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# Preparation and characterization of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PMA: AS an efficient and recyclable nanocatalyst for the synthesis of 1amidoalkyl-2-naphthols

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## **Research Highlight**

- Preparation of the magnetic nanocatalyst.
- Immobilization of PMA nanoparticles on imidazole functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.
- Identification of catalyst by XRD, TEM, DLS, FE-SEM, FT-IR, BET and VSM.
- Catalyst recycling by external magnetic field.
- The preparation of 1-amidoalkyl-2-naphthols as biologically compounds.

#### Graphical abstract

#### Abstract

In this paper, we report a method for preparation of functionalized superparamagnetic

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> that is synthesized based on several stages. First of all, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>

nanosphere core-shell is synthesized. Then,  $H_3PMo_{12}O_{40}$  nanoparticles were synthesized by the treatment of  $H_3PMo_{12}O_{40}$  with n-Octane as solvent by a solvothermal method and this nano hetero polyacid immobilized onto imidazole functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. The structure of the samples was characterized by XRD, TEM, DLS, FE-SEM, FT-IR, N<sub>2</sub> adsorption–desorption isotherm analysis and VSM. Moreover, an efficient and direct protocol is described for the preparation of amidoalkyl naphthols employing a multi-component, onepot condensation reaction of  $\beta$ -naphthol, aldehydes and acetamide, benzamide and urea in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> under solvent-free and microwave conditions. Also, nanocatalyst can be easily recovered by a magnetic field and reused for the next reactions for at least 5 times without distinct deterioration in catalytic activity.

**KEYWORDS**: A. Nanostructures; A. organic compounds; B. magnetic structure; B. chemical synthesis; D. catalytic properties

#### **1. Introduction**

Nanomaterials have been interested extensively because of their unique properties [1] and used extensively in biology [2], physics [3] and chemistry [4]. Also, nanoparticles have gained an interest because of their potential applications in areas such as ceramics [5], optics [6], electronics [7], magnetic data storage [8], catalysis [9-11] and nanocomposites. When size of the particle is decreased to nanometer scale, the surface area of them significantly increased and those activities could be improved [12]. In the past decade, the synthesis of superparamagnetic nanoparticles had been intensively developed due to their different applications such as magnetic inks for jet printing [13], targeted drug delivery [14,15], contrast agents in magnetic resonance imaging (MRI) [16], catalysts for carbon nanotube formation[17], sorbents for

environmental remediation [18,19] and hyperthermia treatment of cancer cells [20]. These applications attributed to those unique properties, such as size, superparamagnetism, the crystallinity, size distribution and monodispersity. Currently, much attention has been focused on the synthesis of magnetic metal oxide structures that coating with a silica shell [21]. In contrast to most of solid catalysts that recovery and reusability of them are very difficult, recovery and reusability of core-shell nanostructure magnetic catalysts could be easily carried out under magnetic field. Therefore, the magnetic core–shell structures are a good supports for the catalysts [22].

In recent years, brønsted acids such as Keggin-type heteropolyacids have been used as efficient catalysts for a variety of organic reactions because of their superacidic and redox properties, low toxicity, ease of handling, low cost, high thermal stability, high proton mobility, water tolerance, recoverability and reusability [23]. Although HPAs are versatile compounds in their acidic form, their main disadvantages are high solubility in polar solvents and low surface area (<10 m<sup>2</sup>/g). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult [23]. Therefore, in order to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon and etc.) which possess large surface area. The use of support allows the heteropolyacids to be dispersed over a large surface area and increases theirs catalytic activity [24].

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 ironoxide nanoparticles have been reported [25]. Therefore in this work, we report the immobilization of  $H_3PMo_{12}O_{40}$  nanoparticles (PMA<sup>n</sup>) on imidazole functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> as a convenient building block for the grafting of catalysts and reagents (scheme1).

Multicomponent reactions (MCRs) have attracted considerable attention in organic synthesis as they can produce the target products in a single operation without isolating the intermediates, thus reducing reaction times and energy consumption. MCRs have merits over conventional linear type syntheses in several aspects including simple procedures, possible structural variations, and rapid access to complex molecules [26]. Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of their ability to synthesize small drug-like molecules with several degrees of structural diversity [27]. Therefore, discovery and development of new MCRs is highly desirable.

1-Amidoalkyl-2-naphthol derivatives are of prominence as they can be easily hydrolyzed to 1-aminoalkyl-2-naphthol. 1-Aminoalkyl-2-naphthols have been commonly applied as hypotensive and bradycardiac agents [28-29]. 1-Amidoalkyl-2naphthols can also be converted to 1,3-oxazine derivatives [30] with different biological activities, such as antitumor [31], antibiotic [32], antipsychotic [33], anticonvulsant [34], antimalarial [35], analgesic [36], antihypertensive [37], antirheumatic [38], and antianginal [39] properties.

