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A green one-pot three-component synthesis of tetrahydrobenzo [b]pyran and 3,4-dihydropyrano[c]chromene derivatives using Fe₃O₄@SiO₂-imid-PMAⁿ magnetic nanocatalyst under ultrasonic irradiation or reflux conditions

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Abstract

An efficient and environmentally benign procedure for the synthesis of tetrahydrobenzo [b]pyran and 3,4-dihydropyrano[c]chromene derivatives has been developed by one-pot three-component reaction of various aldehydes, malononitrile, and dimedone or hydroxycoumarin in the presence of Fe₃O₄@SiO₂-imid-PMAⁿ nanoparticles as magnetic catalysts under ultrasonic irradiation or reflux conditions in water. This new procedure has the notable advantages such as operational simplicity, excellent yields, short reaction time, and absence of any tedious workup or purification. In addition, the excellent catalytic performance in water medium and the easy preparation, thermal stability and separation of the catalyst make it a good heterogeneous system and a useful alternative to other heterogeneous catalysts. Also, the catalyst can be easily recovered by a magnetic field and reused for eight consecutive reaction cycles without significant loss of activity.

Keywords

Fe₃O₄@SiO₂-imid-PMAⁿ magnetic nanocatalyst; Multicomponent reactions; Green synthesis; Tetrahydrobenzo[b]pyrans; 3,4-Dihydropyrano[c]chromenes; One-pot reactions; Ultrasonic irradiation.

1. Introduction

Today the efficiency of a chemical synthesis can be measured, not only by parameters such as selectivity and overall yield but also by its raw material, time, human resources, and energy requirements, as well as the toxicity and hazards of the chemicals and the protocols involved [1]. Multi-component reactions (MCRs) have developed as efficient and powerful tool in modern synthetic organic chemistry because the synthesis of

complex organic molecules from simple and readily available substrates can be achieved in a very fast and efficient manner without the isolation of any intermediate[2]. In addition, the employment of several transformations in a single manipulation is highly compatible with the goals of sustainable and “green” chemistry[3]. Developing MCR procedures in aqueous medium is an active area of research in this direction that have many advantages, such as devoid of any carcinogenic effects, reduced pollution, lower cost, and simplicity in processing, which are valuable to the industry as well as to the environment[4]. On the other hand, the use of ultrasound irradiation represents very powerful green chemical protocols from both the economic and synthetic point of view[5]. The use of ultrasonic irradiation accelerates an organic transformation at ambient conditions which otherwise require harsh conditions of temperature and pressure[6]. The interaction between molecules and ultrasound isn't direct but the energy of these long wavelength can cause cavitation which makes the reaction faster[7].

Pyran derivatives have received significant attention due to their important biological and pharmacological properties[8]. Among the pyrans, the substituted tetrahydrobenzo[*b*]pyran have a special importance among the 6-membered oxygen-containing heterocycles as they have been utilized in synthesis of blood anticoagulant warfarin[9], they have been also used as anticancer and antimicrobial agents[10], and photoactive materials[11].

The conventional synthetic method for the preparation of tetrahydrobenzo[*b*]pyran derivatives is a three-component reaction of cyclic 1,3-diketones, aryl aldehydes, and activated methylene compounds under various reaction conditions, e.g., in the presence of piperidine and triethylamine in acetic acid or DMF[12]. Other methods include use of microwaves[13], ultrasonic radiation[14], and electrogenerated base[15] or using some catalysts such as triethylbenzylammonium chloride (TEBA)[16], perfluorooctanoate[17], (S)-proline[18], silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride [19], n-TiO₂/H₁₄[NaP₅W₃₀O₁₁₀][20], nanozeolite clinoptilolite[21], SO₃H-bearing carbonaceous solid catalyst (PEG-SAC)[22], Multi-walled carbon nanotube supported Fe₃O₄ nanoparticles[23], Free-ZnO nanoparticles[24], acetic acid functionalized imidazolium salts[25], Nano α -Al₂O₃ supported ammonium dihydrogenphosphate (NH₄H₂PO₄/Al₂O₃)[26] and amino functionalized ionic liquids[27]. However, these methods show varying degrees of success as well as limitations such as long reaction times, low yields, and use of toxic solvents. Thus, the development of an alternate milder and cleaner procedure, which surpasses those limitations, is very much relevant for the synthesis of tetrahydrobenzo[*b*]pyran.

Also, Dihydropyrano[3,2-*c*]chromene and its derivatives are very useful compounds in various fields of chemistry, biology and pharmacology[28]. Some of these compounds exhibit spasmolytic, diuretic, anticoagulant, anticancer, and anti-inflammatory activity[28]. Moreover they can be used as cognitive enhancers, for the handling of neurodegenerative diseases, including amyotrophic lateral sclerosis, Alzheimer's disease, Parkinson's disease, Huntington's disease, AIDS associated dementia and Down's

syndrome as well as for the treatment of schizophrenia and myoclonus[29]. Despite their importance from pharmacological, industrial and synthetic point of views, comparatively few methods for the preparation of dihydropyrano[3,2-c]chromenederivatives have been reported[30]. Some of the reported procedures require long reaction times; afford products with only modest yields and non-reusability of the catalyst. Therefore, the development of more effective methods for their preparation is still necessary.

