Synthesis of 3,4-Dihydroquinoxalin-2-Amine, Diazepine-Tetrazole and Benzodiazepine-2-Carboxamide Derivatives with the Aid of $H_6P_2W_{18}O_{62}$/Pyridino-Fe_3O_4

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ABSTRACT: *In the current study, a magnetic inorganic–organic nanohybrid material (HPA/TPI-Fe_3O_4) was produced and used as an efficient, highly recyclable and eco-friendly catalyst for the one-pot and multi-component synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives with high yields and in a short range of time (20–35 min). The nanohybrid catalyst was prepared by the chemical anchoring of $H_6P_2W_{18}O_{62}$ onto the surface of modified Fe_3O_4 NPs with N-[3-(triethoxysilyl)propyl]isonicotinamide (TPI) linker. The magnetically recoverable catalyst was easily recycled at least ten times without any loss of catalytic activity. The structures of obtained products are certified by ^1H and ^{13}C NMR spectra.*

KEYWORDS: *$H_6P_2W_{18}O_{62}$/pyridino-Fe_3O_4; 3,4-Dihydroquinoxalin-2-amine; Diazepine-tetrazole; Benzodiazepine-2-carboxamide.*

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 atom which displays a broad spectrum of biological and pharmacological activities

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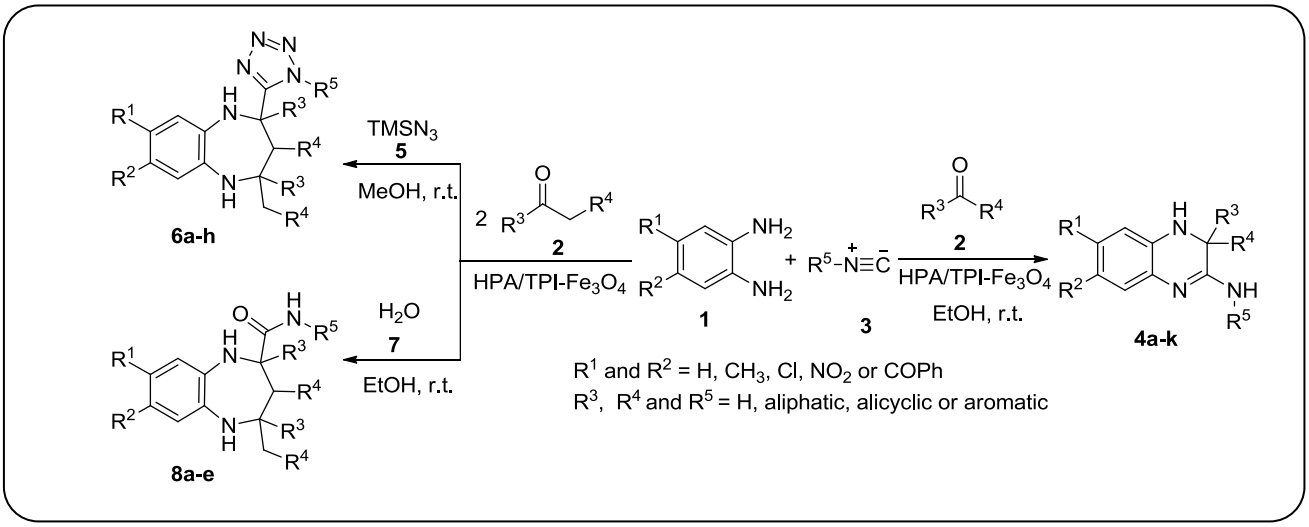


Scheme 1: Synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives.

such as insecticide, fungicide, herbicide, anthelmintic, antibacterial, antimycobacterial, antiprotozoal, anticancer and antibiotic properties [2-3].

Benzodiazepines are an important class of bioactive compounds. These compounds have been extremely applied as anxiolytic, anticonvulsant, hypnotic, sedative, skeletal muscle relaxant, amnestic, diabetic nephropathy, glomerulosclerosis and peptide hormones properties [4-6].

