



Full paper/Mémoire

Tribromide ion supported on boehmite nanoparticles as a reusable catalyst for organic reactions

Arash Ghorbani-Choghamarani^{*}, Zeinab Seydyosefi, Bahman Tahmasbi

Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran



ARTICLE INFO

Article history:

Received 26 January 2018

Accepted 3 September 2018

Available online 5 October 2018

Keywords:

Boehmite nanoparticles

Tribromide

Sulfoxides

Dihydroquinazolines

Polyhydroquinolines

ABSTRACT

Boehmite nanoparticles are not air or moisture sensitive; therefore, they were prepared in water at room temperature using inexpensive materials, without inert atmosphere, by a very simple and inexpensive procedure. When the surface of boehmite nanoparticles was modified by *N,N,N',N'*-tetraethyldiethylenetriamine (TEDETA), tribromide ions became immobilized on modified boehmite nanoparticles ($\text{Br}_3\text{-TEDETA@Boehmite}$). These materials were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, Brunauer–Emmett–Teller, X-ray diffraction, energy-dispersive X-ray spectroscopy, and scanning electron microscopy techniques. Finally, the catalytic activity of $\text{Br}_3\text{-TEDETA@Boehmite}$ was examined in the selective oxidation of sulfides to sulfoxides. Besides, the catalytic activity of $\text{Br}_3\text{-TEDETA@Boehmite}$ was extended to the synthesis of organic heterocyclic compounds, such as 2,3-dihydroquinazolin-4(1*H*)-one and polyhydroquinoline derivatives. This catalyst was reused several times without significant loss of its catalytic efficiency.

© 2018 Published by Elsevier Masson SAS on behalf of Académie des sciences.

1. Introduction

To reach an excellent degree of catalyst reusability, during recent years immobilization of homogeneous catalysts on various heterogeneous supports has been used as recyclable catalysts in organic synthesis [1,2]. However, many supports such as SBA-15 [3], MCM-41 [4], TiO_2 nanoparticles [5], and iron oxide [6,7] have been used for catalyst supports; the preparation of these supports requires high temperature for calcination or inert atmosphere and also a lot of time and tedious conditions. It is worth mentioning that other heterogeneous supports such as heteropolyacids [8], carbon nanotubes [9], ionic liquids [10,11], graphene oxide [12], or some polymers [13,14] are expensive. Boehmite nanoparticles ($\gamma\text{-AlOOH}$) are not air or moisture sensitive; therefore, they were prepared in

water at room temperature using inexpensive and available materials [15]. Nanoboehmite has several attractive features, such as thermal, chemical, and mechanical stability, high specific surface area ($>120\text{ m}^2/\text{g}$), easy and ready availability, nontoxicity, ease of surface modification, and favorable biocompatibility [16–18]. In this regard, the surface of boehmite (aluminum oxyhydroxide) nanoparticles, which are covered with high density of hydroxyl groups, can be modified using other functional groups to immobilize homogeneous catalysts [19,20]. Although modification of boehmite has been rarely reported as a heterogeneous support [17–20]. Herein, $\text{Br}_3\text{-TEDETA@Boehmite}$ (TEDETA, *N,N,N',N'*-tetraethyldiethylenetriamine) has been reported as a new metal-free catalyst for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one and polyhydroquinoline derivatives and also for the selective oxidation of sulfides to sulfoxides. Sulfoxides are valuable synthetic intermediates for the production of chemically and biologically active molecules including therapeutic agents such as antiulcer, antifungal, antibacterial,

* Corresponding author.

E-mail addresses: arashghch58@yahoo.com, a.ghorbani@ilam.ac.ir (A. Ghorbani-Choghamarani).

antiatherosclerotic, antihypertensive, and psychotropic and vasodilators [21–24]. Furthermore, allicin, sulindac, modafinil, garlicnin B-2, garlicnin L-1, and omeprazole are several typical examples of the extensive application of these intermediates in the pharmaceutical and fine chemical industries [22,25]. In addition, sulfoxides are also valuable in the C–C bond formation and molecular rearrangements [26]. Besides, 2,3-dihydroquinazolin-4(1*H*)-one and polyhydroquinoline derivatives have been reported to possess a wide range of biological properties and pharmaceutical activities [27,28]. For example, altanserin and nitroaltanserin are drugs for 5-HT_{2A} receptor antagonists [29], also 2-(2-hydroxyphenyl)-4(3*H*)-quinazolinone was used in the detection of metal ions [30]. Furthermore, 2,3-dihydro-4(1*H*)-quinazolinones are starting materials for the preparation of 4-(3*H*)-quinazolinones [31]. The novelty of this work is that it is for the first time that an ion has been grafted on boehmite nanoparticles, which have been rarely used as catalyst supports. In addition, synthesis of 2,3-dihydroquinazolin-4(1*H*)-one and polyhydroquinoline derivatives has been commonly reported in the presence of Louise or protonic acid [39–41]. In this study, tribromide ions supported on boehmite nanoparticles were used as catalysts for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one and polyhydroquinoline derivatives. Furthermore, Br₃-TEDETA@Boehmite is a selective catalyst for the sulfoxidation reaction.

2. Result and discussion

2.1. Catalyst preparation

Br₃-TEDETA@Boehmite was prepared by the concise route outlined in Scheme 1. Modified boehmite nanoparticles were prepared according to the new reported procedure [15].

2.2. Catalyst characterization

The mentioned nanocatalyst has been characterized by thermogravimetric analysis/differential thermal analysis (TGA/DTA), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectroscopy techniques.

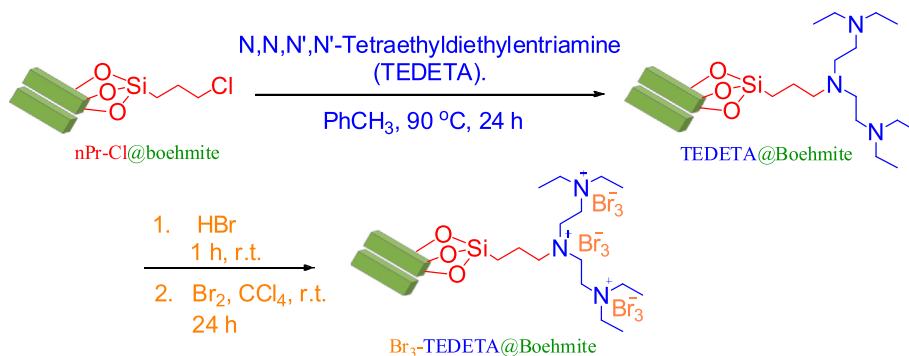
The size of particles was evaluated by SEM technique. The several SEM images of Br₃-TEDETA@Boehmite are shown in Fig. 1. These SEM images illustrated that the particles of the catalyst were formed as nanometer-sized particles of about 20–60 nm (Fig. 1). To indicate the content of element type in catalyst, EDS analysis of Br₃-TEDETA@Boehmite was performed (Fig. 2). As depicted, the EDS spectrum of catalyst shows the presence of Al, Si, O, C, N, and Br species in the catalyst.

