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One-pot synthesis of 4*H*-benzo[*b*]pyrans and dihydropyrano[*c*]chromenes using inorganic–organic hybrid magnetic nanocatalyst in water

Mehdi Khoobi^a, Leila Ma'mani^a, Faezeh Rezazadeh^b, Zeinab Zareie^b, Alireza Foroumadi^a, Ali Ramazani^b, Abbas Shafiee^{c,*}

^a Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran 14176, Iran

^b Chemistry Department, Zanjan University, PO Box 45195-313, Zanjan, Iran

^c Department of Medicinal Chemistry, Faculty of Pharmacy and Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran 14176, Iran

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ABSTRACT

The synthesized nanocatalyst in this work provides a green and useful method to obtain 4*H*-benzo[*b*]pyrans and dihydropyrano[*c*]chromenes in aqueous media. The catalyst shows environmental benign character, which can be easily prepared, stored, recovered without obvious significant loss of activity. Due to water-resistant and superparamagnetic nano-nature of the catalyst, it could be easily separated by the application of an external magnetic device and reused conveniently. The synthesized inorganic–organic hybrid nanocatalyst has fully been characterized by magnetic, adsorptive and thermal techniques (transmission and scanning electron microscopy (TEM & SEM), Fourier transform spectroscopy infrared (FTIR), thermo gravimetric analysis (TGA), X-ray Diffraction (XRD), Brunauer Emmett Teller (BET) and vibrational sampling magnetometer (VSM)), which reveal of the superparamagnetic nano-nature of the particles. In summary, the magnetically inorganic–organic hybrid nanocatalyst supported on hydroxyapatite encapsulated γ -Fe₂O₃ was found to be quite excellent and clean catalytic system for the synthesis of 4*H*-benzopyrans and 2-amino-5-oxo-4-aryl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitriles.

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1. Introduction

The last decade has witnessed much advancement in organocatalysis. Their stability to moisture and oxygen make inconvenient air sensitive techniques unnecessary. The term "organocatalysis" has emerged during the last decade as one of the major issues in the development of catalytic chemical technology [1]. Although many organocatalysts have been designed and applied in this area, however, the design and development of new, effective and easily accessible organic catalysts continue to be a major challenge. In recent years, the utilization of secondary amines-aminocatalysis as organocatalysts has emerged as a viable strategy for different organic transformations [2]. For example, the generally accepted enamine mechanism for α -functionalization is an extension of the work by Stork et al. [3].

Tetrahydrobenzo[*b*]pyrans and dihydropyrano[*c*]chromenes have recently attracted much attention as an important class of heterocycles having useful biological and pharmacological properties, such as diuretic, anti-cancer, anticoagulant, and anti-anaphylactic activities [4–9]. Also, they possess a wide range of application as cognitive enhancers, for the treatment of neurodegenerative diseases, including Parkinson's disease, Down's syndrome, Alzheimer's disease and AIDS associated dementia as well as for the treatment of schizophrenia [10].

Consequently, several methods have been reported for the promoting preparation of tetrahydrobenzo[*b*]pyrans or dihydropy-rano[*c*]chromenes, for example applying of microwave [11] and ultrasonic irradiation [12]. In addition, there are several modified procedures using a variety of reagents, including the use of hexadecyldimethylbenzyl ammonium bromide (HDMBAB) [13], tetrabutylammonium bromide (TBAB) [14,15], fluoride ion [16], ionic liquids [17–20], rare earth perfluorooctanoate [RE(PFO)₃] [21], Na₂SeO₄ [22], high surface area MgO [23,24], nanosized MgO [25], solid acid [26,27], diammonium hydrogen phosphate [28,29], silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride [30], and DBU [31].

