Received: 2 October 2016 | Revised: 30 November 2016 | Accepted: 5 December 2016

DOI 10.1002/aoc.3729

WILEY Applied Organometallic Chemistry

FULL PAPER

Eco-friendly synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives with the aid of MCM-48/$H_5PW_{10}V_2O_{40}$

Esmail Vessally[1] | Rahim Hosseinzadeh-Khanmiri[1,2] | Ebrahim Ghorbani-Kalhor[2] | Moosa Es'haghi[2] | Ladan Ejlali[2]

[1] Department of Chemistry, Payame Noor University, Tehran, Iran

[2] Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

Correspondence
Ebrahim Ghorbani-Kalhor, Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran.
Email: ekalhor@iaut.ac.ir

A heterogeneous material composed of MCM-48/$H_5PW_{10}V_2O_{40}$ was produced and used as an efficient, eco-friendly and highly recyclable catalyst for the one-pot and multicomponent synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives in aqueous media and at room temperature with high yields in short reaction times (40–60 min). The recoverable catalyst was easily recycled at least five times without any loss of catalytic activity. The structures of obtained products were confirmed using ^{1}H NMR and ^{13}C NMR spectra.

KEYWORDS

3,4-dihydroquinoxalin-2-amine, benzodiazepine-2-carboxamide, diazepine-tetrazole, green chemistry, MCM-48/$H_5PW_{10}V_2O_{40}$

1 | INTRODUCTION

Heterocyclic chemistry is one of the most important branches in organic chemistry which accounts for nearly one-third of modern publications.[1]

Quinoxaline is one of the heterocyclic compounds containing nitrogen atoms that display a broad spectrum of biological and pharmacological activities such as insecticidal, fungicidal, herbicidal, anthelmintic, antibacterial, antimycobacterial, antiprotozoal, anticancer and antibiotic properties.[2,3]

Benzodiazepines are an important class of bioactive compounds. These compounds have been widely applied for their anxiolytic, anticonvulsant, hypnotic, sedative, skeletal muscle relaxant, amnestic, diabetic nephropathy, glomerulosclerosis and peptide hormone properties.[4–6]

Catalysis based on heteropolyacids (HPAs) and related compounds, especially those comprising the strongest Keggin-type HPAs, is an important field in which new and promising developments are being realized in both academia and technological fields. The major disadvantages of HPAs lie in extremely low surface area, water solubility, difficult recovery and recycling which always limit their practical applications.[7,8]

It is known that high active phase dispersion or high surface area as well as fast mass transfer of products and reactants are necessary for any active catalyst. Hence, designing a heterogeneous catalyst involving a rigorous control of the surface geometry and proper control of surface chemistry at the mesoscales need to be explored for the successful development of environmentally compatible catalytic systems. New heterogeneous materials based on mesoporous molecular sieves have attracted much research interest and have opened new vistas for the same. The use of these mesoporous materials from the Mobile Composition of Matter (MCM) family has provided attractive possibilities for development of highly active solid catalysts and they have found a number of applications in various industrially important classes of reactions.[9]

Mesoporous materials are widely used in various fields according to their high surface area and tunable structures.[10–17] MCM-48 is a type of mesoporous silica tube-like material with uniformly sized three-dimensional mesopores. These compounds have been of interest as solid supports in catalysis and sorption. The mesoporous silica material MCM-48 has been considered as an ideal support for various HPAs, because of its special pore structure and

large surface area; moreover, this support is easy to produce at a low cost.[18]

MCM-48 has an interesting bicontinuous cubic structure (with Ia3d symmetry) centred on the gyroid minimal surface that divides available pore space into two nonintersecting subvolumes. This three-dimensional bicontinuous structure is preferred over the two-dimensional hexagonal structure for catalytic applications, because the unique three-dimensional channel network is thought to provide a highly opened porous host that offers easy and direct access for guest species, thus facilitating inclusion or diffusion throughout the pore channels without pore blocking.[19,20]

Recently, science and technology have been shifting emphasis to environmentally friendly and sustainable resources and processes, and for these reasons a few heterogeneous materials with supported HPW, such as HPW/C,[21] HPW/CNTS,[22] HPW/TiO_2,[23] HPW/SnO_2,[24] HPW/C-Al_2O_3,[25] HPW/Nb_2O_5,[26] HPW/ZrO_2,[27] HPW/hydrous zirconia,[28] HPW/SiO_2[29] and HPW/MCM-48,[30,31] have been studied.

