

Magnetic 4-aminobenzenesulfonic acid-functionalized periodic mesoporous organosilica as a highly efficient heterogeneous catalyst for the Green synthesis of dibenzo[1,4]diazepine derivatives

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Abstract

Magnetic 4-aminobenzenesulfonic acid (PABSA)-functionalized periodic mesoporous organosilica ($\text{Fe}_3\text{O}_4@$ PMO-ICS-Pr-PABSA) was prepared as a green and recoverable nanocatalyst. This nanocatalyst was able to efficiently catalyze synthesis of dibenzo[1,4]diazepine derivatives *via* one-pot three-component reactions of *o*-phenylenediamine, dimedone and various aldehydes at room temperature. This method have the key advantages such as simplicity of operation, high to excellent products yield and short reaction times, easy work-up, accessible catalyst and purification of products by crystallization (non-chromatographic) of this work.

Keywords: Magnetic 4-aminobenzenesulfonic acid-functionalized periodic mesoporous organosilica; dibenzo[1,4]diazepine derivatives; Three-Component reactions; Nanocatalyst.

1. Introduction

In recent years, the use of heterogeneous catalysts has become highly desirable in chemical catalytic process systems, because they incorporate many green chemistry principles [1]. Furthermore, the recovery and reuse of the homogeneous catalysts is always challenging. Alternatively, the heterogeneous catalysts have the advantages of easy separation and recycling after the completion of the reactions [2].

In this regard, periodic mesoporous organosilica (PMO) has a unique structure for catalytic studies due to high mesoporosity and surface area [3, 4]. Fe_3O_4 magnetic

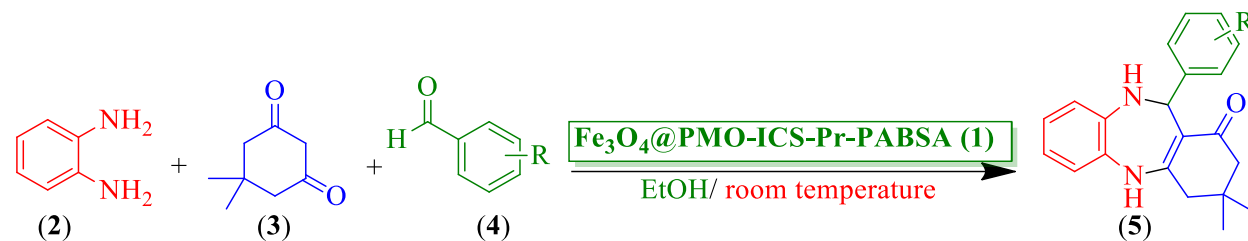
nanoparticles (MNPs) with their diverse physical and chemical properties have been applied in the modified various materials [5].

Fe₃O₄ magnetic nanoparticles (MNPs) with their diverse physical and chemical properties have been applied in the modified various materials [6]. This nanoparticles conveniently performed by an external magnetic. The essential fields of MNPs application in organic chemistry are the catalytic process and biomedicine fields [7].

Multicomponent reactions (MCRs) are one of the practical and ideal synthesis methods in organic synthesis has been applied to synthesize a vast range of heterocyclic compounds [8]. The unique properties of MCR includes atom-economy, simple design, environmental benignity and synthesis of highly functionalized molecules in a one-pot reaction [9-12].

Dibenzo[1,4]diazepine derivatives are a very noteworthy class of heterocyclic compounds that have attracted a major value of attention because there have various medicinal and biological properties [13, 14].

In this work, we report the preparation of Fe₃O₄@PMO-ICS-Pr-PABSA (**1**) as a novel, unique, efficient, and recoverable heterogeneous catalyst for the synthesis of dibenzo[1,4]diazepine derivatives.



Scheme 1. Synthesis of dibenzo[1,4]diazepine derivatives catalyzed by Fe₃O₄@PMO-ICS-Pr-PABSA (**1**).

2. Experimental Section

2.1. Reagents and Apparatus

All chemical reagents were purchased from Merck. To determine the completion of the reaction, analytical thin-layer chromatography (TLC) was performed on pre-coated silica-gel plates (Merck Silica Gel F254). Product stains were detected either

under UV light or by placing in an iodine chamber. Also, melting points were determined in open capillaries using an Electrothermal 9100 apparatus.