However aforementioned methods suffer from the disadvantages, such as expensive or unavailability or toxicity of the reagent, extended reaction times, toxic solvents, additionally the main drawback of almost existing methods is that the catalysts are decomposed under aqueous work-up conditions and their recoveries are often impossible. Therefore, to overcome these drawbacks a great deal of efforts is directed to develop an efficient, catalytic system for synthesis of these compounds. According to the

^{*} Corresponding author. Tel.: +98 21 66406757; fax: +98 21 66461178. *E-mail address*: ashafiee@ams.ac.ir (A. Shafiee).

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successful usage of magnetic catalytic systems as vastly powerful and clean recoverable supports for a variety of catalysts, nowadays their applying is growing [32-41]. In other hand, science and technology are shifting emphasis on economically and environmentally benign and sustainable processes. In this regard, various magnetic nanoparticles including γ -Fe₂O₃ coating with hydroxyapatite has been considered as ideal biocompatible and high-performance heterogeneous catalytic supports [42-45] owing to its excellent thermal and chemical stability, high surface area and their ability to design new functionalized materials considered as "inorganic-organic hybrids" [46-49]. Bearing in mind the usefulness and efficiency of organocatalysts and in connection with our previous works using hydroxyapatite-encapsulated γ -Fe₂O₃ nanocrystallites [50–56] and functionalized iron oxide nanoparticle with amino pyridine moiety [57], we decided to explore on novel magnetically immobilized organocatalyst fabricated by covalently anchoring (2-aminomethyl)phenol moiety on the surface of hydroxyapatite encapsulated maghemite nanoparticles (denoted as $[\gamma-Fe_2O_3@HAp-Si-(CH_2)_3-AMP]$), for the preparation of tetrahydrobenzo[b]pyrans and dihydropyrano[c] chromenes

2. Experimental

2.1. Synthesis of inorganic–organic hybrid magnetic nanocatalyst: (2-aminomethyl)phenol supported on HAp-encapsulated- γ -Fe₂O₃ ([γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP])

A sample of magnetic hydroxyapatite $[\gamma - Fe_2O_3@HAp]$ [55] (500 mg) was pre-activated by heating under vacuum for 48 h at 120 °C and suspended in a mixture of 150 ml of dry toluene containing a stoichiometric amount (92 mg, 0.5 mmol) of 3aminopropyltrimethoxysilane. The amounts of this agent were estimated by assuming two hydroxyl groups per formula of phosphate. The mixture was refluxed under Ar atmosphere for 48 h. The product was separated by filtration, washed with ethanol, and dried under vacuum for 24 h at 50 °C after Soxhelet extraction with hot ethanol to give the solid surface bonded amine group at a loading 0.75 mmol g^{-1} (calculated by the back-titration analysis). The resulting $[\gamma - Fe_2O_3@HAp - Si - (CH_2)_3 - NH_2]$ (0.75 mmol g⁻¹, 10 g) was allowed to react with equimolar of 2-hydroxybenzaldehyde in super dry EtOH for 24h under Ar atmosphere. Then, the solid product was magnetically separated by an external magnet and washed with dry EtOH. The resulting solid was allowed to react with an excess NaBH₃CN in super dry MeOH for 72 h. The used solvent was evaporated and dried over Mg for subsequent application. The product was magnetically separated by an external magnet and washed with diethyl ether and after Soxhelet extraction by hot ethanol dried under vacuum for 24 h at 70 °C to give the ([γ - $Fe_2O_3@HAp-Si-(CH_2)_3-AMP]$ at a loading $0.72 \pm 0.01 \text{ mmol g}^{-1}$ $[\gamma$ -Fe₂O₃@HAp] (determined by TGA analysis).

