chemistry proceedings

Proceeding Paper

Magnetic 4-Aminobenzenesulfonic Acid-Functionalized Periodic Mesoporous Organosilica as a Highly Efficient Heterogeneous Catalyst for the Green Synthesis of Dibenzo[1,4]Diazepine Derivatives †

Hamidreza FaniMoghadam, Mohammad G. Dekamin * and Negin Rostami

Pharmaceutical and Heterocyclic Compounds Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran
* Correspondence: mdekamin@iust.ac.ir; Tel.: +98-21-772-406-4050; Fax: +98-21-730-215-84
† Presented at the 25th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2021; Available online: https://ecsoc-25.sciforum.net/.

Abstract: Magnetic 4-aminobenzenesulfonic acid (PABSA)-functionalized periodic mesoporous organosilica (Fe_3O_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

Citation: FaniMoghadam, H.; Dekamin, M.G.; Rostami, N. Magnetic 4-Aminobenzenesulfonic Acid-Functionalized Periodic Mesoporous Organosilica as a Highly Efficient Heterogeneous Catalyst for the Green Synthesis of Dibenzo[1,4]Diazepine Derivatives. **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Published: date

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].

Fe_3O_4 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 Fe_3O_4@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 Fe_3O_4@PMO-ICS-Pr-PABSA (**1**).

2. Experimental Section

2.1. Reagents and Apparatus

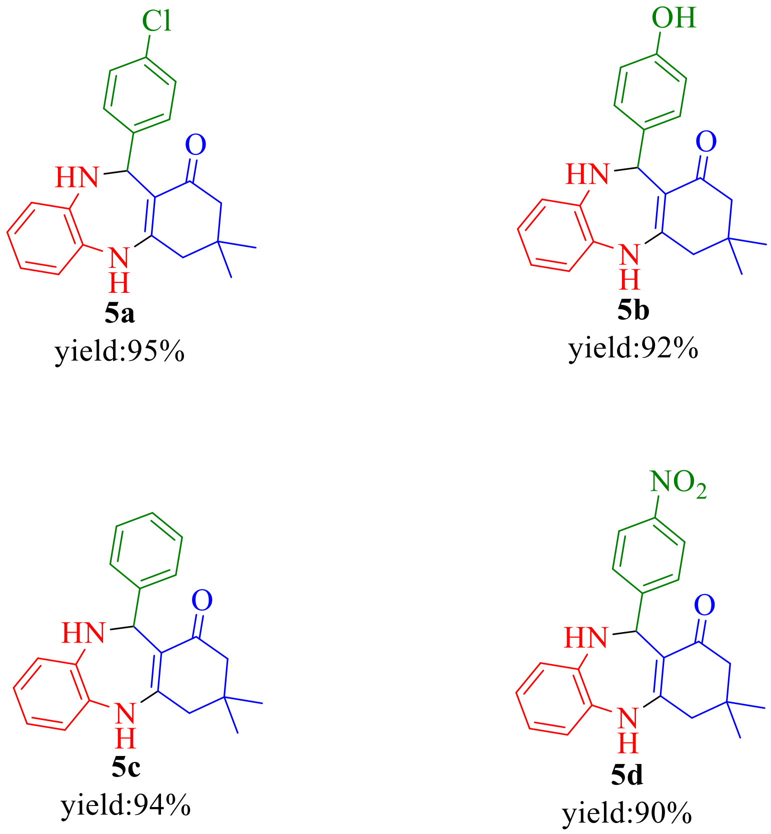
All chemical reagents were purchased from Merck. To determine the completion of the reaction, analytical thin-layer chromatography (TLC) was performed on pre-coated silica-gel plates (Merck Silica Gel F254). Product stains were detected either under UV light or by placing in an iodine chamber. Also, 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 Fe_3O_4@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 Fe_3O_4@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 Fe_3O_4@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 Fe_3O_4@PMO-ICS-Pr-PABSA (**1**) nanoparticles in EtOH at room temperature

4. Conclusions

In summary, the new magnetic 4-aminobenzenesulfonic acid (PABSA) functionalized periodic mesoporous organosilica (Fe_3O_4@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.

Acknowledgments: We are grateful for the financial support from The Research Council of Iran University of Science and Technology (IUST), Tehran, Iran (Grant No. 160/19108).

