One-pot synthesis of substituted imidazole derivatives by a new designed $BiFeO_3/CuWO_4$ heterojunction nanocatalyst

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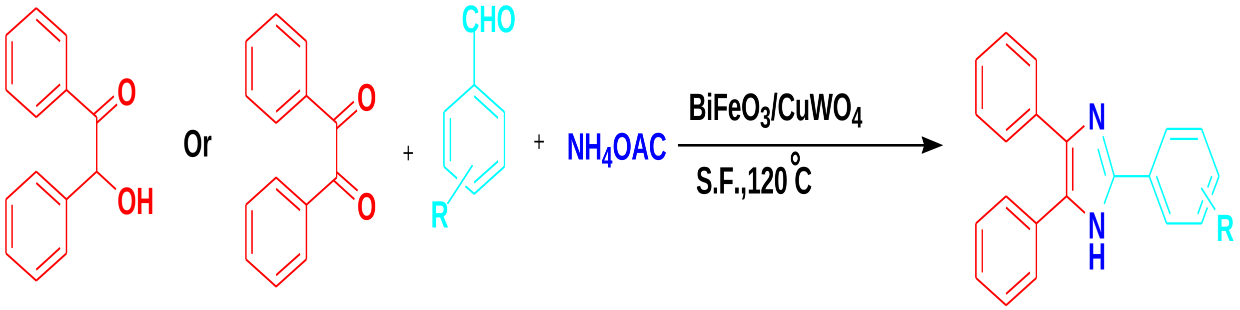
Abstract

In this work a novel heterojunction nanocatalyst have been synthesized and employed as a highly efficient and recoverable heterogeneous catalyst for the one pot three-component synthesis of substituted imidazoles under mild reaction conditions in short reaction times and good to excellent yields. Analytical methods including Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) were used for the catalyst characterization.

1. Introduction

Development of new multicomponent reactions (MCRS) are an area of considerable interest due to the fact that the products are formed in a single step and also the variety could be achieved only by changing the reaction components [1]. Imidazole derivatives are a very interesting class of heterocyclic compounds because they have many pharmacological properties and play important roles in biological process. The imidazole compounds are known to possess NO synthase inhibition and antifungal, antimycotic, antitumor, antibiotic, antibacterial, antiulcerative, and CB1 receptor antagonistic activities [2,3]. Various substituted imidazoles act as B-Raf kinase [4], glucagon receptors [5], inhibitirs of p38 MAP kinase [6], plant grown regulators [7], therapeutic agents [8], and pesticides [9,10]. These propellants have engendered considerable interest among synthetic organic and medicinal chemists in recent years. Accordingly, a number of synthetic methods have been reported for the synthesis of 2,4,5-trisubstituted imidazoles. These methods involve condensation of benzil or benzoin, aryl aldehydes and ammonium acetate by using various catalytic systems [11,12]. But, some of these synthetic methods are associated with one or more drawbacks such as using expensive reagents, long reaction times, purifications, complex work-up, generation of large amount of toxic wastes, strongly acidic conditions, high temperature, poor yields and occurrence of side reactions. Owing to the wide range of pharmacological and biological activities, the development of effective, high yielding, economical, clean and mild environmental benign protocols is still desirable and is in demand. Moreover, the design of valuable, effective and recoverable catalysts is important for the both environmental and economical point of view. Herein we wish to report a new efficient and practical route for the synthesis of trisubstituted imidazoles by the condensation reaction of benzil or benzoin, aryle aldehydes and ammonium acetate catalyzed by novel $BiFeO_3/CuWO_4$ heterojunction particles. To the best of our knowledge, this is the first report of design, preparation, and characterization of $BiFeO_3/CuWO_4$ heterojunction and its application as a heterogeneous catalyst in organic reactions. This novel approach has several superiorities as a compared with the previous reports for the synthesis of substituted imidazole derivatives and opens an important area to the use of environmentally benign and recoverable heterogeneous nanocatalyst in the synthesis of pharmaceutically important heterocyclic compounds (Scheme 1).



Scheme 1. One-pot synthesis of trisubstituted imidazoles catalyzed by $BiFeO_3/CuWO_4$.

