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ORIGINAL PAPER

$[Bmim]_5[PNiW_{11}O_{39}]\cdot 3H_2O$ an organic–inorganic hybrid as catalyst for one-pot pseudo-five-component synthesis of tetrazolyldiazepines

Sajad Mousavifaraz[1] · Zahra Nadealian[1] · Valiollah Mirkhani[1] · Abbas Rahmati[1]

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Abstract In this research, two heterogeneous organic–inorganic hybrid catalysts, $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and $[bmim]_5[PNiW_{11}O_{39}]\cdot 3H_2O$, have been prepared. The catalysts were fully characterized by several techniques such as elemental analyses, Fourier transform infrared spectroscopy, thermo-gravimetric analysis, scanning electron microscope and energy-dispersive X-ray analysis. Next, the hybrid catalysts have been used for the synthesis of functionalized diazepines containing tetrazole ring. Tetrazolyl-1*H*-spiro[benzo[b]cyclopenta[e][1,4] diazepines products were obtained in excellent yields and mild experimental conditions using $[bmim]_5[PNiW_{11}O_{39}]\cdot 3H_2O$ as catalyst. This process was carried out via a one-pot, pseudo-five-component condensation reaction by means of a 1,2-diamine, isocyanide, TMSN3 and two molecules of a linear or cyclic ketone in methanol, at ambient temperature.

Keywords Diazepine · Multi-component reaction · Organic–inorganic hybrid catalyst · Isocyanide

Introduction

Nowadays chemists are trying to design low-cost and environment-friendly reactions. Multi-component reactions (MCRs) in the presence of heterogeneous catalysts can meet the above criteria [1]. Because MCRs are more facile, fast, atom-efficient, practical, economical, green approaches and environmentally benign process [2, 3]. In MCRs, three or more different starting materials react together and produce products without a need for isolation and purification of intermediates [2, 3]. Because of the good reactivity, vast variety and commercially availability of isocyanides, they have been broadly used in MCRs [4, 5]. The use of heterogeneous catalysts in IMCRs has been well documented in the literature [6]. One type of heterogeneous catalysts is organic–inorganic hybrid polyoxometalates [7–11]. They have been extensively used in various organic reactions owing to their unique features such as high thermal stability, low cost and toxicity, simple separation, facility of preparation and recyclability [9].

Heterocyclic compounds, especially heterocyclic compounds containing nitrogen atom, are the main scaffold in the structure of natural compounds and pharmaceutically active compounds [12]. Two types of these compounds are diazepines and tetrazoles [13–15]. Many of benzodiazepines have received great attention because of their broad range of biological properties such as anti-HIV [16], antipsychotics [17] and antitumor agents [18]. Similarly, tetrazoles rings have also been used as anti-TMV [19, 20], antifungal [21], antiulcer [22] and anti-HCV compounds [23]. Diazepines and tetrazoles have been synthesized using MCRs and IMCRs [24–26]. It was reported that heterocyclic compounds containing two or more heterocyclic rings have synergic effect and increase pharmaceutical properties [27, 28]. A few syntheses of tetrazolodiazepines and tetrazolyldiazepines were already reported [29–35]. Shaabani et al. recently have synthesized tetrazolylbenzodiazepine using two different methods. In their first method, the problems were a two-step process, the use of expensive and very toxic compounds, harsh reaction condition and tedious workup, the use of large amount of organic solvents and low atom economy of process. Although in their second report, a part of problems was moderated with using of the one-pot MCR

✉ Abbas Rahmati
a.rahmati@sci.ui.ac.ir

[1] Department of Chemistry, University of Isfahan, P. O. Box 81746-73441, Isfahan, Iran

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method, the main problem (the use of *p*-TSA and HCl homogeneous acidic catalyst) is not resolved, yet. These catalysts are not reusable and environmentally benign and are also high corrosive. Therefore, proposing a convenient procedure to use a safer catalyst is of great importance.

In continuation of our studies on IMCRs [36, 37], here a new method is introduced for synthesis of 5-(1*H*-tetrazol-5-yl)-4,5,6,7-tetrahydro-1*H*-1,4-diazepine-2,3-dicarbonitrile derivatives **5a–e** and 2-(1*H*-tetrazol-5-yl)-2,3,4,5-tetrahydro-1*H*-benzo[b] [1, 4] diazepine derivatives **5f–o.** These products are obtained in excellent yields using a catalytic amount of [bmim]5[PNiW11O39]·3H2O in methanol solvent at ambient temperature via one-pot pseudo-five-component reaction (Scheme 1).

Experimental

General

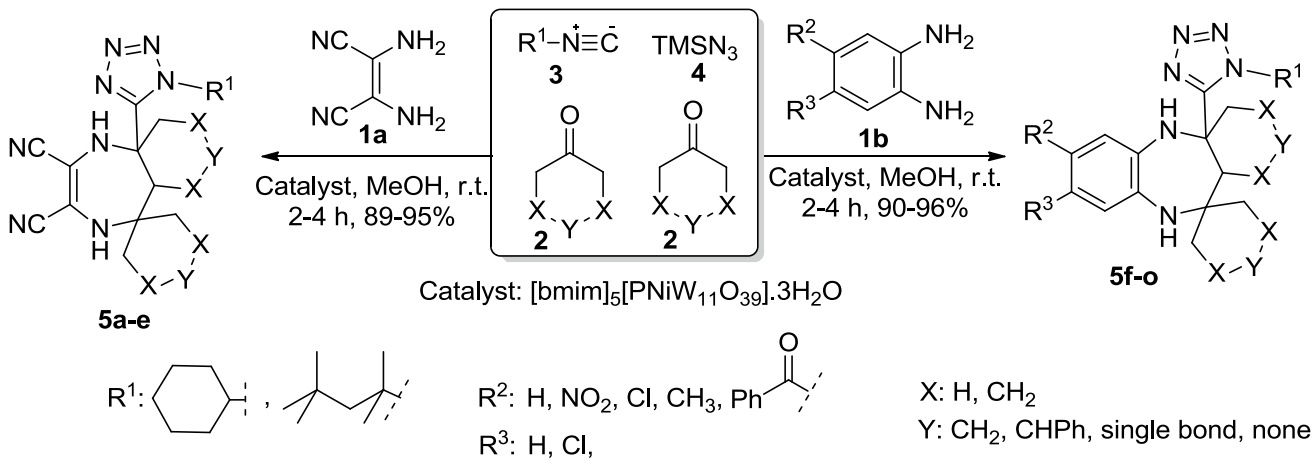
All chemicals and reagents were purchased from Across, Alfa Aesar, Daejung or Merck chemical companies and were used without purification. The known organic products were identified by comparison of their melting points and ^{1}H NMR spectral data with those reported in the literature. New organic compounds fully characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectra and elemental analysis. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. FT-IR spectra were recorded as KBr pellets using a Shimadzu Corporation spectrometer at 400–4000 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX FT-NMR spectrometer at 400 and 100 MHz, respectively (δ in ppm). Thermo-gravimetric analysis (TGA) of the catalyst was carried out on a Mettler TA4000 instrument. Inductively coupled plasma optical emission spectrometer (ICP-OES) was carried out on a Varian Vista PRO Radial. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) studies were carried out with SEM-HITCHI S4160.