In recent years, brønsted acids such as Keggin-type heteropolyacids (HPAs) have been used as efficient catalysts for a variety of organic reactions because of their redox properties and superacidic, high thermal stability, ease of handling, high proton mobility, stronger acids than homogeneous acid catalysts, low toxicity, development of clean technologies and low cost [31]. Although HPAs are versatile compounds in their acidic form, their main disadvantages are high solubility in polar solvents and low surface area ($<10 \text{ m}^2/\text{g}$). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult[32]. Therefore, in order to overcome this problem, these materials disperse on supports (such as active carbon, silica, acidic ion-exchange resins and etc.,) which possess large surface area. The use of support allows the heteropolyacids to be dispersed over a large surface area and increases their catalytic activity [33]. In previous work[34], we introduce a simple, repaid, inexpensive and one step method, solvothermal, for synthesis of $\text{H}_3\text{PMo}_{12}\text{O}_4$ nanoparticles (PMA^{n}) from $\text{H}_3\text{PMo}_{12}\text{O}_4$ bulk particles (PMA^{b}). Acidity of as-prepared nanoparticles was investigated by pyridine adsorption method. Results showed acidity of PMA rise by declining particle size.

Magnetic nanoparticles (MNPs) such as magnetite (Fe_3O_4) have attracted great interest because of magnetic and electrical properties, high specific surface area, their unique catalytic and their wide applications, including drug delivery systems, targeted gene therapy, ion exchange separation, magnetic resonance imaging, biosensors, magnetic data storage, and environmental remediation and catalysis[35]. For many applications, magnetic nanoparticles are suitable to be chemically stable and uniform in size. But the magnetic nanoparticles trend to aggregate due to their nanoscale and strong interaction between each other. This problem can be solved by coating of magnetite nanoparticles with a silica layer as the stabilizer, which prevents direct contact between the nanoparticles. Furthermore, the abundant hydroxyl groups on the surface of composite particles provide the opportunity to conjugate various function molecules for many special applications[36]. Recently, a number of functionalized Fe_3O_4 nanoparticles have been employed in a range of organic transformations, and the studies on immobilization of organo catalysts on silica coated iron oxide nanoparticles have been reported [37]. Therefore, as part of our continuing interest in developing newer methods for the synthesis of useful compounds, we have recently successfully developed $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -imid-PMAⁿ as recyclable catalyst for the one-pot synthesis of 1-amidoalkyl-2-naphthols [38]. Compared to other substrates (silica, acidic ion-exchange resins, active carbon and nanotitania), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -imid nanoparticles have various advantages such as high

loading capacity, low leaching and simple and efficient recovery procedure. Fig. 1 presents the procedure for the preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ stepwise.

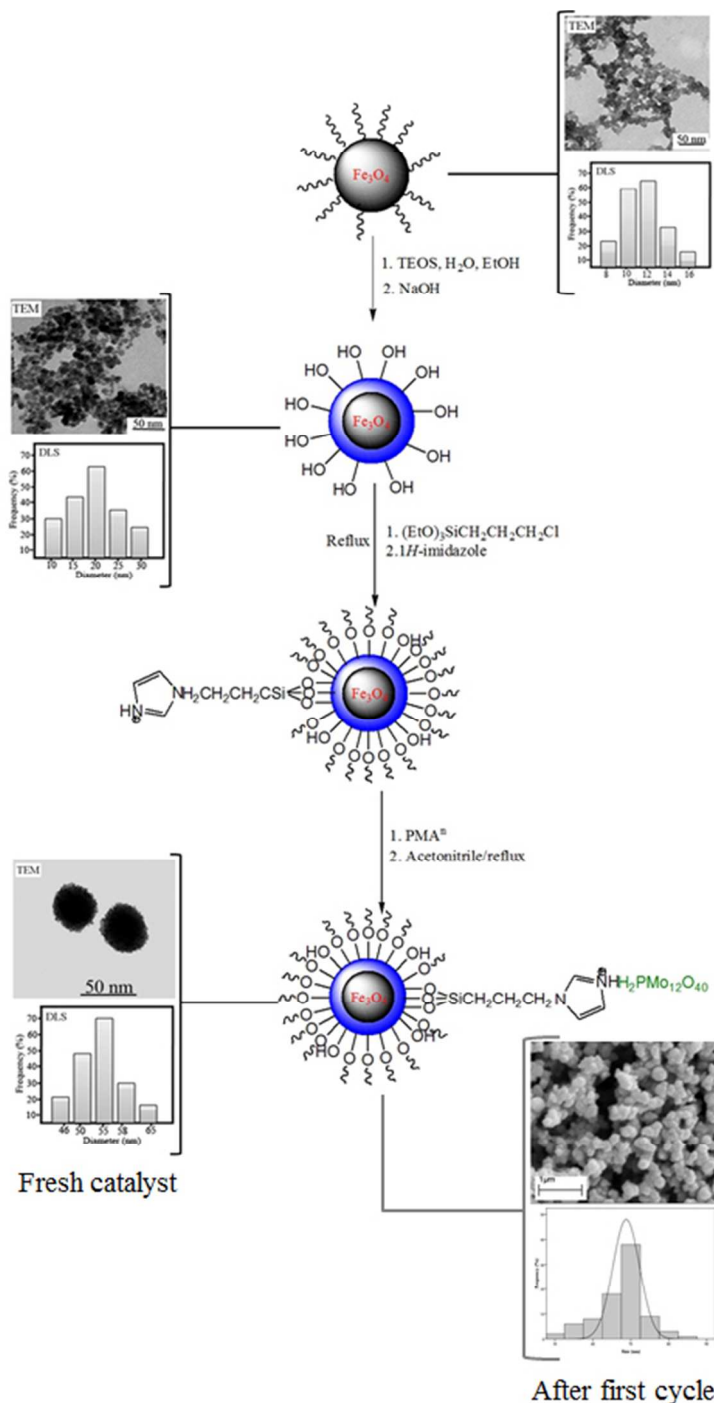
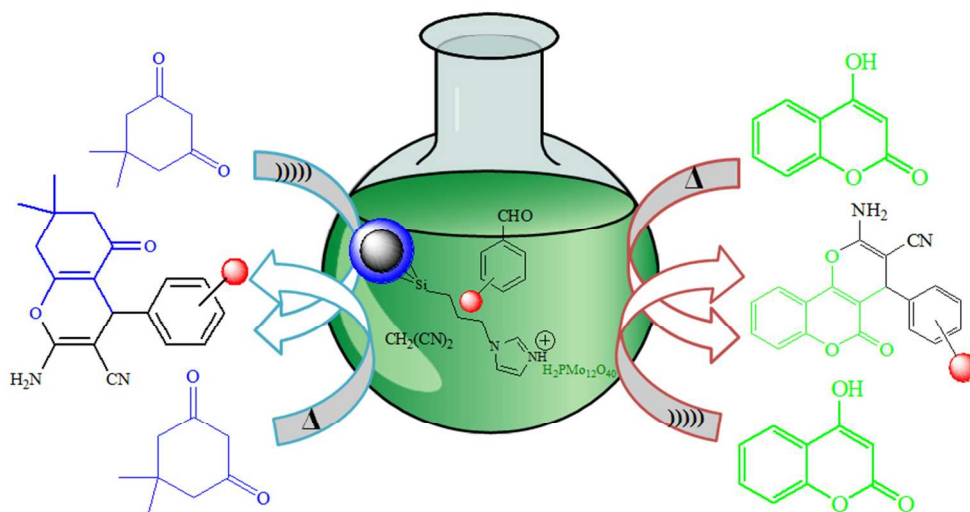