Loading of HPAs on mesoporous silica not only allows transfer of HPA-catalysed reactions from homogeneous to heterogeneous systems to avoid the difficulty in catalyst separation, but also effectively increases the surface area of HPAs.[32]

Heterogeneous catalytic systems have attracted worldwide attention and have been studied extensively due to their technological and biological applications such as in drug delivery, bioseparation, biomolecular sensors and magnetic resonance imaging.[33–37]

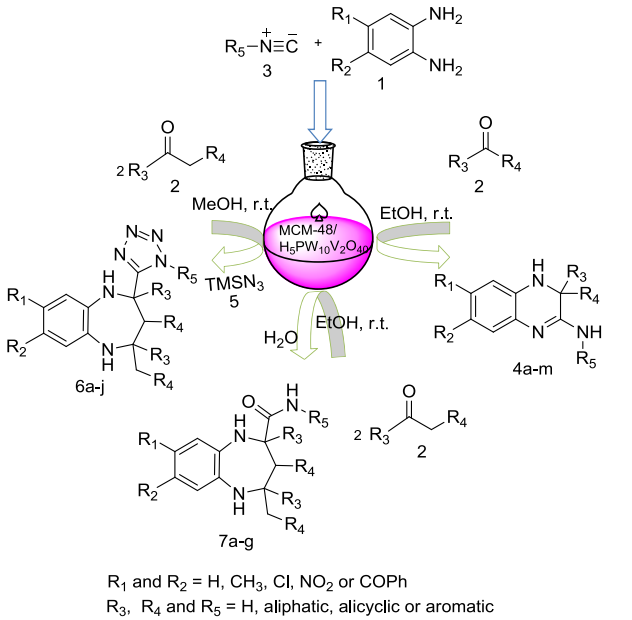
Shaabani and co-workers reported novel routes for the synthesis of quinoxaline and benzodiazepine derivatives using isocyanide-based multicomponent reactions in the presence of non-recyclable catalytic amount of *p*-toluenesulfonic acid, with long reaction times, the reaction not occurring in the absence of this catalyst.[38]

In this paper, a novel method for the synthesis biologically important materials is presented using MCM-48/$H_5PW_{10}V_2O_{40}$. This environmentally benign, heterogeneous and highly reusable catalyst shows very good catalytic activity towards the synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives (Scheme 1).

2 | RESULTS AND DISCUSSION

The Fourier transform infrared (FTIR) spectrum of MCM-48 shows a peak at around 960 cm^{-1}, which is related to Si—OH (silanol) stretching vibration (Figure 1).

The powder low-angle X-ray scattering of calcined mesoporous structure of MCM-48 was studied. This compound shows an intense peak assigned to the reflections at (100) and two low-intensity peaks at (200) and (110),



SCHEME 1 Synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives

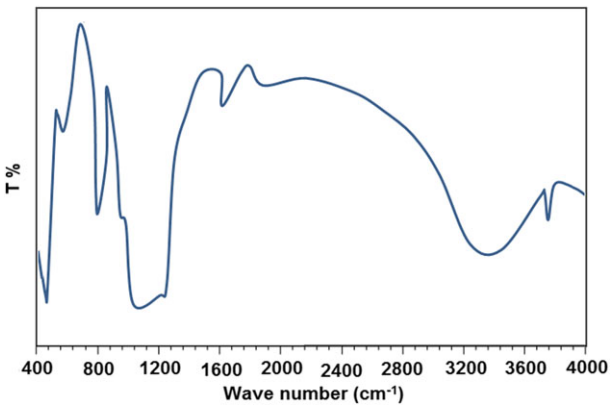


FIGURE 1 FT-IR spectrum of MCM-48

which correspond to a significant degree of long-range ordering in the structure and well-ordered hexagonal pore system. The (100) reflection of MCM-48 is still observed after $H_5PW_{10}V_2O_{40}$ loading (Figure 2). However, modification of MCM-48 with $H_5PW_{10}V_2O_{40}$ results in a loss of crystalline order, as is evidenced by a significant decrease in diffraction intensities.[39]

The scanning electron microscopy (SEM) image of MCM-48 (Figure 3) demonstrates fine, spherical particles of uniform diameter and particle size. The SEM image of $H_5PW_{10}V_2O_{40}$/MCM-48 depicts that the catalyst has a homogeneous distribution of spherical particles and the structure is not significantly affected upon introduction of HPW, although some agglomeration and particle shape deterioration are observed. Further, no change in surface morphology indicates that HPW species are well dispersed inside the three-dimensional pores of the support, which agrees well with the surface area and X-ray diffraction data.

