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Snail shell as a natural and highly efficient catalyst for the synthesis of imidazole derivatives

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ABSTRACT

A convenient, simple and green process for the synthesis of 2,4,5-triaryl-1H-imidazole and 1,2,4,5-tetraaryl-1H-imidazole derivatives using snail shell, which is abundant in Morocco, as a catalyst in ethanol at 40 °C has been developed. Additionally, short reaction times, excellent yields, simple procedure and relative non-toxicity of the catalyst are other noteworthy advantages and make this method an interesting alternative to other methodologies. Finally, this solid catalyst can be recovered and reused at least seven times with negligible loss in activity. The catalyst has been characterized by X-ray diffraction, scanning electron microscope, Fourier transforms infrared spectroscopy (FT-IR) and measuring the specific surface.

Keywords: Heterogeneous catalysis, Green catalysts, Snail shell, 1,2,4,5-tetraaryl-1H-imidazole, 2,4,5-triaryl-1H-imidazole.

1. Introduction

Multi-substituted imidazoles are an important class of compounds in pharmaceutical industries [1]. The imidazole pharmacophore is of therapeutic interest due to its hydrogen bond donor-acceptor capability [2]. Triaryl imidazoles are used as photosensitive material in photography [3]. In addition, they are of interest because of their herbicidal [4], analgesic [5], fungicidal [6], anti-inflammatory [7], anti-allergic activities [8]. They act as ligands in metalloenzymes and non-natural metal complexes [9]. They are components of a number of very significant biomolecules [10]. Various substituted imidazoles act as inhibitors of P38 MAP kinase [11] and B-Raf kinase [12].

A number of methods which have been reported for the synthesis of 2,4,5-triaryl-1H-imidazoles are generally synthesized by condensation of 1,2-diketone, aldehyde with ammonium acetate, in presence of microwaves [13], ionic liquids [14] europium triflate [15], oxalic acid [16], TBAB [17], CAN [18], refluxing in AcOH [19], silica sulfuric acid [20], Silica-bonded S-sulfonic acid [21], acidic ionic liquid [(CH$_2$)$_4$SO$_3$HMIM][HSO$_4$] [22], (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O [23], polyethylene glycol [24], nano crystalline MgO [25] and zeolite-supported [26].

On the other hand, the synthesis of 1,2,4,5-tetraaryl-1H-imidazoles is carried out by four component condensation of a 1,2-diketone, α-hydroxyketone or α-ketomonoxime with an aldehyde, a primary amine and ammonium acetate using microwaves [17], heteropolyacid [18], silica gel/NaHSO$_4$ [19] InCl$_3$·3H$_2$O [20] or HClO$_4$-SiO$_2$ [21]. In addition, they can also be accessed by hetero-Cope rearrangements [22] and condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave irradiation [23].

The snail shell has been utilized as a natural source of calcium carbonate, as a very effective coagulant in the treatment of waste [27] and as a source of calcium for the preparing nanocrystalline hydroxyapatite [28]. However, the use of snail shell as a catalyst in the synthesis of organic compounds in particular 1H-imidazoles derivatives, has not been reported.

In order to continue our work on the growth of simple and efficient heterogeneous catalysts, in this study, we report a straightforward and efficient method for synthesis of 1,2,4,5-tetraaryl-1H-imidazoles and 2,4,5-triaryl-1H-imidazoles derivatives via a one condensation reaction of aldehyde, benzile, ammonium and amine catalyzed by snail shell in EtOH at 40 °C.

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2. Experimental

2.1. Chemicals and apparatus

All the chemicals used were purchased from Sigma-Aldrich. All products were identified by comparison of spectral and physical data with the literature. Melting points were taken on a Kofler hot stage apparatus and are uncorrected. Powder X-ray diffraction (XRD) measurements were performed using a Panalytical X'Pert Pro diffractometer. Scans were taken with a 2θ and with an increment of 0.03° ranging from 10° to 90° using Cu Kα radiation source generated at 45 kV and 40 mA. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker 300-MHz and 75 MHz spectrometer in DMSO-d_6. The elemental analysis was performed on a Perkin Elmer 2400 Serie II CHNS/O microanalyzer.

2.2. Preparation of snail shell (Aragonite) catalyst

The waste of snail shells was collected, cleaned and dried in an oven at 100 °C during 24 h. The obtained shells, which do not contain calcinations, were ground into white soft powder.

