

## EFFICIENT ONE-POT SYNTHESIS OF IMIDAZOLES CATALYZED BY SILICA-SUPPORTED $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ NANO PARTICLES AS A NOVEL AND REUSABLE PEROVSKITE OXIDE

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**ABSTRACT.** Silica-supported  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  nanoparticles were prepared and used as a new perovskite-type catalyst for rapid and efficient synthesis of substituted imidazoles by an one-pot three-component condensation of [9,10]-phenanthraquinone, aryl aldehydes and ammonium acetate in excellent yield under reflux, and also solvent-free conditions.

**KEY WORDS:** Perovskite, Multicomponent reaction, One-pot synthesis, Imidazoles, Nano catalyst, Heterogeneous catalyst

### INTRODUCTION

Imidazole derivatives are an important group of heterocyclic compounds that have biological and chemical properties [1]. Nowadays these compounds are used in pharmacology. They have different capacity such as anti-bacterial, anti-viral, and anti-cancer, anti-inflammatory [2-4]. Also, the imidazole ring system is one of the main substructures found in most of natural products and pharmacologically active compounds, such as the hypnotic agent [5]. Therefore, a great number of synthetic methods have been reported for the synthesis of multi substituted imidazoles [6].

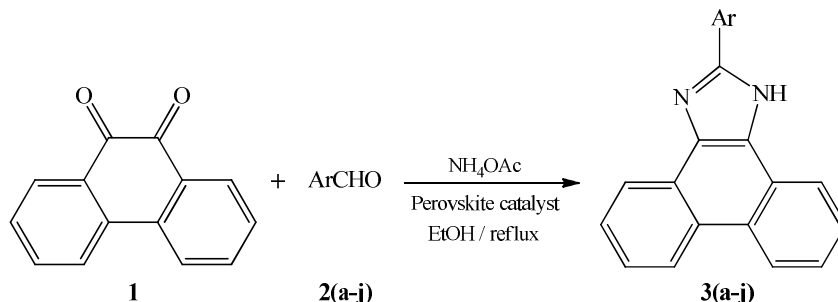
In the last decade, 2,4,5-trisubstituted imidazoles are synthesized by one-pot three-component condensation of an aldehyde and ammonium acetate with an  $\alpha$ -hydroxy ketone, or an  $\alpha$ -keto-oxime, or a 1,2-dicarbonyl compound by using various catalyst such as ionic liquids [7,8], Lewis acids [9,10], protic acids [11-13], and other catalysts [14-17]. However, most of these methodologies are associated with one or more disadvantages, such as low yields, high temperature requirement, longer reaction time, highly acidic conditions, use of expensive reagents and catalysts, requirement of large amount of catalysts, use of harmful solvents, formation of toxic wastes and tedious work-up [8].

Perovskite-type oxides with the chemical formula  $\text{ABO}_3$  can be crystallized with cubic structure. The level of oxygen and defects is affected by the composition because of a wide constancy range of the structure. The greater A-site cation mostly represents a metal cation belonging to one of groups of rare earth metals (La, Sm, Pr), alkaline earth metals (Sr, Ba, Ca), or alkali metals (Na, K) coordinated to 12 oxygen anions. The B-site cation represents typically a smaller transition metal cation, which occupies octahedral spaces in the oxygen framework. Some hybrids of A- and B-site cations can create a steady perovskite-like structure [18]. The catalytic activity of perovskite-type catalysts is mainly because of the existence of the multiplicity of oxidation states [19]. Perovskite-type oxides possess adsorption, acid-base, as well as redox properties, which leads to attractive catalytic activities. They can fulfill the requirements (excellent activity, constancy, and potential to be processed into structured catalysts) [20].

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Herein, in continuation of our interest to perovskite-type oxides [21, 22], and our works with solid acids as heterogeneous catalyst in organic reactions [23-28], in this study we wish to report the synthesis of imidazole derivatives (**3a-j**) via a one-pot three-component condensation of 9,10-phenanthraquinone (**1**), aromatic aldehyde (**2a-j**), and ammonium acetate in the existence of perovskite-type oxide  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  (LPMO) nanoparticles and  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  supported on silica (S-LPMO) as a new catalyst, in reflux and solvent-free conditions (Scheme 1).