2. Experimental

2.1 Synthesis of $BiFeO_3$

Bismuth ferrite, $BiFeO_3$ was synthesized according to a modified sol-gel method [16]. A transparent multi-component solution was prepared by mixing bismuth and iron salts. Bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved at room temperature in a mixture of 2-methoxyethanol and acetic acid. Then it was mixed with equimolar amount of iron nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ by constant stirring at room temperature. The precursor solution was dried at 80 °C for about 12h to obtain the $BiFeO_3$ xerogel powder. Then the xerogel powder was ground, and the powder was annealed at 600 °C for 30 min in air or N_2 atmosphere in the furnace. During the annealing procedure, heating and cooling rates of furnace were maintained at a rate of 4 °C/min.

2.2 Synthesis of $BiFeO_3/CuWO_4$ Composite

The $BiFeO_3/CuWO_4$ heterojunction catalyst were prepared through an impregnation process as follows. The above-obtained $BiFeO_3$ powder with the predetermined amount was impregnated in an aqueous solution containing a given amount of $Cu(NO_3)_2.3H_2O$ and $Na_2WO_4.2H_2O$. The suspension was sonicated for 2 h to make it homogeneous and then was continuously stirred till the water was totally evaporated on a water bath at 70℃. Afterwards, the dried powder was ground and annealed in a furnace at 600 ℃ for 2 h to decompose the $Cu(NO_3)_2.3H_2O$ and $Na_2WO_4.2H_2O$ to $CuWO_4$ which were in close contact with $BiFeO_3$ powder.

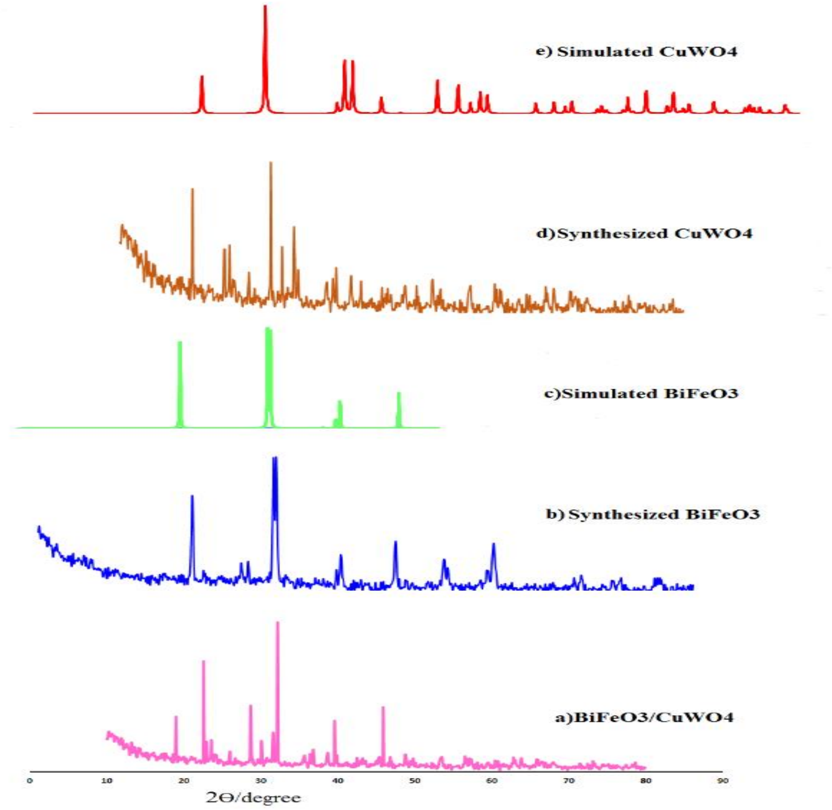


Fig. 1. PXRD patterns of a) $BiFeO_3/CuWO_4$, b) Synthesized $BiFeO_3$, c) Simulated $BiFeO_3$, d) Synthesized $CuWO_4$ and e) Simulated $CuWO_4$.