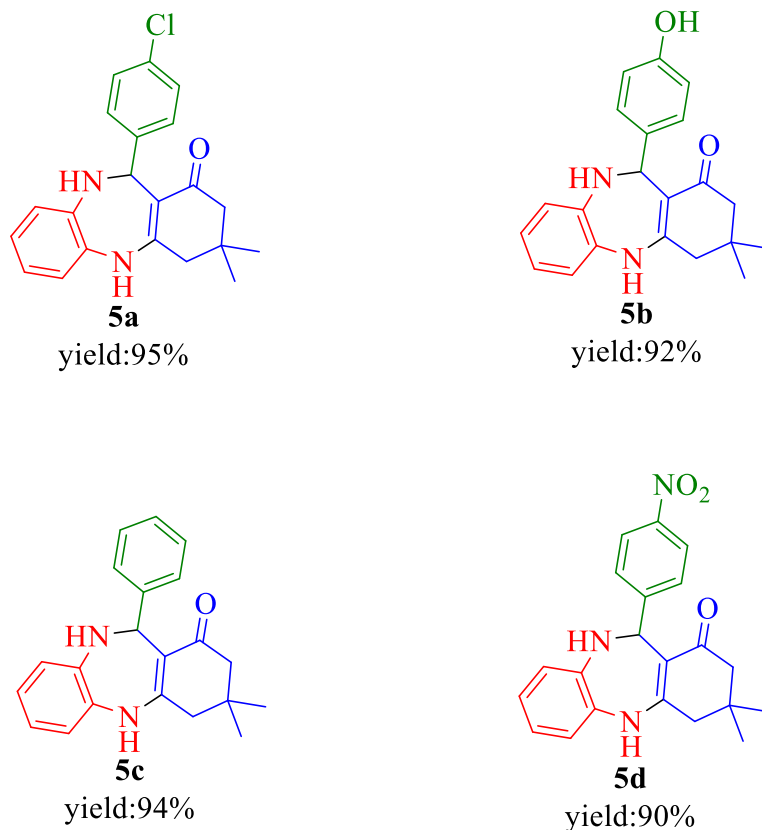
2.2. *General procedure for the synthesis of dibenzo[1,4]diazepine derivatives*

(5a–d)

In a round bottom flask (5 mL), *o*-phenylenediamine (**2**, 1 mmol), dimedone (**3**, 1 mmol), various aldehydes (**4**, 1 mmol), and 10 mg of Fe₃O₄@PMO-ICS-Pr-PABSA (**1**) as catalyst were added to EtOH (3 mL). The resulted mixture was stirred at room temperature and the completion of the reaction indicated by TLC. The magnetic catalyst was separated by an external magnet and washed with water and EtOH, dried in vacuum oven for the next run.

3. Results and Discussion

The catalytic activity of Fe₃O₄@PMO-ICS-Pr-PABSA (**1**) was evaluated in the green and one-pot synthesis of dibenzo[1,4]diazepine derivatives by cyclocondensing *o*-phenylenediamine, dimedone and various aldehydes in EtOH at room temperature. According to Scheme 2, using a small amount of Fe₃O₄@PMO-ICS-Pr-PABSA (**1**) as heterogeneous catalyst (about 10 mg), the desired products were synthesized with green and uncomplicated protocol, high yield and in short times. The ability to magnetically separate and reused for at least five runs with minimal effort is another advantage of this catalyst.



Scheme 2. Synthesis of dibenzo[1,4]diazepine derivatives (**5a-d**) catalyzed by $\text{Fe}_3\text{O}_4@\text{PMO-ICS-Pr-PABSA}$ (**1**) nanoparticles in EtOH at room temperature

Conclusion

In summary, the new magnetic 4-aminobenzenesulfonic acid (PABSA) functionalized periodic mesoporous organosilica ($\text{Fe}_3\text{O}_4@\text{PMO-ICS-Pr-PABSA}$) catalyst was used for three-component reaction *o*-phenylenediamine, dimedone and various aldehydes in EtOH in room temperature to afford pharmacologically active dibenzo[1,4]diazepine compounds. The advantages of this method are high-to-excellent yields of products, low loading of catalyst, magnetically separation and reusability of catalyst, use of green solvent. Furthermore, this catalyst was recovered and reused at least five times without a considerable decrease in its activity.

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