The FT-IR spectra of boehmite nanoparticles, *n*Pr-Cl@boehmite, TEDETA@Boehmite, and Br₃-TEDETA@Boehmite are shown in Fig. 3. Two bands at 3086 and 3308 cm⁻¹ indicated the hydroxyl groups on the surface of boehmite nanoparticles [32]. Several peaks in FT-IR spectra at 480, 605 and 735 cm⁻¹ can be attributed to the Al–O bonds [20]. Also, one band at 1650 cm⁻¹ and two bands at 1164 and 1069 cm⁻¹ correspond to the nitrate impurity vibration and hydrogen bands of OH...OH surface, respectively [32]. In the FT-IR spectra of TEDETA@Boehmite, O–Si and C–H stretching vibrations appear at 1070 and 2930 cm⁻¹, respectively [1].

The TGA/DTA was used to determine the percent of organic functional groups, which were immobilized on the surface of boehmite nanoparticles. Fig. 4 shows the TGA curves for boehmite nanoparticles and catalyst. The weight loss at temperatures <200 °C (about 10%) is caused by the removal of the adsorbed solvents [20,32]. In the TGA/DTA profile of the catalyst, organic layers have been desorbed at temperatures >350 °C (about 29%).

The XRD patterns of Br₃-TEDETA@Boehmite are shown in Fig. 5. As it has been clearly illustrated, XRD pattern of Br₃-TEDETA@Boehmite shows a good agreement with standard XRD pattern of boehmite nanoparticles in which all of the peaks confirmed the crystallization of boehmite with an orthorhombic unit cell [15,18]. This agreement is strong evidence that boehmite phase was stable after modification.

The nitrogen adsorption–desorption isotherms of Br₃-TEDETA@Boehmite are shown in Fig. 6. On the basis of the IUPAC classification, these materials display a typical IV isotherm, which can be regarded as the characteristic of mesoporous materials. On the basis of the BET technique, the surface area for Br₃-TEDETA@Boehmite, which is 37.6 m²/g, is lower than the surface area of boehmite nanoparticles (122.8 m²/g) [32] because of the



Scheme 1. Preparation process of Br₃-TEDETA@Boehmite.

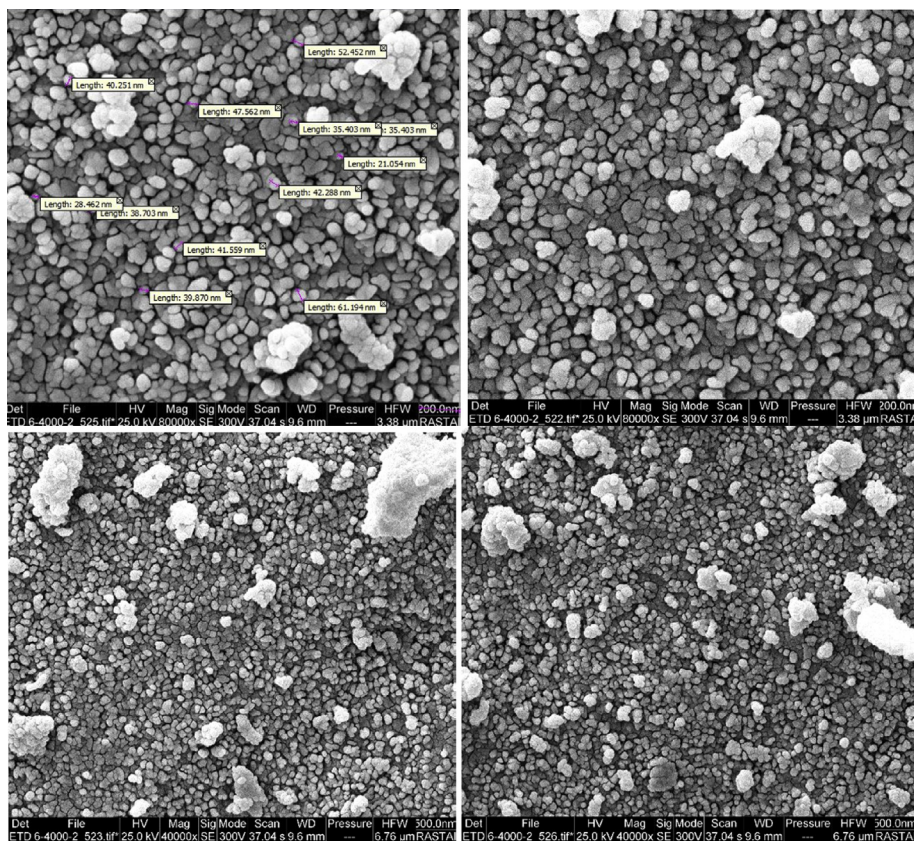


Fig. 1. SEM images of Br₃-TEDETA@Boehmite.

immobilization of organic layers and the catalyst on the surface of boehmite nanoparticles.

2.3. Catalytic study

To study the catalytic activity of Br₃-TEDETA@Boehmite, we were interested in finding a simple and efficient procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives using condensation of aldehydes and

anthranilamide in the presence of Br₃-TEDETA@Boehmite as a recoverable nanocatalyst (Scheme 2).

The reaction conditions for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives were optimized in the condensation of 4-chlorobenzaldehyde with ammonium acetate, dimedone, and ethyl acetoacetate in the presence of different amounts of Br₃-TEDETA@Boehmite in various solvents as a model reaction (Table 1). The sample reaction cannot proceed in the absence of Br₃-

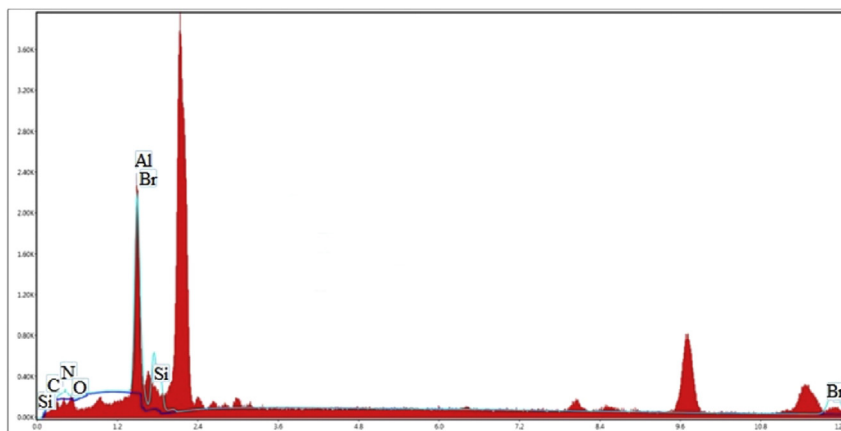


Fig. 2. EDX spectrum of Br₃-TEDETA@Boehmite.