The XRD patterns of five materials including $BiFeO_3/CuWO_4$, synthesized $BiFeO_3$, simulated $BiFeO_3$, synthesized $CuWO_4$ and simulated $CuWO_4$ are shown in (Fig. 1a-e), respectively. All the diffraction peaks in the synthesized $BiFeO_3$ pattern (Fig. 1b) are indexed as the pure $BiFeO_3$ structure (Fig. 1c). The diffraction peaks of pure $BiFeO_3$ sample is in good agreement with pure rhombohedral phase of $BiFeO_3$ (JCPDS No. 2-169) shown in (Fig.1b,c). There are no impure peaks found, suggesting the high purity and crystallinity of the sample. Powder x-ray diffraction compares the simulated and experimental x-ray diffraction patterns (Fig. 1). All the diffraction peaks in the $CuWO_4$ XRD pattern are indexed as the triclinic $CuWO_4$ structure (Fig.1d). According to JCPDS card numbers the peaks at 2Θ values of 18.1^0, 19.0^0, 22.9^0, 23.5^0, 24.1^0, 25.9^0, 26.9^0, 28.7^0, 30.1^0, 30.8^0, 31.6^0, 32.1^0, 34.4^0 and 38.6^0 can be indexed to (0,0,1), (1,0,0), (1,1,0), (0,-1,1), (0,1,1), (-1,0,1), (1,0,1), (-1,-1,1), (1,1,1), (0,2,0), (-1,1,1), (1,-1,1), (1,2,0) and (2,0,0) crystal planes, respectively. No other impurity peaks were detected, indicating the highly crystal structure of $CuWO_4$. Also for the $BiFeO_3/CuWO_4$ product, the XRD pattern of (Fig.1a) matches well with those of $BiFeO_3$ and $CuWO_4$ phases in the composite.

FT-IR spectrum of $BiFeO_3$, $CuWO_4$ and $BiFeO_3/CuWO_4$ structures have also investigated and shown in Fig.2. In the FT-IR spectrum of $BiFeO_3$ shown in Fig.2. the broad band around 3442.5 cm^{-1} arises from the antisymmetric and symmetric structure of H_2O and OH^- groups. Specifically, two strong absorptive peaks around 545.8 and 441.7 cm^{-1} are attributed to the Fe–O stretching and O–Fe–O bending vibrations, being characteristics of the octahedral FeO_6 groups in the perovskite compounds. The formation of perovskite structure can be confirmed by the presence of metal-oxygen band [17]. In the $CuWO_4$ FT-IR spectrum the bands appear at a lower frequency is assigned to the deformation mode of the WO_4 tetrahedra. The absorption bands that appear in the 901 cm^{-1} assigned to stretching mode of W-O bonds in junction with WO_4 tetrahedra. Furthermore, the bands appearing in the 760 cm^{-1} is due to the Cu-O stretching band. The appearing absorption bands below 600 cm^{-1} might be responsible for the deformation modes of W-O bonds in the WO_4 tetrahedra or the deformation modes of W-O-W bridges. Presence of several splitting absorption peaks at 569, 585, 774, and 902 cm^{-1} can attributed to the $CuWO_4$ phase. Furthermore, annealing of the sample at higher temperatures (600°C) creates stronger W-O bonds due to the improvement of the sample crystallinity. As illustrated in the FT-IR spectrum of the $BiFeO_3/CuWO_4$ (Fig. 2.) separate and common absorption peaks of $BiFeO_3$ and $CuWO_4$ can be seen with the composite formation.