Fig. 1: Process for preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ nanoparticles and characterization by TEM, SEM and DLS technique.

Encouraged by these efforts and aiming to show the efficiency and generality of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ as catalysts for further, we have utilized this novel catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans and dihydropyrano[3,2-*c*]chromenes from simple and easily available starting materials under much milder reaction conditions (Scheme.1).



Scheme.1: $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ catalyzed synthesis of tetrahydrobenzo[*b*]pyran and dihydropyrano[3,2-*c*]chromene derivatives under ultrasonic irradiation or reflux conditions.

2. Results and discussion

In our previous work [38], the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ nanocatalysts were characterized by various methods such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), Fourier transform infrared (FT-IR), vibrating sample magnetometer (VSM) and etc. As shown in Fig. 1 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ nanoparticles have spherical shapes with approximately 50 nm diameters. The size distribution of these is centered at a value of 55 nm. The magnetic properties of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ nanoparticles were measured by VSM at room temperature. All the samples show a typical superparamagnetic behavior. Hysteresis phenomenon was not found and the magnetization and demagnetization curves were coincident. The saturation magnetization of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ is 63.4, 39.7, 33.2 emu g^{-1} , respectively.

Due to ability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ as a mild and efficient acid catalyst, we decided to apply this catalyst for synthesis of tetrahydrobenzo[*b*]pyrans. At the first stage,

to obtain the best reaction conditions, the reaction of dimedone, benzaldehyde and malononitrile, as a model reaction was chosen. The model reaction was refluxed in the presence of 0.02 g of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ and a variety of solvents such as H_2O , EtOH, MeOH, EtOAc, CHCl_3 and CH_3CN . The represented data in Table 1, showed the reaction proceeded efficiently in refluxing H_2O and resulted in high yields of the desired product (Table 1, entry 6). This three-component condensation was also accomplished in protic solvents such as EtOH and MeOH under reflux and the corresponding products were obtained in 87% and 79% yield, respectively (Table 1, entries 1 and 3). Aprotic solvents such as CHCl_3 , EtOAc and CH_3CN afforded the desired product in lower yields and longer reaction times (Table 1, entries 2, 4 and 5). Moreover, the model reaction was examined under solvent-free conditions at 100 °C and gave the corresponding product in 71% yield after 70 min (Table 1, entry 7).

Table.1: Optimization of the amount of catalyst, solvent and temperature in a one-pot synthesis of the model reaction.^a

Entry	Catalyst amount (g)	Solvent	Condition	Time (min)	Yield (%) ^b
1	0.02	EtOH	reflux	20	87
2	0.02	EtOAc	reflux	80	43
3	0.02	MeOH	reflux	30	79
4	0.02	CHCl_3	reflux	100	Trace
5	0.02	CH_3CN	reflux	60	28
6	0.02	H_2O	reflux	20	94
7	0.02	Solvent-free	100°C	70	71
8	None	H_2O	reflux	360	-
9	0.005	H_2O	reflux	60	33
10	0.01	H_2O	reflux	60	67
11	0.015	H_2O	reflux	30	87
12	0.025	H_2O	reflux	20	92
13	0.02	H_2O	r.t	120	46
14	0.02	H_2O	60°C	90	77
15	0.02	H_2O	80°C	40	85
16	None	H_2O	Sonication (40 kHz)/r.t	20	-
17	0.005	H_2O	Sonication (40 kHz)/r.t	15	54
18	0.01	H_2O	Sonication (40 kHz)/r.t	10	88
19	0.015	H_2O	Sonication (40 kHz)/r.t	7	96
20	0.02	H_2O	Sonication (40 kHz)/r.t	7	93

^aReaction conditions: benzaldehyde (1 mmol), malonitrile (1.2mmol), dimedone (1 mmol), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ catalyst and solvent (5 mL).