2.3. General procedures for the synthesis of 2,4,5-triaryl-1H-imidazoles and 1,2,4,5-tetraaryl-1H-imidazoles

0.4 mol% aragonite snail shell (0.4 mg) was added to a mixture of benzil (1 mmol), aldehyde (1 mmol) and ammonium acetate (4 mmol) in 1 mL EtOH and was heated at 40 °C at the appropriate time. After completion of the reaction (monitored by TLC), THF was added to the cold reaction mixture and the catalyst was recovered by filtration and washed with THF (2×5 mL) and acetone (2×5 mL). After evaporation of the solvent, an oily residue or an impure solid was obtained. By adding ethanol and water to the residue, a milky to yellow solid was obtained. The solid was then recrystallized from ethanol.

3. Results and Discussion

3.1. General information for the catalyst

The catalyst has been characterized by X-ray diffraction, scanning electron microscope, FT-IR and measuring the specific surface.

3.1.1. XRD analysis for snail shell (aragonite)

The Analysis of the X-ray powder diffraction Fig. 1 showed a well-crystallized phase. The presence of the allotropic aragonite form of calcium carbonate was confirmed by the characteristic 111, 221, and 202 reflections at 26.26°,45.90° and 48.48° respectively (2θ) (Joint Committee on Powder Diffraction International Centre for Diffraction Data (JCPDS: 76-0606). Furthermore, it confirms the absence of the characteristic reflections of calcium carbonate in the different allotropic calcite (JCPDS: 86-2334) and vaterite (JCPDS: 74-1867). [29]

3.1.2. SEM analysis

The analysis by scanning electron microscopy Fig. 2 shows that it was crystallized as irregular needles. The snail shell (aragonite) powder has an average specific surface of 3.15 m[2]/g.

Measurements were carried out by the BET (Brunauer Emmett and Teller).

3.1.3. Fourier transforms infrared spectroscopy (FT-IR)

The FT-IR spectra of snail shell (Aragonite) in Fig. 3 shows that the spectrum can be divided into five parts with peaks around 1786.60, 1456.15, 1080.24, 853.63 and 706.34 cm[1] which can be associated to CO_3^{-2} ions in $CaCO_3$.
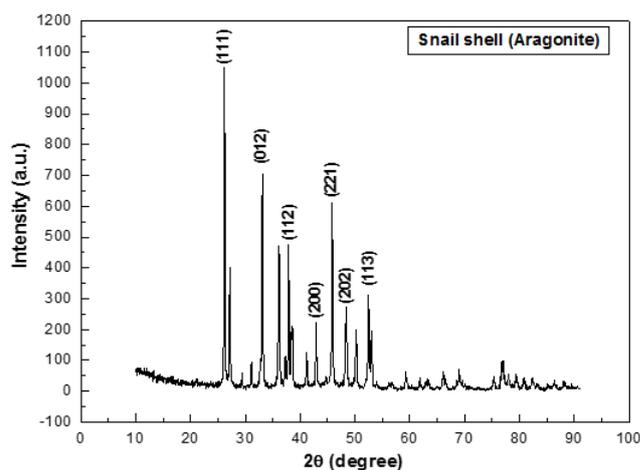

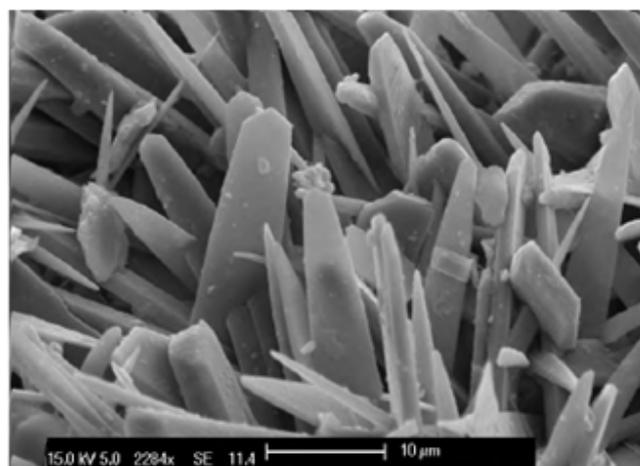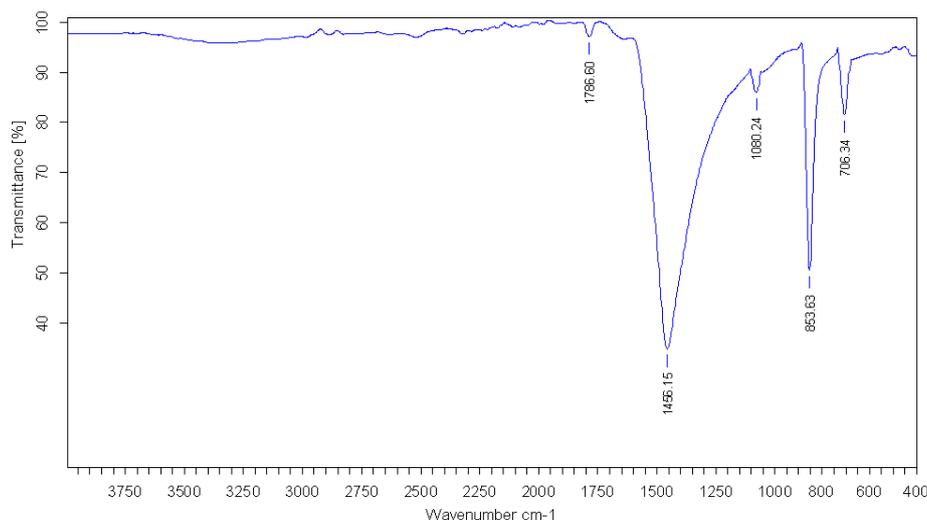**Fig. 1.** XRD analysis for snail shell (aragonite).