Recently, science and technology are shifting emphasis on environmentally friendly and sustainable resources and processes, for these reasons few heterogeneous materials with supported HPW, such as HPW/C [7], HPW/CNTS [8], HPW/TiO_2 [9], HPW/SnO_2 [10], HPW/C-Al_2O_3 [11], HPW/Nb_2O_5 [12], HPW/ZrO_2 [13], HPW/hydrous zirconia [14], and HPW/SiO_2 [15] have been studied.

Paramagnetic Fe_3O_4 nanoparticles have attracted worldwide attention and have been studied extensively due to their technological and biological applications such as drug delivery, bioseparation, biomolecular sensors, and Magnetic Resonance Imaging (MRI) [16-18].

Shaabani et al. 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, long reaction times and reaction did not occur in the absence of this catalyst [19].

In this research, a novel method for the synthesis of these biologically important materials is presented using $H_6P_2W_{18}O_{62}$/pyridino- Fe_3O_4. This environmentally benign, heterogeneous, and highly reusable catalyst showed very good catalytic activity toward the synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives (Scheme 1).

EXPERIMENTAL SECTION

General procedure for the preparation of products 4a-k:

A solution of 1,2-benzodiamine (1.00 mmol), carbonyl compounds (1.00 mmol) and isocyanide (1.00 mmol) was stirred for 20-35 min in the presence of HPA/TPI-Fe_3O_4 (0.02 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 recovered using an external magnet. Then, the solution crystallized to give products **4a-k**.

General procedure for the preparation of products 6a-h

A solution of 1,2-benzodiamine (1.00 mmol) and carbonyl compounds (2.20 mmol) was stirred for 20 min in the presence of HPA/TPI-Fe_3O_4 (0.02 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 recovered using an external magnet. Then, the solution crystallized to give products **6a-h**.

Table 1: Optimization of the catalyst for synthesis of N-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine 4a [a]

Solvents	Time (min)	Yields (%)[b]
HPA	20	64
Fe_3O_4	20	33
TPI-Fe_3O_4	20	52
HPA/TPI-Fe_3O_4	20	95

*[a] Reaction conditions: 1,2-benzodiamine (**1**, 1.00 mmol), aceton (**2**, 1.00 mmol), cyclohexyl isocyanide (**3**, 1.00 mmol), and catalyst (0.02 g) were stirred in ethanol 96% (3.00 mL). [b] Isolated yield.*

Table 2: Optimization of the solvent for synthesis of N-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine 4a[a]

Solvents	Time (min)	Yields (%)[b]
H_2O	20	43
CH_2Cl_2	20	53
$CHCl_3$	20	58
CH_3CN	20	76
C_6H_6	20	8
THF	20	24
MeOH 99%	20	89
EtOH 96%	20	95
EtOH 100%	20	97

*[a] Reaction conditions: 1,2-benzodiamine (**1**, 1.00 mmol), aceton (**2**, 1.00 mmol), cyclohexyl isocyanide (**3**, 1.00 mmol), and catalyst (0.02 g) were stirred in ethanol 96% (3.00 mL). [b]Isolated yield.*

General procedure for the preparation of products 8a-e:

A solution of 1,2-benzodiamine (1.00 mmol) and carbonyl compounds (2.20 mmol) was stirred for 20 min in the presence of HPA/TPI-Fe_3O_4 (0.02 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 H_2O (3 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 using an external magnet. Then, the solution crystallized to give products **8a-e**.

RESULTS AND DISCUSSION

HPA/TPI-Fe_3O_4 nanocatalyst was synthesized according to a previously reported procedure [20-21]. The catalytic efficiency of the HPA/TPI-Fe_3O_4 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 catalyst for these reactions, in a typical experiment, 1,2-benzodiamine **1**, acetone **2** and cyclohexyl isocyanide **3** were stirred in ethanol at room temperature in the absence of catalyst. The yield in this case was trace after 12 h that shows catalyst is an important segment of the reaction.

Thereupon, in a pilot experiment, 1,2-benzodiamine **1**, acetone **2** and cyclohexyl isocyanide **3** were stirred in ethanol at room temperature using HPA, Fe_3O_4, TPI-Fe_3O_4 and HPA/TPI-Fe_3O_4 catalyst. Table 1 summarizes the catalytic performance for synthesis of compound **4a.** The catalytic activity was examined as HPA/TPI-Fe_3O_4 > HPA > TPI-Fe_3O_4 > Fe_3O_4.