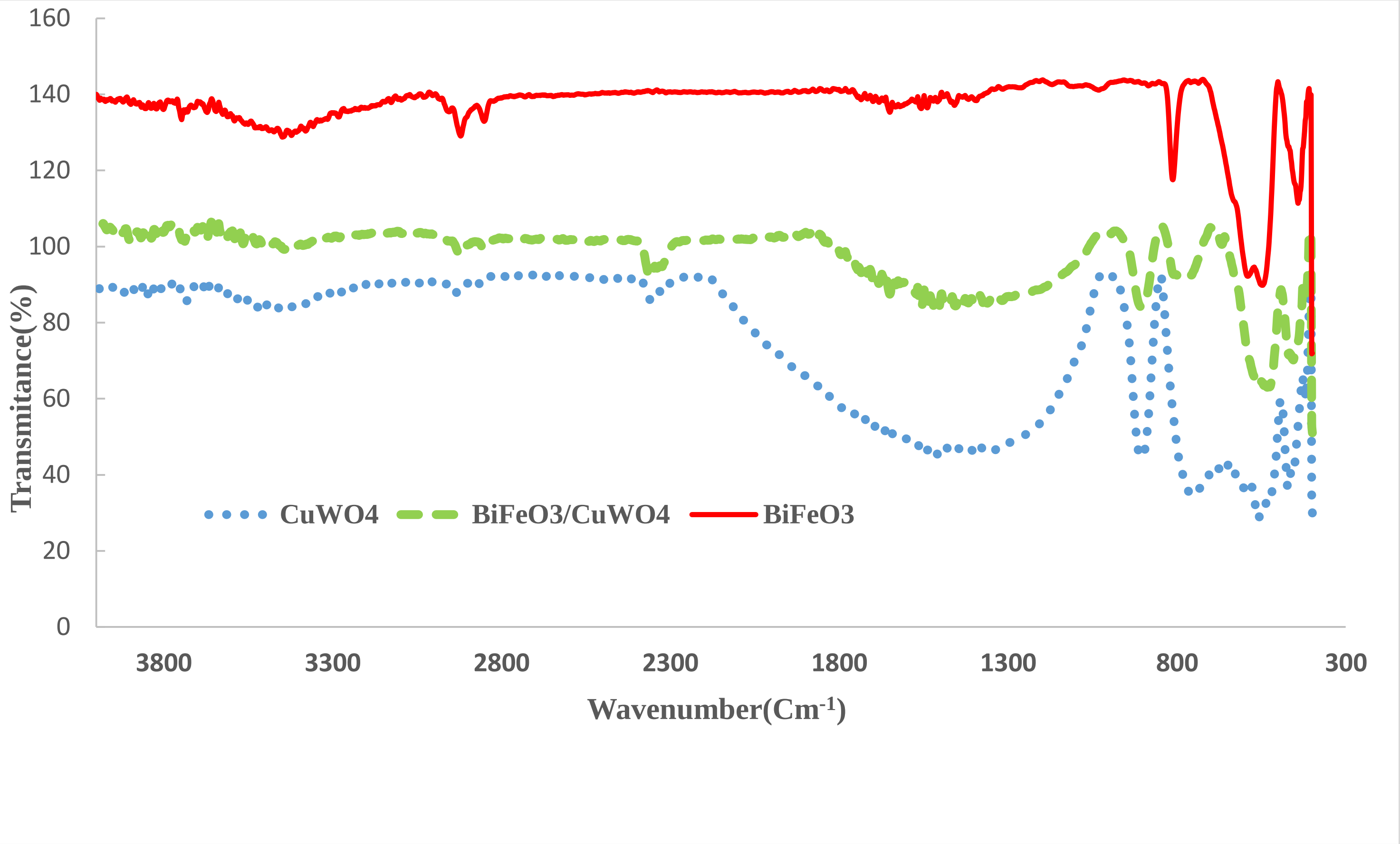
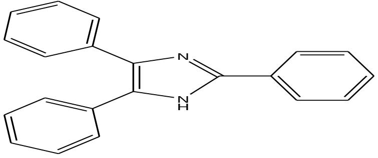
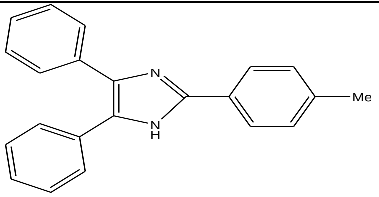
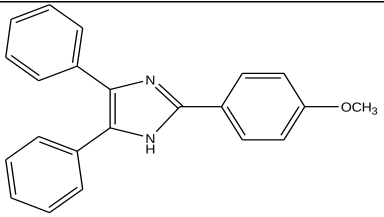
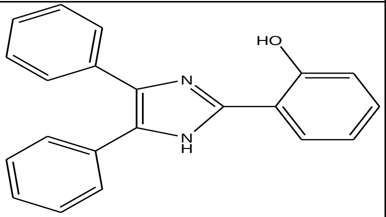
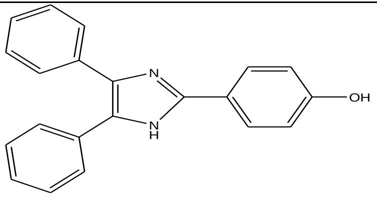
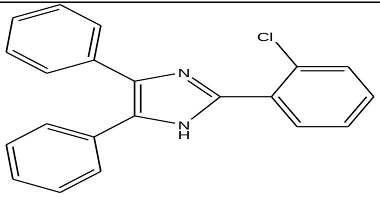
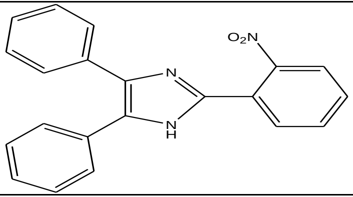
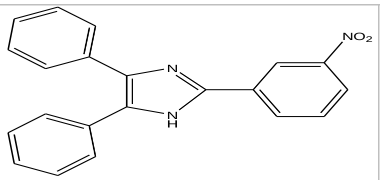
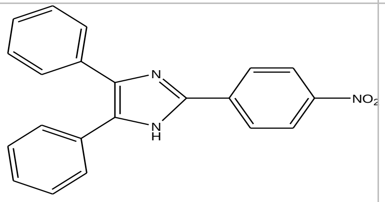
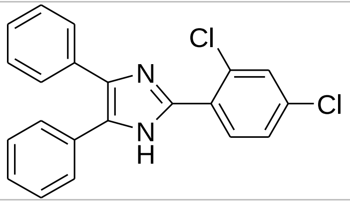
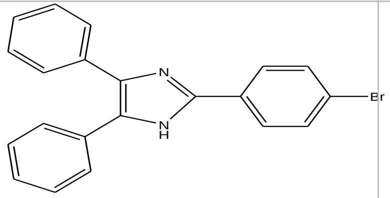
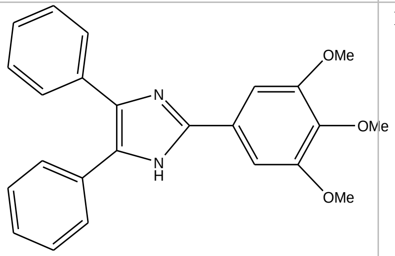
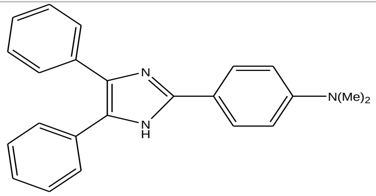
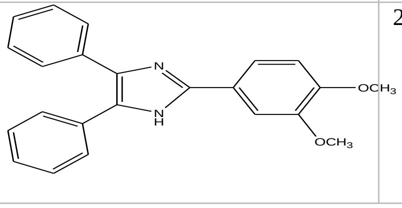


