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A green and efficient method for synthesis of benzimidazoles using nano-Fe_3O_4 in PEG-400/H_2O aqueous system under ambient conditions at room temperature

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In this paper, a green and facile protocol was described which was efficient for synthesis of benzimidazoles using nano-Fe_3O_4 catalyst with continuous bubbling of air as the oxidant in PEG-400/H_2O aqueous system at room temperature. This protocol afforded the target products in good to excellent yields and the catalytic system could be recycled and reused without significant loss of catalytic activity. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: benzimidazoles; nano-Fe_3O_4; PEG-400/H_2O aqueous system; room temperature

Introduction

Benzimidazoles are very useful compounds for development in the pharmaceutical industry, and exhibit significant biological activity against several viruses,[1] such as human immunodeficiency virus (HIV),[1] herpes simplex virus type 1 (HSV-1),[2] influenza[3] and human cytomegalovirus.[1] Although many methods are reported for synthesis of benzimidazole, there are two methods for the synthesis of benzimidazole compounds generally. One is the condensation of carboxylic compounds with *o*-phenylenediamines, which is usually performed under strongly acidic conditions, high temperature or microwave irradiation. The other is oxidative dehydrogenation of Schiff bases, often generated from phenylenediamine and aldehydes. Various oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[4] $FeCl_3$,[5] MnO_2,[6] H_2O_2,[7] $Pb(OAc)_4$,[8] Oxone,[9] $PhI(OAc)_2$,[10] $Na_2S_2O_5$,[11] benzofuroxan[12] and $K_4[Fe(CN)_6]$[13] have been employed in the reaction. Although these methods are effective, some suffer from one or more deficiencies such as the use of strong proton acid, high temperature, long reaction time and recovery of catalysts. Recently, air or oxygen has been used as a green oxidant for the synthesis of benzimidazoles[3] because of its inexpensive, non-toxic, and inexhaustible benign nature. Kawashita *et al.*[14] have reported that 2-phenylbenzimidazole was prepared from *o*-phenylenediamine and benzaldehyde using O_2/activated carbon system in 64% yield at 120°C for 26 h. Lin[15] has also reported the condensation of benzaldehyde with *o*-phenylenediamine in 85% yield using air as the oxidant in 1,4-dioxane at 100°C for 16 h. These methods are effective and practical; however, some still have one or more drawbacks such as high temperature and low product yield. Therefore, much effort is still needed to develop an eco-friendly method.

In the past decade, magnetic nanoparticles (MNPs) have emerged as a new class of catalyst owing to ultrafine size and high surface area, which exhibit higher catalytic activity than conventional heterogeneous catalysts. Among various MNPs, Fe_3O_4 MNPs have been used as a high-performance support because they are inexpensive, environmentally benign, have good chemical stability and are conveniently recovered after reaction by simple magnetic separation using, for example, Fe_3O_4-supportted sulfamic acid,[16] Fe_3O_4-supported dual acidic ionic liquid,[17] Fe_3O_4-supported palladium–bipyridine complex,[18] Fe_3O_4-supported Pd(0)[19] or Fe_3O_4-supported pybox copper(I) catalyst.[20] In addition, Fe_3O_4 MNPs has also been demonstrated as an efficient catalyst for many useful chemical transformations, including thiolysis of epoxides,[21] dehydrogenation of ethylbenzene,[22] synthesis of diverse *N*-heterocycles,[23] synthesis of α-aminonitriles,[24] synthesis of decahydroacridine derivatives,[25] synthesis of quinoxalines,[26] Sonogashira–Hagihara reactions,[27] Friedel–Crafts acylation reaction,[28] trimethylsilyl protection of hydroxyl groups,[29] three-component coupling of aldehyde, alkyne and amine[30] and N-Boc protection of amines.[31]

Recently, many aqueous-phase studies have been reported.[32–37] Water, as the safest reaction medium, is cheap and widely distributed on the Earth, and possesses significant advantages of mild reaction conditions, anti-vice, non-polluting to the environment and effectively preventing loss of product, due to its low solubility of organic products compared with organic solvents. Furthermore, water could provide reactions with a new reaction micro-environment, which is obviously different from traditional solvents, and promote notably improved selectivity of organic reaction. However, owing to its own unique

