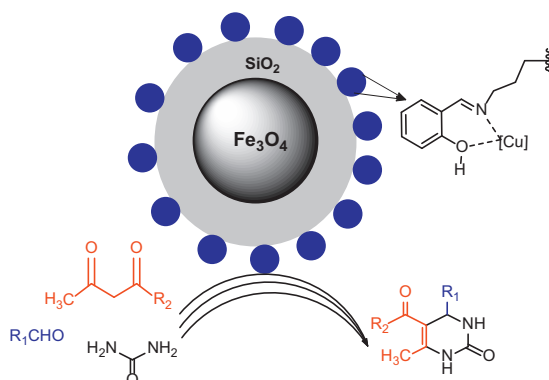
## Regular Article

# Magnetic nanoparticles supported Schiff-base/copper complex: An efficient nanocatalyst for preparation of biologically active 3,4-dihydropyrimidinones

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## GRAPHICAL ABSTRACT

A novel magnetic iron oxide supported Schiff-base/copper complex (Cu/SB-Fe<sub>3</sub>O<sub>4</sub>) is prepared, characterized and applied as efficient nanocatalyst in the one-pot Biginelli reaction.



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## ABSTRACT

A novel magnetic iron oxide supported copper/Schiff-base complex (Cu/SB-Fe<sub>3</sub>O<sub>4</sub>) was prepared, characterized and applied as effective nanocatalyst for the synthesis of biologically active 3,4-dihydropyrimidinones. The Cu/SB-Fe<sub>3</sub>O<sub>4</sub> was prepared by chemical attachment of Schiff-base groups on Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles followed by treatment with copper salt under mild conditions. This was characterized with several techniques such as VSM, TGA, EDX, FTIR, TEM and SEM. The Cu/SB-Fe<sub>3</sub>O<sub>4</sub> nanocatalyst was successfully applied in the Biginelli reaction and gave corresponding biologically active 3,4-dihydropyrimidinones in high yield. Furthermore, this noble catalyst was easily recovered using an external magnet and reused eleven times with keeping its efficiency and stability under applied conditions.

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## 1. Introduction

Since nanoparticles have very small size and are well dispersed in solution, the use of them as support can lead to excellent increase

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of catalyst activity [1–3]. When the nanoparticulate catalyst well dispersed in the reaction media, it forms a stable suspension allowing an elevated rate of reaction [4]. However, the most of nanoparticles are non-reusable and recovery of them from reaction media remains a challenge [1,5,6]. This limitation can be solved by using magnetic nanoparticles (MNPs) that can be certainly isolated from the reaction media using an external magnet. The most of MNPs are non-toxic, easy-accessible, retrievable and reusable, therefore offer advantages in the development of clean and sustainable green processes [7]. Moreover, these nanoparticles are highly valuable support for the immobilization of both homogeneous organic and inorganic catalysts [4]. These properties made MNPs appropriate candidates for a variety of potential applications such as adsorption [4], MRI contrast agents [8,9], drug delivery [10], hyperthermal agents [11] and cell sorting [12]. These have also been successfully used to extract of DNA from agarose gel [13]. Moreover, since magnetic separation has emerged as a highly simple, efficient and fast separation tool in comparison with other product-catalyst isolation methods such as liquid–liquid extraction, chromatography, filtration or centrifugation, these NPs are very important and have key role in the catalytic processes [4,14]. Among different MNPs, magnetic iron oxides are very attracted and widely applied as catalyst and/or support in chemical processes due to their easy preparation, high surface area, low cost and high availability [4,15–17]. Up to now, many applications of these particles in different chemical processes such as oxidation, reduction, hydrogenation, Suzuki, Sonogashira and Heck coupling reactions, degradation, synthesis of sulfonamides, removal of organic pollutants, synthesis of quinoxalines, synthesis of xanthene derivatives, three-component coupling reaction, glucose detection and so on have been reported [18–23]. However, it is well-known that the magnetic iron oxide nanoparticles are unstable, especially under acidic conditions and in the presence of air. Therefore, protect of these NPs with suitable species is a very important challenge between chemists. These magnetic cores are coated with several non-magnetic and relatively inert shells to protect their magnetic properties. To date, some species such as silica, polymer, carbon and different organic ligands have been successfully used for protect of magnetic particles [4,15–17,24–27]. Among these, silica based ones is more attracted due to its high ability for easy immobilization of several organic and inorganic catalysts applicable in chemical transformations. Some of recently developed catalytic systems include  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Pr-NH}_2$  [28],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TEMPO}$  [29],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Mn/porphyrins}$  [30],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Pd}$  [31],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SO}_3\text{H}$  [32],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{dipyridine}$  [33],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{IL/proline}$  [34],  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{diazoniabicyclo[2.2.2]octane}$  [35] and  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{PrSO}_3\text{H}$  [36]. In continuation of these studies and according to high advantage of Biginelli reaction in the production of biologically useful and chemically valuable compounds [37–43], herein a novel  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Schiff-base}$  (SB- $\text{Fe}_3\text{O}_4$ ) supported copper catalyst is prepared, characterized and its catalytic application is developed in the one-pot preparation of 3,4-dihydropyrimidinones *via* Biginelli process (Scheme 1). The recoverability, reusability and durability of this catalyst under applied conditions have also been studied.