Therefore paying attention to the importance of amidoalkyl naphthols, various procedures have been reported. Many of these reported methods employ different homogeneous or heterogeneous catalysts such as *p*-toluenesulfonic acid [40],

dodecylphosphonic acid (DPA) [41], H<sub>2</sub>NSO<sub>3</sub>H [42], oxalic acid [43], Fe(HSO<sub>4</sub>)<sub>3</sub> [44], Sr(OTf)<sub>2</sub> [45], I<sub>2</sub> [46], K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>.3H<sub>2</sub>O [47], HPMo [48], Yb(OTf)<sub>3</sub> in ionic liquid [49], montmorillonite K10 [50], TMSCl/NaI [51], Al<sub>2</sub>O<sub>3</sub>–HClO<sub>4</sub> [52], InCl<sub>3</sub> [53], 2,4,6-trichloro-1,3,5-triazine [54], CuPW and CuPMo [55], H<sub>3</sub>MoO<sub>40</sub>P [56], H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> [57], and P<sub>2</sub>O<sub>5</sub> [58]. However, most of the synthetic protocols for 1amidoalkyl-2-naphthol reported so far suffer from drawbacks such as requiring reagents, which are not readily available, highly toxic and hazardous catalyst, unsatisfactory yields, long reaction times, use of harmful organic solvents and the production of environmental pollutants. Therefore, a great demand still exists for versatile, simple, and environmentally friendly processes whereby 1-amidoalkyl-2naphthols may be formed under simple and practical conditions. Therefore, we utilized H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> nanoparticles (PMA<sup>n</sup>) on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imidazol

nanoparticle in the production of 1-amidoalkyl 2-naphthols.

#### 2. Experimental

#### 2.1. Chemicals and Instrumentation

All the chemical reagents used in our experiments were purchased from the Merck Chemical Company in high purity. All the solvents were distilled, dried and purified by standard procedures. Melting points were determined on a Mel-Temp apparatus. The NMR spectra were recorded on a Bruker avance DPX 250MHz spectrometer in chloroform (CDCl<sub>3</sub>) using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. XRD patterns were recorded by a Bruker AXS D8-advance X-ray

diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5418). The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2000 instrument at 196 °C. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Dynamic light scattering (DLS) were recorded on a HORIBA-LB550. Magnetic properties were obtained on a BHV-55 vibrating sample magnetometer (VSM). Microwave oven (LG Smart Chef MS-255R operating at 2450 MHz having maximum out put power of 960 W) was used for microwave irradiation. Elemental analysis was done on a 2400 series Perkin-Elmer analyzer. Melting points were determined on a Mel-Temp apparatus and were Uncorrected. Therefore, all of the products were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR, and also by comparison with authentic samples. The progress of the reaction was monitored by TLC and purification was achieved by silica gel column chromatography.

## 2.2. Catalyst preparation

#### 2.2.1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Core-Shell

The core–shell  $Fe_3O_4@SiO_2$  nanospheres were prepared by a modified Stober method in our previous work [25]. In a typical procedure, the mixture of  $FeCl_3.6H_2O$  (1.3g, 4.8mmol) in water (15ml) was added to the solution of polyvinyl alcohol (PVA 15000), as a surfactant, and  $FeCl_2.4H_2O$  (0.9g, 4.5mmol) in water (15 ml), which was prepared by completely dissolving PVA in water followed by addition of  $FeCl_2.4H_2O$ . The resultant solution was left to be stirred for 30 min in 80°C. Then,

hexamethylentetraamine (HMTA) (1.0mol/l) was added drop by drop with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The resultant mixture was heated on water bath for 2h at 60°C and the black magnetite solid product was filtered and washed with ethanol three times and was then dried at 80°C for 10h.Then Fe<sub>3</sub>O<sub>4</sub> nanoparticle (0.50g, 2.1mmol) was dispersed in the mixture of ethanol (50mL), deionized water (5mL) and tetraethoxysilane (TEOS) (0.20mL), followed by the addition of 5.0mL of NaOH (10wt%). This solution was stirred mechanically for 30 min at room temperature. Then the product, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, was separated by an external magnet, and was washed with deionized water and ethanol three times and dried at 80°C for 10 h.

#### 2.2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid

 $Fe_3O_4@SiO_2$  (1g) 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 24h 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 xylene to remove any reacted species and dried at 70 °C for 6 h.

#### 2.2.3. Preparation of $H_3PW_{12}O_{40}$ nanoparticles (PMA<sup>n</sup>)

 $PMA^{n}$  nanoparticles were prepared in our previous work [59], which is a simple and single step method. In a typical procedure, 5 mmol of bulk  $H_{3}PMo_{12}O_{40}$  ( $PMA^{b}$ ) 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.

#### 2.2.4. Preparation of $Fe_3O_4$ @SiO<sub>2</sub>-Imid-PMA<sup>n</sup>

Scheme1 represents the anchoring of PMA<sup>n</sup> onto Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid (1.0g) was added to an acetonitrile solution of PMA<sup>n</sup> (1.0mmol) in 20mL was taken in a round-bottom flask. The mixture was refluxed for 24h under nitrogen atmosphere. After 24h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70°C for 6h. FT-IR spectrum of the catalyst showed the expected bands, including distinctive bands due to anchoring of PMA<sup>n</sup> onto Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid. Also, the same method was used for the synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> (PMA<sup>n</sup> = nano H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, PMA<sup>b</sup> = H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>).

# 2.3. General synthesis for the preparation of amidoalkyl naphthols catalyzed by $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup>

A mixture of aldehyde (1 mmol), 2-naphthol (1 mmol), amide or urea (1.1 mmol) and  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> (0.03g) were taken in round bottom flask and stirred for the desired time (as indicated by TLC) at 100 °C in a preheated oil bath or under microwave-irradiation. After completion of the reaction, and separation of

 $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> with using magnetic field, the mixture was diluted with 10 cm<sup>3</sup> ethyl acetate, washed with 10 cm<sup>3</sup> water, and the aqueous layer was then extracted with 2×10 cm<sup>3</sup> ethyl acetate. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to afford the crude product. If further purification was needed it was passed through a short column of silica gel.