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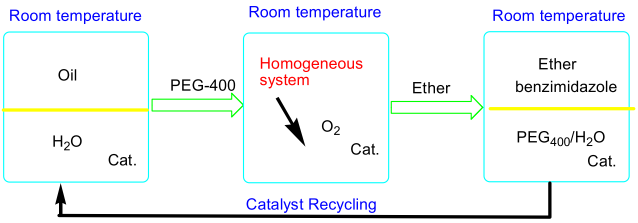
physical properties, such as high molecule cohesive energy density and dielectric constant, the aqueous phase has notable features of a lipophobic effect during organic reactions, in which most organic compounds are non-soluble, thereby severely limiting the application of water in organic reactions. One of the most common approaches is to add surfactants to the aqueous phase to achieve the effect of increasing solubility and performing its hydrophobic effect, which plays a role in the protection of some sensitive reagents to water. However, this method still suffers from the deficiency of cumbersome after-treatment, involving a demulsification operation of the reaction solution, in which the oil phase is dispersed in aqueous solution to form an emulsion when performed with addition of surfactants and vigorous stirring.

Polyethylene glycol (PEG), a commercially available, non-toxic and recyclable polymer, has been widely used in organic transformation as an environmentally benign solvent,[38–45] which is has potential as a substitute for volatile organic solvents, e.g. in *N*-arylation of amines, cross-coupling reaction, asymmetric dihydroxylation, aldol reaction, Baylis–Hillman reaction and multi-component condensation. On the other hand, PEG is an amphiphatic molecule, which presents some interesting characteristics of a surfactant, owing to its special structural properties, with high solubility in water and most common organic compounds. Also, the recovery of products is more easily achieved than using surfactants under mild reaction conditions. In 2012, Zolfigol[46] and co-workers reported the synthesis of benzimidazoles in excellent yields (85–97%) using a nano-Fe_3O_4/O_2 system. In continuation of Zolfigol's investigations, here we report a simple, mild and efficient method for the synthesis of benzimidazoles using Fe_3O_4 nanoparticles with continuous bubbling of air as the oxidant in PEG-400/H_2O aqueous solution at room temperature (Scheme 1). This protocol afforded high catalytic activity and mild conditions due to the surfactant-like property of the PEG molecule, which increased the solubility of organic compounds and effectively transferred the two phases as one component. Also, the reaction products were easily recovered in the organic phase by adding ether to the reaction system, due to the presence of water which could reduce the viscosity of PEG. Moreover, the nano-catalyst could be conveniently recovered and reused without significant agglomeration and sintering, and the PEG-400/H_2O aqueous system could also be reused for further cycles by adding new substrates.

Experimental

General Information

All starting materials were purchased from commercial sources and used without further treatment. X-ray diffraction (XRD) was performed using a Bruker Avance D8 XRD instrument. IR spectral analysis was performed using a Nicolet IS-10 FT-IR spectroscope (KBr). Transmission electron microscopy (TEM) was performed using a JEM-2100 instrument. Melting points were determined on a PerkinElmer differential scanning calorimeter. Elemental analysis was performed using an Elementar Vario Micro spectrometer. ^1H NMR spectra were recorded on a Bruker Avance III (500 MHz) spectrometer with TMS as an internal standard. HPLC experiments were performed using a liquid chromatograph (Shimazhu LC-20AT, Japan).



Scheme 1. Diagram of the catalytic process in the PEG-400/H_2O aqueous system.

Experimental Procedure

Preparation of Fe_3O_4 MNPs

Fe_3O_4 MNPs were prepared by the co-precipitation method according to a previously reported procedure. First, $FeCl_3.6H_2O$ (5.4 g) and $FeCl_2.4H_2O$ (2.0 g) were dissolved in distilled water (50 ml) in a three-necked round-bottom flask (150 ml). The resulting solution was stirred with mechanical stirring for 5 h. A solution of aqueous ammonia (10 ml, 25 wt%) was then added to the solution in a drop-wise manner over a 30 min period. The reaction mixture was then stirred under room temperature for 3 h. The resulting Fe_3O_4 MNPs were collected with a magnet and washed thoroughly with distilled water and ethanol three times, then dried under vacuum for 12 h to give Fe_3O_4 MNPs.