Fig. 2. The FT-IR spectra of pure $BiFeO_3$, $BiFeO_3/CuWO_4$ and $CuWO_4$.

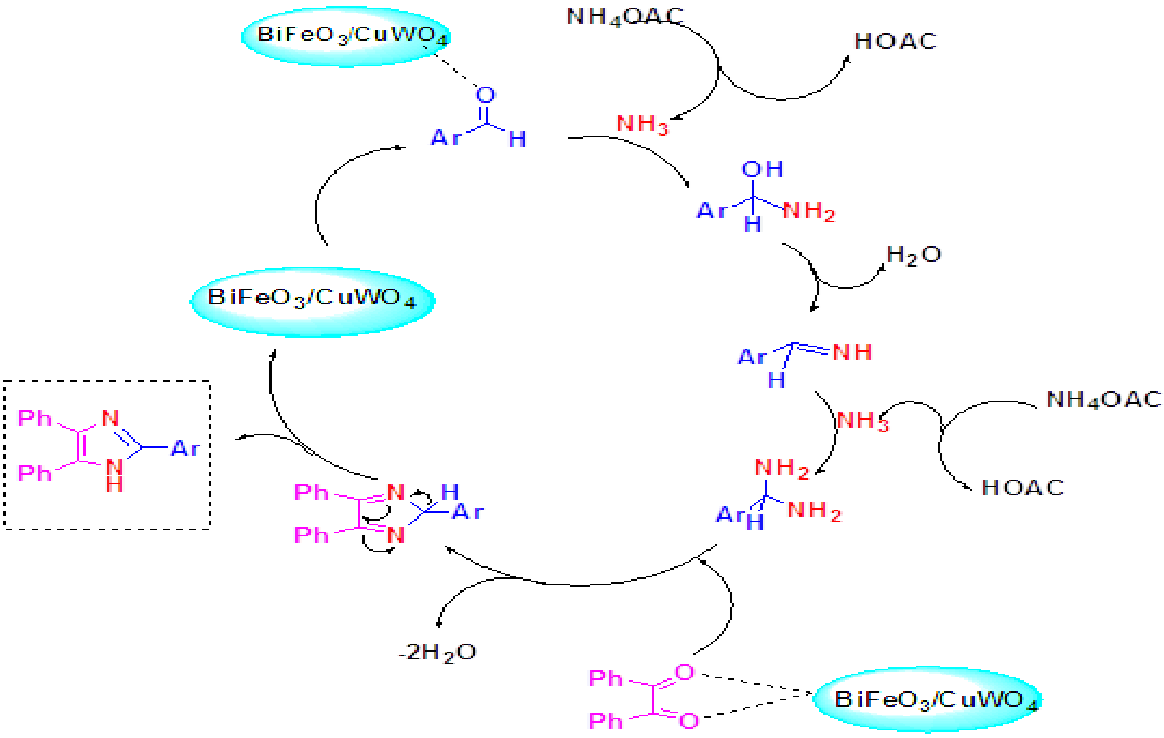
Table 2. Synthesis of 2,4,5-trisubstituted-1H-imidazoles using $BiFeO_3/CuWO_4$ catalyst under solvent-free conditions.