In order to obtain the best synthesis conditions, 1,2-benzodiamine **1**, acetone **2** and cyclohexyl isocyanide **3** in the presence of HPA/TPI-Fe_3O_4 in various organic solvents were allowed to react at room temperature. As shown in Table 2, commercially absolute ethanol, ethanol 96% and methanol 99% are the best solvents for the synthesis of

Table 3: Effect of catalyst amount on the reaction of 1,2-benzodiamine, aceton and cyclohexyl isocyanide 3[a].

Entry	Catalyst (g)	Time (min)	Yields (%)[b]
HPA	0.02	20	64
HPA	0.01	20	44
Fe_3O_4	0.04	20	38
Fe_3O_4	0.02	20	32
Fe_3O_4	0.01	20	24
TPI-Fe_3O_4	0.02	20	52
TPI-Fe_3O_4	0.01	20	39
HPA/TPI-Fe_3O_4	0.02	20	95
HPA/TPI-Fe_3O_4	0.01	20	78

*a) Reaction conditions: 1,2-benzodiamine (**1**, 1.00 mmol), aceton (**2**, 1.00 mmol), cyclohexyl isocyanide (**3**, 1.00 mmol), and catalyst were stirred in ethanol 96% (3.00 mL). b) Isolated 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]	Mp °C	
						Found	Reported
4a	o-Phenylenediamine	Acetone	*c*Hex	25	90	160–162	160-162 [22]
4b	o-Phenylenediamine	Cyclohexanone	*t*-Bu	25	85	104-107	106-108 [22]
4c	4-Methyl-o-phenylenediamine	Cyclohexanone	*c*Hex	20	92	153–154	153-155 [22]
4d	3,4-Diaminobenzophenone	Acetone	*c*Hex	25	89	180–181	181-182 [22]
4e	3,4-Diaminobenzophenone	Cyclohexanone	*c*Hex	25	90	187–189	187-189 [22]
4f	4-Nitro-1,2-phenylenediamine	Acetone	*c*Hex	35	91	mp >250	mp >250 [22]
4g	4-Nitro-1,2-phenylenediamine	Acetone	*t*-Bu	35	88	159–162	158-160 [22]
4h	3,4-Diaminobenzophenone	4-Nitrobenzaldehyde	*c*Hex	25	85	mp >250	mp >250 [22]
4i	4,5-Dichloro-1,2-phenylenediamine	4-Methylbenzaldehyde	*t*-Bu	30	87	mp >250	mp >250 [22]
4j	4-Nitro-1,2-phenylenediamine	Benzaldehyde	*c*Hex	35	80	176–178	178-180 [22]
4k	4-Nitro-1,2-phenylenediamine	4-Methoxybenzaldehyde	*c*Hex	35	86	175-177	175-176 [22]

a) Reaction conditions: diamines (1, 1.00 mmol), carbonyl compounds (2, 1.00 mmol), isocyanides (3, 1.00 mmol), and HPA/TPI-Fe_3O_4 (0.02 g) were stirred in ethanol 96% ((3.00 mL). b) Isolated yield.

compound *N*-cyclohexyl-3,3-dimethyl-3,4-dihydroquinoxalin-2-amine **4a** with respect to the yield and the reaction times.

The catalytic efficiency could be influenced by the catalyst amount. Therefore, a set of experiments using various amounts of catalyst was considered in the reaction of 1,2-benzodiamine **1**, acetone **2** and cyclohexyl isocyanide **3** in ethanol 96% at room temperature (Table 3). The optimum catalyst amount was examined as 0.02 g HPA/TPI-Fe_3O_4 to reach 95% yields of compounds **4a**. Lower amounts of catalyst resulted in a decrease in the efficacy of the reaction, while higher amounts led to complete conversion in a short reaction time.

Using HPA/TPI-Fe_3O_4 in ethanol 96%, we initiated a study to explore the scope of this procedure. Various 1,2-benzodiamines **1**, carbonyl compounds **2** and isocyanides **3** were applied in this reaction (Table 4).