Fig. 2. Scanning electron microscopy of powder of snail shell (aragonite).

Fig. 3. FT-IR spectra for snail shell (Aragonite).

The band at 1786.60 cm[1] could be attributed to C=O bonds of the carbonate groups, while the absorption bands around 1456.15 cm[1] are attributed to the asymmetric stretching. The band at 1080.24 cm[1] corresponds to the symmetric stretching in aragonite, while the bands at 853.63 cm[1] can be attributed to the out-of-plane bending vibrations. Finally, the band at 706.34 cm[1] can be attributed to the symmetric stretching [30].

3.2. Catalytic activity for the synthesis of 2, 4, 5-triaryl-1H-imidazoles

In a model reaction and in the reaction of benzaldehyde **1a** (1 mmol) and benzil **2a** (1 mmol) with ammonium acetate **3a** (4 mmol), the effect of different amounts of the catalyst was investigated. To maximize the formation of the desired product and to achieve good yield, the reaction was optimized by varying amount of catalyst (Table 1). As can be seen in Table 1, the reaction, performed without a catalyst for 90 min, gave no product (Entry 6).

On the other hand, when the catalyst content was increased to 0.05 mol%, the product formation decreased to 62% (Table 1, entry 7) in solvent-free conditions during 5 min. Therefore, it was found that the use of 0.4 mol % (0.4 mg) of the catalyst was sufficient to promote the reaction, and greater amounts of the catalyst did not improve the yields (Table 1, entries 22-23). In addition, to optimize the reaction conditions including solvents and temperature, the reaction model was optimized by the time of the reaction and using various solvents such as EtOH, MeOH, CH₃CN and THF (Table 1). The best results were obtained when the reaction was carried out in methanol or ethanol at 40 °C during 10 min in the presence of catalyst (Table 1, entry

11 and 21). Therefore, ethanol was selected as a solvent for this reaction. Although water is a desirable solvent for chemical reactions due to inexpensive cost, safety and environmental concerns, we found that using water in this reaction gave moderate yields (60%) of the product under reflux condition after long reaction time (90 min).

In order to confirm the generality of the synthesis of 2,4,5-triaryl-1H-imidazoles and to explore the scope and limitations of this reaction, we extended the reaction of benzaldehydes **1**, benzil **2** and ammonium acetate **3** with various aromatic aldehydes carrying either electron-releasing or electron-withdrawing substituents (Scheme 2). We found that the reaction proceeded very efficiently in all cases (Table 2).

To confirm the efficiency of our catalyst in the same conditions, the 1,2,4, 5-tetraaryl-1H-imidazoles were synthesized via a four-component cyclo-condensation of aromatic aldehyde **1**, benzyl **2**, ammonium acetate **3** and aromatic amine **4** (Scheme 2). The results are tabulated in Table 3. Again, it can be seen that electron donating and electron withdrawing groups do not show any difference in the reaction yields.

One of the most important advantages of heterogeneous catalysis is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst were investigated in the imidazole **4a** formation. After completion of the model reaction, the catalyst was separated by simple filtration, washed two times with 3 mL acetone, and dried at 100 °C. Then the recovered catalyst was used in the next run. The results of ten consecutive runs showed that the catalyst can be reused several times without significant loss of its activity (Table 4).