Typical Procedure for Synthesis of Benzimidazole Compounds

o-Phenylenediamine 1.08 g (10 mmol) and benzaldehyde 1.06 g (10 mmol) were thoroughly mixed in PEG_{400}/H_2O aqueous solution ($V(PEG_{400}/H_2O) = 1{:}2$, 15 ml) in a 25 ml three-necked flask equipped with a water-cooled condenser and a gas inlet with vigorous stirring at room temperature. Then, Fe_3O_4 nanoparticles 0.46 g (2 mmol) were added, and air was continuously bubbled by a small pump at an average speed of 60 bubbles per minute. When the reaction was complete, as monitored by TLC analysis, Fe_3O_4 nanoparticles were collected by magnetic force, subsequently washed with ethanol and dried under vacuum to give recycled Fe_3O_4 nanoparticles. The reaction mixture was extracted with ether three times, and the organic layer was dried using anhydrous magnesium sulfate and rotary evaporation under reduced pressure. The residue was purified by column chromatograph on a silica gel using *n*-hexane–ethyl acetate (10:1) as eluent to afford the pure product in 92% yield; m.p. 292–294°C. The next run was performed under identical reaction conditions.

Results and Discussion

XRD, FT-IR adsorption and TEM analysis of Fe_3O_4 MNPs are shown in Fig. 1. The position and relative intensities of all peaks ($2\theta = 30.1°, 35.4°, 43.1°, 53.4°, 57°, 62.6°$), which are assigned to (2 2 0, 3 1 1, 4 0 0, 4 2 2, 5 1 1, 4 4 0) were consistent with the JCPDS file (JCPDS19-0629),[47] indicating the crystalline cubic spinel of Fe_3O_4 MNPs. The strong FT-IR adsorption at 578 cm^{-1} was the Fe—O stretching vibration and the broad band at around 3500–3000 cm^{-1} was attributed to adsorbed solvents. Also, the control experiment of FT-IR adsorption showed no obvious differences in characteristic adsorption peaks between fresh Fe_3O_4 MNPs and reused Fe_3O_4 MNPs. These results revealed that the catalyst was stable and could endure the reaction conditions. TEM images of nano-Fe_3O_4 show that the synthesized nanoparticles