Entry	**Product**	**Time (min)**		**Yield (%)**[a]		**Mp (°C)**
		Benzil	**Benzoin**	**Benzil**	**Benzoin**	
1		10	14	95	93	270-271
2		10	15	94	90	228-230
3		15	20	90	86	227-229
4		12	16	92	85	203-205
5		15	20	95	92	230-232
6		20	25	94	91	190-192
7		15	25	87	85	230-231

8		7	15	95	93	290-291
9		8	10	94	91	199-201
10		10	15	98	93	177-178
11		12	20	94	92	261-263
12		15	20	95	91	262-263
13		15	30	89	84	260-261
14		20	25	95	92	216-218

[a] Yields refer to isolated pure products. The known products were characterized and compared by their physical properties with authentic samples.

A probable mechanistic pathway for the formation of 2,4,5-trisubstituted imidazoles is outlined in scheme 2. According to the mechanism, it can be proposed that the enormous active centers or unsaturated metals in the $BiFeO_3/CuWO_4$ heterostructure composite are responsible for the initial activation of the carbonyl group of aldehydes to facilitate nucleophilic addition of ammonia. In more details, it can be proposed that the hydrogen atoms in ammonia and free-orbitals of the metal centers in $BiFeO_3/CuWO_4$ having the lewis acidic properties, are responsible for the activation of carbonyl groups, and thus increase the rate of imine production through coordination bonding for nucleophilic attack of amines (Scheme 2). It is noteworthy that ammonia itself is produced in situ by decomposition of ammonium acetate in the presence of catalyst. It is considerable that the byproducts of this tandem MCR reaction are mainly water molecules which can be sorbed to the $BiFeO_3/CuWO_4$. Highly catalytic activity of magnetic $BiFeO_3/CuWO_4$ can be attributed to the catalytic temper of metal centers in both of $BiFeO_3$ and $CuWO_4$ structure that can easily coordinate with the substrates.



Scheme 2. Plausible mechanism of the reaction.

4. Conclusions

In summary, we have introduced a novel $BiFeO_3/CuWO_4$ heterojunction structure as a highly effective and recoverable heterogeneous catalyst for the one-pot synthesis of trisubstituted imidazoles under mild solvent free conditions. The high catalytic activity of $BiFeO_3/CuWO_4$ is further highlighted when compare with the other catalysts in this reaction. The several advantages of $BiFeO_3/CuWO_4$ as catalyst are easy to prepare,recycled several times and easiness of separation. In addition to the mild reaction conditions, easy work up, operational simplicity, giving the desired products in good to high yields are the key advantages of this protocol. We have believe that this procedure is appropriate, user-friendly process and economic for the synthesis of substituted imidazoles of biological and medicinal procedure.

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Graphical Abstract