#### 3. Results and discussion

FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid, PMA<sup>b</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> are shown in Fig 1a, b, c, d and e. Some of the important bands which are observed in the spectra are given in Table 1. From the IR spectra presented in Fig1a, the absorption peak at 554cm<sup>-1</sup> belonged to the stretching vibration mode of Fe-O bonds in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, the absorption peak presented at 1000-1150 cm<sup>-1</sup> most due to stretching vibration of framework and Si–O-Si groups. Also, the peaks at around 3400 cm<sup>-1</sup> and 1622 cm<sup>-1</sup> in Fig1a are due to the adsorbed water in the sample. In Fig1b, the presence of vibration bands in 556, 1000-1150 and 3400 cm<sup>-1</sup>, which is due to the Fe-O, Si-O-Si, and -OH respectively, demonstrates the existence of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-Imid. IR spectral analysis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid in the range of 1360-1490  $\text{cm}^{-1}$  indicated three band at 1369, 1443, and 1484  $\text{cm}^{-1}$ , can be attributed, respectively, to the vibrations  $\omega(CH_2)$ ,  $\nu$  (C=N) and  $\delta(CH_2)$  of the CH<sub>2</sub> groups linked to imidazol ring. Also, the presence of several bands with medium intensity in 2808-2993cm<sup>-1</sup> region is allocated to C-H stretching of methylene groups (Fig1b). FT-IR spectroscopy, as a means of providing the structure of the HPAs, is convenient and widely used for the characterization of heteropolyacid [60].

The FT-IR spectrum for PMA<sup>n</sup> shows four bands in the range 500–1250 cm<sup>-1</sup> are assigned at 786, 856, 954 and 1057 cm<sup>-1</sup>, which correspond to  $v_{as}$ (Mo–O<sub>e</sub>–Mo),  $v_{as}$ (Mo–O<sub>c</sub>–Mo),  $v_{as}$ (Mo–O<sub>t</sub>) and  $v_{as}$ (P–O<sup>\*</sup>), respectively [61] (Fig1c). According to FT-IR spectroscopy data that was shown in Table1, the characteristic bands of Keggin structure for PMA<sup>n</sup> compared to PMA<sup>b</sup> (Fig1d), are shifted to higher wave numbers (blue shift).

The presence of vibration bands in 556, 794, 864, 956, 1055, 1095, 1454 and 2792-2985 which is due to the Fe-O, Mo-O<sub>e</sub>-MO, Mo-O<sub>c</sub>-MO, Mo-O<sub>t</sub>, P-O, Si-O-Si, C=N and CH respectively, demonstrates the existence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> in the spectrum (Fig 1e). The band at 1443 cm<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid is assigned to the C=N of the imidazole group, which is shifted toward 1454 cm<sup>-1</sup> in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> which could be due to the change in environment of the double-bonded nitrogen in imidazole. Also, a small band between 1400-1420 cm<sup>-1</sup> in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> is the characteristic band of the C-N bond which can be attributed to anchoring of imidazole to the propyl group [23].

Fig. 2 shows the XRD patterns for  $Fe_3O_4$ ,  $Fe_3O_4@SiO_2$ ,  $PMA^n$  and  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> nanoparticles.

The characteristic peaks at  $2\theta$ : 30.1°, 35.4°, 43.1°, 53.4°, 57° and 62.6° for Fe<sub>3</sub>O<sub>4</sub> nanoparticles, which were marked respectively by their indices (220), (311), (400), (422), (511) and (440), were also observed for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (reference JCPDS card no.19-629) (Fig2a,b). This revealed that the surface modification of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles does not lead to their phase changes. The XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> shows an obvious diffusion peak at  $2\theta = 15-25^\circ$  that appeared because

of the existence of amorphous silica (Fig2b).The strong characteristic peaks at  $20=9.05^{\circ}$ , 23.7°, 26.35°, 28.25° and 32.4 in Fig2c, are assigned to Keggin structure of PMA<sup>n</sup> [JCPDS File 1-32] [59]. For Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> nanoparticles, the broad peak was transferred to lower angles due to the synergetic effect of amorphous silica and Imid-PMA<sup>n</sup> (Fig2d). Also, the presence of the silica and Imid-PMA<sup>n</sup> layers on the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, leads to amorphous structure and the disappearance of peaks corresponding to Fe<sub>3</sub>O<sub>4</sub> and PMA<sup>n</sup> (Fig2d). The average sizes of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and PMA<sup>n</sup> are determined according to calculation with the Scherrer formula method (D=  $0.9\lambda/\beta \cos\theta$ ), where D is the average diameter in A°,  $\beta$  is the broadening of the diffraction line measured at half of its maximum intensity in radians,  $\lambda$  is the wavelength of the X-rays and  $\theta$  is the Bragg diffraction angle. The mean crystallite sizes of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and PMA<sup>n</sup> nanoparticles were found to be around 12, 20 and 12 nm, respectively.

The morphology of the synthesized (a)  $Fe_3O_4$ , (b)  $Fe_3O_4@SiO_2$ , (c) PMA<sup>n</sup> and  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> particles were determined by TEM (Fig3).

TEM image of  $Fe_3O_4$  clearly shows that  $Fe_3O_4$  nanoparticles are almost spheroidal in shape with diameters in the 8–16nm range, which is almost the same with average particle size obtained from XRD (Fig3a).

Fig.3b display the TEM image of  $Fe_3O_4$  nanoparticles coated with silica layers. The size of nanoparticles obtained from the TEM images, turned out to be approximately 20 and 15nm for  $Fe_3O_4@SiO_2$ , PMA<sup>n</sup> respectively, and their shapes are nearly spherical (Fig3b,c). Fig.3d displays the high resolution TEM images of  $Fe_3O_4$  nanoparticles coated with silica layers and PMA<sup>n</sup> nanoparticles. Fig3e shows FE-SEM

image of  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup>. As it is shown, these nanoparticles have spherical shapes with approximately 50 nm diameters.