^bIsolated yield.

After that we checked the model reaction in presence of H_2O as a green solvent under reflux conditions and various amount of catalyst. As it was shown in Table 1 the best result was obtained when we carried out the model reaction in the presence of 0.02 g of catalyst. This condensation was carried out with low amounts of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ of 0.005, 0.01 and 0.015 g and the corresponding products were obtained in 33%,

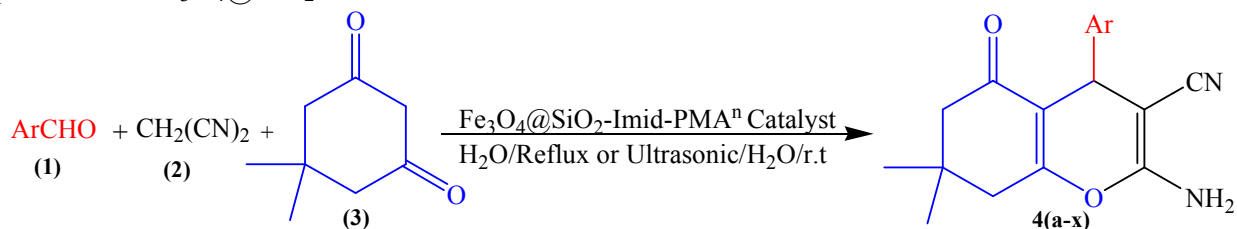
67% and 87% yield, respectively (Table 1, entries 9-11). The effect of temperature was also studied by carrying out the model reaction in the presence of water as a solvent and 0.02 g of catalyst at room temperature, 60°C and 80°C. It was observed that the yield was increased when the reaction temperature was increased (Table 1, entries 13-15).

The reaction was also checked without the catalyst in which the reaction did not proceed even after 6 h (Table 1, entry 8). These observations established the crucial role of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ for the expedition of the reaction time and the product yield.

For investigation of the ability of ultrasonic irradiation for the acceleration of organic reactions, we examined the model reaction under ultrasonic irradiation at room temperature in presence of H_2O as a green solvent and various amount of catalyst. As it is revealed from Table 1, the best results were obtained in the presence of 0.015 g of catalyst (Table 1, entry 19). However, synthesis of organic compounds under ultrasound irradiation has been limited by the need for a specialized apparatus that may not be available in many laboratories. Because of this limitation, herein we report both ultrasonic irradiation in H_2O in presence of 0.015 g of catalyst at room temperature and also refluxing water in presence of 0.02 g of catalyst (Table 1, entries 6 and 19) for the synthesis of tetrahydrobenzo[b]pyrans.

After optimizing the reaction conditions, the generality of this catalytic system was confirmed by the employment of a series of aldehydes, dimedone and malononitrile to obtain desired products under the optimized conditions. The results are summarized in Table 2.

Table.2: Synthesis of derivatives of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[b]pyran in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$.



Entry	Ar	Product	H ₂ O/Reflux		Ultrasonic/H ₂ O/r.t		M.p. °C (Lit.)
			Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	
1	C ₆ H ₅	4a	20	94	7	96	238-240 (227-239) ^[39]
2	4-Me-C ₆ H ₄	4b	30	85	10	91	212-214 (214-216) ^[39]
3	2-Me-C ₆ H ₄	4c	40	82	12	92	210-211 (210-212) ^[26]
4	4-MeO-C ₆ H ₄	4d	25	87	10	94	201-203 (198-202) ^[21]
5	3-MeO-C ₆ H ₄	4e	30	88	10	92	195-197 (196-198) ^[26]
6	4-Me ₂ N-C ₆ H ₄	4f	25	90	8	95	212-214 (210-213) ^[21]
7	3,4-(MeO) ₂ -C ₆ H ₃	4g	30	84	12	93	229-231 (227-229) ^[24]
8	2,3-(MeO) ₂ -C ₆ H ₃	4h	50	85	12	90	216-218 (216-217) ^[21]
9	4-OH-C ₆ H ₄	4i	30	92	9	96	225-227 (224-226) ^[12]

10	4-OH-3-MeO-C ₆ H ₃	4j	40	88	12	91	230-231 (227-229) ^[24]
11	4-Cl-C ₆ H ₄	4k	10	95	5	97	212-213 (213-214) ^[21]
12	2-Cl-C ₆ H ₄	4l	18	90	7	93	213-214 (212-213) ^[21]
13	4-NO ₂ -C ₆ H ₄	4m	10	96	4	97	179-181 (180-182) ^[26]
14	3-NO ₂ -C ₆ H ₄	4n	15	93	7	95	209-211 (210) ^[4]
15	2-NO ₂ -C ₆ H ₄	4o	10	93	5	92	237-238 (238-239) ^[24]
16	4-Cl-3-NO ₂ -C ₆ H ₃	4p	5	97	5	96	214-216 (216-217) ^[24]
17	4-CN-C ₆ H ₄	4q	10	94	5	97	227-228 (225-228) ^[26]
18	4-F-C ₆ H ₄	4r	12	96	5	95	188- 189 (190-191) ^[26]
19	2,4-(Cl) ₂ -C ₆ H ₄	4s	10	95	4	97	192-194 (190-192) ^[26]
20	3-OPh-C ₆ H ₄	4t	30	89	12	90	191-193 (193-194) ^[19]
21	2-Naphthalene	4u	25	92	8	93	232-233 (232-234) ^[8]
22	4-C ₃ H ₇ -C ₆ H ₄	4v	40	90	14	91	190-191 (187-189) ^[8]
23	2-Thionyl	4w	35	92	10	94	221-222 (223-225) ^[21]
24	2-Furyl	4x	30	90	10	89	219-221 (220-223) ^[21]

^aReaction conditions: aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2mmol), water (5 mL, reflux), Fe₃O₄@SiO₂-imid-PMAⁿ (0.02 g) or water (5 mL, ultrasonic irradiation (40 kHz), r.t), Fe₃O₄@SiO₂-imid-PMAⁿ(0.015 g).

