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A recyclable polymer anchored copper(II) catalyst for oxidation reaction of olefins and alcohols with *tert*-butylhydroperoxide in aqueous medium

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Keywords: Olefin oxidation Alcohol oxidation Polymer anchored Copper complex tert-Butylhydroperoxide Aqueous medium ABSTRACT

A new reusable polymer anchored Cu(II) complex was synthesized which can acts as an efficient heterogeneous catalyst for oxidation of olefins and alcohols with *tert*-butylhydroperoxide (TBHP) in aqueous medium. The present catalyst well oxidized styrene and other olefins to their allylic products and alcohols were converted to their corresponding aldehydes in good-to-moderate yields. This catalyst can be easily recovered by filtration and recycled without significant loss of its catalytic performances.

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The use of transition metal complexes as catalysts for the oxidation reactions has been a subject of great interest [1,2], oxidation being carried out by using several oxidants, such as oxygen, hydrogen peroxide, and tert-butylhydroperoxide (TBHP) [3,4]. Many soluble metal complexes have been found to be active catalysts in the oxidation reaction during the last few decades. Recently, soluble compounds of early transition metals such as rhenium [5], vanadium [6], manganese [7] and molybdenum [8] have been used for alkene oxidations. Good activities and selectivities have been pointed out as the main advantages of homogeneous catalysts. However, some industrial problems such as corrosion, deposition on reactor wall, difficulty in recovery and separation of the catalyst from the reaction mixtures are associated with these homogeneous catalysts. These disadvantages were minimized if homogeneous complexes were immobilized onto insoluble solid supports. Amorphous silica [9], modified MCM-41 [10] and alumina [11] have been used for immobilization of homogeneous compounds and applied them as catalysts for alkene oxidation. Nowadays, polystyrene is one of the most widely employed solid supports for the synthesis of functionalized polymer anchored catalysts [12–15]. Immobilization of active homogeneous metal complexes on polymeric supports has evolved as a promising strategy for combining the advantages of both homogeneous and heterogeneous catalysts [16-19].

In the chemical processes, traditional organic solvents are used in large quantities, which has led to various environmental and health concerns. As part of green chemistry efforts, a variety of cleaner solvents have been used as replacements [20]. As an alternative solvent, water has been paid extraordinary attention. Apart from being a chemically interesting solvent, water provides a cheap (both in cost price and in ecotax) alternative for organic solvents, making it environmentally and economically interesting as well. However, for organic synthetic chemists, who are trained to put compounds in solution and frequently approach organic reactions from a "like-need like perspective", it is less important, because water is traditionally not a popular choice of solvent. It is commonly accepted that a mixture of water and one or more nonpolar organic reactants will usually have low reaction rates and low yields of the desired products [21]. K. Barry Sharpless and his colleagues report [22] that the above assumption does not hold for a variety of organic reactions (ene reactions, nucleophilic substitutions. Claisen rearrangements and Diels-Alder reactions) in the 'on water' approach that they have pioneered [21]. Phase transfer catalysis is becoming an interestingly important technique in organic synthesis. But there is one limitation in this method that many phase transfer catalysts promote stable emulsion which renders work-up difficult. Regen introduced the new concept of triphase catalysis, in which the catalyst and each of a pair of reagents are located in separated phase [23,24]. The major advantage of triphase catalysis over phase transfer catalysis is that the catalyst can be removed from the reaction mixture by simple filtration. So, based on the above two concepts, we tried to synthesize a new polymer anchored metal complex which can catalyze the organic reactions in aqueous medium without any phase transfer catalyst.

Here, we have developed polymer anchored Cu(II) catalyst and characterized it. Catalytic performances were investigated in liquid phase oxidation of olefins in water. The influences of various reaction parameters on the conversion of styrene have been studied in order to optimize the reaction conditions. Furthermore, this catalyst can

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catalyze the epoxidation of cyclooctene and oxidation of aromatic alcohols. The results illustrated that the heterogeneous copper catalyst was effective for the oxidation reaction with a variety of organic compounds using TBHP as oxidant in water and found to be easily recoverable, recyclable up to five times.

The polymer supported copper complex was prepared by the complexation of copper salts with polymer anchored ligand (3) (Scheme 1) [25]. Amino polystyrene was synthesized and characterized in earlier studies [26]. After that it was reacted with di-bromo ethane under refluxing condition using K₂CO₃ as base and produced ligand (2). Under refluxing conditions, functionalized polymer supported ligand (2) reacted with o-aminophenol successfully to yield the corresponding polymer supported ligand (3) as shown in Scheme 1. Finally a solution of copper chloride was added to the ligand (3) and dark brown polymer supported copper catalyst was obtained. Due to insolubilities of the polymer anchored Cu(II) catalyst in all common organic solvents, the characterization of the catalyst was done on the basis of infrared spectroscopy, diffuse reflectance spectra of solid, thermogravimetric analysis and by using scanning electron microscope. The metal content in the catalyst determined by atomic absorption spectroscopy suggests 2.23 wt.% Cu in the heterogeneous catalyst.