Table 1. Effect of the amounts of catalyst, solvent and temperature on the synthesis of imidazole **4a** in the reaction of benzaldehyde, ammonium acetate and benzil.[a]

Entry	Catalyst loading (mol %)	Solvent (1 mL)	Temp. (°C)	Time (min)[b]	Yield (%)[c]
	0.1	Solvent-free	40	5	60
2	0.1	MeOH	40	13	74
3	0.1	EtOH	40	40	71
4	0.1	THF	40	90	62
5	0.1	CH_3CN	40	60	53
6	no catalyst	MeOH	40	90	-
7	0.05	MeOH	40	20	62
8	0.1	MeOH	40	13	74
9	0.2	MeOH	40	8	82
10	0.3	MeOH	40	6	88
11	0.4	MeOH	40	10	96
12	0.5	MeOH	40	12	93
13	1	MeOH	40	13	47
14	0.4	MeOH	r.t	60	--
15	0.4	MeOH	50	60	94
16	0.4	MeOH	70	31	94
17	0.4	MeOH	90	28	93
18	0.4	MeOH	100	16	93
19	0.4	MeOH	110	12	90
20	0.4	MeOH	120	10	90
21	0.4	EtOH	40	10	95
22	0.5	MeOH	40	10	96
23	0.6	MeOH	40	10	95
24	0.4	H_2O	100	90	60

[a]Reaction conditions: Benzaldehyde **1a** (1 mmol), benzil **2a** (1 mmol) and ammonium acetate **3a** (4 mmol) under condition.
[b]Time reported in min monitored by thin layer chromatography (TLC).
[c]Isolated yield.
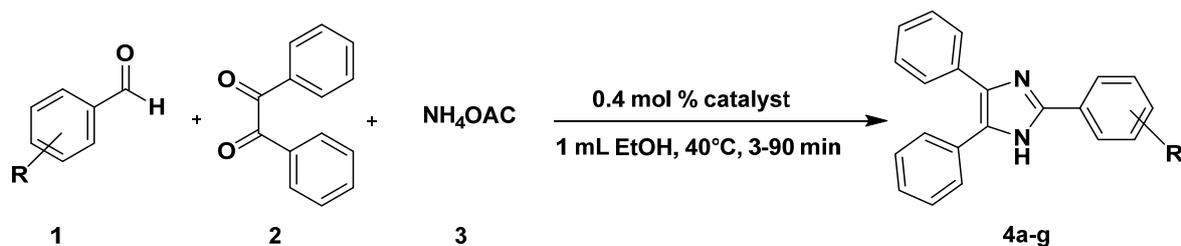
Scheme 1. Synthesis of 2,4,5-triaryl-1H-imidazoles catalyzed by snail shell.

Table 2. Snail shell catalyzed the synthesis of 2,4,5-triaryl-1*H*-imidazoles.[a]

Product	R	Time (min)	Yield (%)[a]	m.p. (°C) Found	m.p. (°C) Reported	Ref.
4a	H	10	96	274-275	275-276	[34]
4b	4-Cl	16	99	261-263	260-262	[31]
4c	4-Me	25	84	228-230	227-229	[32]
4d	4-NO$_2$	3	92	241-243	240-242	[33]
4e	2-Cl	31	97	187-189	187-188	[33]
4f	2,4-Cl$_2$	90	82	174-176	173-174	[33]
4g	4-OMe	30	95	227-229	228-231	[32]
4h	4-Br	30	94	251-253	252-254	[32]

[a]Isolated yields.
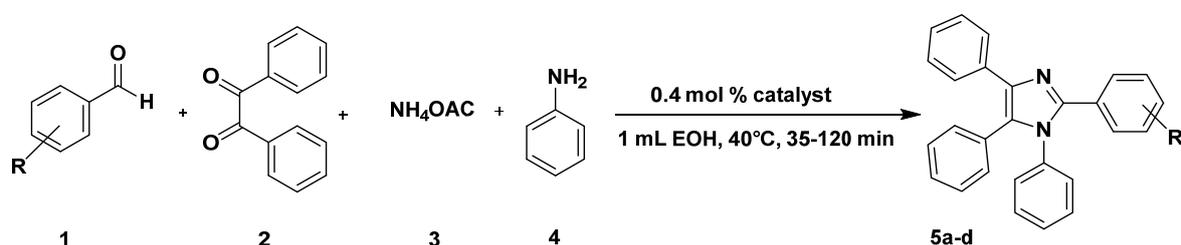
Scheme 2. Synthesis of 1, 2, 4, 5-tetraaryl-1H-imidazoles catalyzed by snail shell.