To investigate the size distribution of these nanoparticles, particle size histograms were prepared for  $Fe_3O_4$ ,  $Fe_3O_4@SiO_2$ ,  $PMA^n$  and  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> (Fig 4a to d respectively) by DLS analysis. This size distribution is centered at a value of 12, 20, 12 and 55 nm for  $Fe_3O_4$ ,  $Fe_3O_4@SiO_2$ ,  $PMA^n$  and  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup>, respectively.

The surface areas of PMA<sup>b</sup>, PMA<sup>n</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid- $PMA^n$  and  $Fe_3O_4@SiO_2$  were measured by  $N_2$  adsorption. While the BET (Calculated by the BJH method) surface area was 10.0 and 250.0  $m^2/g$  for PMA<sup>b</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> respectively (Table2, entries 1,3), nano HPAs have the much higher surface area (Table2, entries 2,4). Reducing the particle size from bulk powder to nanometer scale, caused the surface area was increased from 10 to  $270 \text{ m}^2/\text{g}$ for PMA and from 250 to 422  $m^2/g$  for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid- PMA (Table2, entries 1-4). The magnetic properties of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> nanoparticles were measured by VSM at room temperature. As it is shown in the Fig5A, 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 samples (a-c) is 63.4, 39.7, 33.2 emu/g, respectively (Fig 5Aa, b, c). These results indicated that the magnetization of  $Fe_3O_4$ decreased considerably with the increase of SiO<sub>2</sub> and functionalization of Fe<sub>3</sub>O<sub>4</sub>. Nevertheless, in all cases, the separation of the catalyst was achieved by applying an external permanent magnet, making the recovery of the catalyst very straightforward.

The magnetic  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> stably dispersed in acetonitrile can be readily separated from the dispersion when an external magnetic field is applied (Fig5B). After the external magnet is removed, the accumulation can be redispersed into acetonitrile by mild shaking.

The acidity of HPAs compounds has been investigated with different methods of analysis: (i) Hammett indicators + visual inspection [62], (ii) ammonia + temperature programmed desorption (TPD) [63,64], FT-IR spectroscopy [65], calorimetry [66,67], (iii) pyridine + TPD, FT-IR spectroscopy [68, 69], (iv) H<sup>1</sup> NMR [70] and O<sup>17</sup> NMR [71].

The interaction of pyridine with HPAs was confirmed by FT-IR spectroscopy. Pyridinium ions can be identified by the band at 1540 cm<sup>-1</sup> [72]. The characteristic chemisorbed pyridium ion was detected after the removal of physisorbed pyridine from HPAs by evacuation. The absorption band corresponding to the Mo=O stretch might be expected to track the extent of proton transfer upon interaction with basic molecules such as pyridine. As shown in Fig6 1d, the P–O, Mo=O (terminal oxygen), and Mo–O–Mo (corner sharing and edge-sharing) bands of fresh H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> appeared at 1051, 950, 853 and 781 cm<sup>-1</sup>, respectively. The P–O, Mo=O (terminal oxygen), and Mo–O–Mo (corner sharing and edge-sharing) bands of pyridine-exposed Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> appeared at 1032, 927, 838 and 769 cm<sup>-1</sup>, respectively (Fig6e). Shifting of IR bands of pyridine-exposed HPAs were attributed to the interaction of the cationic species, pyridinium ions, with the heteropolyanions. In the FT-IR analyses of pyridine-exposed HPAs shown in Fig.6, the quantification of bridging oxygen bands was not simple. Thus the absorption band corresponds to the

Mo=O stretch might be expected to track the extent of proton transfer upon interaction with basic molecules such as pyridine. We measured the IR intensity of pyridium ion at 1540 cm<sup>-1</sup> of the pyridine-exposed PMA and calculated the intensity ratio of I (1540 cm<sup>-1</sup>)/I (Mo=O) bands in an attempt to track the acidic properties of PMA. I value for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> were 1.1 and 2.8 respectively, these indicated that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> have more acidic site then Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> (Fig6 c,e).

Herein we report a new, convenient, mild and efficient procedure for one-pot threecomponent synthesis of amidoalkyl naphthol derivatives from various aldehydes, 2naphthol and different amides in the presence of  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> nanocatalyst as an effective and recoverable catalyst under solvent-free and microwave conditions (Scheme 2).

Initially, to find the best optimum conditions, a model reaction of benzaldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide (1.1 mmol) in the presence of  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> (0.03 g) was performed in different solvents such as 1,2-dichloroethane, ethylacetate, DMF, ethanol, acetonitrile, dichloromethane, toluene, cyclohexane, 1,4- dioxane under reflux conditions (Table3, Entries 1-9). Among these solvents, 1,2-dichloroethane and ethylacetate provided the highest yields at refluxed temperature after 4 h (Table3, Entries 1,2). However, a higher yield of product could be obtained under solvent-free condition in the presence of (0.03g) catalyst at 100°C only after 25 min in 95% yield (Table3, Entry 10). Decrease of the yield was observed when the reaction was repeated in the presence of lower amount of the catalyst so that in the absence of any catalyst no product was observed, even after a prolonged

reaction time (Table3, Entries 11-14). Enhancement of the catalyst loading did not show any effect on the yield or the reaction time (Table 3, Entries 15-16). In addition, the effect of temperature was studied and the results indicated that at lower temperatures, the reaction did not proceed properly and most of the initial substances remained unreacted. (Table3, Entry 17). In order to find the best conditions, the model reaction was performed in the presence of  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> (0.03g) under solvent free condition in microwave (Table3, Entry 18). The result showed that under this condition, the corresponding product was obtained in 96% yield after very short time (6 min).