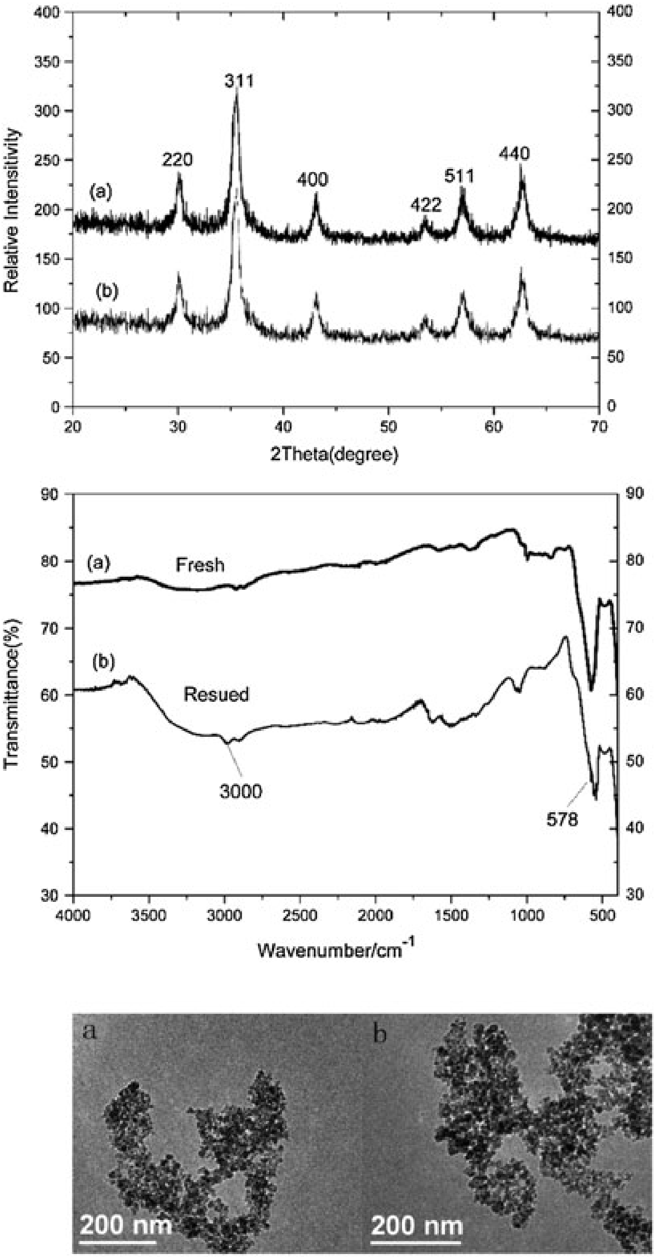


Figure 1. XRD, FT-IR adsorption and TEM analysis: (a) fresh; (b) after using five times.

were of uniform size (average size ~25 nm); the aggregation phenomenon was not clearly presented after the catalyst had been used five times. Notably, PEG polymer acts not only as a reaction solvent but also as a green stabilizer, limiting particle growth and effectively preventing their agglomeration and sintering.[48,49]

As we know, PEGs are amphiphatic molecules as a result of their special long chain structure consisting of ether bonds. The oxygen atom of ether bonds could combine with a water molecule to afford oxonium compounds, and the —CH units of PEG increase the solubility of organic compounds, which is derived from the hydrophobic gathering effect of the hydrocarbon chain. The mechanism for transferring the two phases as one component involves the PEG molecules being arranged between the two phases through the separate affinity of different parts of the molecule for the two phases, making their surfaces turn to face the inside of the PEG molecule. This could increase the oil–water contact area and effectively reduce surface tension.

The catalytic system was investigated for the synthesis of 2-phenylbenzimidazole via a model reaction of *o*-phenylenediamine with benzaldehyde. First, the reaction was performed in the absence of air under an N_2 atmosphere, when extremely little product was observed by HPLC analysis. The result suggests that oxygen played an oxidant role in this reaction. When the reaction was run under a static atmosphere of air, the product yield was good after a long reaction time of 12 h. Following on from the above results, the reaction was subsequently run using continuous bubbling of air, with the best performance in terms of reaction time and product yield. This indicates that continuous bubbling of air is more efficient than reaction just under air atmosphere, probably as a result of the increase of gas–liquid contact area and mass transfer efficiency. However, when the reaction was run under continuous bubbling of oxygen, the product yield was lower than using continuous bubbling of air, in spite of lower reaction time, which can probably be attributed to excessive oxidation of substrates in the pure oxygen atmosphere (Fig. 2).

The reaction was then carried out in the presence of various metal oxides as catalyst under the same conditions (Table 1, entries 1–3 and 6). We were delighted to find that the reaction with nano-Fe_3O_4 completed in 5 h to give a yield of 92%. The high efficiency here could be attributed to the large surface area and ultrafine size offered by the Fe_3O_4 nanoparticles, which dispersed well during the reaction process to form a pseudo-homogeneous system and alleviate the disadvantage of the corresponding heterogeneous catalysts. The influence of catalyst amount was investigated in the range of 0–40 mol% with a maximum activity at 20 mol% (Table 1, entries 4–8). As control experiments, we tested the effects of solvents by using commercial solvents under the same reaction conditions (Table 1, entries 6 and 9–14). The use of CH_2Cl_2 and $CH_3COOC_2H_5$ afforded low yields of product, whereas CH_3CN and DMF gave moderate yields. When the experiment was run in ethanol and methanol, the results were good and similar. As we expected, the best result was obtained with the PEG/H_2O system, which might be attributed to the high binding capacity of the PEG/H_2O system with oxygen derived from hydrogen bonding between molecules and excellent oxygen solubility of the PEG polymer. Moreover,