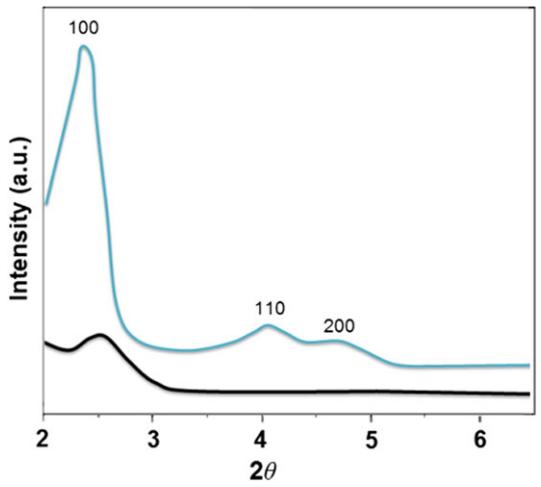


FIGURE 2 Low-angle X-ray diffraction patterns of calcined MCM-48(blue curve) and $H_5PW_{10}V_2O_{40}$/MCM-48 (black curve)

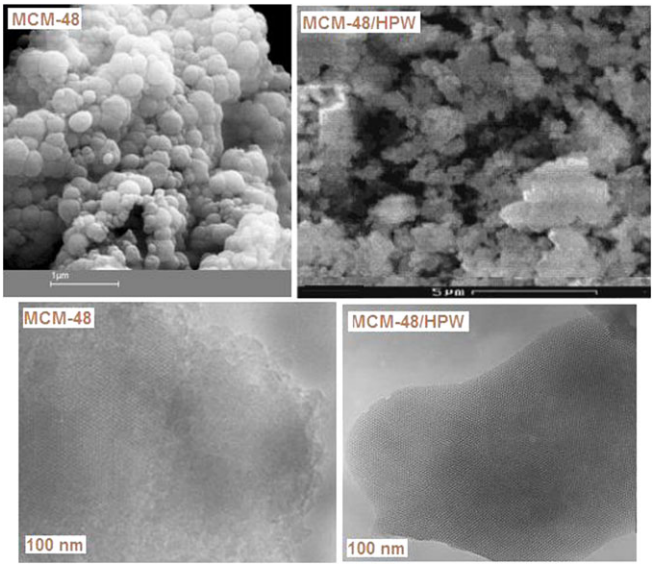


FIGURE 3 SEM and TEM images of MCM-48 and MCM-48/$H_5PW_{10}V_2O_{40}$

The transmission electron microscopy (TEM) image of MCM-48 shows a very well-ordered pore system with pore diameter of between 2 and 4 nm (Figure 3). It is well known in the literature, that MCM-48 has a three-dimensional pore system with two nonintersecting gyroidal pores which can assist dispersion of material having diameters in the range 1–3 nm. The TEM image of $H_5PW_{10}V_2O_{40}$/MCM-48 (Figure 3) shows ordered three-dimensional channels that are well arranged over a large scale. Furthermore, the absence of characteristic peaks of the crystalline phase of HPW in the catalyst indicates that HPW is highly dispersed inside the channels of MCM-48. The results are in good agreement with the X-ray diffraction data.

The catalytic efficiency of the MCM-48/$H_5PW_{10}V_2O_{40}$ heterogeneous catalytic system was studied for the preparation of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives (Scheme 1). To illustrate the need of a catalyst for these reactions, in a typical experiment, 1,2-benzenediamine (**1a**), acetone (**2a**) and cyclohexyl isocyanide (**3a**) were stirred in ethanol at room temperature in the absence of catalyst. The yield in this case is a trace after 12 h that shows the catalyst is important for the reaction.

Thereupon, in a pilot experiment, **1a**, **2a** and **3a** were stirred in ethanol at room temperature using HPA, MCM-48 and MCM-48/$H_5PW_{10}V_2O_{40}$ catalyst. Table 1 summarizes the catalytic performance results for the synthesis of *N*-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**4a**). The catalytic activity is found to be in the order MCM-48/$H_5PW_{10}V_2O_{40}$ > $H_5PW_{10}V_2O_{40}$ > MCM-48.

In order to obtain the best synthesis conditions, **1a**, **2a** and **3a** in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$ in various organic solvents were allowed to react at room temperature. As evident from Table 2, commercially absolute ethanol, ethanol 96% and methanol 99% are the best solvents for the synthesis of **4a** with respect to yield and reaction time.

The catalytic efficiency could be influenced by the amount of catalyst. Therefore, a set of experiments using various amounts of catalyst was considered for the reaction of **1a**, **2a** and **3a** in ethanol 96% at room temperature (Table 3). The optimum amount of MCM-48/$H_5PW_{10}V_2O_{40}$ catalyst is

TABLE 1 Optimization of catalyst for synthesis of *N*-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**4a**)[a]

Catalyst	Time (min)	Yield (%)[b]
MCM-48	50	33
HPA	50	62
MCM-48/$H_5PW_{10}V_2O_{40}$	50	92

[a]Reaction conditions: 1,2-benzenediamine (**1a**, 1.00 mmol), acetone (**2a**, 1.00 mmol), cyclohexyl isocyanide (**3a**, 1.00 mmol) and catalyst (0.04 g) were stirred in ethanol 96% (3.00 ml).

[b]Isolated yield.