Procedure for the preparation of $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ catalyst (catalyst A)

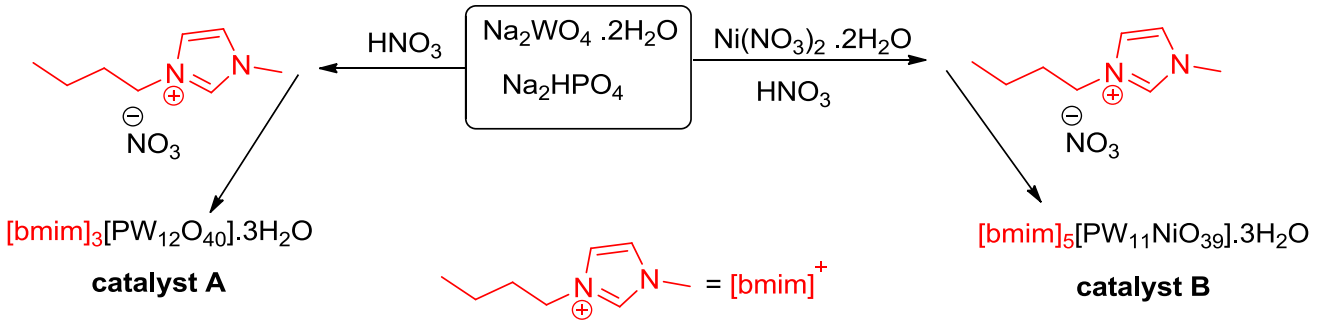
A mixture of sodium tungestate·$2H_2O$ (8.250 g, 25 mmol) and sodium monohydrogen phosphate (0.320 g, 2.3 mmol) was dissolved in a 50 mL of water in a round-bottomed flask (250 mL) and stirred at room temperature for 1 h. Next, pH of the solution was tuned to 4.8 by means of HNO_3. Then, [bmim]NO_3 (2.412 g, 12 mmol) ionic liquid was poured slowly to solution into 2 h. The precipitated catalyst was filtered off, washed with cooled water and dried. Finally, the product was obtained (5.725 g).

Procedure for the preparation of $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ catalyst (catalyst B)

A mixture of sodium tungestate·$2H_2O$ (8.250 g, 25 mmol) and sodium monohydrogen phosphate (0.320 g, 2.3 mmol) was dissolved in a 50 mL of water in a round-bottomed flask (250 mL) and stirred at room temperature. After 1 h, nickel nitrate (0.546, 3 mmol) was added to the solution and stirred for 1 h. Next, the pH of the solution was tuned to 4.8 using HNO_3. Then, [bmim]NO_3 (2.412 g, 12 mmol) was added slowly to solution in 2 h. The precipitated catalyst was filtered off, washed with cooled water and dried. Finally, the product was obtained (4.938, g).



Scheme 1 Synthesis of tetrazolyldiazepines **5a–o** in the presence of $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$



Scheme 2 Synthesis of $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ catalysts

Table 1 EA, ICP and AA for determination of type and element wt% in catalysts by various methods

Entry	Method of determination	wt% of element	Catalyst A		Catalyst B	
			Experimental	Theoretical	Experimental	Theoretical
Elemental analyses						
1	CHNS	C	8.72	8.61	13.78	13.78
		H	1.52	1.54	2.30	2.34
		N	2.53	2.51	4.10	4.02
2	ICP	P	0.92	0.92	0.87	0.89
		Ni	–	–	1.62	1.68
		W	65.75	65.88	58.27	58.01
3	Atomic absorption	Ni	–	–	1.50	1.68
		W	65.60	65.88	58.49	58.01

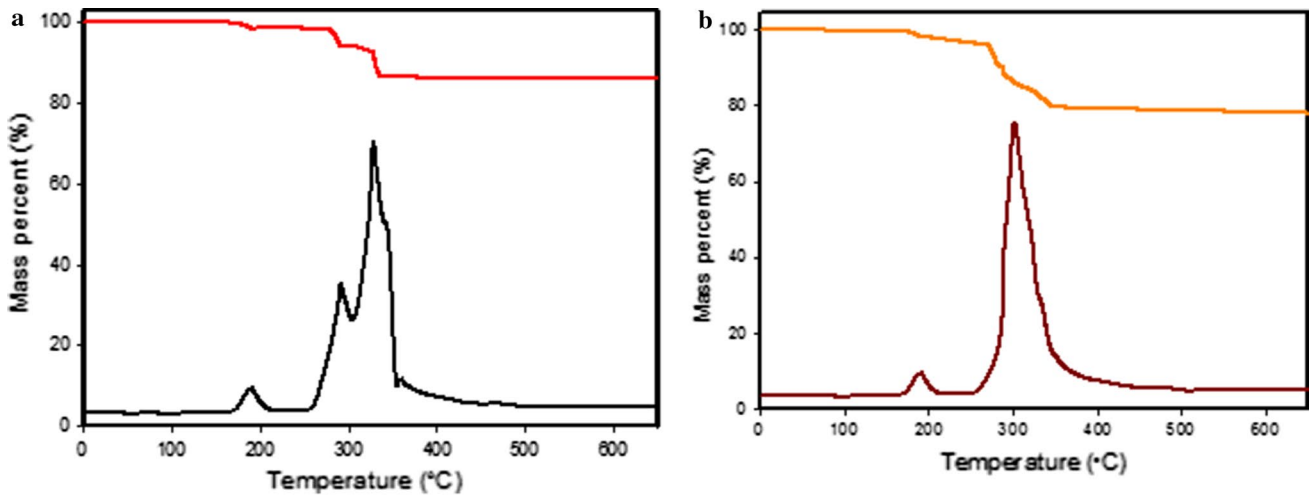


Fig. 1 TGA of **a** $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and **b** $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$