This three-component condensation of various aldehydes and amides with 2-naphthol catalyzed by  $Fe_3O_4@SiO_2-Imid-PMA^n$  was then explored under the optimized reaction conditions described above. The results are summarized in Table 4. Aldehydes bearing electron-donating and withdrawing substituents in the reaction with acetamide as an aliphatic amide and 2-naphthol led to good yields of the desired 1- amidoalkyl-2-naphthols (Table 4, Entries 1-13). Using benzamide as an aromatic amide, instead of acetamide, resulted in the corresponding 1-amidoalkyl-2- naphthols in good yields when it was treated with 2-naphthol and aldehydes in the presence of  $Fe_3O_4@SiO_2-Imid-PMA^n$  under solvent free and in microwave conditions (Table 4, Entries 14-26). In addition, the reaction of aldehydes and 2-naphthol with urea afforded the corresponding products in high yields (Table 4, Entries 27-30). To test the worth of the present work in comparison with results in the literature, we compared results of  $Fe_3O_4@SiO_2-Imid-PMA^n$  and  $Fe_3O_4@SiO_2-Imid-PMA^b$  with other applied Lewis and Bronsted acids in synthesis of 1-amidoalkyl-2-naphthols.

These data, which are shown in Table 5, revealed that  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> is a better catalyst than most of the conventional catalysts mentioned with respect to reaction times and yields of the obtained products.

The recyclability of the  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> was also investigated using the above model reaction. In order to confirm the reusability and stability of magnetic nanocatalyst it was separated from the reaction mixture after it was first used in the preparation of amidoalkyl naphthol. The recovered catalyst was found to be reusable for five cycles with a slight loss in activity (Fig7A,B).

#### 4. Conclusions

In conclusion, superparamagnetic  $Fe_3O_4@SiO_2$ -Imidazol- PMA<sup>n</sup> nanospheres have been prepared by immobilizing  $H_3PMo_{12}O_{40}$  nanoparticles on the surface of  $Fe_3O_4@SiO_2$ -Imidazol.  $H_3PMo_{12}O_{40}$  nanoparticles (PMA<sup>n</sup>) were synthesized by the reaction of  $H_3PMo_{12}O_{40}$  with n-Octane as solvent by a solvothemal method. The nanocatalyst was successfully synthesized and structural, surface, morphological, and magnetic properties of these nanoparticles were evaluated. The nanospheres possessed a spherical shape and a porous structure and the crystalline structure of  $Fe_3O_4$  was unchanged during the synthesis process of magnetic nanocatalyst. FT-IR spectroscopy, as a means of providing the structure of the heteropolyacids, is convenient and widely used for catalyst characterization. TEM microscopy revealed the formation of very fine layer of  $SiO_2$  on the  $Fe_3O_4$ . The crystallite size obtained from X-ray line profile fitting is comparable with the particle size obtained from TEM. Magnetization curves demonstrated a high degree of superparamagnetism and

magnetic nanocatalyst with saturation magnetization value of about 33.2 emu/g can be easily recover under an external magnetic field.

Therefore, considering the importance of this catalyst, we have elaborated an efficient and expeditious synthesis of 1-amidoalkyl-2-naphthol derivatives accomplished via three-component reactions of aldehydes, 2-naphthol and benzamide, acetamide or urea in the presence of  $Fe_3O_4$ @SiO<sub>2</sub>-Imid-PMA<sup>n</sup> by two methods. These two methods offer several significant advantages such as: high conversions, easy handling, short reaction times, easy and green work up, recovery and reusability of catalyst, cost efficient and versatility. These advantages, in general, highlight this protocol as a useful and attractive methodology, among the methods reported in the literature, for the rapid synthesis of 1-amidoalkyl-2-naphthols as precursors of biological active 1aminoalkyl-2-naphthols.

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#### **Spectral data**

N-((2-hydroxynapthalen-1-yl)(4-methyl-phenyl) methyl] acetamide (Table 4, Entry9) <sup>1</sup>HNMR (250 MHz, DMSO-*d*<sub>6</sub>): δ=1.96 (s, 3H), 2.21 (s, 3H), 7.03—7.08 (m, 5H), 7.19 (d, J= 4.4 Hz, 1H), 7.24 (t, J= 3.6 Hz, 1H), 7.33-7.35 (m, 1H), 7.74 (d, J= 4.4 Hz, 1H), 7.78 (d, J=3.8 Hz, 1H), 7.82 (br, 1H), 8.36 (d, J= 4.1 Hz, 1H), 9.91 (s, 1H); <sup>13</sup>C NMR (125 MHz,

DMSO-*d*<sub>6</sub>): 20.4, 22.6, 47.6, 118.4, 118.9, 122.2, 123.1, 125.9, 126.1, 128.3, 128.4, 128.9, 132.2, 134.9, 139.4, 143.2, 152.9, 168.9; Anal. Calcd: C, 78.66; H, 6.27; N, 4.59; Found: C, 78.58; H, 6.18; N, 4.61%.

**N**-((2-hydroxynaphthalen-1-yl)(4-nitrophenyl) methyl) benzamide (Table 4, Entry17) <sup>1</sup>HNMR (250 MHz, DMSO-*d*<sub>6</sub>): δ= 7.24 (d, 1H), 7.45 (d, 1H), 7.39-7.54 (m, 7H), 7.79-7.90 (m, 4H), 8.11 (m, 3H), 9.04 (d, 1H), 10.49 (s. 1H). <sup>13</sup>CNMR (62 MHz, DMSO-*d*<sub>6</sub>): δ= 49.75, 115.46, 118.63, 121.66, 122.58, 123.24, 126.43, 128.34, 128.86, 128.94, 129.26, 132.34, 134.31, 145.96, 148.98, 153.54, 167.71; Anal. Calcd: C, 72.35; H, 4.55; N, 7.03; Found: C, 72.29; H, 4.66; N, 7.08%.