Scheme 1. One-pot three component synthesis of substituted imidazoles in the presence of perovskite catalyst.

## EXPERIMENTAL

### General

All materials and reagents were purchased from Merck and Aldrich and utilized with no more purification. Determination of melting points were carried out using an Electro thermal type 9100 melting point apparatus and are uncorrected. The IR spectra were recorded on a Thermo Nicolet AVATAR-370 FT-IR spectrophotometer. A Bruker DRX250 spectrometer was used to obtain  $^1\text{H}$  NMR spectra.

### Preparation of $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ nano particles

In current study, the perovskite precursor was synthesized using the citrate-based sol-gel improved Pechini technique [21]. Chemicals of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_9\text{MnO}_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$  and citric acid (99.5%) were utilized as raw materials. Next, a mixture of metal nitrates solutions with nominal La:Pb:Mn ratios of 0.5:0.5:1 (LPMO) was prepared in deionized water. The addition of citric acid to the metal solution was performed proportionally to have the similar equivalents. The solution was concentrated through evaporation at nearly  $50^\circ\text{C}$  with agitating for 1 h for converting them to steady (La, Pb)/CA complexes. The solution was agitated on a hot plate at about  $75^\circ\text{C}$  for removing excess water and accelerating polyesterification reaction. Next, the dry gel was achieved through heating gradually to  $120^\circ\text{C}$  in an oven. The gel pieces were milled to create a fine powder. Finally,  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  NPs were synthesized through thermal treating the precursor at  $650^\circ\text{C}$  for 9 h in air. Most of the residual carbon was removed through annealing of the amorphous precursor and the hexagonal perovskite phase was achieved.

### Preparation of silica-supported $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ nanoparticles (30% w/w)

Initially silica was put into oven for 2 hours with  $90^\circ\text{C}$ , then catalyst (0.3 g) with silica (0.7 g) were worn out into glass mortar about 1 hour when mixture were bright and unify.

*Typical procedure synthesizing imidazole derivatives in reflux condition*

A mixture of aldehyde (1 mmol), 9,10-phenanthraquinone (1 mmol), ammonium acetate (2.5 mmol) and S-LPMO nanoperovskite (0.04 g) in 10 mL ethanol was stirred. The resulted mixture was refluxed for described time. At the end of the reaction (the reaction progress was monitored by TLC using *n*-hexan:ethylacetate as eluent solution) the catalyst was separation with filtering, and solid perovskite catalyst was isolated and could be reused. The solid product resulted after evaporation of organic phase, was washed with cold water (3 × 20 mL), and recrystallized in ethanol to provide pure product.

*Typical process for synthesizing imidazole derivatives in solvent-free condition*

A mixture of aldehyde (1 mmol), 9,10-phenanthraquinone (1 mmol), ammonium acetate (2.5 mmol) and S-LPMO nano perovskite (0.04 g) was stirred. Then, the mixture was heated at a temperature of 100 °C for described time (the reaction progress was monitored by TLC using *n*-hexan:ethylacetate as eluent). After cooling, the filtration of mixture was carried out and the filtrated mixture was washed using ethanol to separated catalyst. The filtrate was concentrated through evaporation under reduced pressure using a rotary evaporator. To obtain pure products, the recrystallization of remaining solid from ethanol was carried out.

*Analytical data for selected compounds*

*2-(4-Nitrophenyl)-1H-phenanthro[9,10-d]imidazole (3b)*. Yellow crystal, m.p. = 316 °C. IR (KBr):  $\nu$  = 3260 (N-H), 1591 (C=N), 1536 (NO<sub>2</sub>), 1450 (C=C), 1383 (NO<sub>2</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.63-8.83 (m, 12 H, Ar-H), 13.80 (s, 1H, NH) ppm.

*2-(2-Chlorophenyl)-1H-phenanthro[9,10-d]imidazole (3e)*. Yellow crystal, m.p. = 232-234 °C. IR (KBr):  $\nu$  = 3435 (N-H), 1594 (C=N), 1450 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.37-8.88 (m, 12H, Ar-H), 13.57 (s, 1H, NH) ppm.