General procedure for the synthesis tetrazolyldiazepines (5a–o) using $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$

A solution of 1,2-diamine (1 mmol), ketone (2.2 mmol), isocyanide (1 mmol) and trimethylsilylazide (1.2 mmol) and $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ (5 mol%) in MeOH (5 mL) was stirred for 2–4 h at room temperature. After completion of the reaction, as indicated by TLC, the precipitate and catalyst was filtered off. The residue of products and catalyst was separated by washing with acetone. Then the product was crystallized from acetone:ethanol to give pure products **5a**–**o**.

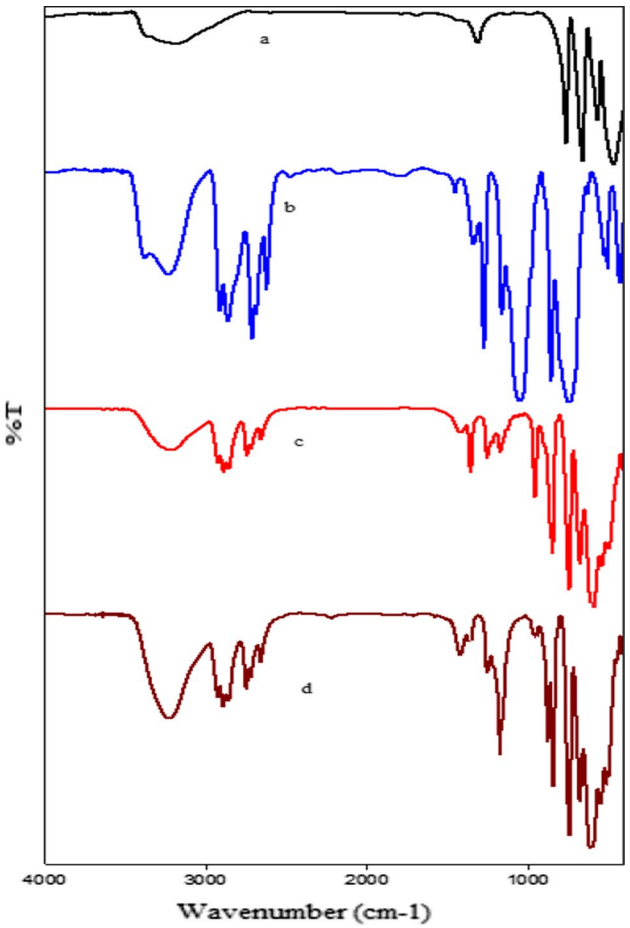


Fig. 2 FT-IR spectra of **a** $H_3[PW_{12}O_{40}]$, **b** $[bmim]NO_3$, **c** $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$

Characterization data for new compounds

3a-(1-cyclohexyl-1*H*-tetrazol-5-yl)-2,3,3a,4,9,10a-hexahydro-1*H*-spiro[benzo[b]cyclopenta [e] [1, 4] diazepine-10,1′-cyclopentane] **(5 g)**: Yield 94%. White powder; mp 251–253 °C. IR (KBr) υ: 3382, 3018, 2937, 2872, 1598, 1505, 1472, 1444, 1400, 1310, 1261, 740 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d6*) δ: 1.12–2.22 (24H, m, $5CH_2$ of Cyclohexyl and $7CH_2$ of Cyclopentyl), 3.63 (1H, m, CH of Cyclopentyl), 4.43 (1H, s, NH), 4.82 (1H, m, CH of Cyclohexyl), 5.62 (1H, s, NH), 6.39–6.71 (4H, m, H-Ar) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 21.84, 23.76, 24.10, 24.57, 27.44, 32.27, 32.73, 33.99, 40.54, 42.06, 53.42, 56.74, 64.47, 65.78, 117.89, 117.97, 118.33, 119.49, 134.21, 135.71, 160.14 ppm. Anal. Calcd for $C_{23}H_{32}N_6$: C, 70.37; H, 8.22; N, 21.41; found C, 69.60; H, 7.69; N, 21.55.

3a-(1-cyclohexyl-1*H*-tetrazol-5-yl)-6-methyl-2,3,3a,4,9,10a-hexahydro-1*H*-spiro[benzo [b]cyclopenta[e] [1, 4] diazepine-10,1′-cyclopentane] **(5 k)**: Yield 96%. White powder; mp 262-264 °C. IR (KBr) υ: 3371, 3306, 2935, 2859, 1594, 1502, 1448, 1395, 1315, 1251, 799 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d6*) δ: 1.06–2.20 (27H, m, $5CH_2$ of Cyclohexyl, $7CH_2$ of Cyclopentyl and $1CH_3$), 3.60 (1H, m, CH of Cyclopentyl), 4.39 (1H, s, NH), 4.83 (1H, m, CH of Cyclohexyl), 5.45 (1H, s, NH), 6.21–6.59 (3H, m, H-Ar) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 20.23, 22.00, 23.78, 24.14, 24.60, 27.59, 32.53, 32.83, 33.99, 40.49, 41.94, 53.39, 56.70, 64.50, 65.81, 118.41, 118.76, 119.91, 128.11, 131.55, 135.85, 160.12 ppm. Anal.