^bThe yields refer to isolated products.

As shown in Table 2, we investigated the reaction with a wide range of aromatic aldehydes with electron donating and electron withdrawing groups. Both electron-rich and electron-deficient aldehydes worked well and give high yields of products under both refluxing H₂O and ultrasonic irradiation.

Electron-deficient aldehydes furnished excellent yields of the corresponding products in the shorter reaction times (Table 2, entries 11-19), but the aromatic aldehydes with electron-donating substituents carried out the reaction at longer reaction times in lower yields of the corresponding tetrahydrobenzo[b]pyrans (Table 2, entries 2-10). Moreover, it is clear that, under the same reaction conditions, reactions under ultrasonic irradiation led to shorter reaction times.

Also both of our methodologies have been successfully used for heteroaromatic aldehydes that are acid sensitive species such as thiophene-2-carbaldehyde and furan-2-carbaldehyde and the corresponding tetrahydrobenzo[b]pyrans were obtained in excellent yields without the formation of any byproduct (Table 2, entries 23 and 24).

Encouraged by these results, we replaced the dimedone with 4-hydroxycoumarin to explore its further applications toward the synthesis of dihydropyrano[3,2-c]chromene derivatives. Initially, we optimized the reaction conditions. For this purpose, the reaction of 4-hydroxycoumarin, benzaldehyde and malononitrile was chosen as a model reaction then the model reaction was refluxed in the presence of 0.025 g of Fe₃O₄@SiO₂-imid-PMAⁿ and a variety of solvents such as H₂O, EtOH, MeOH, EtOAc, CHCl₃, CH₂Cl₂, THF and CH₃CN. As shown in Table 3, the best result in terms of the reaction time (15 min) and yield (96%) was obtained when the reaction was carried out in refluxing H₂O (Table 3, entry 8). This condensation was also accomplished efficiently in refluxing EtOH and MeOH and resulted in high yields of the desired products (Table 3, entries 1, 2). The model reaction was also examined under solvent-free conditions at 100

°C and gave the corresponding product in 81% yield after 60 min (Table 3, entry 9). Due to green nature and cost effective of the reactions in H₂O, we decided to choose H₂O as a solvent in this condensation and checked the model reaction in presence of H₂O as a solvent under reflux and various amount of catalyst. As shown in Table 3 the best result was obtained when the model reaction carried out in the presence of 0.025 g of catalyst. The results show clearly that the catalyst is effective for this transformation and in its absence; the reaction did not take place even after higher reaction time (Table 3, entry 13). Use of a higher amount of catalysts did not improve the yield (Table 1, entry 17) while a decrease in the amount of catalysts decreases the yield (Table 3, entry 13).

We also checked the model reaction in presence of water as a solvent and 0.025 g of catalyst at room temperature, 60°C and 80°C and observed that the corresponding product was formed in longer reaction time and lower yield (Table 3, entries 10-12).

Because of the ability of ultrasonic irradiation for the synthesis of tetrahydrobenzo[b]pyrans, we examined the model reaction under ultrasonic irradiation at room temperature in presence of H₂O as a green solvent and various amount of catalyst at room temperature. As shown in Table 3, the best results were obtained in the presence of 0.025 g of catalyst (Table 3, entry 22).

Table 3: Effect of solvent, temperature and catalyst amount on the condensation of benzaldehyde, malononitrile, and 4-hydroxycoumarin.^a

Entry	Catalyst amount (g)	Solvent	Condition	Time (min)	Yield (%) ^b
1	0.025	EtOH	reflux	15	92
2	0.025	MeOH	reflux	25	87
3	0.025	CHCl ₃	reflux	90	22
4	0.025	CH ₂ Cl ₂	reflux	90	Trace
5	0.025	CH ₃ CN	reflux	60	48
6	0.025	THF	reflux	90	35
7	0.025	EtOAc	reflux	60	52
8	0.025	H ₂ O	reflux	15	96
9	0.025	Solvent-free	100°C	60	81
10	0.025	H ₂ O	r.t	100	56
11	0.025	H ₂ O	60°C	60	75
12	0.025	H ₂ O	80°C	30	88
13	None	H ₂ O	reflux	300	-
14	0.01	H ₂ O	reflux	60	22
15	0.015	H ₂ O	reflux	40	44
16	0.02	H ₂ O	reflux	15	81
17	0.03	H ₂ O	reflux	15	94
18	None	H ₂ O	Sonication (40 kHz)/r.t	20	-
19	0.01	H ₂ O	Sonication (40 kHz)/r.t	15	44
20	0.015	H ₂ O	Sonication (40 kHz)/r.t	10	77
21	0.02	H ₂ O	Sonication (40 kHz)/r.t	8	94
22	0.025	H ₂ O	Sonication (40 kHz)/r.t	6	97
23	0.03	H ₂ O	Sonication (40 kHz)/r.t	8	96