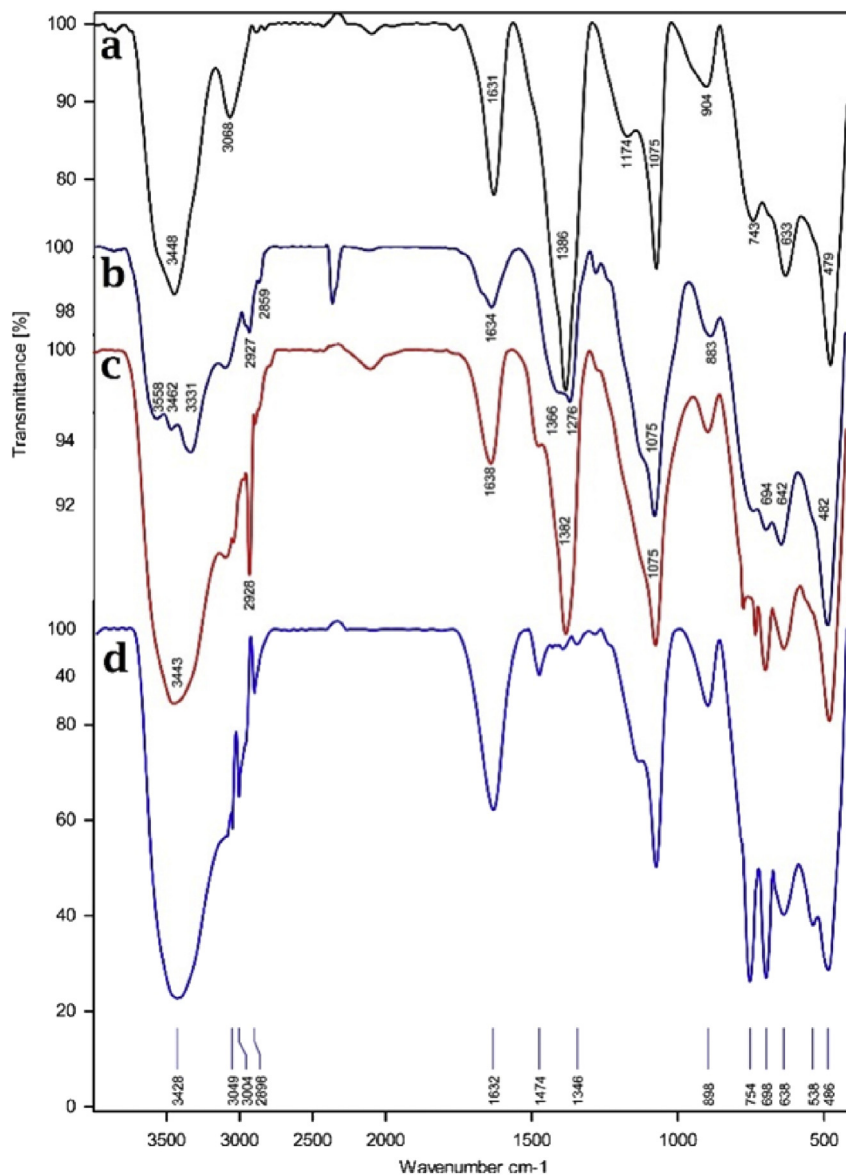


Fig. 3. FT-IR spectra of boehmite nanoparticles (a), *n*Pr-Cl@boehmite (b), TEDETA@Boehmite (c), and Br₃-TEDETA@Boehmite (d).

TEDETA@Boehmite even after 3 h (Table 1, entry 8). Although increasing the amount of catalyst from 30 mg (Table 1, entry 6) to 40 mg (Table 1, entry 5) led to an increase in the yield of the product from 50% to 96%, increasing the amount of catalyst (from 40 to 50 mg) had no significant effect on the yield of product or reaction time. The model reaction was also carried out in the presence of a little amount of the catalyst (Table 1, entries 6 and 7), which caused low yields of the products. To find the best reaction conditions, different temperatures were examined for the model reaction. As shown in Table 1, best results were obtained at 70 °C. In this sense, it is worth noting that when the model reaction was tested at 50 °C, the reaction yield decreased to 63% (Table 1, entry 9). Among the different solvents such as PEG, ethyl acetate, DMSO, and H₂O, the best results were obtained in ethyl acetate.

As shown in Table 1, 40 mg of Br₃-TEDETA@Boehmite in ethyl acetate at 70 °C was found to be the best reaction conditions for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones.

To demonstrate the generality and efficiency of this method, different aldehydes were tested under optimized reaction conditions (Table 2). As shown in Table 2, the catalytic system worked exceedingly well in the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones with a wide range of functional groups. The pure products were obtained in short reaction times and high yields.

In the second phase of our study, the catalytic activity of Br₃-TEDETA@Boehmite in the one-pot synthesis of polyhydroquinoline derivatives (Scheme 3) was reported.

To find the best reaction conditions, various parameters such as different amounts of catalyst and various solvents

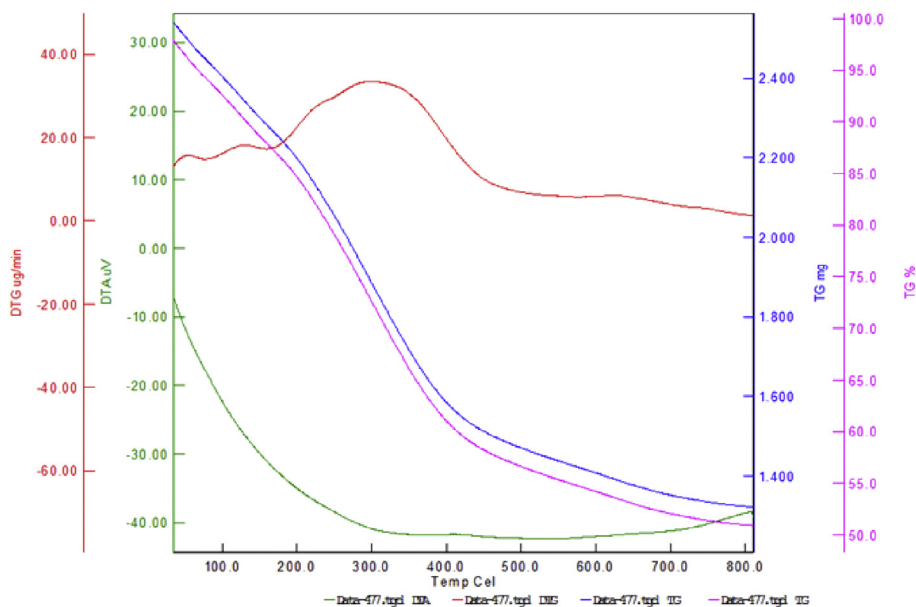


Fig. 4. TGA/DTA diagram of Br₃-TEDETA@Boehmite.

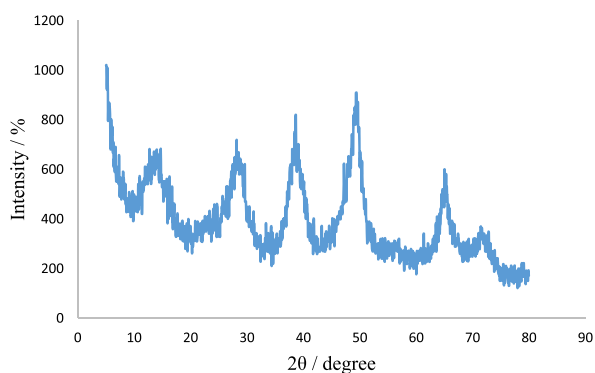


Fig. 5. XRD pattern of Br₃-TEDETA@Boehmite.