TABLE 2 Optimization of solvent for synthesis of *N*-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine (**4a**)[a]

Solvent	Time (min)	Yield (%)[b]
H_2O	50	76
CH_2Cl_2	50	71
$CHCl_3$	50	69
CH_3CN	50	85
C_6H_6	50	32
THF	50	62
MeOH 99%	50	90
EtOH 96%	50	92
EtOH 100%	50	94

[a]Reaction conditions: 1,2-benzodiamine (**1a**, 1.00 mmol), acetone (**2a**, 1.00 mmol), cyclohexyl isocyanide (**3a**, 1.00 mmol) and catalyst (0.04 g) were stirred in ethanol 96% (3.00 ml).

[b]Isolated yield.

TABLE 3 Effect of catalyst amount on reaction of 1,2-benzodiamine, acetone and cyclohexyl isocyanide[a]

Catalyst	Catalyst amount (g)	Time (min)	Yield (%)[b]
MCM-48	0.06	50	38
MCM-48	0.05	50	36
MCM-48	0.04	50	33
MCM-48	0.02	50	29
$H_5PW_{10}V_2O_{40}$	0.06	50	66
$H_5PW_{10}V_2O_{40}$	0.05	50	63
$H_5PW_{10}V_2O_{40}$	0.04	50	62
$H_5PW_{10}V_2O_{40}$	0.02	50	48
MCM-48/$H_5PW_{10}V_2O_{40}$	0.06	50	96
MCM-48/$H_5PW_{10}V_2O_{40}$	0.05	50	95
MCM-48/$H_5PW_{10}V_2O_{40}$	0.04	50	92
MCM-48/$H_5PW_{10}V_2O_{40}$	0.02	50	76

[a]Reaction conditions: 1,2-benzodiamine (**1a**, 1.00 mmol), acetone (**2a**, 1.00 mmol), cyclohexyl isocyanide (**3a**, 1.00 mmol) and catalyst were stirred in ethanol 96% (3.00 ml).

[b]Isolated yield.

0.04 g to reach 92% yield of compound **4a**. Lower amounts of catalyst result in a decrease in the efficacy of the reaction, while higher amounts lead to complete conversion in a short reaction time. Clearly, immobilizing the HPA on the MCM-48 increases its catalytic activity towards the condensation reaction.

Using MCM-48/$H_5PW_{10}V_2O_{40}$ in ethanol 96%, we initiated a study to explore the scope of this procedure. Various derivatives of **1a**, carbonyl compounds **2** and isocyanides **3** were applied in this reaction (Table 4).

In continuation, by using a two-step condensation reaction between **1a**, two moles of ketone derivatives (**2**), an isocyanide (**3a**) and $TMSN_3$ (**5**) as a nucleophile in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$, 1*H*–tetrazol-5-yl-4-methyl-1*H*-benzo[*b*][1,4]diazepines **6a–j** were obtained (Scheme 1).

In a pilot experiment, **1a** and **2a** were stirred in the presence of a catalytic amount of MCM-48/$H_5PW_{10}V_2O_{40}$ in methanol at room temperature. The progress of the reaction was monitored by TLC. After 30 min, trimethylsilyl azide and **3a** were added to the reaction mixture and stirring was continued for 20 min. After completion of the reaction, the catalyst was removed by filtration. The residue was crystallized from acetone to give 5-(1-cyclohexyl-1*H*-tetrazol-5-yl)-5,7,7-trimethyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine-2,3-dicarbonitrile (**6a**) in 91% yield. This reaction does not proceed in the absence of catalyst.

Using MCM-48/$H_5PW_{10}V_2O_{40}$ as the best catalyst in methanol, we initiated a study to explore the scope of this reaction. Various derivatives of **1a**, ketones **2** and isocyanides **3** were examined in this reaction. The results are summarized in Table 5.

In view of the success of the reactions discussed above for the synthesis of benzodiazepine derivatives, we decided to extend our study by using water instead of $TMSN_3$ (**5**) for the preparation of **7a–g** (Scheme 1). The reaction proceeds cleanly under mild conditions at room temperature and no undesirable side reactions are observed under these reaction conditions.

In a pilot experiment, 4-nitro-1,2-phenylenediamine and **2a** were stirred in methanol at room temperature in the presence of a catalytic amount of MCM-48/$H_5PW_{10}V_2O_{40}$. The progress of the reaction was monitored by TLC. After 30 min, **3a** and water were added to the reaction mixture, and stirring was continued for 25 min. After completion of the reaction, an aqueous workup afforded compound **7a** in 92% yield.