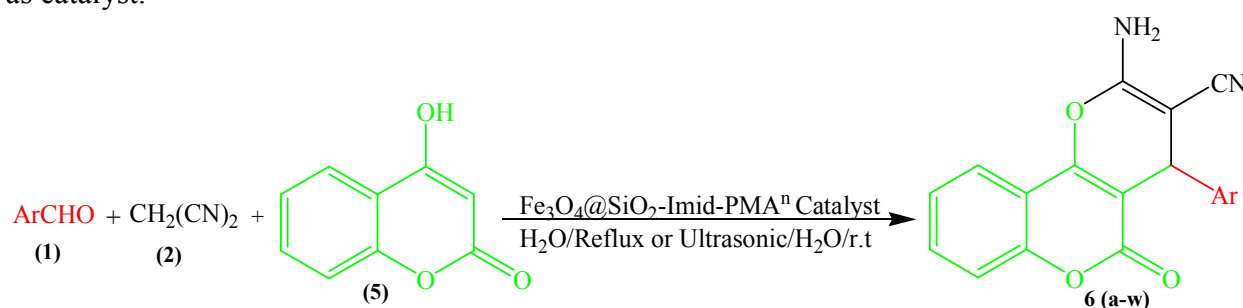
^aReaction conditions: benzaldehyde (1 mmol), malonitrile (1.2mmol), 4-hydroxycoumarin (1 mmol), Fe₃O₄@SiO₂-imid-PMAⁿ catalyst and solvent (5 mL).

^bIsolated yield.

So, the best results were obtained when the reaction was carried out under ultrasonic irradiation in H₂O at room temperature and also refluxing water in presence of 0.025 g of catalyst (Table 3, entries 8 and 22).

In order to develop the scope of these reactions, we conducted the reaction with a series of aromatic aldehydes bearing different substituent groups, heteroaromatic and aliphatic aldehydes under the determined optimized conditions. The results are summarized in Table 4.

Table.4: Synthesis of dihydropyrano[3,2-c]chromenederivatives using Fe₃O₄@SiO₂-imid-PMAⁿ as catalyst.^a



Entry	Ar	Product	H ₂ O/Reflux		Ultrasonic/H ₂ O/r.t		M.p. °C (Lit.)
			Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	
1	C ₆ H ₅	6a	15	96	6	97	260-261 (256-258) ^[40]
2	4-MeO-C ₆ H ₄	6b	25	88	8	93	244-246 (247-249) ^[19]
3	4-Me-C ₆ H ₅	6c	25	90	8	95	253-255 (254-255) ^[19]
4	4-OH-C ₆ H ₅	6d	25	93	10	96	261-263 (258-260) ^[41]
5	3-OH-C ₆ H ₅	6e	30	95	7	95	268-270 (269-270) ^[42]
6	4-OH-3-MeO-C ₆ H ₅	6f	30	86	12	92	254-256 (256-257) ^[41]
7	4-Me ₂ N-C ₆ H ₄	6g	20	91	10	94	224-226 (224-225) ^[19]
8	3,4-(MeO) ₂ -C ₆ H ₃	6h	30	86	10	90	225-227 (228-230) ^[43]
9	3,4,5-(MeO) ₃ -C ₆ H ₂	6i	40	89	12	88	234-236 (236-238) ^[42]
10	4-Br-C ₆ H ₄	6j	15	92	6	95	250-251 (252-254) ^[40]
11	4-Cl-C ₆ H ₅	6k	12	95	5	96	265-267 (264-266) ^[22]
12	2-Cl-C ₆ H ₅	6l	15	88	8	90	267-269 (266-268) ^[44]
13	2,4-(Cl) ₂ -C ₆ H ₄	6m	8	93	5	97	260-261 (258-259) ^[40]
14	4-F-C ₆ H ₄	6n	10	93	6	91	260 (259-261) ^[19]
15	4-CN-C ₆ H ₄	6o	12	96	6	95	281-283 (284-286) ^[30]
16	4-NO ₂ -C ₆ H ₅	6p	5	96	5	97	252- 254 (250-252) ^[41]
17	3-NO ₂ -C ₆ H ₅	6q	10	91	6	93	266-267 (263-265) ^[41]
18	2-NO ₂ -C ₆ H ₅	6r	10	89	5	96	257-259 (258-260) ^[42]
19	2-Furyl	6s	30	87	12	92	255-256 (253-255) ^[41]
20	2-Thionyl	6t	30	92	10	90	225-227 (228-229) ^[17]
21	CH ₃ (CH ₂) ₂	6u	40	90	12	93	240-242 (243-245) ^[40]
22	(CH ₃) ₂ CH	6v	35	86	12	89	251-253 (250-252) ^[19]

23	Cyclohexyl	6w	40	91	12	94	283-285 (281-283) ¹⁷¹
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^aReaction conditions: aldehyde (1 mmol), 4-hydroxycoumarin (1 mmol), malononitrile (1.2mmol), water (5 mL, reflux), or water (5 mL, ultrasonic irradiation (40 kHz), r.t), Fe₃O₄@SiO₂-imid-PMAⁿ (0.025 g).

^bThe yields refer to isolated products.

According to [Table 4](#), aromatic aldehydes bearing electron-withdrawing groups ([Table 4](#), entries 10-18) generally exhibit higher reactivity in this reaction compared to those bearing electron-releasing groups ([Table 4](#), entries 2-9). In contrast, as seen in [Table 4](#), the present method is not only suitable for aromatic aldehydes but can also successfully be applied to aliphatic and heteroaromatic aldehydes.

Heteroaromatic aldehydes such as thiophene-2-carbaldehyde and furan-2-carbaldehyde were also converted to the corresponding products in excellent yields under both of our methodologies ([Table 4](#), entries 19 and 20).