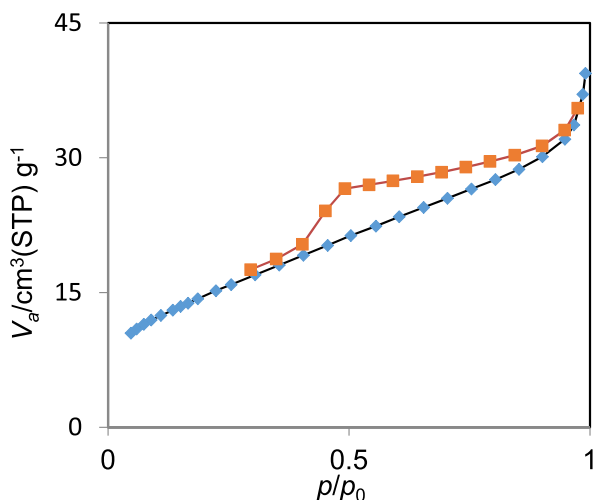
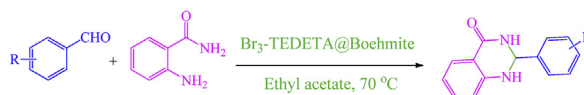


Fig. 6. Nitrogen adsorption–desorption isotherms of Br₃-TEDETA@Boehmite.

were investigated in the condensation of 4-chloro benzaldehyde, dimedone, ethyl acetoacetate, and ammonium acetate as a model reaction (Table 3). Initially, the amount of catalyst was optimized and, as a result, the best results were obtained with 0.04 g of Br₃-TEDETA@Boehmite (Table 3, entry 4). Moreover, the experiments show that the reaction does not occur in the absence of the catalyst (Table 3, entry 7). As shown in Table 3, increase in the amount of the catalyst led to an increase in the yield of obtained products. Meanwhile, the best results were obtained in the presence of 40 mg of catalyst. When the



Scheme 2. Br₃-TEDETA@Boehmite catalyzed the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives.

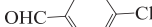
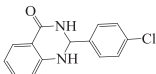
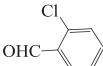
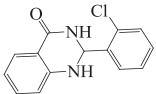
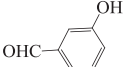
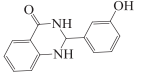
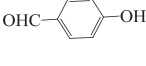
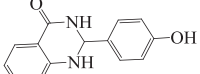
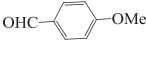
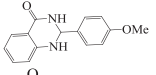
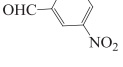
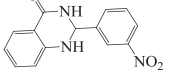
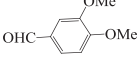
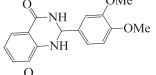
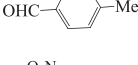
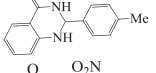
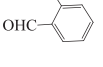
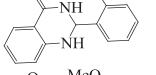
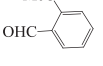
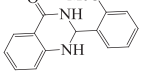
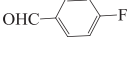
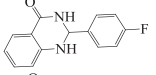
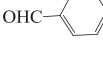
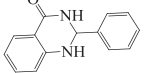
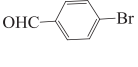
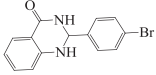
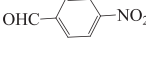
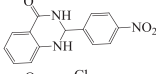
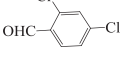
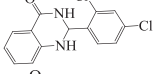
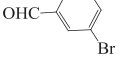
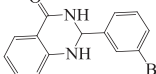
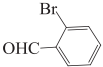
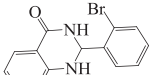
Table 1

Optimization of the reaction conditions for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones in the condensation of 4-chlorobenzaldehyde with anthranilamide.

Entry	Solvent	Catalyst (mg)	Time (min)	Temperature (°C)	Yield (%) ^a
1	H ₂ O	40	35 min	70	20
2	PEG	40	35 min	70	25
3	DMSO	40	35 min	70	45
4	Ethyl acetate	50	35 min	70	97
5	Ethyl acetate	40	35 min	70	96
6	Ethyl acetate	30	90 min	70	50
7	Ethyl acetate	20	90 min	70	39
8	Ethyl acetate	–	3 h	70	Trace
9	Ethyl acetate	40	35 min	50	63

^a Isolated yields.

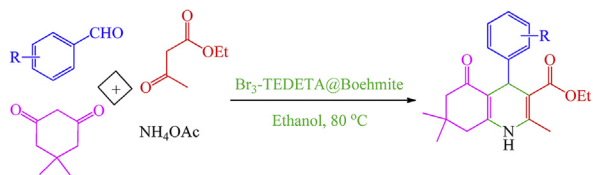
Table 2
Synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by Br₃-TEDETA@Boehmite.

Entry	Aldehyde	Product	Time (min)	Yield (%) ^a	Melting point (°C)	Reported melting point [reference]
1			35	96	193–195	193–194 [33]
2			60	94	204–206	206–208 [33]
3			60	91	195–197	190–192 [34]
4			105	93	268–270	278–280 [35]
5			90	85	183–185	182–183 [36]
6			160	87	196–198	193–195 [33]
7			70	86	207–209	210–212 [37]
8			80	87	219–221	220–222 [37]
9			90	89	190–191	188–190 [27]
10			40	91	163–165	165–167 [38]
11			135	88	197–199	197–199 [39]
12			90	91	218–220	219–220 [33]
13			70	92	201–203	201–202 [37]
14			275	86	195–197	200–201 [37]
15			170	90	167–169	166–169 [33]
16			270	92	171–174	174–176 [40]
17			270	93	176–178	174–176 [37]

^a Isolated yield.

amount of catalyst was increased to 50 mg (Table 3, entry 3), no significant change in the yield of product or reaction time was observed. Consequently, the effect of different solvents was examined (Table 3, entries 1–3). Among the

various solvents, the highest yield has been obtained in ethanol with short reaction time. Finally, the effect of temperature on the model reaction was studied and best results were obtained at 80 °C (Table 3, entry 4).



Scheme 3. Br₃-TEDETA@Boehmite catalyzed the synthesis of polyhydroquinoline derivatives.

Table 3

Optimization of reaction conditions for the synthesis of polyhydroquinoline for condensation of 4-chlorobenzaldehyde with dimedone, ethyl acetoacetate, and ammonium acetate.

Entry	Solvent	Catalyst (mg)	Time (min)	Temperature (°C)	Yield (%) ^a
1	Ethyl acetate	40	75	80	84
2	PEG	40	75	80	55
3	Ethanol	50	75	80	95
4	Ethanol	40	75	80	93
5	Ethanol	30	100	80	75
6	Ethanol	20	100	80	70
7	Ethanol	–	100	80	– ^b
8	Ethanol	40	75	60	44
9	Ethanol	40	75	40	40

^a Isolated yield.

^b No reaction.

Table 4

Synthesis of polyhydroquinoline derivatives catalyzed by Br₃-TEDETA@Boehmite.