TABLE 4 Synthesis of 3,4-dihydroquinoxalin-2-amines with various diamines, carbonyl compounds and isocyanides[a]

Entry	Amine compound	Carbonyl compound	R^5	Time (min)	Yield (%)[b]	M.p. (°C)	
						Found	Reported[22]
4a	*o*-Phenylenediamine	Acetone	*c*Hex	50	92	161–163	160–162
4b	*o*-Phenylenediamine	Cyclohexanone	*t*-Bu	50	87	104–107	106–108
4c	4-Methyl-*o*-phenylenediamine	Cyclohexanone	*c*Hex	45	94	154–155	153–155
4d	3,4-Diaminobenzophenone	Acetone	*c*Hex	50	91	180–182	181–182
4e	3,4-Diaminobenzophenone	Cyclohexanone	*c*Hex	50	90	187–190	187–189
4f	4-Nitro-1,2-phenylenediamine	Acetone	*c*Hex	55	92	>250	>250
4 g	4-Nitro-1,2-phenylenediamine	Acetone	*t*-Bu	60	89	158–161	158–160
4 h	3,4-Diaminobenzophenone	4-Nitrobenzaldehyde	*c*Hex	50	86	>250	>250
4i	4,5-Dichloro-1,2-phenylenediamine	4-Methylbenzaldehyde	*t*-Bu	55	87	>250	>250
4j	4-Nitro-1,2-phenylenediamine	Benzaldehyde	*c*Hex	60	81	177–180	178–180
4 k	4-Nitro-1,2-phenylenediamine	4-Methoxybenzaldehyde	*c*Hex	60	85	176–179	175–176
4 l	4-Methyl-*o*-phenylenediamine	Acetone	*c*Hex	50	91	171–173	—
4 m	*o*-Phenylenediamine	Acetone	1,1,3,3-Tetramethylbutyl	55	83	>250	—

[a]Reaction conditions: diamines (**1**, 1.00 mmol), carbonyl compounds (**2**, 1.00 mmol), isocyanides (**3**, 1.00 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) were stirred in ethanol 96% (3.00 ml).

[b]Isolated yield.

TABLE 5 Synthesis of 1*H*–tetrazolylbenzo[*b*][1,4]diazepine derivatives with various diamines, carbonyl compounds and isocyanides[a]

Entry	Amine compound	Carbonyl compound	R^5	Time (min)	Yield (%)[b]	M.p. (°C)	
						Found	Reported[19]
6a	*o*-Phenylenediamine	Acetone	*c*Hex	50	91	241–243	241–242
6b	4-Methyl-*o*-phenylenediamine	Acetone	*c*Hex	45	89	203–205	202–204
6c	3,4-Diaminobenzophenone	Acetone	*c*Hex	40	90	293–295	293–295
6d	3,4-Diaminobenzophenone	Cyclohexanone	*c*Hex	50	90	>300	>300
6e	4-Nitro-1,2-phenylenediamine	Acetone	TOSMIC	55	81	197–199	196–198
6f	4-Nitro-1,2-phenylenediamine	Cyclohexanone	*c*Hex	55	87	>300	>300
6 g	4-Nitro-1,2-phenylenediamine	4-*tert*-Butylcyclohexanone	*c*Hex	50	75	>300	>300
6 h	4,5-Dichloro-1,2-phenylenediamine	Cyclohexanone	*c*Hex	50	86	>300	>300
6i	*o*-Phenylenediamine	Cyclohexanone	*c*Hex	35	89	>300	—
6j	4-Methyl-*o*-phenylenediamine	4-*tert*-Butylcyclohexanone	*t*-Bu	30	85	283–285	—

[a]Reaction conditions: diamines (**1**, 1.00 mmol), carbonyl compounds (**2**, 1.00 mmol), isocyanides (**3**, 1.00 mmol), $TMSN_3$ (**5**, 1.3 mmol) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) were stirred in methanol (3.00 ml).

[b]Isolated yield.

TABLE 6 Synthesis of 2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine-2-carboxamide derivatives with various diamines, carbonyl compounds and isocyanides[a]

Entry	Amine compound	Carbonyl compound	R^5	Time (min)	Yield (%)[b]	M.p. (°C)	
						Found	Reported[23]
7a	4-Nitro-1,2-phenylenediamine	Acetone	*c*Hex	55	92	186–188	185–187
7b	4-Nitro-1,2-phenylenediamine	Acetone	*t*-Bu	55	89	225–227	224–226
7c	4,5-Dichloro-1,2-phenylenediamine	Acetone	*c*Hex	50	86	170–173	169–172
7d	4,5-Dichloro-1,2-phenylenediamine	Cyclohexanone	*t*-Bu	50	85	169–172	168–170
7e	3,4-Diaminobenzoic acid	Cyclohexanone	*c*Hex	55	87	214–216	213–214
7f	*o*-Phenylenediamine	Cyclohexanone	*c*Hex	50	82	211–213	—
7g	*o*-Phenylenediamine	4-*tert*-Butylcyclohexanone	*c*Hex	55	88	191–193	—

[a]Reaction conditions: diamines (**1**, 1.00 mmol), carbonyl compounds (**2**, 1.00 mmol), isocyanides (**3**, 1.00 mmol), H_2O (1.00 ml) and MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) were stirred in methanol (3.00 ml).