2.2. General procedure for the synthesis of 2-amino-5-oxo-4-aryl-4, 5-dihydropyrano [3,2-c]chromene-3-carbonitrile or tetrahydrobenzo[b]pyran derivatives

A stirring mixture of an aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), magnetic catalytic system ([γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP], 1.5 mol%) and water (5 mL) were heated under refluxing conditions for a few minutes. To this stirred mixture, 4-hydroxycoumarin or dimedone (1 mmol) was added. The reaction mixture was refluxed for an appropriate time as mentioned in Table 1 or Table 2. The progress of the reaction was monitored by TLC, for disappearance of aldehyde. After completion



Fig. 1. VSM curve of [γ-Fe₂O₃@HAp] (line) vs. [γ-Fe₂O₃@HAp—Si—(CH₂)₃—AMP)] nanocrystallites (dotted line).

of the reaction, the reaction mixture was allowed to cool at room temperature. The reaction mixture was diluted with ethyl acetate and the catalyst was easily separated from the reaction mixture with an external magnet and washed twice with ethyl acetate. The combined organic layers were concentrated in vacuum and the resulting residue was purified by recrystallization from ethanol. All compounds gave satisfactory spectral data (¹H NMR and ¹³C NMR) and they were identical with those reported in the literature [17–31].

3. Result and discussion

Magnetic hydroxyapatite encapsulated γ -Fe₂O₃ supported (2-aminomethyl) phenol ([γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP]) was synthesized according to the procedure shown in Scheme 1. [γ -Fe₂O₃@HAp] were synthesized via co-precipitation of ferrous (Fe²⁺) and ferric (Fe³⁺) ions followed by coating of the γ -Fe₂O₃ nanoparticles with hydroxyapatite [55]. The nanocrystallities of [γ -Fe₂O₃@HAp] were functionalized by 3-aminopropyltrimethoxysilane to produce an organic–inorganic hybrid. Then, this synthesized hybrid was reacted with 2-hydroxy benzaldehyde followed by sodium cyanoborohydride reduction to obtain the (2-aminomethyl) phenol functionalized core-shell magnetic nanocrystallities of [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)].

 $[\gamma$ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)] nanocrystallites were fully characterized by VSM (Fig. 1), SEM, TEM, XRD and TGA (Fig. 2). Due to the superparamagnetic nature of the nanoparticle core, nuclear magnetic resonance (NMR) technique could not be used to confirm surface modification of the –Si—(CH₂)₃NHCH₂—PhOH.

It is important that the core-shell material should possess sufficient magnetic and superparamagnetic properties for practical applications. Magnetic hysteresis measurements for the $[\gamma$ -Fe₂O₃@HAp] and $[\gamma$ -Fe₂O₃@HAp-Si-(CH₂)₃-AMP] nanocrystallites were done in an applied magnetic field at r.t., with the field sweeping from -8000 to +8000 Oe. As shown in Fig. 1, the M(H) hysteresis loop for the samples was completely reversible, showing that the nanoparticles exhibit superparamagnetic characteristics. The hysteresis loops of them reach saturation up to the maximum applied magnetic field. The magnetic saturation values of the $[\gamma$ -Fe₂O₃@HAp] and $[\gamma$ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)] nanocrystallites are 7.24 and 4.37 emu g^{-1} at r.t., respectively. Lower magnetic saturation of later nanoparticles could be due to the influence of the functional group. Both particles shown high permeability in magnetization and their magnetization is sufficient for magnetic separation with a conventional magnet. The reversibility in hysteresis loop confirms that no aggregation imposes to the nanoparticles in the magnetic fields.

The SEM and TEM showed that the average size of synthesized encapsulated nanoparticles is less than 100 nm and they present

Table 1

Synthesis of dihydropyrano[c]chromenes (via condensation of aldehydes. 4-hydroxy coumarin and malononitrile using magnetic nano-organocatalyst)

Entry	Product	Yield ^a	Time	m.p.	Ref.
	NH ₂ O CN				
1	(4a)	10	10 h ^b	253-255	[20]
2	(4a)	10	10 h ^c	253-255	[20]
3	(4a)	78	10 min ^d	253-255	[20]
4	(4b)	84	10 min ^d	257-258	[20]
5	(4c)	78	10 min ^d	220-222	[20]
6	(4d)	75	10 min ^d	255-256	[59]
7	(4e)	79	10 min ^d	255–257	-
8	(4f)	70	10 min ^d	270-272	[60]

^a Yields refer to isolated pure products.