Entry	Aldehyde	Product	Time (min)	Yield (%) ^a	Melting point (°C)	Reported melting point [reference]
1			400	93	214–216	216–218 [41]
2			75	96	228–230	233–235 [42]
3			75	98	253–257	254–256 [41]
4			340	87	234–237	239–241 [43]
5			500	85	178–180	178–180 [44]

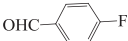
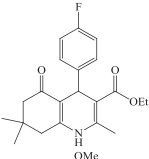

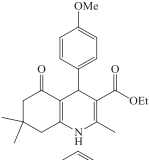
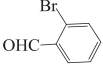
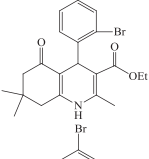
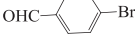
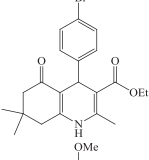
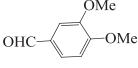
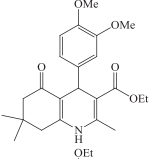
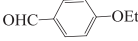
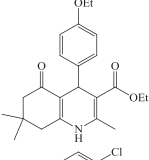
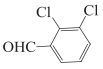
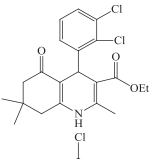
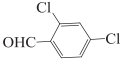
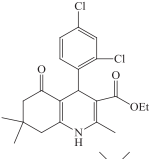
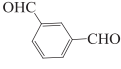
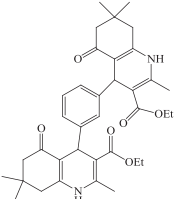

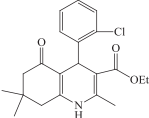
(continued on next page)

To explore the activity of these catalysts, various aldehydes, including a wide range of electron-donating and electron-withdrawing (Table 4) functional groups, have been described in optimum conditions. Besides, the corresponding polyhydroquinoline compounds were obtained in good to excellent yields. As a point of note, 1,4-benzenedicarboxaldehyde was converted to bis-polyhydroquinoline in 90% of yield (Table 4, entry 14).

Finally, the oxidation of sulfides to sulfoxides has been examined using H₂O₂ in the presence of these nano-materials (Scheme 4).

To optimize the reaction conditions, we selected the oxidation of methyl phenyl sulfide using H₂O₂ in various solvents and in the presence of different amounts of the catalyst (Table 5). Different amounts of the catalyst were examined and the best results were obtained using 0.04 g of the catalyst (Table 5, entry 4). As shown in Table 5, increase in the amount of the catalyst (from 0.04 to 0.05 g) did not cause a significant change in reaction time or yield. Also, amount of hydrogen peroxide needed in the model reaction was studied and 0.4 mL of hydrogen peroxide was selected for oxidation sulfides to sulfoxides (Table 5, entry 4). Decreasing the amount of hydrogen peroxide from 0.4 mL (Table 5, entry 4) to 0.3 mL (Table 5, entry 8) led to decrease in yield of the product from 88% to 53% even during long reaction times. Moreover, to find the best reaction conditions, various solvents and solvent-free conditions were examined in the model reaction and the best

Table 4 (continued)

Entry	Aldehyde	Product	Time (min)	Yield (%) ^a	Melting point (°C)	Reported melting point [reference]
6			30	90	187–190	183–185 [27]
7			560	96	246–248	247–249 [36]
8			90	89	192–194	–
9			240	88	248–250	247–248 [41]
10			180	92	202–204	201–202 [36]
11			360	92	169–171	172–174 [27]
12			330	87	231–234	229–234 [45]
13			360	88	234–236	238–241 [46]
14			210	93	157–159	–
15			200	90	194–195	202–204 [47]

^a Isolated yields.



Scheme 4. Br₃-TEDETA@Boehmite catalyzed the oxidation of sulfides to sulfoxides.

Table 5

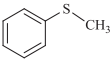
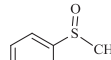
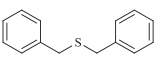
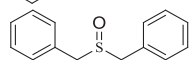
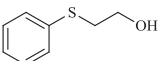
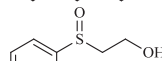
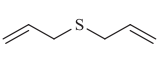

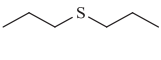
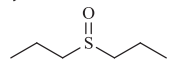

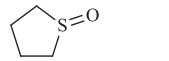

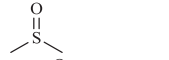
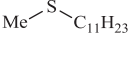
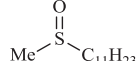
Optimization of the reaction conditions for oxidation of methyl phenyl sulfide as a model substrate.

Entry	Solvent	Catalyst (mg)	H ₂ O ₂ (mL)	Time (min)	Yield (%) ^a
1	Acetonitrile	40	0.4	90	75
2	Ethanol	40	0.4	100	79
3	Solvent-free	40	0.4	90	46
4	Ethyl acetate	40	0.4	60	88
5	Ethyl acetate	20	0.4	80	75
6	Ethyl acetate	50	0.4	80	90
7	Ethyl acetate	60	0.4	20	93
8	Ethyl acetate	40	0.3	100	53

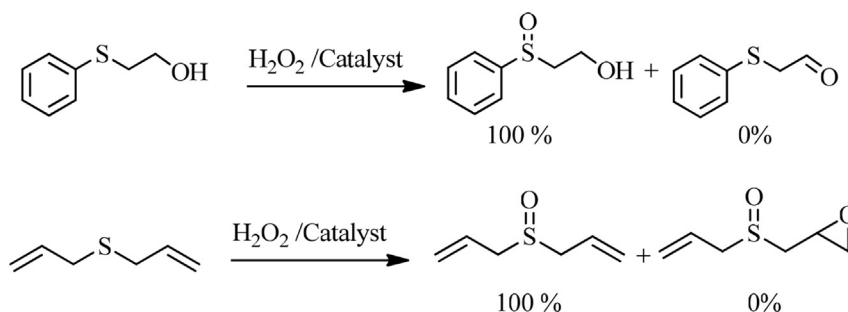
^a Isolated yield.

Table 6

Synthesis of polyhydroquinoline derivatives catalyzed by Br₃-TEDETA@Boehmite.

Entry	Sulfide	Product	Time (min)	Yield (%) ^a	Melting point (°C)	Reported melting point [reference]
1			20	93	Oil	Oil [48]
2			25	90	130–132	131–133 [49]
3			20	80	Oil	Oil [50]
4			25	83	Oil	Oil [49]
5			40	91	Oil	Oil [55]
6			35	85	Oil	Oil [48]
7			45	80	Oil	Oil [49]
8			40	94	59–62	61–64 [57]

^a Isolated yields.



Scheme 5. Chemoselective oxidation of sulfides in the presence of other functional groups using Br₃-TEDETA@Boehmite as a catalyst.

results were obtained in ethyl acetate. As shown in Table 5, methyl phenyl sulfide (1 mmol) in the presence of Br₃-TEDETA@Boehmite (0.04 g) and ethyl acetate at room temperature was found to be the ideal reaction conditions for the formation of methyl phenyl sulfoxide.