[b]Isolated yield.

Under optimal conditions, various derivatives of **1a**, ketones **2** and isocyanides **3** were examined in this reaction. The results are summarized in Table 6.

The catalyst is very active, stable, nontoxic and inexpensive. To explore the reusability of MCM-48/$H_5PW_{10}V_2O_{40}$, it was easily separated from the reaction medium by filtration and washed thoroughly with ethanol. Then, the catalyst was dried in air and then was activated in a vacuum oven at 70 °C for 3 h. Finally, the recycled catalyst was reused for another condensation reaction. Findings exhibited the same catalytic activity as the fresh catalyst, without any loss of its activity. In addition, to ensure reproducibility of the transformation, repeated typical experiments were carried out under identical reaction conditions (Table 7).

The changes in the structure of the recovered MCM-48/$H_5PW_{10}V_2O_{40}$ were determined using FT-IR methods. As depicted in Figure 4, the structure of the recycled catalyst does not change and a very slight decrease in the reaction yield may be due to the covering of the surface of catalyst by impurities.

A possible mechanism for the formation of products **6a–j** is shown in Figure 5. It is conceivable that the initial event is

TABLE 7 Recycling of catalyst[a]

Cycle	Catalyst (g)	Yield (%)
1	0.040	92
2	0.040	92
3	0.040	92
4	0.037	91
5	0.037	91
6	0.036	90

[a]Reaction conditions: 1,2-benzodiamine (**1a**, 1.00 mmol), acetone (**2a**, 1.00 mmol), cyclohexyl isocyanide (**3a**, 1.00 mmol) and catalyst were stirred in ethanol 96% (3.00 ml).

the formation intermediate **8** from condensation between diamine **1** and 2 mol of ketone **2**. Then, an intramolecular imine–enamine cyclization of **9** affords seven-membered ring **10**. On the basis of the well-established chemistry of the reaction of isocyanides with imines,[19] intermediate **11** is produced by nucleophilic attack of isocyanide **3** to iminium **10** followed by nucleophilic attack of an azide molecule on the nitrilium moiety and production of compound **12**. Finally, the [2 + 3] intermolecular cycloaddition reaction between

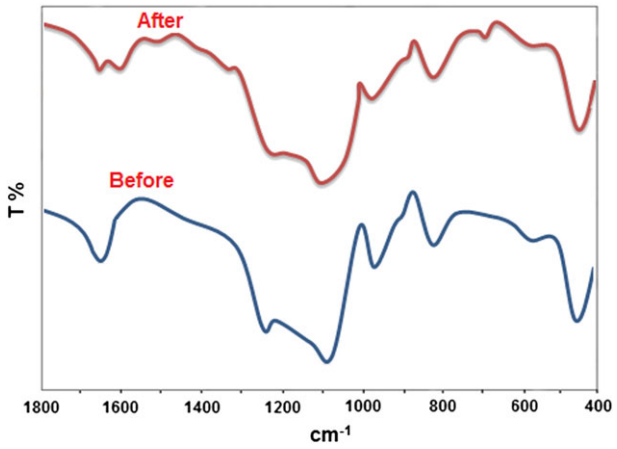


FIGURE 4 FT-IR spectra of MCM-48/$H_5PW_{10}V_2O_{40}$ before and after reaction

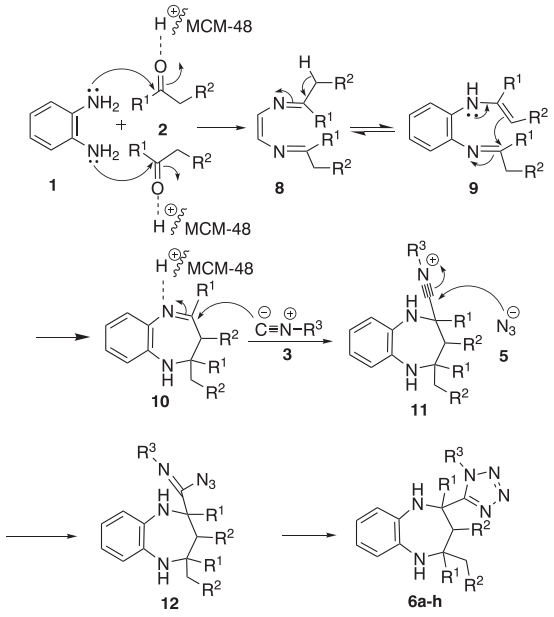


FIGURE 5 Possible mechanism for the formation of products **6a–j**

the C═N and N_3 group of the intermediate **12** leads to **6a–j** (Figure 5).