*2-(p-Tolyl)-1H-phenanthro[9,10-d]imidazole (3h)*. Yellow crystal, m.p. = 290-292 °C. IR (KBr):  $\nu$  = 3377 (N-H), 1612 (C=N), 1593 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 2.38 (s, 3H, CH<sub>3</sub>), 7.28-8.82 (m, 12 H, Ar-H), 13.36 (s, 1H, NH) ppm.

*2-(4-(Benzyloxy)phenyl)-1H-phenanthro[9,10-d]imidazole (3i)*. Yellow crystal, m.p. = 228-230 °C. IR (KBr):  $\nu$  = 3432 (N-H), 1592 (C=N), 1673 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 5.11 (s, 2H, CH<sub>2</sub>), 7.16-8.83 (m, 17 H, Ar-H), 9.83 (s, 1H, NH) ppm.

*N-(4-(1H-Phenanthro[9,10-d]imidazol-2-yl)phenyl)acetamide (3j)*. Yellow crystal, m.p. = 246-248 °C. IR (KBr):  $\nu$  = 3212 (N-H), 1591 (C=N), 1562 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 2.08 (s, 3H, CH<sub>3</sub>), 7.28-8.82 (m, 12H, Ar-H), 10.17 (s, 1H, NH), 13.40 (s, 1H, NH) ppm.

**RESULTS AND DISCUSSION**

After synthesis of La<sub>0.5</sub>Pb<sub>0.5</sub>MnO<sub>3</sub> nanoparticles [21], for characterization of this catalyst, the morphology of the sample was determined using SEM analysis. Figure 1 demonstrates the micrograph related to the samples prepared through the sol-gel modified Pechini technique and calcined 650 °C.

According to the SEM images, the surface is obviously porous and it appears that the size of grown particles is uniform. The size of pores is in the range of 30-188 nm. Moreover, SEM

image shows that besides the presence of bigger particles, there were relatively smaller particles on the surface. However, the main particles on the surface were the bigger ones. The aggregation of smaller particles (in the nm scale) may cause the creation of larger LPMO NPs on the surface.

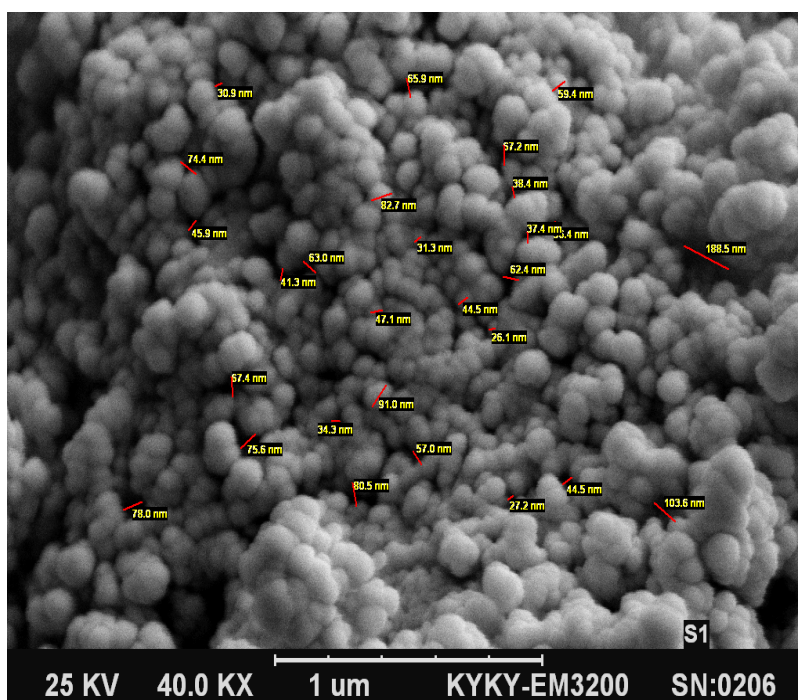


Figure 1. SEM image of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  nanoparticles.