**N-(1-(2-hydroxynaphthalen-1-yl) propyl) acetamide (Table 4, Entry13)** <sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>): 0.77 (t, J= 3.7 Hz, 3H), 1.81 (s, 3H), 1.89–1.84 (m, 2H), 5.63 (q, J= 3.8 Hz, 1H), 7.13 (d, J= 4.6 Hz, 1H), 7.21 (t, J= 3.7 Hz, 1H), 7.39 (t, J= 3.7 Hz, 1H), 7.64 (d, J= 4.4 Hz, 1H), 7.72 (d, J= 4.0Hz, 1H), 8.03 (s, 1H), 8.08 (d, J= 4.3 Hz, 1H), 9.94 (s, 1H). <sup>13</sup>C NMR (62 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ = 11.9, 23.2, 27.2, 48.0, 119.1, 120.0, 122.7, 123.1, 126.6, 128.7, 128.9, 129.0, 132.9, 153.5, 169.1; Anal. Calcd: C, 74.05; H, 7.04; N, 5.75. Found: C, 74.11; H, 6.96; N, 5.71%.

**N-(1-(2-hydroxynaphthalen-1-yl) propyl) benzamide (Table 4, Entry24)** <sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ = 0.90 (t, J= 3.6 Hz, 3H,), 1.89 (m, 2H), 5.85 (t, J= 3.7 Hz, 1H), 7.09 (d, J= 4.4 Hz, 1H), 7.29 (dd, J= 3.6 Hz, 1H), 7.43–7.53 (m, 4H), 7.66 (d, J= 4.4 Hz 1H), 7.75 (t, J= 3.6 Hz, 3H), 8.18 (d, J= 4.4 Hz, 1H), 8.61 (d, J= 4.0 Hz, 1H),  $\delta$ =10.08 (s, 1H). <sup>13</sup>C NMR (62 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ = 11.35, 26.91, 48.49, 118.57, 119.53, 122.34, 126.22, 126.87, 128.19, 131.06, 132.23, 134.71, 152.85, 165.37; Anal. Calcd: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.57; H, 6.21; N, 4.54.

N-(1-(2-Hydroxynaphthalen-1-yl)-3-phenylpropyl) benzamide (Table 4, Entry25) <sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>): δ= 2.04 (m, 2H), 2.74 (t, 2H), 5.98 (d, 1H), 7.13–7.24 (m, 6H), 7.40–7.47 (m, 4H), 7.66– 7.82 (m, 4H), 8.02 (d,1H), 8.66 (d, 1H), 10.16 (s, 1H). <sup>13</sup>C NMR (62 MHz, DMSO-*d*<sub>6</sub>): δ= 32.46, 35.60, 46.70, 118.59, 119.62, 122.38, 125.66, 126.22, 126.96, 127.33, 128.18, 128.26, 128.35, 128.45, 128.52, 131.13, 132.02, 134.63, 141.68, 152.90, 165.55; Anal. Calcd: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.80; H, 6.01; N, 3.55.

## (E)-N-(1-(2-Hydroxynaphthalen-1-yl)-3-phenylallyl benzamide (Table 4, Entry26) <sup>1</sup>H

NMR (250 MHz, DMSO- $d_6$ ):  $\delta$ = 7.08 (d, 1H), 7.17 (d, 1H), 7.21 (m, 4H), 7.41 (m, 3H), 7.75 (m, 3H), 8.07 (d, 1H), 9.01 (d, 1H), 10.43 (s, 1H). <sup>13</sup>C NMR (62 MHz, DMSO- $d_6$ ):  $\delta$ = 48.15, 123.51, 127.61, 128.30, 131.27, 132.47, 133.60, 135.81, 137.28, 141.84, 158.24, 165.54; Anal. Calcd: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.24; H, 5.53; N, 3.65.

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#### **Figure captions:**

**Scheme1:** Process for preparation of immobilization of  $H_3PMo_{12}O_{40}$  nanoparticles (PMA<sup>n</sup>) on imidazole functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticle.

Scheme.2: Synthesis of amidoalkyl naphthol using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup>.

**Fig.1:** FT-IR spectra a)  $Fe_3O_4@SiO_2[25]$ , b)  $Fe_3O_4@SiO_2$ -Imid, c) PMA<sup>n</sup> [59], d) PMA<sup>b</sup>[59] and e)  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup>.

**Fig. 2**: XRD patterns of a)  $Fe_3O_4$  [25] b)  $Fe_3O_4@SiO_2$  [25] c) PMA<sup>n</sup> [59] d)  $Fe_3O_4@SiO_2$ -Imid- PMA<sup>n</sup>.

**Fig.3**: TEM images of  $Fe_3O_4$  (a) [25]  $Fe_3O_4@SiO_2$  (b) [25] PMA<sup>n</sup> (c) [59] and HRTEM and FE-SEM images  $Fe_3O_4@SiO_2$ -Imid- PMA<sup>n</sup> (d), (e) respectively.

**Fig.4:** DLS size distributions of  $Fe_3O_4$  (a) [25]  $Fe_3O_4@SiO_2$  (b) [25] PMA<sup>n</sup> (c) [59] and  $Fe_3O_4@SiO_2$ -Imid- PMA<sup>n</sup> (d).