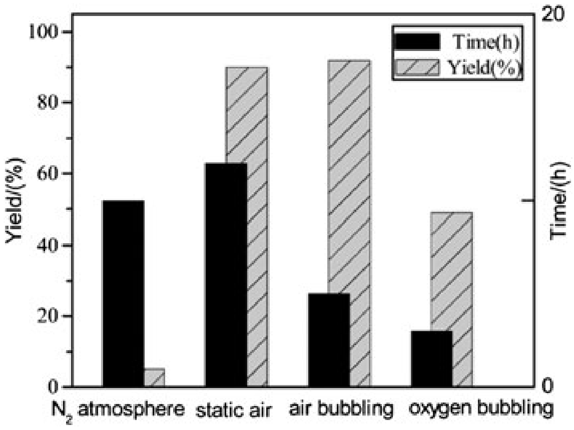
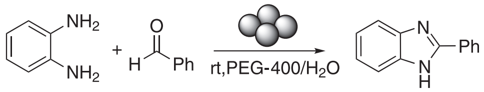


Figure 2. Effect of oxidant with different oxygen sources.

Table 1. Influence of reaction conditions on the synthesis of 2-phenyl benzimidazoles[a,b]



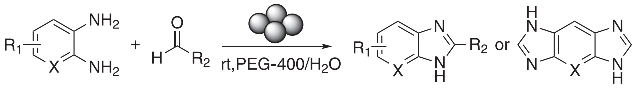
Run	Catalyst (mol%)	Solvent	Temperature (°C)	Yield[c] (%)
1	Al_2O_3 (20)	PEG/H_2O	r.t.	80
2	MnO_2 (20)	PEG/H_2O	r.t.	87
3	CuO (20)	PEG/H_2O	r.t.	75
4	Fe_3O_4 (0)	PEG/H_2O	r.t.	58
5	Fe_3O_4 (10)	PEG/H_2O	r.t.	82
6	Fe_3O_4 (20)	PEG/H_2O	r.t.	92
7	Fe_3O_4 (30)	PEG/H_2O	r.t.	91
8	Fe_3O_4 (40)	PEG/H_2O	r.t.	92
9	Fe_3O_4 (20)	Ethanol	r.t.	88
10	Fe_3O_4 (20)	Methanol	r.t.	85
11	Fe_3O_4 (20)	Dichloromethane	r.t.	45
12	Fe_3O_4 (20)	Ethyl acetate	r.t.	50
13	Fe_3O_4 (20)	Acetonitrile	r.t.	70
14	Fe_3O_4 (20)	DMF	r.t.	68
15	Fe_3O_4 (20)	PEG/H_2O	40	86
16	Fe_3O_4 (20)	PEG/H_2O	60	64
17	Fe_3O_4 (20)	PEG/H_2O	80	51
18	Fe_3O_4 (20)	PEG/H_2O	Reflux	40

[a] Reaction conditions: *o*-phenylenediamines 1.08 g (10 mmol) and benzaldehyde 1.06 g (10 mmol), nano-Fe_3O_4 0.46 g (2mmol), PEG/H_2O (15 ml). The reaction was stirred under ambient conditions for 5 h.

[b] Continuous bubbling of air as oxidant.

[c] Yield of isolated product.

Table 2. Synthesis of benzimidazoles from aldehydes and diamines[a]



Entry	X	R_1	R_2	Time (h)	Yields[b] (%)
1	H	H	Ph	5	92
2	H	H	4-OHC_6H_4	6	86
3	H	H	4-$Me_2NC_6H_4$	10	81
4	H	H	2-ClC_6H_4	4.5	91
5	H	H	4-ClC_6H_4	4	95
6	H	H	4-BrC_6H_4	4	93
7	H	H	2, 4-ClC_6H_3	3	96
8	H	H	3-$NO_2C_6H_4$	5	94
9	H	4-NO_2	Ph	10	84
10	H	H	H[c]	12	85
11	N	H	H	14	80
12	N	5,6-Diamno	H	15	74

[a] Reaction conditions: diamines (10 mmol) and aldehyde (10 mmol), nano-Fe_3O_4, 0.46 g (2 mmol), PEG/H_2O (15 ml). The reaction was monitored by TLC analysis.

[b] Products were purified by column chromatography and confirmed by HPLC, ^1H NMR, elemental analysis and melting point.

[c] 37% formaldehyde solution was used.

the PEG/H_2O system is thought to offer a practical advantage over methanol or ethanol in regard to considerations of toxicity and volatility. In addition, the impact of reaction temperature is shown in Table 1, and it appears that room temperature gave the highest product yield. A high reaction temperature (>30°C) would cause a gradual decrease in conservation due to escape of oxygen from the reaction system (Table 1, entries 6 and 15–18).