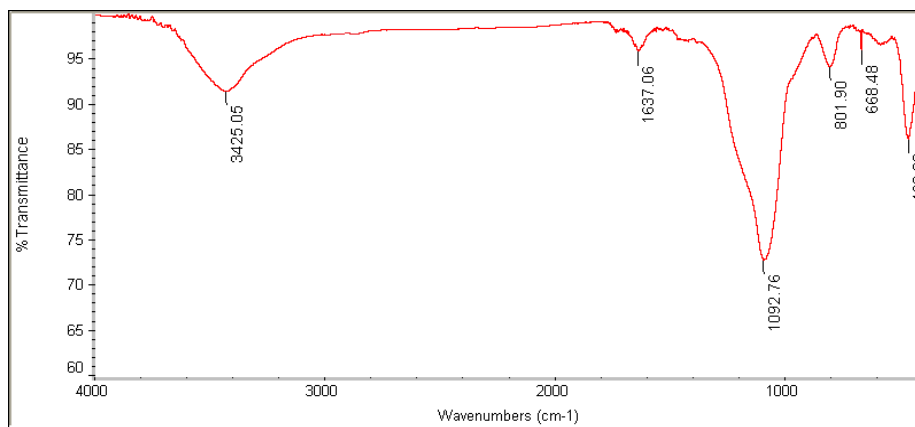


Figure 2. FTIR spectrum of  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  nanoparticles.

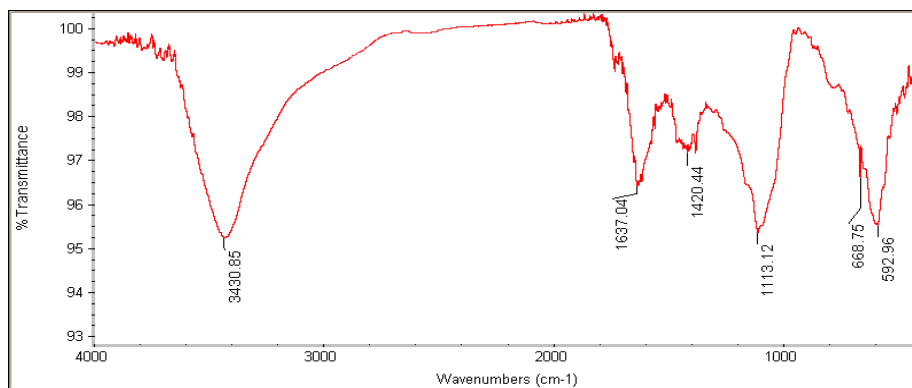


Figure 3. FTIR spectrum of silica-supported  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  nanoparticles.

FT-IR spectra were obtained for single LPMO and S-LPMO samples in range of 400-4000  $\text{cm}^{-1}$ . Figure 2 shows the FT-IR spectrum of LPMO perovskite nanoparticle, and Figure 3 shows the FT-IR spectrum of S-LPMO sample. The IR bands at 3430 and 1638  $\text{cm}^{-1}$  is due to the stretching and bending vibration of  $\text{H}_2\text{O}$  molecules, respectively. The very strong and IR band at 1113  $\text{cm}^{-1}$  is usually assigned to the Si-O-Si asymmetric vibrations. The picks at 668 and 592  $\text{cm}^{-1}$  corresponding to LPMO perovskite coated on  $\text{SiO}_2$  are clearly observed in this spectrum [18, 21].

For the purpose of optimization of the amount of catalyst and the reaction time, initially we were executed various amount catalyst in presence ethanol solvent. A model study was carried out on the synthesis of 2-(4-chlorophenyl)-1*H*-phenanthro[9,10-*d*]imidazole (3 g) via condensing [9,10] phenanthraquinone (1 mmol), 4-choloro benzaldehyde (1 mmol), ammonium acetate (2.5 mmol) in ethanol. For establish effectiveness of LPMO, a test reaction done without catalyst at ambient temperature. We were performed trace amount of product in the absence of catalyst (entry 1). We increased temperature up to reflux condition, but final product was not appreciable (entry 2). After that, reactions were reacted with different amounts of LPMO catalyst. Results summarized in Table 1 indicated the best result was with 0.04 g amount of catalyst but increasing the amount of catalyst did not improve the yield (entry 6 and 7). Also, when we supported LPMO on silica (S-LPMO), the amount of product was increased (entry 8).