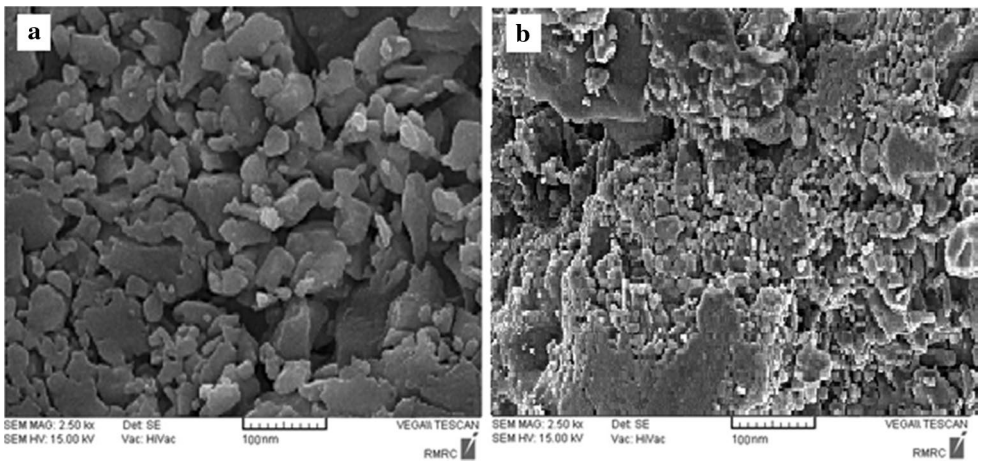


Fig. 3 SEM images of **a** $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and **b** $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$

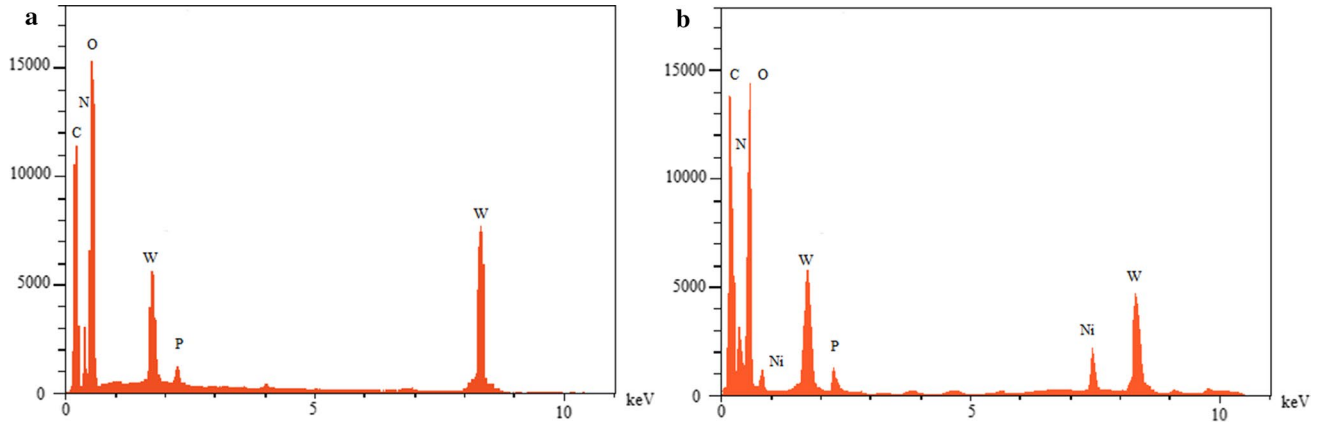


Fig. 4 EDX images of **a** $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and **b** $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$

Calcd for $C_{24}H_{34}N_6$: C, 70.90; H, 8.43; N, 20.67; found C, 69.89; H, 8.70; N, 20.55.

(3a-(1-cyclohexyl-1*H*-tetrazol-5-yl)-2,3,3a,4,9,10a-hexahydro-1*H*-spiro[benzo[b]cyclopean ta[e] [1, 4] diazepine-10,1′-cyclopentane]-6-yl)(phenyl)methanone **(5n)**: Yield 94%. White powder; mp >300 °C. IR (KBr) υ: 3369, 3345, 2938, 2861, 1628, 1584, 1566, 1496, 1444, 1395, 1336, 1290, 1132 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d6*) δ: 1.02–2.24 (24H, m, $5CH_2$ of Cyclohexyl and $7CH_2$ of Cyclopentyl), 3.80 (1H, m, CH of Cyclopentyl), 4.71 (1H, m, CH of Cyclohexyl), 5.71 (1H, s, NH), 5.94 (1H, s, NH), 6.43–7.56 (8H, m, H-Ar) ppm. ^{13}C NMR (100 MHz, DMSO-*d6*) δ: 22.14, 24.04, 24.35, 24.49, 24.74, 27.82, 32.90, 33.02, 34.07, 40.86, 42.14, 52.17, 56.65, 64.28, 66.16, 116.45, 120.40, 124.14, 125.81, 128.12, 128.64, 130.97, 133.09, 139.00, 142.09, 159.63, 193.65 ppm. Anal. Calcd for $C_{30}H_{36}N_6O$: C, 72.55; H, 7.31; N, 16.92; found C, 72.10; H, 7.26; N, 15.98.

6,7-dichloro-3a-(1-cyclohexyl-1H-tetrazol-5-yl)-2,3,3a,4,9,10a-hexahydro-1Hspiro[benzo[b] cyclopenta[e] [1, 4] diazepine-10,1′-cyclopentane] **(5o)**: Yield 92%. White powder; mp >300 °C. IR (KBr) υ: 3375, 2941, 2872, 1590, 1490, 1463, 1400, 1298, 1224, 1132, 860 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 1.15–2.17 (24H, m, 5CH2 of Cyclohexyl and 7CH2 of Cyclopentyl), 3.69 (1H, m, CH of Cyclopentyl), 4.74 (1H, m, CH of Cyclohexyl), 5.01 (1H, s, NH),6.01 (1H, s, NH), 6.59 (1H, s, H–Ar), 6.90 (1H, s, H–Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.80, 23.85, 24.39, 24.54, 24.66, 27.42, 32.36, 33.24, 34.00, 40.65, 42.15, 55.91, 56.84, 64.30, 65.87, 118.20, 118.39, 120.09, 134.83, 136.66, 159.61 ppm. Anal. Calcd for $C_{23}H_{30}C_{l2}N_6$: C, 59.87; H, 6.55; N, 18.21; found C, 60.18; H, 6.81; N, 18.14.