Moreover, it is clear that, about all of above results, reactions under ultrasonic irradiation led to shorter reaction times. The generality of this catalytic system was also checked for aliphatic aldehydes and a high yield of desired product was obtained ([Table 4](#), entry 21-23).

A proposed mechanism for the synthesis of tetrahydrobenzo[b]pyransis was outlined in [Supplementary information](#). Based on this mechanism, as shown in [S1](#), the intermediate (**I**) is produced upon initial condensation of aldehyde with malononitrile under the catalytic activity of Fe₃O₄@SiO₂-imid-PMAⁿ.

Subsequent nucleophilic addition of dimedone to the intermediate (**I**) followed successively by intramolecular cyclization to the intermediate (**II**), and rearrangement to furnish the corresponding product. A similar mechanism may occur for the formation of dihydropyrano [3,2-c]chromene derivatives.

To compare the reactivity of the Fe₃O₄@SiO₂-imid-PMAⁿ with previously reported catalysts/reagents a comparative chart is presented in [S2](#). Although, all the catalysts listed in [S2](#) were able to produce good yields of corresponding products, however some of these reactions were carried out under harsh reaction conditions such as toxic solvents. Moreover, some of the catalysts listed in [S2](#) are not reusable and thus, our reusable catalyst and green methodologies in water have been established as a better alternative compared to the reported methods for the fabrication of corresponding products.

We also compared the catalytic activity of Fe₃O₄@SiO₂-imid-PMAⁿ with H₃PMO₁₂O₄₀ (PMA^b) and nano H₃PMO₁₂O₄₀ (PMAⁿ) in these condensations and we observed the best results in terms of the reaction times and yields were obtained when the reaction was carried out in the presence of Fe₃O₄@SiO₂-imid-PMAⁿ as a catalyst ([S2](#), entries 17-19 and 35-37).

Fe₃O₄@SiO₂-imid-PMAⁿ magnetic catalyst dispersed in H₂O can be easily separated by external magnetic field within several minutes without the need for a centrifugation or filtration step or a tedious workup of the final reaction mixture. However, magnetic

separation performance makes the nanoparticles more effective and convenient in applications.

The reusability and recovery of the catalyst are important issues, especially when the reactions use solid catalysts. Thus, the recovery and reusability of catalyst were investigated for the preparation of 2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (**4k**) and 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**6k**) at reflux conditions or ultrasonic irradiation under optimized conditions in water (Table 5). The catalyst was recovered by a magnetic field and the remaining solid was washed with hot ethanol (2×10 mL). Then, the recovered catalyst was dried under vacuum at 60°C. The performance of the recycled catalyst in reaction up to eight successive runs was shown in Table 5. These bar diagrams clearly suggest that the desired products were obtained in high yields without distinct deterioration in catalytic activity.

To determine the exact PMAⁿ species responsible for the observed reactions and to measure the extent of molybdenum (Mo) leaching after the reactions, we have used the hot filtration test [63]. For this aim, we have studied the model reaction between 4-chlorobenzaldehyde, malononitrile and dimedone under reflux conditions in water. The hot reaction mixture was filtered after 27% conversion (GC) to remove the catalyst. Continuation of the reaction upon the resulting filtrate under the same conditions showed 32% conversion (GC) after 6h. This result shows that the amount of leaching of the catalyst into the reaction mixture should be low and confirms that the catalyst acts heterogeneously in the reaction.

To determine the degree of leaching of the metal from the heterogeneous catalyst, the catalyst was removed by using a magnetic field and the molybdenum amount in reaction medium after each reaction cycle was measured through Inductively Coupled Plasma (ICP) analyzer. The analysis of the reaction mixture by the ICP technique showed that the leaching of H₃PMo₁₂O₄₀ was negligible (Table 5).

SEM and DLS images of the catalyst after the first recycle have been represented in Fig. 1. As shown in Fig. 1, Fe₃O₄@SiO₂-imid-PMAⁿ nanoparticles had an average diameter of 70 nm, were of uniform size, and showed good dispersity. Additionally, the hydrodynamic diameter of catalyst was investigated by DLS technique. This size distribution is centered at a value of 70 nm. Generally, leaching of H₃PMo₁₂O₄₀ and increasing of catalyst size lead to decrease the yield after each cycle.

Table 5 Recyclability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ in the synthesis of **4k** and **6k** under the optimized conditions and PMAⁿ leaching (%) in each reaction cycle.

Run	1	2	3	4	5	6	7	8
Yield (%)								
a	95	95	94	94	94	92	92	92
b	97	97	96	95	95	95	92	92
c	95	95	95	93	93	92	92	92
d	96	96	95	94	94	93	93	93
Leaching (%)								
a	0.43	0.61	0.85	1.47	1.92	2.42	3.16	3.71
b	0.27	0.43	0.78	1.15	1.89	2.12	2.57	2.91
c	0.63	1.17	1.57	1.88	2.70	2.98	3.63	4.11
d	0.51	0.77	1.07	1.20	1.50	1.62	1.96	2.33

- (a) Reaction conditions: 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2mmol), water (5 mL), reflux, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ (0.02 g), 10 min.
- (b) Reaction conditions: 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2mmol), water (5 mL), ultrasonic irradiation (40 kHz), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ (0.015 g), r.t, 5 min.
- (c) Reaction condition: 4-chlorobenzaldehyde (1 mmol), 4-hydroxycoumarin (1 mmol), malononitrile (1.2mmol), water (5 mL), reflux, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ (0.025 g), 15 min.
- (d) Reaction condition: 4-chlorobenzaldehyde (1 mmol), 4-hydroxycoumarin (1 mmol), malononitrile (1.2mmol), water (5 mL), ultrasonic irradiation (40 kHz), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ (0.025g), 5 min.