Table 1. Effect of catalyst on the one-pot three component synthesis of substituted imidazole<sup>a</sup>

Entry	Catalyst/g	Temperature ( $^{\circ}\text{C}$ )	Time (h)	Yield (%)
1	0.0	R.T.	12	Trace
2	0.0	Reflux	12	<25
3	LPMO/0.01	Reflux	2	40
4	LPMO/0.02	Reflux	2	53
5	LPMO/0.03	Reflux	2	62
6	LPMO/0.04	Reflux	2	74
7	LPMO/0.05	Reflux	2	73
8	S-LPMO/0.04	Reflux	2	94

<sup>a</sup>Reaction conditions: 4-choloro benzaldehyde (1 mmol), [9,10]phenanthraquinone (1 mmol), ammonium acetate (2.5 mmol) in ethanol.

Considering solvent plays a key role in reactions, reaction was reacted in presence different solvents. Results are presented in Table 2. We observed protic solvent including ethanol and methanol have higher yield in this method. The best result was achieved using ethanol (entry 3). This reaction had proper result in free solvent condition. Thus this reaction was considered in free solvent reaction similarly.

Table 2. Effect of solvent on the one-pot three component synthesis of substituted imidazole<sup>a</sup>

Entry	solvent	Yield (%)
1	CHCl <sub>3</sub>	64
2	MeOH	78
3	EtOH	94
4	DMF	42
5	Solvent free (100°C)	80

a. Reaction conditions: 4-choloro benzaldehyde (1mmol), [9,10]phenanthraquinone(1mmol), ammonium acetate (2.5 mmol) and S-LPMO catalyst (0.04 gr) at reflux condition after 2 hours.

At the end of the model reaction, the nano catalyst was separated from the reaction mixture, washed with acetone and dried at 100°C under vacuum for 2 h and reapplied four times for the same reaction. As presented in Table 3, the catalyst can be reused at least four times with no change in its activity.

Table 3. Effect of catalyst recycling on the one-potthree component synthesisof substituted imidazole<sup>a</sup>