Fig.5: A) Magnetization curves at 300°K for a) Fe<sub>3</sub>O<sub>4</sub> b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-

PMA<sup>n</sup> nanoparticles. B) The dispersion (a) and separation (b) process of magnetic

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid- PMA<sup>n</sup> nanocatalyst.

Fig.6: FT-IR spectra a) Pyridine b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup>-

Pyridine d) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> e) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup> - Pyridine.

**Fig.7:** Recyclability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> in the synthesis of amidoalkyl-2-naphthols.

<b>Table.1</b> : Infrared spectroscopic data for Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid, PMA <sup>b</sup> , PMA <sup>n</sup> and
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>n</sup> before the catalytic reaction.

vibration	Fe <sub>3</sub> O <sub>4</sub> @SiO	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -	PMA	PMA	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-
mode	$_{2} \text{ cm}^{-1}$	Imid	b	n	PMA <sup>n</sup>
assignment		cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>
Fe-O	554	556	_	-	556
Mo-O <sub>e</sub> -MO	-	-	781	786	794
Mo-O <sub>c</sub> -MO			853	856	864
Mo-O <sub>t</sub>	-	-	950	954	956
P-O	-	-	1051	1057	1055
Si-O-Si	1000-1150	1000-1150	. 0	-	1095
C=N	-	1443		-	1454
С-Н	-	2808-2993	-	-	2792-2985

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Entry	Sample	$BET(m^2/g)$	Pore volume (cm <sup>3</sup> /g)
1	PMA <sup>b</sup>	10	-
2	$PMA^n$	270	0.465
3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>b</sup>	250	0.333
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>n</sup>	422	0.535
5	$Fe_3O_4@SiO_2$	430	0.755

**Table2.** BET result of PMA<sup>b</sup>, PMA<sup>n</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>b</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid- PMA<sup>n</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.<sup>a</sup>

<sup>a</sup>Calculated by the BJH method.

**Table3.** Optimization of different proportions of  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup> catalyst and also effect of solvents and temperature on the model reaction of benzaldehyde,  $\beta$ -naphthol, and acetamide.

Entry	Solvent	Amount of Catalyst	Temperature	Time	Yield
		(g)	(°C)	(h)	(%) <sup>a</sup>
1	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.03	reflux	4	81
2	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	0.03	reflux	4	83
3	DMF	0.03	reflux	4	69
4	EtOH	0.03	reflux	4	41
5	CH <sub>3</sub> CN	0.03	reflux	4	67
6	$CH_2Cl_2$	0.03	reflux	4	63
7	Toluene	0.03	reflux	4	35
8	Cyclohexane	0.03	reflux	4	72
9	1,4-Dioxane	0.03	reflux	4	48
10	Solvent-free	0.03	100	25 min	95
11	Solvent-free		100	16	0
12	Solvent-free	0.01	100	4	53
13	Solvent-free	0.02	100	2	79
14	Solvent-free	0.025	100	45 min	87
15	Solvent-free	0.035	100	30 min	94
16	Solvent-free	0.04	100	30 min	95
17	Solvent-free	0.03	r.t	4	18
18	Solvent-free	0.03	MW/450w	6 min	96

<sup>a</sup>Isolated yield.

**Table4.** One-pot preparation of 1-amidoalkyl-2-naphthols with different aldehydes andamides catalyzed by  $Fe_3O_4@SiO_2$ -Imid-PMA<sup>n</sup>.

Mp (lit. mp) <sup>ref</sup>	Method B <sup>b</sup>	Method A <sup>a</sup>	$R_2$	$R_1$	ıtry
	Time(min)/Yield	Time (min)/Yield			En
	(%) <sup>c</sup>	(%)			
243-244 (241-243)	6/96	25/95	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	1
[73]					
217-219 ( 218–	10/91	30/88	$CH_3$	2- $NO_2C_6H_4$	2
219) <sup>[58]</sup>					
255-257 (256–	5/95	25/92	CH <sub>3</sub>	$3-NO_2C_6H_4$	3
<b>258</b> ) <sup>[58]</sup>					
235-237 (237–	5/96	20/96	CH <sub>3</sub>	$4-NO_2C_6H_4$	4
238) <sup>[58]</sup>					
208-2010 (206-	12/89	35/86	CH <sub>3</sub>	2-ClC <sub>6</sub> H <sub>4</sub>	5
207) <sup>[58]</sup>					
227-229 (224-	8/91	25/90	CH <sub>3</sub>	$4-ClC_6H_4$	6
227) <sup>[73]</sup>					
(224—226) <sup>[74]</sup>	10/92	35/91	CH <sub>3</sub>	$2,4-Cl_2C_6H_4$	7
229-231 (228-	12/87	35/88	CH <sub>3</sub>	$4-BrC_6H_4$	8
230) <sup>[75]</sup>					
222-224(224-	12/85	35/83	CH <sub>3</sub>	$4-CH_3C_6H_4$	9
225) <sup>[58]</sup>					
183-185 (184–	12/87	40/84	CH <sub>3</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	10
186) <sup>[73]</sup>					
201-203 (203-	10/87	30/86	CH <sub>3</sub>	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	11
205) <sup>[75]</sup>					
123-125 (123) <sup>[76]</sup>	15/89	40/87	CH <sub>3</sub>	4-	12
				$(CH_3)_2NC_6H_4$	