To explore the catalytic activity of Br₃-TEDETA@Boehmite, various sulfides, including aromatic and aliphatic sulfides, were converted to their corresponding sulfoxides in the presence of Br₃-TEDETA@Boehmite under optimized conditions as all of the products were obtained with high to excellent yields (Table 6). To show the chemoselectivity of this protocol, sulfides, including other functional groups such as hydroxyl groups or olefin, were subjected to the oxidation reaction. These functional groups remained intact during the conversion of sulfides into sulfoxides (Scheme 5). Also, because of mild conditions of the described heterogeneous system, overoxidation to sulfone after oxidation of sulfides to sulfoxide was not observed.

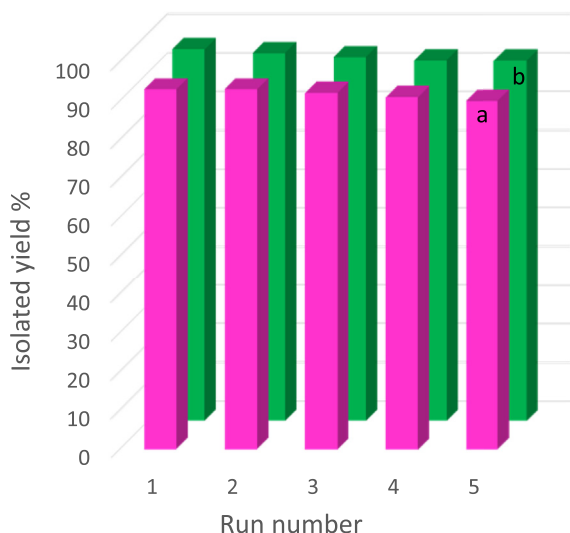


Fig. 7. The recycling experiment of $\text{Br}_3\text{-TEDETA@Boehmite}$ in the synthesis of polyhydroquinoline (a) and 2,3-dihydroquinazolin-4(1H)-one (b) using 4-chlorobenzaldehyde as a model substrate.

2.4. Recyclability of the catalyst

Regarding the aforementioned statements, we examined the recycling of $\text{Br}_3\text{-TEDETA@Boehmite}$ for the synthesis of 2,3-dihydroquinazolin-4(1H)-one and polyhydroquinoline derivatives using 4-chlorobenzaldehyde as the model compound. After completion of the reaction, the catalyst was separated from the product. The remaining catalyst was washed with ethyl acetate and subjected to the next run. The recovered catalyst was reused up to five runs without any significant loss of its catalytic activity (Fig. 7).

Besides, the recycled catalyst has been characterized by FT-IR spectroscopy technique. FT-IR spectra of the recycled catalyst are shown in Fig. 8. As illustrated in Fig. 8, FT-IR

spectrum of recycled $\text{Br}_3\text{-TEDETA@Boehmite}$ (Fig. 8) shows a very good agreement with FT-IR spectrum of fresh $\text{Br}_3\text{-TEDETA@Boehmite}$ (Fig. 3d). Stability of $\text{Br}_3\text{-TEDETA@Boehmite}$ after recycling was confirmed by position of stretching vibrations in FT-IR spectra of the fresh and recycled catalyst. This agreement is strong evidence for the high stability of $\text{Br}_3\text{-TEDETA@Boehmite}$ after being recycled.

2.5. Comparison of the catalyst

The efficiency of $\text{Br}_3\text{-TEDETA@Boehmite}$ was demonstrated by comparing the obtained results in the present work with previous methods for synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives using 4-chlorobenzaldehyde and oxidation of methyl phenyl sulfide (Table 7). As shown, better reaction times and higher yields were obtained using $\text{Br}_3\text{-TEDETA@Boehmite}$ as compared with other reported catalysts. In addition, $\text{Br}_3\text{-TEDETA@Boehmite}$ can be reused for several runs.

3. Experimental section

3.1. Materials

The sodium hydroxide, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3-chloropropyltrimethoxysilane, TEDETA, solvents, and other chemicals used in the present study were purchased from Merck, Aldrich, or Fluka companies and used without further purification.

3.2. Characterization techniques

Powder XRD of the catalyst was performed with $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA using a PW1730 instrument from Philips Company. FT-IR spectra were recorded with KBr pellets using a VRTEX 70 model Bruker FT-IR spectrometer. The component analysis was carried out by the

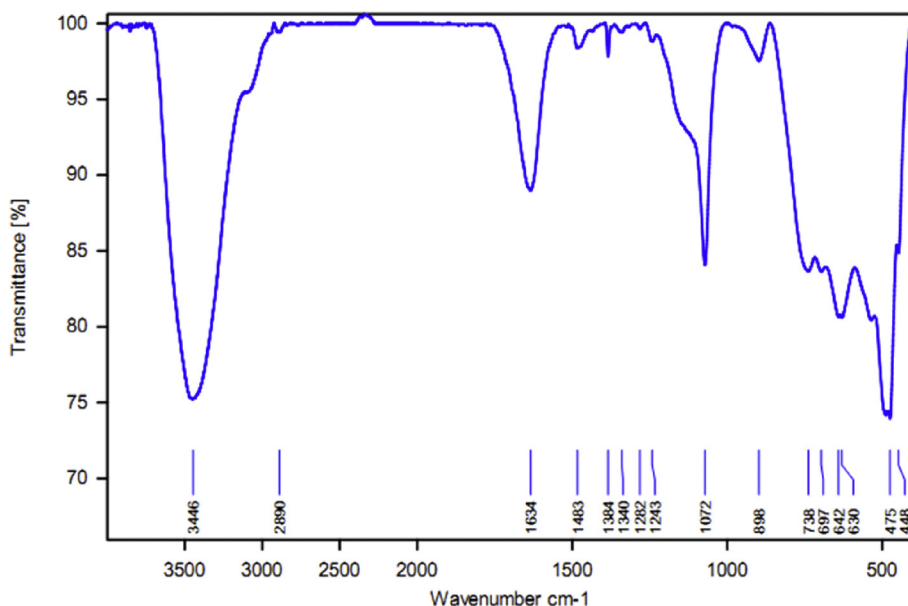


Fig. 8. FT-IR spectra of recycled $\text{Br}_3\text{-TEDETA@Boehmite}$.

Table 7

Comparison of Br₃-TEDETA@Boehmite for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones using 4-chlorobenzaldehyde and oxidation of methyl phenyl sulfide with previously reported procedures.