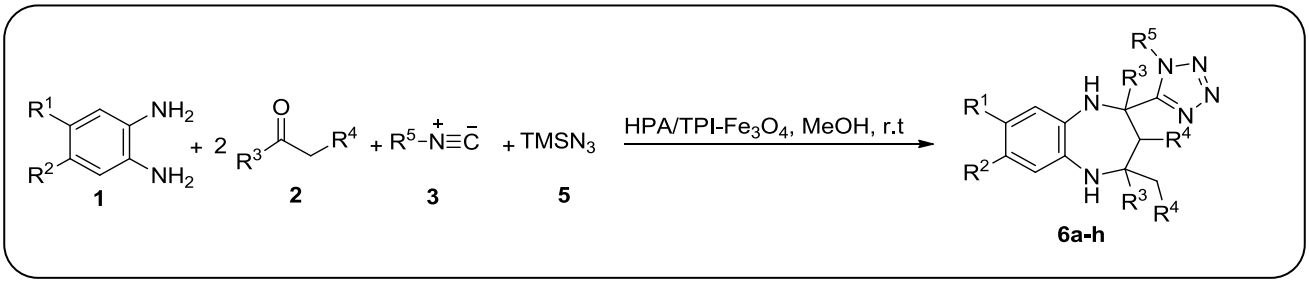
In continue, by using a two-step condensation reaction between 1,2-benzodiamine **1**, two moles of ketone derivatives **2**, an isocyanide **3** and $TMSN_3$ **4** as a nucleophile in the presence of HPA/TPI-Fe_3O_4 , 1*H*-tetrazol-5-yl-4-methyl-1*H*-benzo [*b*][1,4] diazepines **6a-h** were obtained (Scheme 2).

n a pilot experiment, 1,2-benzodiamines **1** and acetone were stirred in the presence of a catalytic amount

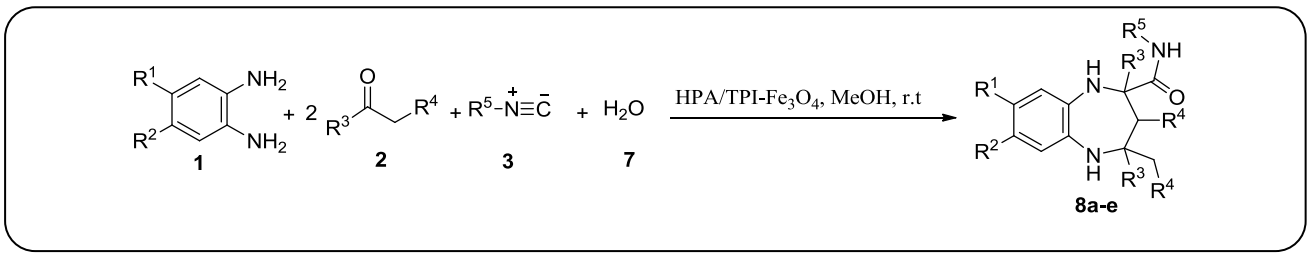
Table 5: Synthesis of 1H-tetrazolyl-benzo[b][1,4]diazepine derivatives with various diamines, carbonyl compounds and isocyanides[a].

Entry	Amine compound	Carbonyl compound	R^5	Time (min)	Yield (%)[b]	Mp °C	
						Found	Reported
6a	o-Phenylenediamine	Acetone	*c*Hex	30	89	240–242	241–242 [19]
6b	4-Methyl-o-phenylenediamine	Acetone	*c*Hex	25	88	203–204	202–204 [19]
6c	3,4-Diaminobenzophenone	Acetone	*c*Hex	20	91	293-294	293-295 [19]
6d	3,4-Diaminobenzophenone	Cyclohexanone	*c*Hex	30	91	> 300	> 300 [19]
6e	4-Nitro-1,2-phenylenediamine	Acetone	TASMIC	35	80	196–199	196–198 [19]
6f	4-Nitro-1,2-phenylenediamine	Cyclohexanone	*c*Hex	35	88	> 300	> 300 [19]
6g	4-Nitro-1,2-phenylenediamine	4-*tert*-Butylcyclohexanone	*c*Hex	30	77	> 300	> 300 [19]
6h	4,5-Dichloro-1,2-phenylenediamine	Cyclohexanone	*c*Hex	30	85	> 300	> 300 [19]

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 HPA/TPI-Fe_3O_4 (0.02 g) were stirred in methanol (3.00 mL). [b] Isolated yield.