Encouraged by the previous results, we continued to study the scope of reaction, which could be extended to a series of structurally variable arylamines and aromatic aldehydes. In most cases, *o*-phenylenediamine reacted smoothly with various benzaldehydes to give the corresponding products with good yields. It appeared that benzaldehyde bearing electron-deficient groups on the aromatic rings gave a higher yield of products than those bearing electron-rich groups (Table 2, entries 2–8). The reason might be that the electron-withdrawing groups enhanced the electrophilicity of the carbon atom of the aldehyde group to increase the reaction rate. In addition, the position of the substitute group relative to the aldehyde group on the aromatic rings also influenced the reaction rate and yield. The sterically hindered *o*-chlorobenzaldehyde reacted with *o*-phenylenediamine to give the target product in lower yield than *p*-chlorobenzaldehyde (Table 2, entries 4 and 5). Moreover, aromatic aldehydes like benzaldehydes reacted faster with *o*-phenylenediamine than aliphatic aldehydes such as formaldehyde (Table 2, entries 1 and 10), probably due to the conjugated effect of the phenyl group of benzaldehyde, which promoted an increase of the positive electrical property of the carbon atom of aldehyde and facilitated nucleophilic attack of the amine group. On the other hand, a diamine-bearing electron-deficient group on the aromatic rings or containing a hetero atom proceeded more inefficiently than *o*-phenylenediamine in terms of longer reaction time and lower yield (Table 2, entries 1, 9, 11 and 12).

The reuse of catalyt is highly preferable for a green process. Thus the recyclability of Fe_3O_4 MNPs was investigated by using *o*-phenylenediamine and benzaldehyde as a model reaction. The catalyst was easily separated by using an external magnet after the reaction and reused in a subsequent reaction. Nearly quantitative Fe_3O_4 MNP catalyst could be recovered from each run. In a test of five cycles, the catalyst could be reused without significant loss of catalytic activity (Fig. 3).

The mechanism for synthesis of benzimidazoles from aromatic diamines and aldehydes is shown in Scheme 2. The first step was dehydration to form a schiff base with *o*-phenylendiamine. During the next steps, ring closure led to a five-membered ring, and dehydrogenation with air oxidation to form benzimidazole.[50,51]

Conclusions

We have developed a green and efficient method for the synthesis of benzimidazole compounds using Fe_3O_4 MNPs with continuous bubbling of air as the oxidant in PEG-400/H_2O aqueous solution at room temperature. Owing to the high efficiency of nanomaterials and the surfactant-like property of the

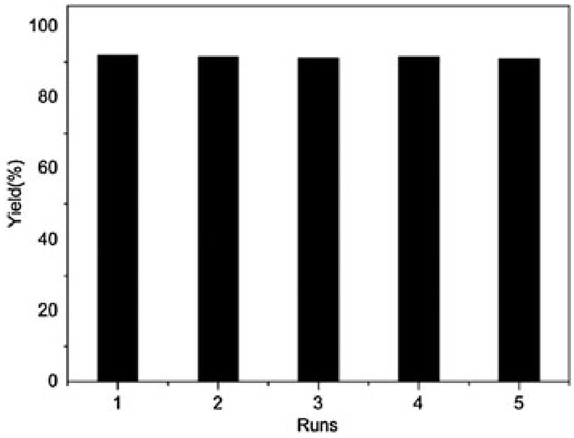
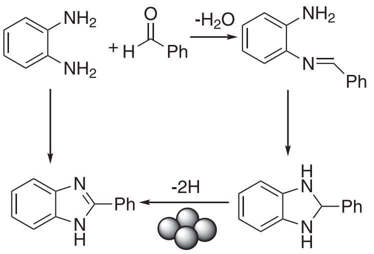


Figure 3. Cycling reaction of Fe_3O_4 MNPs.



Scheme 2. Mechanism for synthesis of benzimidazole.

PEG molecule, our protocol presents outstanding advantages including simplicity of operation, good yields, low cost and excellent recyclability of the catalytic system. The scope and synthetic application of this reaction are currently under study in our laboratory.

Acknowledgment

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