Results and discussion

Synthesis and characterization of catalysts

Both the organic–inorganic hybrid catalysts were synthesized via two-step one-pot method (Scheme 2).

Table 2 Comparison of catalysts with other catalysts in model reaction[a]

Entry	Catalyst	Time (h)[b] (Yield (%)[d])	Time (h)[c] (Yield (%)[d])
1	–	24(–)	–
2	$H_3[PW_{12}O_{40}]$	6(60)	8(76)
3	$H_4[SiW_{12}O_{40}]$	6(62)	8(72)
4	$[Bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$	6(71)	7(86)
5	$[Bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$	6(94)	4(94)
6	HCl	6(30)	11(51)
7	H_2SO_4	6(22)	14(35)
8	$MgCl_2$	6(9)	10(12)
9	$NiCl_2$	6(35)	10(48)
10	$[Bmim]NO_3$	24(–)	–

[a] Benzene-1,2-diamine (1 mmol), cyclopentanone (2.2 mmol), cyclohexylisocyanide (1 mmol) and trimethylsilylazide (1.2 mmol) in methanol (5 mL), in the presence of catalyst (20 mol %), [b] constant time (6 h), [c] completion of reaction time by TLC, [d] isolated yield

Table 3 Effect of solvent, time and temperature on the model reaction[a]

Entry	Solvent	Amount of catalyst (mol%)	Temperature (°C)	Time (h) (Yield (%)[b])
1	EtOAc	20	r.t.	6(–)
2	Toluene	20	r.t.	6(–)
3	EtOH	20	r.t.	6(15)
4	CH2Cl2	20	r.t.	6(–)
5	H2O	20	r.t.	6(–)
6	MeCN	20	r.t.	6(–)
7	MeOH	20	r.t.	6(94)
8	MeOH	20	r.t.	4(94)
9	MeOH	20	r.t.	3(90)
10	MeOH	20	r.t.	2(74)
11	MeOH	20	r.t.	1(53)
12	MeOH	20	45	3(94)
13	MeOH	20	60	3(94)
14	MeOH	10	r.t.	4(94)
15	MeOH	5	r.t.	4(94)
16	MeOH	2	r.t.	4(81)

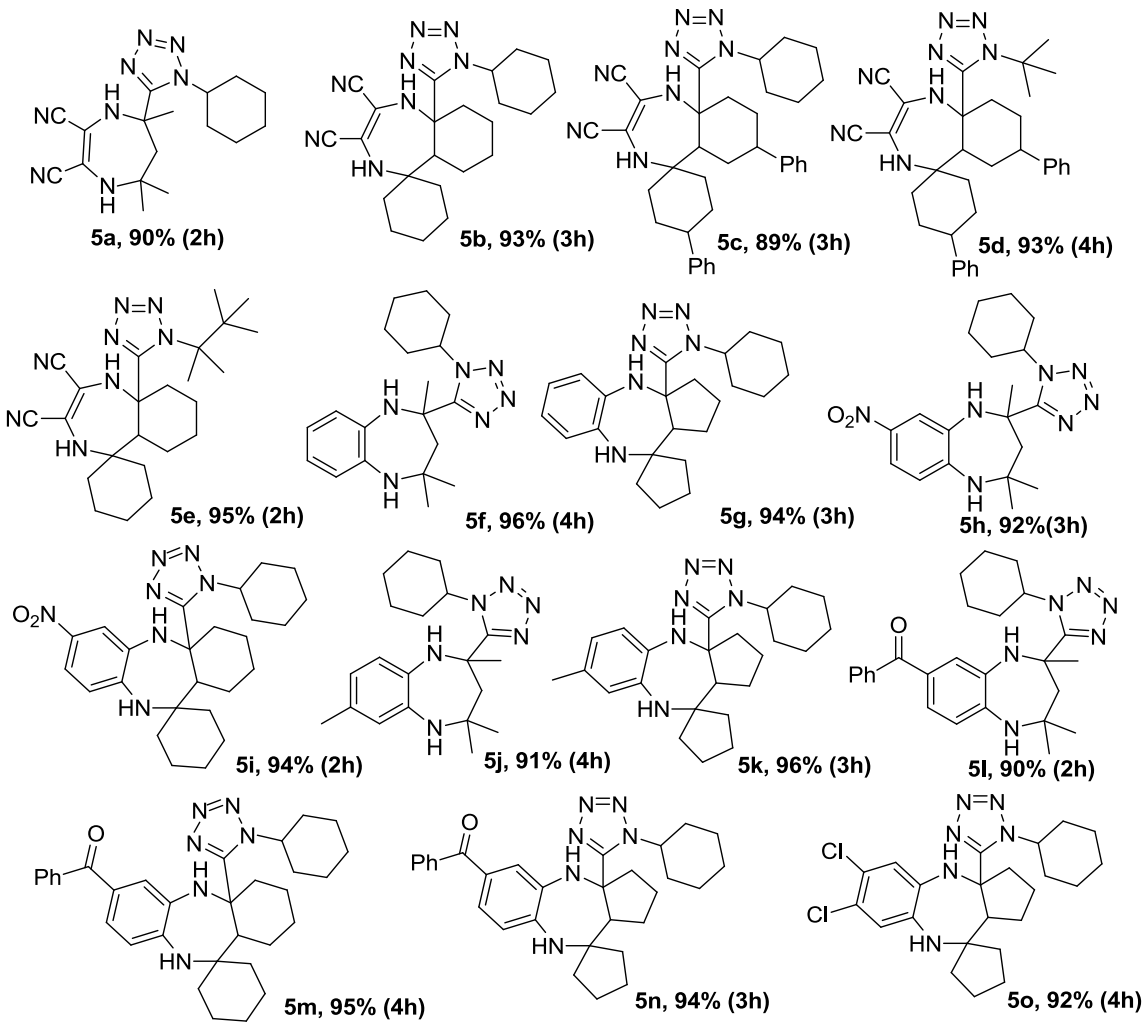
[a] Benzene-1,2-diamine (1 mmol), cyclopentanone (2.2 mmol), cyclohexylisocyanide (1 mmol) and trimethylsilylazide (1.2 mmol) in the presence of $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ (20 mol%), [b] isolated yield

EA, AA, ICP-OES, TG-DTG, FT-IR, SEM and EDX have been used to confirm the formation of the catalysts.