Scheme 2: Synthesis of 1H-tetrazol-5-yl-4-methyl-1H-benzo[b][1,4] diazepines 6a-h.



Scheme 3: Synthesis of 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine-2-carboxamide 8a-e.

of HPA/TPI-Fe_3O_4 in methanol at room temperature. The progress of the reaction was monitored by TLC. After 20 min, trimethylsilyl azide **5** and cyclohexyl isocyanide were added to the reaction mixture and stirring was continued for 10 min. After completion of the reaction, catalyst was recovered by using an external magnet. 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 89 % yield. This reaction does not proceed in the absence of catalyst.

Using HPA/TPI-Fe_3O_4 as the best catalyst in methanol, we initiated a study to explore the scope of this reaction. Various 1,2-benzodiamine **1**, ketones **2** and isocyanides **3** were examined in this reaction and results are summarized in Table 5.

In view of the success of the above reactions for the synthesis of benzodiazepines derivatives, we decided to extend our results using water 7 instead of trimethylsilyl azide **5** for preparation of **8a-e** (Scheme 3). The reaction proceeds cleanly under mild conditions at room temperature and no undesirable side reactions were observed under these reaction conditions.

Table 6: Synthesis of 2,3,4,5-tetrahydro-1H-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]	Mp °C	
						Found	Reported
8a	4-Nitro-1,2-phenylenediamine	Acetone	*c*Hex	35	90	185-187	185-187 [23]
8b	4-Nitro-1,2-phenylenediamine	Acetone	*t-But*	35	88	224-225	224-226 [23]
8c	4,5-Dichloro-1,2-phenylenediamine	Acetone	*c*Hex	30	85	169-171	169-172 [23]
8d	4,5-Dichloro-1,2-phenylenediamine	Cyclohexanone	*t-But*	30	85	168-171	168-170 [23]
8e	3,4-Diaminobenzoic acid	Cyclohexanone	*c*Hex	35	85	213-214	213-214 [23]

*a) Reaction conditions: diamines (**1**, 1.00 mmol), carbonyl compounds (**2**, 1.00 mmol), isocyanides (**3**, 1.00 mmol), H_2O (**7**, 1.00 mL) and HPA/TPI-Fe_3O_4 (0.02 g) were stirred in methanol (3.00 mL). b) Isolated yield.*

Table 7: Recycle of the catalyst[a].

Cycle	Cat. (g)	Yield (%)
1	0.020	95
2	0.020	95
3	0.020	95
4	0.019	94
5	0.019	94
6	0.019	93
7	0.019	93
8	0.018	92
9	0.018	92
10	0.018	91

*a) Reaction conditions: 1,2-benzodiamine (**1**, 1.00 mmol), aceton (**2**, 1.00 mmol), cyclohexyl isocyanide (**3**, 1.00 mmol), and catalyst were stirred in ethanol 96% (3.00 mL)*

In a pilot experiment, 4-nitro-1,2-phenylenediamine and acetone **2** were stirred in methanol at room temperature in the presence of a catalytic amount of HPA/TPI-Fe_3O_4. The progress of the reaction was monitored by TLC. After 20 min, cyclohexyl isocyanide and water **7** were added to the reaction mixture, and stirring was continued for 15 min. After completion of the reaction, an aqueous workup afforded compound **8a** in 90 % yield.

Under optimal conditions, various 1,2-benzodiamine **1**, ketones **2** and isocyanides **3** were examined in this reaction and results showed in Table 6.