^b No catalyst, H₂O, reflux, 10 h. ^c [γ -Fe₂O₃@ HAp], H₂O, reflux, 10 h. ^d [γ -Fe₂O₃@ HAp—Si—(CH₂)₃—<u>AMP</u>], H₂O, reflux, 10 min.



i. Ca(NO₃)₂, (NH4)₂HPO₄, NH₄OH, *ii*. a) 3-aminopropyltrimethoxysilane, dry toluene, reflux, 48h, b) 2-hydroxybenzaldehyde, dry EtOH, reflux, 24h, c) NaBH₃CN, dry MeOH, r.t., 72h

Table 2

Synthesis of 4H-benzo[b]pyrans (via condensation of aldehydes, dimedone and malononitrile using [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP] as recoverable nanocatalyst in water).

5			017 2 3 1	2,55 1	5 ,
Entry	Product	Yield ^a	Time	m.p.	Ref.
1	O O O O O O O O	80	10 min	225-226	[61]
2	(6b)	84	10 min	198–201	[61]
3	CN NH_2 (6c) S CN CN	87	10 min	195–198	[61]
4	H_2N (6d)	74	10 min	191–194	[62]
5		55	10 min	295–297	[61]

^a Yields refer to isolated pure products.

as uniform particles SEM (Fig. 2a and b). The obtained histogram confirmed the fact that the size of distribution for 75 observed nanoparticles was a narrow normal one with a 69 nm average value and a 2.1 nm standard deviation. The theoretical curve of standard distribution from our studies (Fig. 2c) was calculated by means of origin program.

The XRD pattern of $[\gamma$ -Fe₂O₃@HAp] nanocrystallities agrees well with that of the tetragonal structure of γ -Fe₂O₃ (1999 JCPDS file No 13-0458). No other phase except the maghemite is detectable [58] (Fig. 2d). Diffraction peaks at around 18.4°, 30.2°, 35.7°, 43.6°, 56.2° and 63.1° corresponding to the (111), (220), (311), (400), (440) and (511) are readily recognized from the XRD pattern. Nitrogen adsorption-desorption isotherms are shown in Fig. 2e and reveal that the adsorption-desorption process is not reversible. This is a result of the hysteresis loops due to capillary condensation. The surface area was calculated using BET method, and that was found 122 m² g⁻¹ for synthetic hydroxyapatite coated magnetic nanoparticle ([γ -Fe₂O₃@HAp]). This average was reduced to 87 m² g⁻¹ for functionalized hydroxyapatite coated magnetic nanoparticle powder $[\gamma$ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)]. The synthetic powder showed a type (IV) nitrogen adsorption-desorption isotherm (Fig. 2e).

Quantitative determination of the functional group contents of the surface-bonded [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)] nanocrys-tallites was performed using thermo-gravimetric analysis (TGA) and a loading of 0.72 \pm 0.01 mmol g⁻¹ was obtained. TGA analysis of

the immobilized (2-aminomethyl) phenol moiety was performed and showed a first peak due to desorption of the water (centered at 95 °C). This is followed by a second peak around 300 until 500 °C, corresponding to the loss of the organic spacer group (Fig. 2f).

In connection with our previous work using synthesized magnetic nano-catalysts, and our interest in multi-component reactions, herein the facile synthesis of dihydropyrano[*c*]chromene and 4*H*-drobenzo[*b*]pyran derivatives in the presence of catalytic amounts of [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)] nanocrystallites in aqueous medium is reported. On the basis of the optimal conditions established (1.5 mol%, [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP)], we examined the condensing of malononitrile, 4-hdroxycoumarine and various aromatic aldehyde in aqueous medium. As shown in Scheme 2 the reactions proceed smoothly and corresponding 2-amino-5-oxo-4-aryl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile derivatives were obtained in high yields. Furthermore, the three-component reaction of dimedone, aldehydes, and malononitrile for preparation of tetrahydrobenzo[*b*]pyrans was investigated (Scheme 2).