3 | CONCLUSIONS

Mesoporous silica-supported HPAs have attracted much attention in heterogeneous catalysis. HPA anchored to MCM-48 proved to be an excellent solid acid catalyst for the synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives upon mixing readily available substrates in short reaction times at room temperature. Recyclability of the catalyst with no loss in its activity, mild reaction conditions, ease of product isolation, use of nontoxic substrates and excellent yields are important features of this new protocol to prepare 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives.

4 | EXPERIMENTAL

4.1 | Preparation of Supported MCM-48/$H_5PW_{10}V_2O_{40}$ Catalyst

MCM-48 and $H_5PW_{10}V_2O_{40}\cdot 30H_2O$ were synthesized according to a previously reported procedure.[26] MCM-48-supported $H_5PW_{10}V_2O_{40}\cdot 30H_2O$ was prepared by mixing dried MCM-48 (2.00 g) with a solution of $H_5PW_{10}V_2O_{40}\cdot 30H_2O$ (0.50 g) in the minimum amount of deionized water. The resulting mixture was stirred continuously with a magnetic stirrer for 15 h. After removal of water, the solid powder was first dried at 100 °C for 4–5 h, and then dried at 140 °C for 3 h.

4.2 | General Procedure for Preparation of Products 4a–m

A solution of 1,2-benzenediamine (1.00 mmol), carbonyl compound (1.00 mmol) and isocyanide (1.00 mmol) was stirred for 40–60 min in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) in 3.00 ml of ethanol 96% at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 3:1), the precipitate was filtered off and the product was dissolved in acetone. The catalyst was removed by filtration and the filtrate solution was crystallized to afford pure crystalline products **4a–m**.

4.3 | General Procedure for Preparation of Products 6a–j

A solution of 1,2-benzenediamine (1.00 mmol) and carbonyl compound (2.20 mmol) was stirred for 30 min in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) in 3.00 ml of methanol at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 2:1), isocyanide (1.00 mmol) and trimethylsilyl azide (1.30 mmol) were added to the reaction mixture and stirred at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 3:1), the precipitate was filtered off and the product was dissolved in acetone. The catalyst was removed by filtration. Then, the solution crystallized to afford products **6a–j**.

4.4 | General Procedure for Preparation of Products 7a–g

A solution of 1,2-benzenediamine (1.00 mmol) and carbonyl compound (2.20 mmol) was stirred for 30 min in the presence of MCM-48/$H_5PW_{10}V_2O_{40}$ (0.04 g) in 3.00 ml of methanol at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 2:1), isocyanide (1.00 mmol) and water (1 ml) were added to the reaction mixture and stirred at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate–*n*-hexane, 3:1), the precipitate was filtered off and the product was dissolved

in acetone. The catalyst was recovered by filtration. Then, the solution crystallized to afford products **7a–g**.

ACKNOWLEDGEMENT

The authors thank Tabriz Branch, Islamic Azad University for the financial support of this research.

REFERENCES

[1] A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York **1985**.

[2] A. A. Abu-Hashem, *Am. J. Org. Chem.* **2015**, *5*, 14.

[3] M. Ayaz, G. Martinez-Ariza, C. Hulme, *Synlett* **2014**, *25*, 1680.

[4] P. Aastha, K. Navneet, A. Anshu, S. Pratima, K. Dharma, *Res. J. Chem. Sci.* **2013**, *3*, 90.

[5] W. Lan-Zhi, L. Xiao-Qing, A. Ying-Shuang, *Org. Biomol. Chem.* **2015**, *13*, 5497.

[6] A. Shaabani, H. Sepahvand, S. E. Hooshmand, M. Borjian Boroujeni, *Appl. Organometal. Chem.* **2016**, *30*, 414.

[7] M. Riahi Farsani, F. Jalilian, B. Yadollahi, H. A. Rudbari, *Appl. Organometal. Chem.* **2015**, *29*, 7.

[8] T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641.

[9] D. T. On, D. D. Giscard, C. Danumah, S. Kaliaguine, *Appl. Catal. A* **2003**, *253*, 545.

[10] M. Behbahani, A. Aliakbari, M. M. Amini, A. S. Behbahani, F. Omidi, *RSC Adv.* **2015**, *5*, 68500.

[11] J. Tashkhourian, M. Daneshi, F. Nami-Ana, M. Behbahani, A. Bagheri, *J. Hazard. Mater.* **2016**, *318*, 117.

[12] F. Omidi, M. Behbahani, M. Kalate Bojdi, S. Jamaleddin Shahtaheri, *J. Magn. Magn. Mater.* **2015**, *395*, 213.

[13] J. Abolhasani, M. Behbahani, *Environ. Monit. Assess.* **2015**, *187*, 1.

[14] M. Behbahani, J. Abolhasani, M. M. Amini, O. Sadeghi, F. Omidi, A. Bagheri, M. Salarian, *Food Chem.* **2015**, *173*, 1207.