Entry	Substrate	Catalyst	Time (min)	Yield ^a (%) [reference]
1	Ph-SCH ₃	Ni-SMTU@Boehmite	75	97 [50]
2	Ph-SCH ₃	Polymer-anchored Cu(II)	180	90 [51]
3	Ph-SCH ₃	Cu-SPATB/Fe ₃ O ₄	95	98 [52]
4	Ph-SCH ₃	Cd-salen-MCM-41	150	98 [53]
5	Ph-SCH ₃	TsOH	240	88 [54]
6	Ph-SCH ₃	Ni-salen-MCM-41	156	95 [53]
7	Ph-SCH ₃	DSA@MNPs	360	98 [55]
8	Ph-SCH ₃	VO ₂ F(dmpz) ₂	300	95 [56]
9	Ph-SCH ₃	Br ₃ -Fe ₃ O ₄	50	98 [57]
10	Ph-SCH ₃	Br ₃ -TEDETA@Boehmite	20	93 [this work]
11	4-ClC ₆ H ₄ CHO	GSA@MNPs	50	99 [39]
12	4-ClC ₆ H ₄ CHO	[Bmim]PF ₆	40	90 [58]
13	4-ClC ₆ H ₄ CHO	TBAB/100 °C	60	75 [59]
14	4-ClC ₆ H ₄ CHO	SiO ₂ -FeCl ₃	420	87 [60]
15	4-ClC ₆ H ₄ CHO	2-(N-morpholino)ethanesulfonic acid	180	89 [61]
16	4-ClC ₆ H ₄ CHO	ZrCl ₄	37	91 [62]
17	4-ClC ₆ H ₄ CHO	[NMP][H ₂ PO ₄]	38	79 [63]
18	4-ClC ₆ H ₄ CHO	Boehmite-SSA	50	98 [27]
19	4-ClC ₆ H ₄ CHO	Pd-SBTU@Fe ₃ O ₄	140	95 [41]
20	4-ClC ₆ H ₄ CHO	Br ₃ -TEDETA@Boehmite	35	96 [this work]

^a Isolated yield.

energy dispersive X-ray spectroscopy (EDS) using an FEI Quanta 200 Scanning Electron Microscope. TGA of the samples was obtained between 30 and 800 °C with heating rate of 10 °C min⁻¹ using Perkin Elmer Pyris Diamond Thermogravimetric Analyzers. The particle size and morphology were performed using an FEI Quanta 200 Scanning Electron Microscope at an accelerating voltage of 25 kV. Melting points of all compounds were determined using Griffin melting point apparatus. Nitrogen adsorption isotherms were determined using a standard gas manifold at 77 K to surface characteristics of the catalyst using a BELSORP MINI II device. Also, the catalyst sample was degassed at 120 °C for 2 h using a BEL PREP VAC II device before analysis.

3.3. Preparation of the catalyst

Initially, modified boehmite nanoparticles using 3-chloropropyltrimethoxysilane (*n*Pr-Cl@Boehmite) were prepared according to the newly reported procedure [17]. Besides, the obtained *n*Pr-Cl@Boehmite (1.0 g) was dispersed in toluene and mixed with 1.5 mL of TEDETA. The mixture was stirred at 90 °C for 24 h. The solid product (TEDETA@Boehmite) was obtained after being washed with ethanol and dried at 50 °C. Then, 1 mL of HBr was added to TEDETA@Boehmite (1 g) and stirred for 1 h at room temperature. Finally, the resultant product (1 g) was dispersed in CCl₄ (5 mL). Subsequently, Br₂ (2.5 mL) was added to the mixture and stirred for 24 h at room temperature. Then, the final product (Br₃-TEDETA@Boehmite) was separated and washed with CCl₄ to remove the unattached substrates.

3.4. General procedure for the oxidation of sulfides

A mixture of sulfide (1 mmol), H₂O₂ (0.4 mL), and Br₃-TEDETA@Boehmite (0.06 g) was stirred at room temperature in ethyl acetate, and the progress of the reaction was monitored by TLC (thin-layer chromatography). After

completion of the reaction, the catalyst was separated using filtration and washed with ethyl acetate. Accordingly, the product was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ (1.5 g). Finally, the organic solvents were evaporated, and products were obtained in good to high yield.

3.5. General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol), and Br₃-TEDETA@Boehmite (0.04 g) was stirred in ethanol under reflux conditions, and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated and washed with ethyl acetate. Then, the solvent was evaporated and all of the products were recrystallized in ethanol. It is worth mentioning that pure polyhydroquinoline derivatives were obtained in good to excellent yields.

3.6. General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives

A mixture of Br₃-TEDETA@Boehmite (0.01 g), anthranilamide (1 mmol), and aldehyde (1 mmol) was stirred at 80 °C in ethanol (2 mL). The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. Afterward, CH₂Cl₂ (2 × 5 mL) was added and the catalyst was separated. CH₂Cl₂ was evaporated under reduced pressure to afford the essentially pure products. Finally, all products were recrystallized in ethanol for further purification.

4. Conclusions

Tribromide ions on boehmite nanoparticles (Br₃-TEDETA@Boehmite) were prepared and characterized by FT-IR

spectroscopy, TGA, BET, XRD, EDS, and SEM techniques. Br₃-TEDETA@Boehmite has been used as a highly efficient and reusable nanocatalyst in the selective oxidation of sulfides and the synthesis of polyhydroquinoline, and 2,3-dihydroquinazolin-4(1H)-one derivatives. All products were obtained in good yields. The reusability of this catalyst was studied. Finally, this catalyst, which is compatible with the environment because of metal-free and nontoxicity, was prepared using inexpensive and available materials.

Acknowledgments

This work was supported by the research facilities of Ilam University, Ilam, Iran.