The catalyst was very active, stable, nontoxic and inexpensive. To explore the reusability of the HPA/TPI-Fe_3O_4 nanoparticles, it was easily separated from the reaction medium by an external magnet and washed thoroughly with CH_2Cl_2. Then, the catalyst was dried in air and then was activated in a vacuum oven at 70 °C for 4 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 HPA/TPI-Fe_3O_4 were determined by FT-IR methods. As can be depicted in Fig. 1, the structure of the recycled catalyst does not change and a very slight decrease in the reaction yield is may be due to the covering the surface of catalyst by impurities.

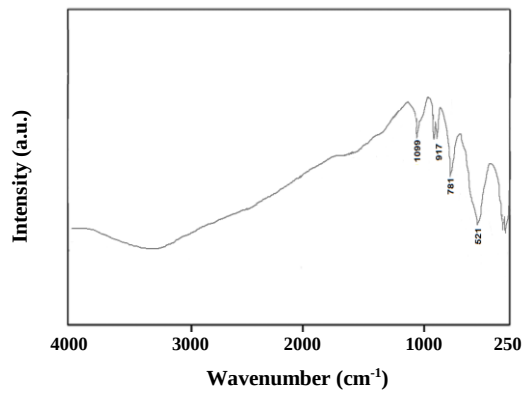


Fig. 1: FT-IR spectrum pattern of HPA/TPI-Fe_3O_4.

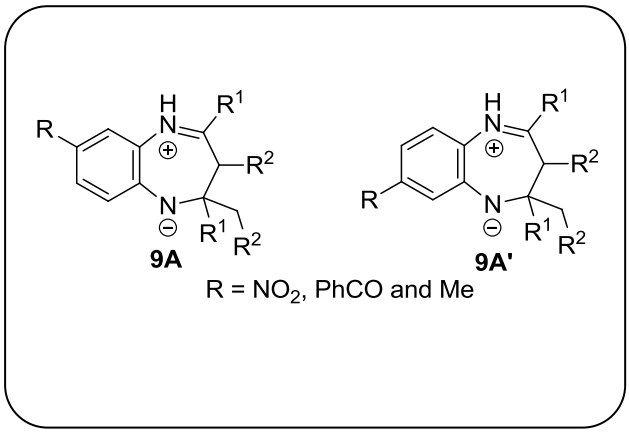


Fig. 2: Structure of intermediates 9A and 9A'.