Subsequently, a series of differently substituted dihydropyrano[c]chromene and tetrahydrobenzo[b]pyran derivatives was prepared successfully under aqueous conditions. The results are listed in Tables 1 and 2. The results clearly indicate that reactions can tolerate a wide range of differently substituted aldehydes. The reactions were complete within 10–15 min and excellent yields of products were obtained by this method. However, in case of



Fig. 2. (a) SEM image; (b) TEM micrograph; (c) histogram of sizes using SEM image; (d) XRD spectra; (e) the isotherm plot of [γ -Fe₂O₃@HAp] and (f) TGA diagram of [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP] nanocrystallites.



Scheme 2. The one-pot synthesis of dihydropyrano[c]chromene-3-carbonitrile and 4H-benzo[b]pyran derivatives.



Fig. 3. The recycling of catalyst (left) and catalyst ability to effective recovery at the end of reactions (right).



Scheme 3. Possible mechanism for one-pot synthesis of 2-amino-5-oxo-4-aryl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile.

aliphatic aldehydes, reactions were not complete under the above conditions and desired products were obtained in low yields.

In continuation to this research, a simple and an efficient onepot synthetic approach was used for the preparation of biologically interesting spirooxindole derivatives in good yields by means of three-component reactions of isatin, malononitrile, and dimedone catalyzed by mentioned magnetic catalytic system in water (Table 2, entry 5).

Finally, to determine the applicability of catalyst recovery, we decanted the vessel by use of an external magnet and remained catalyst was washed with diethyl ether to remove residual product, dried under vacuum and reused in a subsequent reaction. In 10 consecutive runs, the conversion stayed with no detectable loss, higher than 90%. To rule out any contribution of homogeneous catalysis, we tested the reaction leached by a catalytic amount of catalyst (after 2 h stirring in H_2O and removal of the catalyst) and observed that the reaction did not carried out even after 12 h. This clearly confirmed that no active species were present in the supernatant (Fig. 3).

A possible mechanism for the reaction using $[\gamma$ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP] nanocrystallities as clean catalyst is shown in Scheme 3. According to the mechanism $[\gamma$ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP] nanocrystallities catalyzed the readily in situ formation of Knoevenagel product **8.** The higher reactivity of the iminium ion compared to the carbonyl species facilitates Knoevenagel reaction between aryl aldehyde and malononitrile. In the presence of magnetic catalyst, enamine **9** is formed from amine functional group and 4-hydroxycoumarin. Reaction of compound **9** with **8** followed by hydrolysis afforded compound **4a**. The substituent on the aromatic ring did not show any electronic effects in terms of yields under these reaction conditions.

4. Conclusion

In summary, we showed that (2-aminomethyl)phenol moiety supported on HAp-encapsulated- γ -Fe₂O₃ [γ -Fe₂O₃@HAp—Si—(CH₂)₃—AMP] was a novel and effective

heterogeneous catalyst for the one-pot synthesis 4H-benzo[b]pyran and 2-amino-5-oxo-4-aryl-4,5of dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives from commercially available starting materials. The present method requires remarkably small amounts of non-toxic and environmentally friendly $[\gamma$ -Fe₂O₃@HAp-Si-(CH₂)₃-AMP] as catalyst (1.5 mol%). In addition the aqueous conditions, excellent yields, operational simplicity, practicability, product purity, cost efficiency and environmentally benefits are the worthy advantages of this protocol. The introduced magnetically inorganic-organic hybrid nanocatalyst supported on hydroxyapatite encapsulated γ -Fe₂O₃ was highly stable and could be reused in 10 successive runs with no significant structural change and loss of activity.

Based on these observations, it could be concluded that this green and cost-effective catalyst, with simple experimental and work-up procedure, which avoids the use of large volumes of hazardous organic solvents, makes it a useful alternative to the previous methodologies for the scale-up of these three component reactions.

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Appendix A. Supplementary data

Supplementary this artidata associated with found, in the online version, cle can he at http://dx.doi.org/10.1016/j.molcata.2012.03.023.

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