## 2. Experimental section

### 2.1. Preparation of $\text{Fe}_3\text{O}_4$ nanoparticles supported Schiff-base (SB- $\text{Fe}_3\text{O}_4$ )

For this purpose, firstly magnetic iron oxides coated with silica ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) were prepared according to Stöber method [44]. For this, 1 g of  $\text{Fe}_3\text{O}_4$  was added to a solution of water (20 mL) and ethanol (40 mL) while stirring at room temperature. After 10 min, the reaction vessel was charged with 0.7 mL of

tetramethylorthosilicate (TMOS) and stirring was continued at the same temperature. After 8 h, the resulted product was collected with an external magnet and it was washed completely with distilled water and EtOH. This was dried at 70 °C for 12 h under vacuum and denoted as  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ . For preparation of  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-PrNH}_2$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  (1 g) was added in toluene (40 mL) and the mixture was stirred at room temperature. After complete dispersion of this material, 3-aminopropyltrimethoxysilane (1 mmol) was added and obtained mixture was refluxed for 24 h. The solid material was collected with a magnet, dried similar to the previous sample and denoted as  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-PrNH}_2$ . The SB- $\text{Fe}_3\text{O}_4$  sample was finally prepared as following:  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-PrNH}_2$  (1 g) was added in toluene (40 mL) while stirring at room temperature. After complete dispersion, ortho-hydroxy-benzaldehyde (3 mmol) was added and this was refluxed for 24 h. Then, the resulted material was collected using an external magnet, dried at 70 °C and denoted as SB- $\text{Fe}_3\text{O}_4$ .

### 2.2. Preparation of $\text{Cu/SB-Fe}_3\text{O}_4$

For the preparation of  $\text{Cu/SB-Fe}_3\text{O}_4$ , the SB- $\text{Fe}_3\text{O}_4$  (1 g) was added in DMSO (40 mL) while sonicating at room temperature. After complete dispersion of this material, a DMSO solution of  $\text{Cu}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$  (3 mmol) was added and obtained mixture was stirred for 24 h at room temperature. The resulted material was then collected by an external magnet, washed completely with absolute EtOH and water, dried under vacuum and denoted as  $\text{Cu/SB-Fe}_3\text{O}_4$ .

### 2.3. General procedure for the Biginelli reaction using $\text{Cu/SB-Fe}_3\text{O}_4$ nanocatalyst

To do this, the  $\text{Cu/SB-Fe}_3\text{O}_4$  catalyst (0.01 g) was added into a mixture of aldehyde (1 mmol), ethylacetoacetate (1 mmol) and urea (1.5 mmol). This was magnetically stirred at 80 °C while progress of the reaction was monitored using TLC. After finishing of the process, hot EtOH (10 mL) was added and the  $\text{Cu/SB-Fe}_3\text{O}_4$  catalyst was removed using an external magnet. The catalyst-free solution was then put in an ice bath to precipitate crude crystals. The pure Biginelli products were obtained after recrystallization in ethanol. For performing the reaction under ultrasonic conditions, a flask containing the above mentioned starting materials was put in an ultrasonic bath. The reaction progress was monitored using TLC at 60 °C under ultrasonic irradiations. After completion of the reaction, the pure products were obtained as above. These products were characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and *via* comparison of their melting points with the reported ones.

### 2.4. General procedure for the recovery of the $\text{Cu/SB-Fe}_3\text{O}_4$ catalyst

For this, to a homogeneous mixture of aldehyde, ethylacetoacetate and urea,  $\text{Cu/SB-Fe}_3\text{O}_4$  catalyst was added and the reaction progress was monitored using TLC at 60 °C under ultrasonic irradiations. After completion of the reaction, the catalyst was separated using an external magnet and the product was obtained as previous procedure. The recovered catalyst was dried and applied in the next run under the same conditions as the first run. These steps were repeated at least eleven times and corresponding yields were calculated.

### 2.5. IR, $^1\text{H}$ NMR and $^{13}\text{C}$ NMR data of some Biginelli products

#### 2.5.1. 5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one

IR (KBr,  $\text{cm}^{-1}$ ): 3347, 3110, 2953, 1670, 1699, 1403, 1653, 1242.  
 $^1\text{H}$  NMR (400 MHz, DMSO, 25 °C):  $\delta$  = 2.53 (s, 3H), 2.23 (s, 3H), 5.2 (d, 1H, CH,  $J$  = 4.5), 7.20–7.33 (m, 5H), 7.73 (s, 1H, NH), 9.20

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