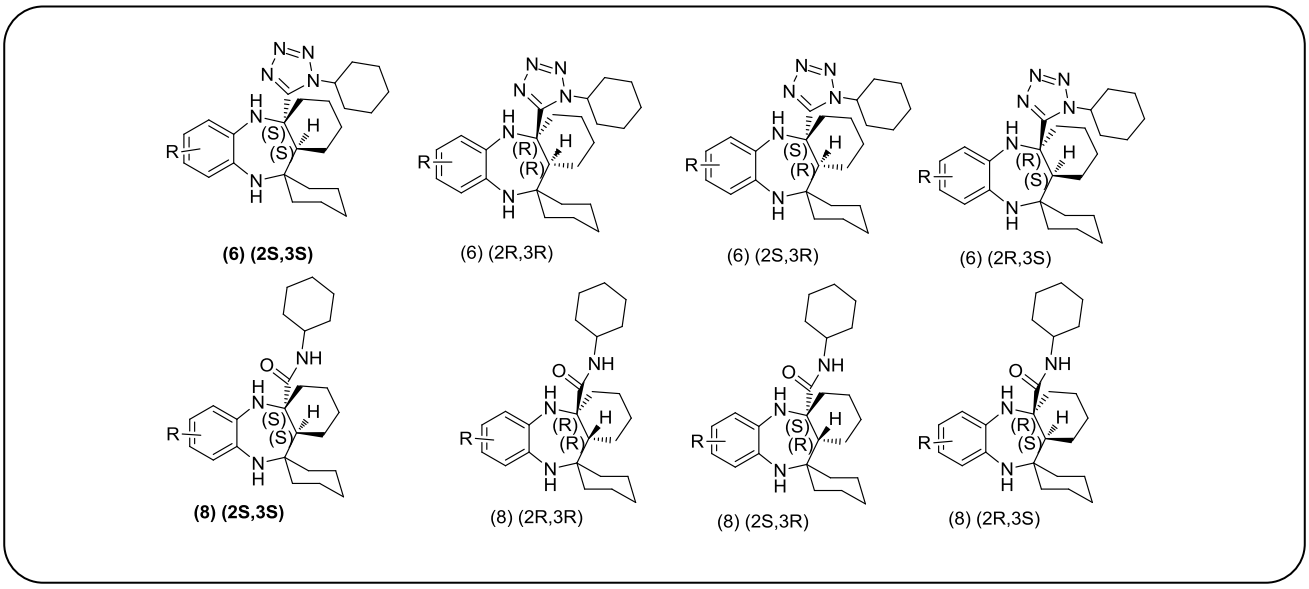


Fig. 3: Structures of four possible stereoisomers for compounds 6d-h and 8d-e.

The synthetic route was highly regioselective because of the regioselectivity of the first step (scheme 1). The ^{1}HNMR and ^{13}CNMR spectra obtained from products with electrone-withdrawing or donating groups such as NO_2, PhCO and CH_3 was consistent with the presence of only one isomer. It may be explained that the selectivity is the result of the electronic effect of the electron-withdrawing or electron-donating group such as NO_2, PhCO and CH_3 [19]. Electron-donating groups at the para position (e.g., CH_3) are activated exclusively, and to give iminium ion 9A' (not 9A). While electron-withdraving groups (e.g., NO_2, PhCO) deactivate the para amino group, the reaction is favored by the meta amino group to give 9A (not 9A') as the favored product (Fig 2).

Also stereochemistry of compounds was assigned by single crystal X-ray diffraction reported by *Shaabani et al.* [19, 23]. As can be seen in the structure of the product, this reaction leads to creation of two stereogenic centers, and among the four different stereoisomers, only one isomer (2S, 3S) was obtained in high yield (Fig. 3).

The stereochemistry of **6f** and **8d** is shown in Fig 4. The hydrogen is in a cis position relative to the tetrazole and amide groups on the adjacent carbon atoms in compounds **6f** and **8d**.

The possible mechanism for the formation of products **6a-h** is shown in Scheme 5. It is conceivable that the initial event is the formation intermediate **10** from condensation between diamine **1** and 2 mol of ketone **2**.

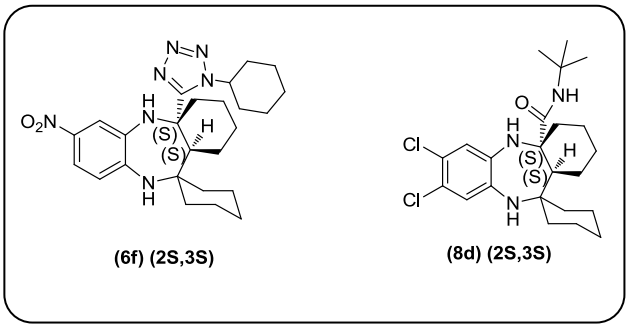


Fig. 4: Stereochemistry assignment for compounds 6f and 8d.

Then, an intramolecular imine-enamine cyclization of **11** affords seven-membered ring **12**. On the basis of the well- stablished chemistry of the reaction of isocyanides with imines,[19] intermediate **13** was produced by nucleophilic attack of isocyanide **3** to iminium **12** followed by nucleophilic attack of an azide molecule on the nitrilium moiety and production of compound **14**. Finally, the [2+3] intermolecular cycloaddition reaction between the C=N and N_3 group of the intermediate **14** led to **6a-h**. (Fig. 3).

CONCLUSIONS

We reported HPA/TPI-Fe_3O_4 as a new and efficient solid acid catalyst for the synthesis of 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives upon mixing readily available substrates under short reaction times at room temperature. Recyclability of the catalyst with no loss in its activity, mild reaction conditions and product isolation, use of nontoxic and excellent yields, are important features of this new protocol to prepare 3,4-dihydroquinoxalin-2-amine, diazepine-tetrazole and benzodiazepine-2-carboxamide derivatives.

Acknowledgements

The authors would like to thank Marand Branch, Islamic Azad University for the financial support of this research.

Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/

Received : Feb. 10, 2015 ; Accepted : Apr. 19, 2016

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