References

- [1] A. Ghorbani-Choghamarani, B. Tahmasbi, N. Noori, R. Ghafouri-nejad, *J. Iran. Chem. Soc.* 14 (2017) 681.
- [2] D. Wang, D. Astruc, *Chem. Rev.* 114 (2014) 6949.
- [3] V.F. Vavsari, G.M. Ziarani, A. Badiie, S. Balalaie, *J. Iran. Chem. Soc.* 13 (2016) 1037.
- [4] M. Nikoorazm, A. Ghorbani-Choghamarani, N. Noori, B. Tahmasbi, *Appl. Organometal. Chem.* 30 (2016) 843.
- [5] S.S. Soni, D.A. Kotadia, *Catal. Sci. Technol.* 4 (2014) 510.
- [6] S. Shylesh, V. Schunemann, W.R. Thiel, *Angew. Chem. Int. Ed.* 49 (2010) 3428.
- [7] C.W. Lim, I.S. Lee, *Nano Today* 5 (2010) 412.
- [8] M.M. Heravi, S. Sadjadi, *J. Iran. Chem. Soc.* 1 (2009) 6.
- [9] M. Blanco, P. Álvarez, C. Blanco, M.V. Jiménez, J. Fernández-Tornos, J.J. Pérez-Torrente, L.A. Oro, R. Menéndez, *ACS Catal.* 3 (2013) 1307.
- [10] M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, G. Chehardoli, F. Derakhshan-Panah, A. Zare, O. Khaledi, *Sci. Iran. C* 19 (2012) 1584.
- [11] M.A. Zolfigol, A.R. Moosavi-Zare, M. Zarei, *C. R. Chim.* 17 (2014) 1264.
- [12] W. Zhang, Q. Zhao, T. Liu, Y. Gao, Y. Li, G. Zhang, F. Zhang, X. Fan, *Ind. Eng. Chem. Res.* 53 (2014) 1437.
- [13] F. Yu, R. Zhong, H. Chong, M. Smet, W. Dehaen, B.F. Sels, *Green Chem.* 19 (2017) 153.
- [14] A.M. Trzeciak, E. Mieczynska, J.J. Ziolkowski, W. Bukowski, A. Bukowska, J. Noworól, J. Okal, *New J. Chem.* 32 (2008) 1124.
- [15] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, *RSC Adv.* 6 (2016) 43205.
- [16] V. Vatanpour, S.S. Madaenia, L. Rajabi, S. Zinadini, A.A. Derakhshan, *J. Membr. Sci.* 401–402 (2012) 132.
- [17] M. Mirzaee, B. Bahramian, A. Amoli, *Appl. Organometal. Chem.* 593 (2015) 29.
- [18] A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, *RSC Adv.* 6 (2016) 56638.
- [19] M. Mirzaee, B. Bahramian, M. Mirebrahimi, *Chin. J. Catal.* 37 (2016) 1263.
- [20] B. Tahmasbi, A. Ghorbani-Choghamarani, *Catal. Lett.* 147 (2017) 649.
- [21] M. Hajjami, L. Shiri, A. Jahanbakhshi, *Appl. Organometal. Chem.* 668 (2015) 29.
- [22] K.G.M. Koua, V.M. Dong, *Org. Biomol. Chem.* 13 (2015) 5844.
- [23] B. Sreedhar, P. Radhika, B. Neelima, N. Hebbalkar, A.K. Mishra, *Catal. Commun.* 10 (2008) 39.
- [24] G. Li, H. Qian, R. Jin, *Nanoscale* 4 (2012) 6714.
- [25] M.M.D. Pramanikab, N. Rastogi, *Chem. Commun.* 52 (2016) 8557.
- [26] D. Habibi, M.A. Zolfigol, M. Safaiee, A. Shamsian, A. Ghorbani-Choghamarani, *Catal. Commun.* 10 (2009) 1257.
- [27] A. Ghorbani-Choghamarani, B. Tahmasbi, *New J. Chem.* 40 (2016) 1205.
- [28] A. Ghorbani-Choghamarani, M.A. Zolfigol, M. Hajjami, H. Goudarziafshar, M. Nikoorazm, S. Yousefi, B. Tahmasbi, *J. Braz. Chem. Soc.* 22 (2011) 525.
- [29] C.H. Van Dyck, P.Z. Tan, R.M. Baldwin, L.A. Amici, P.K. Garg, C.K. Ng, R. Soufer, D.S. Charney, R.B. Innis, *J. Nucl. Med.* 41 (2000) 234.
- [30] M. Waibel, J. Hasserodt, *Tetrahedron Lett.* 50 (2009) 2767.
- [31] L. He, H. Li, J. Chen, X.F. Wu, *RSC Adv.* 4 (2014) 12065.
- [32] A. Ghorbani-Choghamarani, M. Hajjami, B. Tahmasbi, N. Noori, *J. Iran. Chem. Soc.* 13 (2016) 2193.
- [33] B.B.F. Mirjalili, A. Bamoniri, S. Azad, *J. Iran. Chem. Soc.* 14 (2017) 47.
- [34] M. Ghashang, S.S. Mansoor, K. Aswin, *Res. Chem. Intermed.* 41 (2015) 3447.
- [35] A. Rostami, A. Tavakoli, *Chin. Chem. Lett.* 22 (2011) 1317.
- [36] M. Norouzi, A. Ghorbani-Choghamarani, M. Nikoorazm, *RSC Adv.* 6 (2016) 92387.
- [37] L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Appl. Organometal. Chem.* 31 (2017) e3596.
- [38] F. Havasi, A. Ghorbani-Choghamarani, F. Nikpour, *Microporous Mesoporous Mater.* 224 (2016) 26.
- [39] M. Hajjami, B. Tahmasbi, *RSC Adv.* 5 (2015) 59194.
- [40] M. Hajjami, A. Ghorbani-Choghamarani, R. Ghafouri-Nejad, B. Tahmasbi, *New J. Chem.* 40 (2016) 3066.
- [41] A. Ghorbani-Choghamarani, B. Tahmasbi, Z. Moradi, *Appl. Organometal. Chem.* 31 (2017) 3665.
- [42] M. Tajbakhsh, H. Alinezhad, M. Norouzi, S. Baghery, M. Akbari, *J. Mol. Liq.* 177 (2013) 44.
- [43] K. Mohammadi, F. Shirini, A. Yahyazadeh, *Res. Chem. Intermed.* 42 (2016) 2047.
- [44] A. Zare, F. Abi, A.R. Moosavi-Zare, M.H. Beyzavi, M.A. Zolfigol, *J. Mol. Liq.* 178 (2013) 113.
- [45] G. MohammadiZiarani, A.R. Badiie, Y. Khaniania, M. Haddadpour, *Iran. J. Chem. Chem. Eng.* 29 (2010) 1.
- [46] M. Yarhosseini, S. Javanshir, M.G. Dekamin, M. Farhadnia, *Monatsh. Chem.* 147 (2016) 1779.
- [47] O. Goli-Jolodar, F. Shirini, M. Seddighi, *RSC Adv.* 6 (2016) 26026.
- [48] A. Ghorbani-Choghamarani, G. Azadi, B. Tahmasbi, M. Hadizadeh-Hafshejani, Z. Abdi, *Phosphorus Sulfur Silicon* 189 (2014) 433.
- [49] P. Gogoi, M. Kalita, T. Bhattacharjee, P. Barman, *Tetrahedron Lett.* 55 (2014) 1028.
- [50] A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, *RSC Adv.* 6 (2016) 56458.
- [51] S.M. Islam, A.S. Roy, P. Mondal, K. Tuhina, M. Mobarak, J. Mondal, *Tetrahedron Lett.* 53 (2012) 127.
- [52] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, N. Havasi, *Appl. Organometal. Chem.* 30 (2016) 619.
- [53] M. Nikoorazm, A. Ghorbani-Choghamarani, H. Mahdavi, S.M. Esmaeili, *Microporous Mesoporous Mater.* 211 (2015) 174.
- [54] B. Yu, C.X. Guo, C.L. Zhong, Z.F. Diao, L.N. He, *Tetrahedron Lett.* 55 (2015) 1818.
- [55] A. Ghorbani-Choghamarani, H. Rabiei, B. Tahmasbi, B. Ghasemi, F. Mardi, *Res. Chem. Intermed.* 42 (2016) 5723.
- [56] S. Hussain, D. Talukdar, S.K. Bharadwaj, M.K. Chaudhuri, *Tetrahedron Lett.* 53 (2012) 6512.
- [57] L. Shiri, B. Tahmasbi, *Phosphorus Sulfur Silicon* 192 (2017) 53.
- [58] J. Chen, W. Su, H. Wu, M. Liu, C. Jin, *Green Chem.* 9 (2007) 972.
- [59] A. Davoodnia, S. Allameh, A.R. Fakhari, N. Tavakoli-Hoseini, *Chin. Chem. Lett.* 21 (2010) 550.
- [60] M. Ghashang, K. Azizi, H. Moulavi-Pordanjani, H.R. Shaterian, *Chin. J. Chem.* 29 (2011) 1617.
- [61] V.B. Labade, P.V. Shinde, M.S. Shingare, *Tetrahedron Lett.* 54 (2013) 5778.
- [62] M. Abdollahi-Alibeik, E. Shabani, *Chin. Chem. Lett.* 22 (2011) 1163.
- [63] H.R. Shaterian, M. Aghakhanizade, *Res. Chem. Intermed.* 40 (2014) 1655.