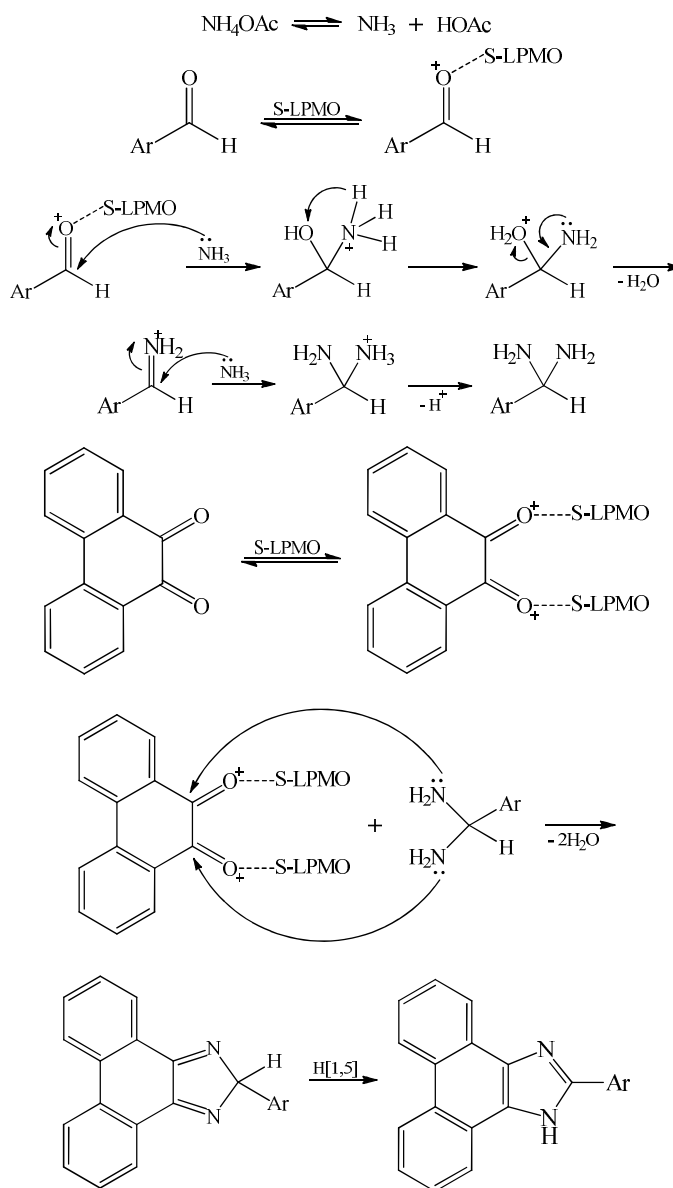
Runs	Yield (%)
1	94
2	93
3	93
4	90

a. Reaction conditions: 4-choloro benzaldehyde (1mmol), [9,10]phenanthraquinone (1mmol), ammonium acetate (2.5 mmol) and S-LPMO catalyst (0.04 gr) at reflux condition in ethanol after 2 hours.

Table 4. One-pot three component synthesis of substituted imidazoles using La<sub>0.5</sub>Pb<sub>0.5</sub>MnO<sub>3</sub> nanoparticles supported on silicaas an acidic catalyst<sup>a</sup>

Entry	Ar	Product	Yield (%) reflux/solvent- free	m.p. (°C) found/reported [Ref.]
1	C <sub>6</sub> H <sub>5</sub>	<b>3a</b>	89 / 78	286-288/>300 [17]
2	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3b</b>	92 / 77	>300/>300 [17]
3	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3c</b>	89 / 75	269-271/278-280 [13]
4	4-CNC <sub>6</sub> H <sub>4</sub>	<b>3d</b>	86 / 71	>300/>300 [17]
5	2-ClC <sub>6</sub> H <sub>4</sub>	<b>3e</b>	87 / 79	232-234/236-237 [17]
6	4-ClC <sub>6</sub> H <sub>4</sub>	<b>3f</b>	94 / 80	268-270/263-265 [13]
7	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>3g</b>	83 / 76	258-260/265-267 [13]
8	4-MeC <sub>6</sub> H <sub>4</sub>	<b>3h</b>	84 / 82	290-292/292-294 [13]
9	4- PhCH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub>	<b>3i</b>	68 / 60	228-230/ new
10	4-H <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub>	<b>3j</b>	74 / 66	246-248/ new

<sup>a</sup>Reaction conditions: aldehyde (1 mmol), [9,10]phenanthraquinone (1 mmol), ammonium acetate (2.5 mmol) and S-LPMO catalyst (0.04 g), at reflux condition in ethanol after 2 hours.



Scheme 2. Plausible mechanism for the formation of imidazole derivatives in the presence of S-LPMO catalyst.

Finally, after optimizing the reaction conditions, we prepared a range of replaced imidazoles (Table 4). In all cases, aldehydes reacted effectively with replaced carrying either electron-donating (entries 7-10) or electron-withdrawing (entry 2-4) groups and provided the estimated products in good to yields.

The mechanism of the reaction was proposed in Scheme 2. Ammonia molecules are obtained from ammonium acetate. We think that the aldehyde and 1,2-dicarbonyl compounds including 9,10-phenanthraquinone at first activated by S-LPMO as Lewis acid, in the rate determining step.

### CONCLUSION

In conclusion, we benefit from one pot synthesis for the preparation of substituted imidazoles through three-component condensation of aldehyde, 9,10-phenanthroquinone, and ammonium acetate in presence of silica-supported  $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$  nanoparticles as an efficient, re-usable and green solid acid catalyst, in reflux and solvent-free conditions. This catalyst has enhanced specific surface area, therefore increasing the contact between the catalyst and reactant. Excellent yields, short reaction times, simplicity of operation and easy separation and re-usability of catalyst are several advantages of this technique. Recovery of both products and inorganic support/catalyst is generally possible, leading to an effective and low-waste route to a range of products.

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