The structure of the catalysts was determined using EA, AA, ICP-OES (Table 1) and TG-DTG analysis (Fig. 1). Elemental analysis by CHNS analyzer showed that cationic part of $[bmim]NO_3$ ionic liquid connected to the polyoxometalate in both of the catalysts. Also, EA revealed that total wt% of the H, C and N atoms was 12.77 and 20.18% in structures of A and B catalysts. Atomic absorption and ICP results showed that polyoxometalate moiety of heteropolyacid exist in the final structure of catalysts. Correspondingly, these analyses revealed that total wt% of the P and W atoms is 66.59% in structure of A catalyst and that of P, Ni and W was 52.81% in structure of B catalyst. On the other hand, the weight loss of the catalysts was determined in the range of 25–650 °C using TGA (Fig. 1). TGA analysis showed thermal decomposition for both catalysts. The first step was removal of water that takes placed in the range of 170–200 °C. The second step was for organic parts decomposition that occurred in the range of 250–380 °C. In A catalyst, decomposition of organic part take placed in two stages. In the first step of decomposition, the amount of the weight loss was 1.60 and 1.53% for A and B catalysts, respectively. Calculations, exactly confirmed the presence of three water molecules in structure of both catalysts. In the second part of decomposition, 12.45 and 19.96% the amount of the weight loss were observed for A and B catalysts, respectively. Therefore, total weight loss for A and B catalysts was 14.05 and 21.49%, respectively. This 14.05% was equal with three water molecules and three cationic [bmim] unit that connected to an anionic $[PW_{12}O_{40}]$ unit. Also, 21.49% was equal with three water molecules and five cationic [bmim] unit that connected to an anionic $[PW_{11}NiO_{39}]$ unit. The results of theoretical weight percent for both catalysts are presented in Table 1. There is good agreement between theoretical and experimental wt% which confirmed the proposed structures. In addition, the weight percents of elements in catalysts exactly confirmed that $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ (catalyst A) and $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ (catalyst B) are the structures of catalysts.

FT-IR spectra of the catalysts ($[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$) were compared with those from the starting material ($[bmim]NO_3$) and a well-known catalyst $H_3[PW_{12}O_{40}]$ (Fig. 2). FT-IR spectra confirm the formation of the catalysts. The broad peak related to O–H stretching of the water appeared at 3400–3600 cm^{-1}. The vibrational frequency of CH_2 and CH_3 groups was observed at 2850–2950 cm^{-1}, and the vibrations at 1637 and 1450 cm^{-1} were attributed to stretching frequencies of C=N and C=C functional groups in the starting material and the catalysts. Based on the literature [38, 39], the stretching frequencies observed at 891, 984 and 1079 cm^{-1} are attributed to P–O, W=O and W–O–W bands of the terminal oxygen of polyoxometalate moiety, respectively. These bands demonstrate the presence of [bmim] and polyoxometalate moieties in the structure of catalysts.

The scanning electron microscope (SEM) micrographs of the catalysts showed that the particles did not



Scheme 3 Structure products, isolated yields and reaction times of synthesized tetrazolyldiazepines in the presence of [bmim]5[PW11NiO39]·3H2O catalyst