[15] M. Kalate Bojdi, M. Behbahani, M. H. Mashhadizadeh, A. Bagheri, S. S. Hosseiny Davarani, A. Farahani, *Mater. Sci. Eng. C* **2015**, *48*, 213.

[16] M. Behbahani, A. Ali Akbari, M. M. Amini, A. Bagheri, *Anal. Methods* **2014**, *6*, 8785.

[17] H. Hosseini, M. Behbahani, M. Mahyari, H. Kazerooni, A. Bagheri, A. Shaabani, *Biosens. Bioelectron.* **2014**, *59*, 412.

[18] P. I. Ravikovitch, A. V. Neimark, *Langmuir* **2000**, *16*, 2419.

[19] N. Thanabodeekij, W. Tanglumlert, E. Gulari, S. Wongkasemjit, *Appl. Organometal. Chem.* **2005**, *19*, 1047.

[20] W. Thitsartarn, E. Gulari, S. Wongkasemjit, *Appl. Organometal. Chem.* **2008**, *22*, 97.

[21] E. Assady, B. Yadollahi, M. Riahi Farsani, M. Moghadam, *Appl. Organometal. Chem.* **2015**, *29*, 561.

[22] A. Micek-Ilnicka, E. Bielańska, L. Lityńska-Dobrzyńska, A. Bielański, *Appl. Catal. A* **2012**, *91*, 421.

[23] K. M. Su, Z. H. Li, B. W. Cheng, L. Zhang, M. L. Zhang, J. Ming, J. Fuel, *Process. Technol.* **2011**, *92*, 2011.

[24] A. E. R. S. Khder, *Appl. Catal. A* **2008**, *343*, 109.

[25] E. Caliman, J. A. Dias, S. C. L. Dias, G. S. Prado, *Catal. Today* **2005**, *816*, 107.

[26] A. M. Alsalme, E. F. Kozhevnikova, I. V. Kozhevnikov, *Appl. Catal. A* **2010**, *390*, 219.

[27] B. M. Devassy, F. Lefebvre, S. B. Halligudi, *J. Catal.* **2005**, *231*, 1.

[28] M. Luciana, J. E. Somavilla, G. M. Zorzi, G. R. Ramos, C. L. G. de Amorim, A. Cláudio, *J. Am. Ceram. Soc.* **2011**, *94*, 2640.

[29] V. V. Costa, K. A. D. Rocha, I. V. Kozhevnikovb, E. V. Gusevskaya, *Appl. Catal. A* **2010**, *383*, 217.

[30] M. Babazadeh, R. Hosseinzadeh-Khanmiri, S. Zakhireh, *Appl. Organometal. Chem.* **2016**, *30*, 514.

[31] R. Tayebee, B. Maleki, *J. Chem. Sci. (Bangalore)* **2013**, *125*, 335.

[32] I. V. Kozhevnikov, A. Sinnema, R. J. J. Jansen, K. Pamin, H. Vanbekkum, *Catal. Lett.* **1995**, *30*, 241.

[33] M. Babazadeh, R. Hosseinzadeh-Khanmiri, J. Abolhasani, E. Ghorbani-Kalhor, A. Hassanpour, *RSC Adv.* **2015**, *5*, 19884.

[34] E. Ghorbani-Kalhor, R. Hosseinzadeh-Khanmiri, J. Abolhasani, M. Babazadeh, A. Hassanpour, *J. Sep. Sci.* **2015**, *38*, 1179.

[35] J. Abolhasani, R. Hosseinzadeh-Khanmiri, E. Ghorbani-Kalhor, A. Hassanpour, A. A. Asgharinezhad, N. Shekari, A. M. Fathi, *Anal. Methods* **2015**, *7*, 313.

[36] E. Ghorbani-Kalhor, R. Hosseinzadeh-Khanmiri, M. Babazadeh, J. Abolhasani, A. Hassanpour, *Can. J. Chem.* **2015**, *93*, 518.

[37] A. Hassanpour, R. Hosseinzadeh-Khanmiri, M. Babazadeh, J. Abolhasani, E. Ghorbani-Kalhor, *Food Addit. Contam. A* **2015**, *32*, 725.

[38] H. Mofakham, A. Shaabani, S. Mousavifaraz, F. Hajishaabanha, S. Shaabani, S. W. Ng, *Mol. Divers.* **2012**, *16*, 351.

[39] G. Karthikeyana, A. Pandurangana, *J. Mol. Catal. A* **2009**, *311*, 36.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Vessally E, Hosseinzadeh-Khanmiri R, Ghorbani-Kalhor E, Es'haghi M, Ejlali L. Eco-friendly synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives with the aid of MCM-48/$H_5PW_{10}V_2O_{40}$. *Appl Organometal Chem*. 2017; e3729. https://doi.org/10.1002/aoc.3729