178-180	12/92	30/91	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub>	13
239-241 (238-	8/93	35/92	$C_6H_5$	$C_6H_5$	14
240) <sup>[58]</sup>					
264-266 (266-	12/88	45/87	$C_6H_5$	$2-NO_2C_6H_4$	15
267) <sup>[58]</sup>					
241-243 (242-	12/90	35/89	$C_6H_5$	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	16
243) <sup>[58]</sup>					
229-231 (231-	8/93	25/94	$C_6H_5$	$4-NO_2C_6H_4$	17
232) <sup>[75]</sup>					
285-287 (284-	16/84	55/85	C <sub>6</sub> H <sub>5</sub>	$2-ClC_6H_4$	18
285) <sup>[58]</sup>					
169-171(168-	10/94	35/93	C <sub>6</sub> H <sub>5</sub>	$4-ClC_6H_4$	19
170) <sup>[58]</sup>					
262-264 (262-	12/89	40/90	$C_6H_5$	2,4-ClC <sub>6</sub> H <sub>4</sub>	20
263) <sup>[30]</sup>					
215-216 (214-	15/86	55/85	$C_6H_5$	$4-CH_3C_6H_4$	21
215)	10/04	55/70	CII		22
204-208 (200-	18/84	55/19	$C_6H_5$	$4-CH_3OC_6H_4$	22
218-220 (220-	18/86	70/81	C.H.	1	23
221) <sup>[58]</sup>	18/80	/0/01	C <sub>6</sub> 115	4-	23
,				$(CH_3)_2NC_6H_4$	
244-246	10/90	30/91	$C_6H_5$	CH <sub>3</sub> CH <sub>2</sub>	24
156-158	15/85	50/86	$C_6H_5$	$C_6H_5CH_2CH_2$	25
232-233	15/81	50/80	$C_6H_5$	$C_6H_5CH = CH$	26
174-176 (175–	8/95	25/92	$\mathrm{NH}_2$	$C_6H_5$	27
177) <sup>[75]</sup>					
170-172 (170–	8/93	25/91	$\mathrm{NH}_2$	$4-ClC_6H_4$	28
171) <sup>[75]</sup>					

141-143 (140-	10/91	35/92	$NH_2$	$2,4\text{-}Cl_2C_6H_4$	29
142) <sup>[77]</sup>					
188-190 (191–	10/94	25/94	$\mathrm{NH}_2$	$3-NO_2C_6H_4$	30
193) <sup>[75]</sup>					

<sup>a</sup>Reaction conditions: β-naphthol 1 mmol, aldehyde 1 mmol, amide 1.1 mmol, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> (0.03g), solvent-free,100 °C.

<sup>b</sup>Reaction conditions:  $\beta$ -naphthol 1 mmol, aldehyde 1 mmol, amide 1.1 mmol, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> (0.03g), solvent-free, microwave.

<sup>c</sup>Isolated yields.

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itry	Catalyst	Conditions	Time	Yield(%) <sup>re</sup>
En				f
1	Molybdophosphoric Acid (0.12 g)	Ethyl acetate/65 °C	3.5h	95 <sup>[48]</sup>
2	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> .xH <sub>2</sub> O/SiO <sub>2</sub> (3.17	Solvent-free/120°C	15min	91 <sup>[77]</sup>
	mol%)			
3	$H_{3}PW_{12}O_{40} (2 \text{ mol } \%)$	Et <sub>4</sub> NCl/120°C	80 min	90 <sup>[78]</sup>
4	$K_5CoW_{12}O_{40}.3H_2O(1 \text{ mol}\%)$	Solvent-free/125°C	2h	90 <sup>[47]</sup>
5	$Al_2O_3$ -HClO <sub>4</sub> (0.1 g)	Solvent-free, 125 °C	30 min	90 <sup>[44]</sup>
6	SiO <sub>2</sub> -HClO <sub>4</sub> (12 mg)	Solvent-free, 110 °C	40 min	89 <sup>[79]</sup>
7	Silica sulfuric acid (0.02 g)	Solvent-free, rt	2 h	85 <sup>[80]</sup>
8	Ce(SO <sub>4</sub> ) <sub>2</sub> (100 mol%)	Solvent-free/reflux	36 h	72 <sup>[73]</sup>
9	$I_2$ (5 mol%)	Solvent-free, 125 °C	5.5 h	85 <sup>[46]</sup>
10	Montmorillonite K10 clay (0.1 g)	Solvent-free, 125 °C	1.5 h	89 <sup>[50]</sup>
11	p-TSA (10 mol%)	Solvent-free/125 °C	300min	88 <sup>[40]</sup>
12	Sulfamic acid (50 mol %)	Solvent-free, ultrasonic; 28–30	15 min	89 <sup>[42]</sup>
		°C		
13	ZrOCl <sub>2</sub> (10 mol %)	ClCH <sub>2</sub> CH <sub>2</sub> Cl/rt	11 h	79 <sup>[81]</sup>
14	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>n</sup> (0.03g)	Solvent-free, 100 °C	25min	95
15	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>n</sup> (0.03g)	Solvent-free, MW 360 w	6min	96
14	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>b</sup> (0.03g)	Solvent-free, 100 °C	40min	89
15	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Imid-PMA <sup>b</sup> (0.03g)	Solvent-free, MW 360 w	20min	92

### **Table5:** Reaction of 2-naphthol, benzaldehyde and acetamide using different acid catalysts.



Scheme1



Scheme.2





Fig. 2



Fig.3





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Fig.5

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<sup>A</sup>Reaction conditions:  $\beta$ -naphthol 1 mmol, benzaldehyde 1mmol, acetamide 1.1 mmol, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> (0.03g), solvent-free, 100 °C.

<sup>B</sup>Reaction conditions:  $\beta$ -naphthol 1 mmol, benzaldehyde 1mmol, acetamide 1.1 mmol, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Imid-PMA<sup>n</sup> (0.03g), solvent-free, under sonication.

Fig.7