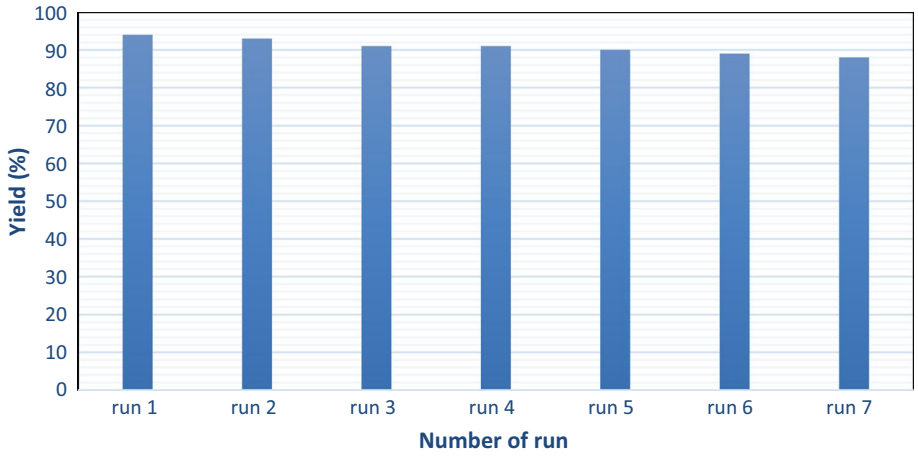


Fig. 5 Recyclability of catalyst B of **5a** product

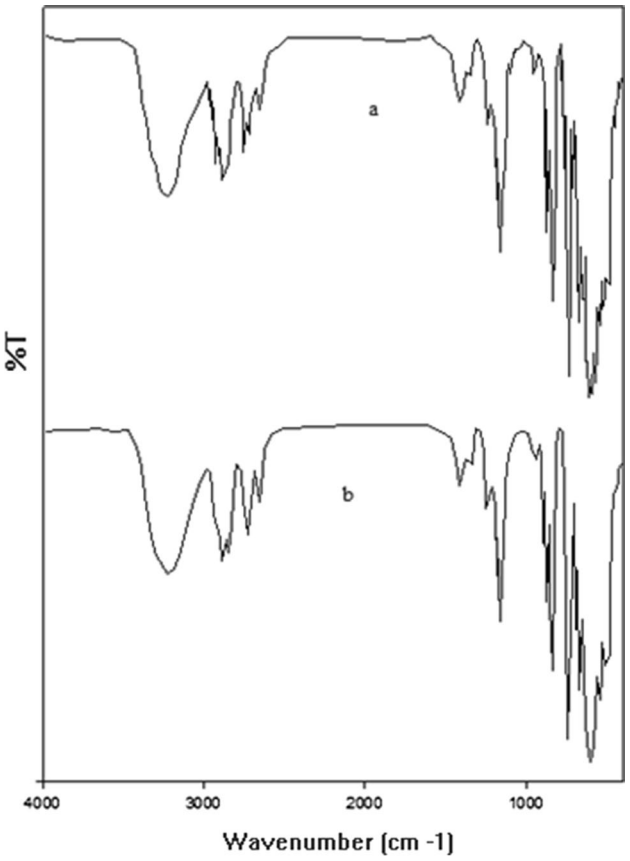


Fig. 6 FT-IR spectra comparing the fresh catalyst B (**a**) and after the 7th run (**b**)

agglomerated completely. The size of the particles is in nanorange (10–100 nm) (Fig. 3).

The energy-dispersive X-ray spectroscopy (EDX) of the nanocatalysts proved the presence of carbon, nitrogen, oxygen, tungsten and phosphorous elements in $[bmim]_3[PW_{12}O_{40}]\cdot 3H_2O$ and carbon, nitrogen, oxygen, nickel, tungsten and phosphorous elements in $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$ as expected (Fig. 4a, b).

Application of the catalysts in synthesis of tetrazolyldiazepines

The catalysts were applied in the synthesis of a tetrazolyldiazepines (**5 g**) in order to compare their efficiency. Benzene-1,2-diamine, cyclopentanone, cyclohexyl isocyanide and trimethyl silylazide were mixed in methanol in the presence of each catalyst at room temperature. The progress of the reactions was monitored by TLC. The reaction was worked up, and the desired products were confirmed by H-NMR and melting point. Good yields of product encouraged us to optimize reaction conditions.

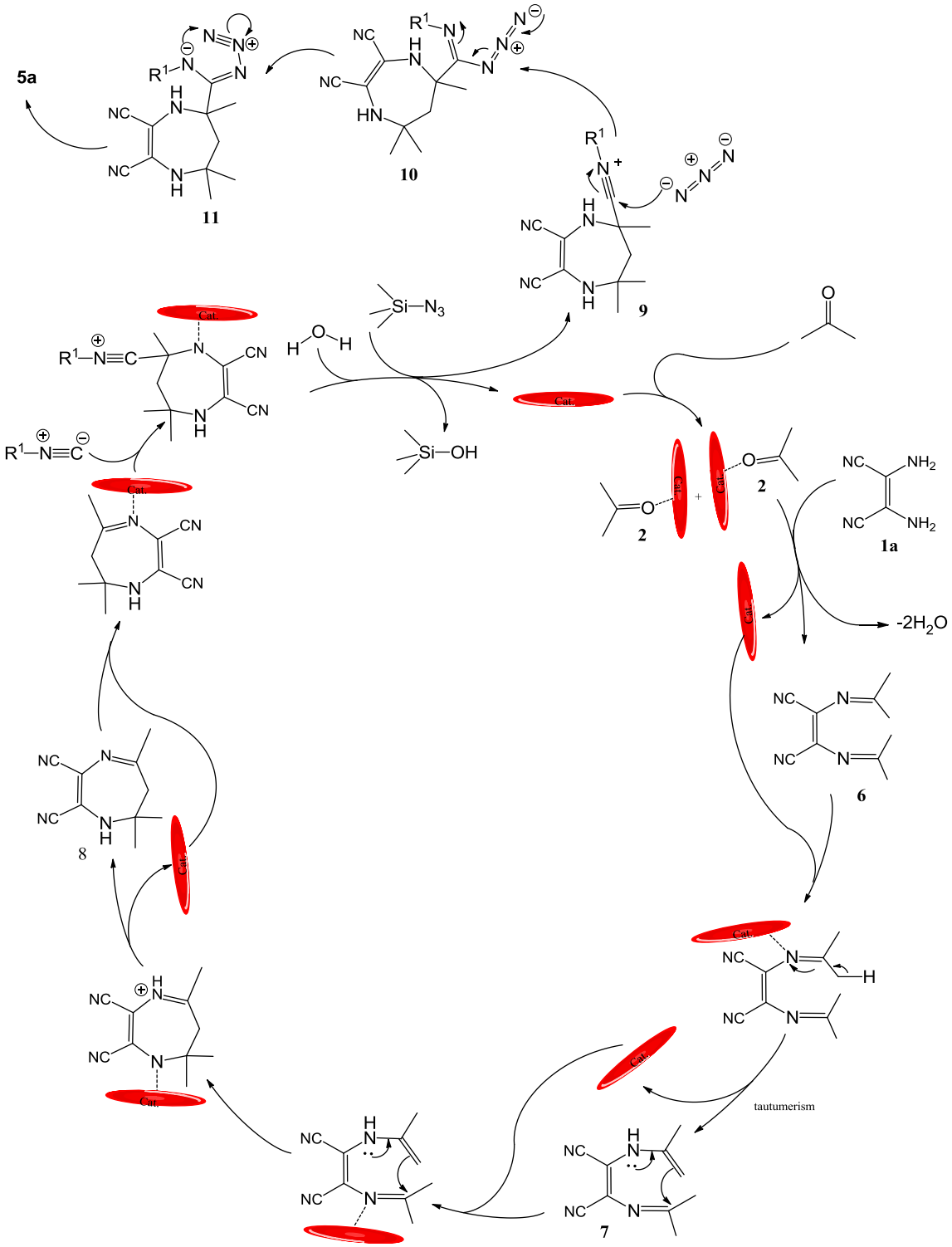
We compared the efficiency of our catalysts with that of the other catalysts. For this purpose, the reaction was performed using commercially polyoxometalates and different Brønsted and Lewis acid catalysts (20 mol%) in methanol at room temperature (entries 2–9, Table 2). For each catalyst two experiments were done: one at a constant time (6 h) and another continued up to disappearance of the starting material on TLC. The polyoxometalate catalysts exhibited better results compared to the normal Brønsted and Lewis acids (Table 2). Among polyoxometalate, the best yield was obtained with [bmim]5[PW11NiO39]·3H2O. On the other hand, no product was obtained in the absence of catalyst after 24 h (entry 1, Table 2). Moreover, the reaction was performed in the presence of $[bmim]NO_3$, and any product was not obtained in this condition after 24 h (entry 10, Table 2).