Table 3. Synthesis of 1, 2, 4, 5-tetraaryl-1H-imidazoles.[a]

Product	R	Time (min)	Yield[a] (%)	m.p. (°C) Found	m.p. (°C) Reported	Ref.
5a	H	50	90	216-218	216-218	[35]
5b	4-Cl	35	94	162-164	160-163	[35]
5c	4-Me	40	91	186-188	186-188	[35]
5d	4-NO$_2$	120	88	193-195	191-193	[36]
5e	4-OMe	60	90	181-183	180-182	[32]

[a]Isolated yields.

Table 4. The reusability of catalyst in the synthesis of 2,4,5-triphenyl-1*H*-imidazole **4a**.

Run	Time (min)	Yield (%)[a]
1	10	96
2	10	96
3	10	94
4	10	93
5	10	93
6	10	91
7	10	91
8	10	90
9	10	89
10	10	87

[a]Isolated yields.

Finally, to demonstrate the efficiency of the present method in the synthesis of 2,4,5-triaryl imidazoles and 1,2,4,5-tetraaryl-1H-imidazoles, it has been compared with the literature protocols summarized in Table 5 and 6. We observed that snail shell is an efficient catalyst with respect to reaction time and product yield.

4. Conclusions

In conclusion, we have developed a highly efficient protocol for the synthesis of 2, 4,5-triaryl-1H-imidazole and 1,2,4,5-tetraaryl-1H-imidazole derivatives using snail shell as a recyclable heterogeneous natural catalyst, in ethanol at 40°C. The attractive features of these procedures are shorter reaction times, mild reaction conditions, high yields and no side reactions, easy preparation and handling of the catalyst, green aspects by avoiding toxic catalysts and solvents, recyclability of the catalyst and simple experimental

procedure. The study on the exact mechanism of $NH_3(CH_2)_4NH_3SiF_6$ which might be applicable to the preparation of these heterocycle derivatives is underway in our laboratory.

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Table 5. Comparison of our catalyst with literature catalysts in the synthesis of 2,4,5-triaryl-1H-imidazoles.

Catalyst	Conditions	Time (min)	Yield %	Ref.
$CuFe_2O_4$	0,05 g, solvent free, 90°C	12-120	85-98	[37]
$Ce(SO_4)_2,4H_2O$	3 mol% , solvent free, 120°C	10-25	86-97	[38]
$NHSO_3H$-KIT-5	0,05 g, solvent free, 120°C	10-25	83-92	[40]
Nano- Al-MCM-41	10 mg, solvent free, 120°C	45-50	86-93	[41]
Nanoparticles onto silica	2.5 mol%, 10 mL EtOH, 50°C	40-170	55-96	[42]
Nano-SiO_2-supported FHS	0,04 g, solvent free, 110°C	30	85-95	[43]
$Fe_3O_4@SiO_2$-Imid-PMA^n	0,03 g, solvent free, 110°C	60-180	73-94	[44]
aspartic acid	0.4 mmol, solvent free,130°C	60-320	70-89	[45]
MCM-41-nPr-$NHSO_3H$	0.1 g, solvent free,130°C	20-150	53-98	[46]
Snail shell	0.4 mol%, 1 mL EtOH, 40°C	3-90	82-99	This work

Table 6. Comparison of snail shell with literature catalysts in the synthesis of 1,2,4,5-tetraaryl-1H-imidazoles.

Catalyst	Conditions	Time (min)	Yield (%)	Ref.
Snail shell	0.4 mol%, 1 mL EtOH, 40°C	35-120	88-94	This work
$CuFe_2O_4$	0,05 g, solvent-free, 90°C	40-100	70-90	[37]
H-ZSM-22	0,08 g, 5 mL EtOH, 140°C	20-30	76-87	[39]
Nano- Al-MCM-41	10 mg, solvent-free, 120°C	30-60	85-92	[41]
$Fe_3O_4@SiO_2$-Imid-PMA^n	0,03 g, solvent-free, 110°C	50-180	81-94	[44]
aspartic acid	0.4 mmol, solvent-free,130°C	160-420	73-92	[45]
MCM-41-nPr-$NHSO_3H$	0.1 g, solvent free,130°C	30-150	91-98	[46]
$BF_3.SiO_2$	37% w/w, solvent-free, 140°C	5-10	82-96	[47]
SBPPSA	0.25 g, solvent-free, 140°C	60-320	72-90	[48]
SASPSPE	1.7 mol%, 5 mL H_2O, 80°C	20-45	75-93	[49]
SBSSA	0.05 g, 5 mL H_2O, 80°C	10-35	75-93	[50]
SASPSPE	0.05 g, solvent-free, 140°C	15-210	70-95	[51]
Snail shell	0.4 mol%, 1 mL EtOH, 40°C	35-120	88-94	This work

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