References

1. Pelckmans, M.; Renders, T.; Van de Vyver, S.; Sels, B. Bio-based amines through sustainable heterogeneous catalysis. *Green Chem.* **2017**, *19*, 5303–5331.
2. Ahadi, A.; Rostamnia, S.; Panahi, P.; Wilson, L.D.; Kong, Q.; An, Z.; Shokouhimehr, M. Palladium comprising dicationic bipyridinium supported periodic mesoporous organosilica (PMO): Pd@ Bipy–PMO as an efficient hybrid catalyst for Suzuki–Miyaura cross-coupling reaction in water. *Catalysts* **2019**, *9*, 140.
3. Akbari, A.; Dekamin, M.G.; Yaghoubi, A.; Naimi-Jamal, M.R. Novel magnetic propylsulfonic acid-anchored isocyanurate-based periodic mesoporous organosilica (Iron oxide@ PMO-ICS-PrSO 3 H) as a highly efficient and reusable nanoreactor for the sustainable synthesis of imidazopyrimidine derivatives. *Sci. Rep.* **2020**, *10*, 1–16.
4. Yaghoubi, A.; Dekamin, M.G.; Karimi, B. Propylsulfonic acid-anchored isocyanurate-based periodic mesoporous organosilica (PMO-ICS-PrSO 3 H): A highly efficient and recoverable nanoporous catalyst for the one-pot synthesis of substituted polyhydroquinolines. *Catal. Lett.* **2017**, *147*, 2656–2663.
5. Öztürk Er, E.; Dalgıç Bozyiğit, G.; Büyükpınar, Ç.; Bakırdere, S. Magnetic nanoparticles based solid phase extraction methods for the determination of trace elements. *Crit. Rev. Anal. Chem.* **2020**, 1–19, doi:10.1080/10408347.2020.1797465.

6. Demin, A.M.; Pershina, A.G.; Minin, A.S.; Mekhaev, A.V.; Ivanov, V.V.; Lezhava, S.P.; Zakharova, A.A.; Byzov, I.V.; Uimin, M.A.; Krasnov, V.P. PMIDA-modified Fe3O4 magnetic nanoparticles: Synthesis and application for liver MRI. *Langmuir* **2018**, *34*, 3449–3458.
7. Karami, S.; Dekamin, M.G.; Valiey, E.; Shakib, P. DABA MNPs: A new and efficient magnetic bifunctional nanocatalyst for the green synthesis of biologically active pyrano [2, 3-c] pyrazole and benzylpyrazolyl coumarin derivatives. *New J. Chem.* **2020**, *44*, 13952–13961.
8. Younus, H.A.; Al-Rashida, M.; Hameed, A.; Uroos, M.; Salar, U.; Rana, S.; Khan, K.M. Multicomponent reactions (MCR) in medicinal chemistry: A patent review (2010–2020). *Expert Opin. Ther. Pat.* **2021**, *31*, 267–289.
9. Sam, M.; Dekamin, M.G.; Alirezvani, Z. Dendrons containing boric acid and 1, 3, 5-tris (2-hydroxyethyl) isocyanurate covalently attached to silica-coated magnetite for the expeditious synthesis of Hantzsch esters. *Sci. Rep.* **2021**, *11*, 1–21.
10. Alirezvani, Z.; Dekamin, M.G.; Valiey, E. Cu (II) and magnetite nanoparticles decorated melamine-functionalized chitosan: A synergistic multifunctional catalyst for sustainable cascade oxidation of benzyl alcohols/Knoevenagel condensation. *Sci. Rep.* **2019**, *9*, 1–12.
11. Alirezvani, Z.; Dekamin, M.G.; Valiey, E. New hydrogen-bond-enriched 1, 3, 5-tris (2-hydroxyethyl) isocyanurate covalently functionalized MCM-41: An efficient and recoverable hybrid catalyst for convenient synthesis of acridinedione derivatives. *ACS Omega* **2019**, *4*, 20618–20633.
12. Rostami, N.; Dekamin, M.; Valiey, E. Urea-Functionalized chitosan as efficient and recoverable organocatalyst for the convenient synthesis of pyrimido [4, 5-b] quinoline-2, 4-dione derivatives. **2020**.
13. Savari, A.; Heidarizadeh, F.; Pourreza, N. Synthesis and characterization of CoFe2O4@ SiO2@ NH-NH2-PCuW as an acidic nano catalyst for the synthesis of 1, 4-benzodiazepines and a powerful dye remover. *Polyhedron* **2019**, *166*, 233–247.
14. Naeimi, H.; Foroughi, H. ZnS nanoparticles as an efficient recyclable heterogeneous catalyst for one-pot synthesis of 4-substituted-1, 5-benzodiazepines. *New J. Chem.* **2015**, *39*, 1228–1236.