Next, using $[bmim]_5[PW_{11}NiO_{39}]\cdot 3H2O$ as the best catalyst, we tried to optimized the reaction condition. Different solvents, such as H2O, CH2Cl2, MeOH, EtOH, EtOAc, CH3CN and toluene were used (entries 1–7, Table 3). The reaction in MeOH had higher yield than the other reactions. Therefore, MeOH was chosen as the reaction solvent. Afterward, reaction time was optimized. The results suggested that 4 h was the best reaction time (entries 7–11, Table 3). We also observed that higher temperature did not improve the yield and reaction time. Finally, the effect of different amount of the catalyst (2, 5, 10 and 20 mol%) was evaluated. The results indicated that 5 mol% of catalyst was optimal amount. Higher amounts of catalyst did not lead to a significant change in yield.

Under the optimized conditions, the ability and limitation of the best catalyst was checked by varying the structure of the diamine, ketone and isocyanide components (Scheme 3). All the reactions showed high yields (89–96%) and the products were purified by crystallization in acetone.

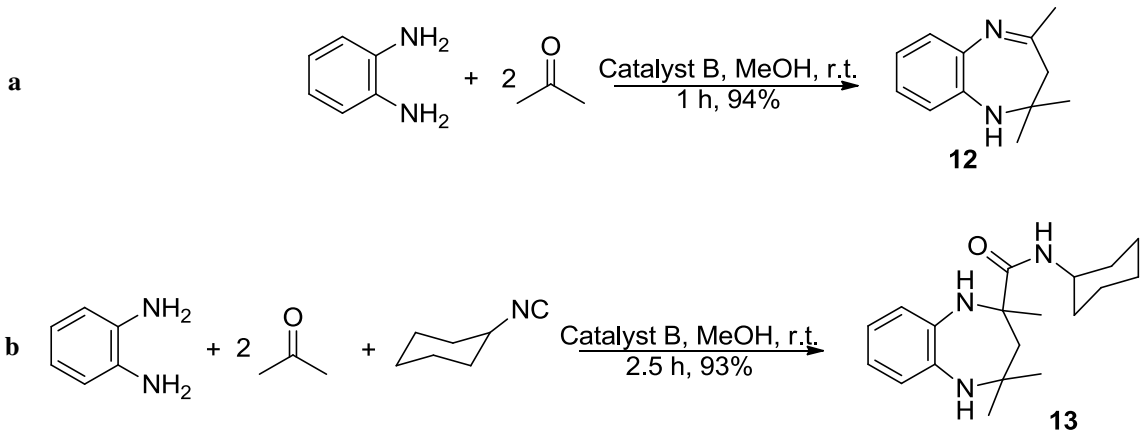
Structure of known compounds was confirmed by melting point and ^{1}H NMR while the structure of new compounds was characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis.

One of the advantages of heterogeneous catalysts is their recyclability. The reusability of this catalyst was investigated in the model reaction under the optimized conditions. For each of the repeated reactions, the catalyst was recovered easily by simple filtration technique and then washed with ethanol (5 mL) twice and dried at 50 °C in an oven. The separated catalyst was reused successively in seven times in model reaction without a considerable loss of catalytic activity (Fig. 5) Comparison of the FT-IR spectra of the catalyst after the 7th run and the fresh catalyst showed that no obvious changes in the structure of catalyst and the characteristic bands (Fig. 6). Also, CHNS analysis after the 7th run from the catalyst illustrated that the results are the similar to the fresh catalyst. Therefore, catalyst is stable and the decreasing of reaction yield undoubtedly is due to the method.



Scheme 4 Possible mechanism for the formation of product **5a** in the presence of catalyst B

The possible mechanism for the formation of product **5a** is shown in Scheme 4. The acid sites in catalyst facilitate the reaction by activating the carbonyl group of ketone **2**. It is feasible that the initial event is the formation of diamine **6** from condensation between diamine **1a** and two molecules of acetone **2**. Then by aid of catalyst imine–enamine tautomerism, compound **7** was created. Next, imine group of 7 was activated by the catalyst and finally intramolecular



Scheme 5 Two reactions to prove the reaction mechanism in the presence of catalyst

cyclizatin produced a seven-membered ring **8**. On the basis of the well-established chemistry of the reaction of isocyanides with imines, intermediate **9** was produced by nucleophilic attack of isocyanide **3** to iminium **8**. Subsequently, by the reaction between intermediate **9** and azide ion (in which was obtained from TMSN3) compound **10** is produced. Followed by the intramolecular electron transfer between the C=N and azide group in **10**, intermediate 11 was achieved. Finally, product **5a** formed from compound **11** using cyclization. In order to prove the reaction mechanism, two different reactions were performed (Scheme 5). The first reaction was the reaction of 1,2-phenylene diamine and two equivalent acetone in the absence of isocyanide and azide ion source that produced benzodiazepine **12** [40]. The other was reaction of 1,2-phenylene diamine, isocyanide and two equivalent acetone without $TMSN_3$ compound that produced benzodiazepine **13** [41].

Conclusion

In summary, we have developed a highly powerful heterogeneous catalyst ($[bmim]_5[PW_{11}NiO_{39}]\cdot 3H_2O$) for one-pot synthesis of highly functionalized tetrazolodiazepines scaffolds from readily available starting materials. The gave the corresponding products in excellent yields. Furthermore, the process was worth from industrially view point because of short reaction time, mild reaction conditions, inexpensive catalyst, reusable catalyst and simple workup.

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Compliance with ethical standards

Conflict of interest None of the authors has any potential conflict of interest.

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