3. Conclusion

In conclusion, we have developed an easy, highly efficient and green methodology for the synthesis of tetrahydrobenzo[b]pyran and dihydropyrano[3,2-c]chromene derivatives via one-pot three-component reaction in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ nanoparticles as efficient and magnetic catalyst under ultrasonic irradiation or reflux conditions in water.

This method gives notable advantages such as easy preparation, heterogeneous nature, thermal stability and easy separation of the catalyst, clean and simple procedure, excellent yields, short reaction time, easy product separation and purification, lower loading of catalyst compared with the other methods, and avoidance of using hazardous organic solvents that makes this method an instrumental alternative to the previous methodologies for the scale up of these one-pot three-component reactions. Furthermore, the catalyst is magnetically separable and eliminates the requirement of catalyst filtration after completion of the reaction, which represents a major advantage for reactions from an economic and environmental point of view. In addition, the catalyst used is easily

recovered by using a permanent magnet and reused without any noticeable loss of activity after at least eight times.

4. Experimental

Chemicals were purchased from Merck and Aldrich Chemical Companies. All the solvents were distilled, dried and purified by standard procedures. Determination of the purity of the substrate and monitoring of the reaction were accomplished by thin-layer chromatography (TLC) on a silica-gel polygram SILG/UV 254 plates. The NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer (using DMSO- d_6 or CDCl₃ with TMS as the standard). Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was taken on a Shimadzu FT-IR 8300 spectrophotometer and the sample and KBr were pressed to form a tablet. Magnetic characterization was carried out on a vibrating sample magnetometer (Meghnatis Daghig Kavir Co., Iran) at room temperature. Dynamic light scatterings (DLS) were recorded on a HORIBA-LB550. Scanning electron microscopy (SEM) image was obtained on Philips XL-30E SEM. Sonication was performed using an ultrasound cleaning bath (KQ-250B, China) with a frequency of 40 Hz and voltage of 220 V. The C, H, N and S elemental analyses were carried out by using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. Melting points were determined by open capillary method and were uncorrected. Therefore, all of the products were characterized by FT-IR, ¹H NMR and ¹³C NMR, and also by comparison with authentic samples.

4.1. General procedure

4.1.1. Preparation of Fe₃O₄@SiO₂ core-shell

The core-shell Fe₃O₄@SiO₂ nanospheres were prepared by a modified Stober method in our previous work (Fig. 1) [64].

4.1.2. Preparation of Fe₃O₄@SiO₂-imid

Fe₃O₄@SiO₂ (1 g) was added to the solution of 3-chlorotriethoxypropylsilane (1 mmol, 0.241 g) and imidazole (1 mmol, 0.0680 g) in *p*-xylene (20 mL) and the resultant mixture was under reflux for 24 h under nitrogen atmosphere. After refluxing for about 24 h, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with *p*-xylene to remove any reacted species and dried at 70 °C for 6 h [38].

4.1.3. Preparation of H₃PMo₁₂O₄₀ nanoparticles (PMAⁿ)

PMAⁿ nanoparticles were prepared in our previous work [34]. In a typical procedure, 5 mmol of bulk H₃PMo₁₂O₄₀ (PMA^b) was dispersed in 50 mL *n*-octane and the resulting dispersion was stirred vigorously for 30 min at room temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80% of the total volume. The autoclave was sealed and maintained at 150 °C for 12 h. The autoclave was then cooled to room temperature. Finally, the resulted powder was filtered and washed for several times by octane, and dried in a vacuum at 80 °C for 12 h (Fig. 1).

4.1.4. Preparation of Fe₃O₄@SiO₂-imid-PMAⁿ

Fig. 1 represents the anchoring of PMAⁿ onto Fe₃O₄@SiO₂-imid. Fe₃O₄@SiO₂-imid (1.0 g) was added to an acetonitrile solution of PMAⁿ (1.0 mmol) in 20 mL was taken in a round-bottom flask. The mixture was refluxed for 24 h under nitrogen atmosphere. After 24 h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70 °C for 6 h [38].

4.1.5. General procedure for the synthesis of tetrahydrobenzo[*b*]pyrans

A mixture of aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol) and Fe₃O₄@SiO₂-imid-PMAⁿ catalyst (0.02 or 0.015 g) in water (5 mL) was refluxed in an oil bath or sonicated at room temperature for an appropriate period of time as indicated in Table 2. During the procedure, the reaction was monitored by TLC. Upon completion, the catalyst was removed by using a magnetic field. Then, the resulting solid product was recrystallized from ethanol to give pure products in high yields.

4.1.6. General procedure for the synthesis of 3,4-dihydropyrano[*c*]chromene derivatives

A mixture of malononitrile (1.2 mmol), aromatic aldehyde (1 mmol), 4-hydroxycoumarin (1 mmol) and Fe₃O₄@SiO₂-imid-PMAⁿ catalyst (0.025 g) in water (5 mL) was refluxed in an oil bath or sonicated at room temperature for an appropriate time as mentioned in Table 4. The progress of the reaction was monitored by TLC, for disappearance of aldehyde. After completion of the reaction, the catalyst was removed by using a magnetic field. Then, for the purification of the product, the precipitates were washed with cold aqueous ethanol and recrystallized from ethanol to give the pure product.

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