The modes of attachment of copper metal onto the support were confirmed by comparison of the FT-IR spectral bands of the copper catalyst over the polymer in various steps of its synthesis. Polymer anchored ligand (2) exhibited a broad band around 3400 cm⁻¹ which is assigned to N-H (secondary amine) stretching frequency. The intensity of this band increased in polymer anchored ligand (3) and also there was a band at 1381 cm^{-1} which is assigned to phenolic C–O stretching frequency. This C-O stretching band is shifted to lower frequency region and appeared at 1367 cm⁻¹ in copper complex which indicates that copper metal is attached with the polymer anchored ligand through the phenolic oxygen. On the other hand, the band at 3400 cm^{-1} region is shifted to lower frequency region and appeared at 3365 $\rm cm^{-1}$ in the complex. Polymer anchored Cu(II) catalyst exhibited important IR peaks at 540 cm⁻¹ (ν Cu-N), 622 cm⁻¹ (ν Cu-O) [27] and at 354 cm⁻¹(v Cu–Cl) [28]. The scanning electron micrographs of polymer anchored ligand (Fig. 1A) and supported copper catalyst (Fig. 1B) clearly show the morphological change which occurred after complexation and suggest the loading of copper metal on the surface of polymer. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for polymer anchored ligand and supported copper catalyst are given in Fig. 2 (A and B). The EDAX data also confirm the attachment of copper metal on the surface of the polymer matrix. Thermal stability of the complex was investigated using TGA at a heating rate of 10 °C/ min in air over a temperature range of 30–600 °C (Fig. S1 in supporting information). Polymer supported ligand decomposed in the temperature range 310-340 °C. After complexation of copper metal on polymer supported ligand, thermal stability of the immobilized complex is improved. Polymer supported Cu(II) complex decomposed at 390–410 °C. So, thermogravimetric study suggests that the polymer anchored copper catalyst degraded at considerably higher temperature.

The electronic spectrum of the immobilized copper catalyst has been recorded in the diffuse reflectance mode. The UV–vis spectra provided further evidence for the presence of metal on the polymer support. The spectrum of the copper catalyst exhibits few spectral bands (Fig. S2 in supporting information). The spectral band at 275 nm is due to intra ligand charge transfer and the bands at 375 nm and at 446 nm are due to LMCT. The band at 446 nm indicates the phenolic oxygen to copper charge transfer [29]. In the complex, the band around 674 nm is due to d–d transition which corresponds to the square-planar geometry [30,31].

In the first stage of the investigation for the catalysis, we tested the oxidation reactions [32] of olefins in water using this catalyst and in all the cases allylic oxidation products are obtained. In order to optimize the reaction conditions, oxidation of styrene with polymer anchored Cu(II) catalyst was taken as probe reaction. In this case styrene selectively converted to benzaldehyde. Effects of various oxidants on the conversion of styrene and selectivity of benzaldehyde using polymer anchored Cu(II) catalyst was summarized in Table 1. We investigated the ability of various oxidants like TBHP, H_2O_2 , NaIO₄, PhIO and KHSO₅ in styrene oxidation reaction (Table 1, Entries 2–6). As shown in Table 1, TBHP is the best oxidant among the five oxidants that are used in catalytic oxidation reaction in the present study (Table 1, Entry 2). Oxidants like H₂O₂, PhIO and NaIO₄ are clearly less efficient than TBHP as is evident from the percentage of conversion of styrene (Table 1, Entries 3-5). The use of KHSO₅ is not favored because a buffer is needed (Table 1, Entry 6). The effect of temperature on the performance of the catalyst was also studied at three different temperatures, viz. 50, 60 and 70 °C at fixed amount of styrene (5 mmol), TBHP (10 mmol), Cu(II) catalyst (0.030 g) in 5 mL water (Table 1, Entries 2 and 7-8). A maximum of 96% conversion was achieved on carrying out the reaction at 60 °C. At 50 °C, the conversion was low. At 70 °C, the initial conversion of styrene was high than at 60 °C but when the reaction continues the conversion of styrene was almost same with conversion at 60 °C. Therefore 60 °C was the optimum temperature and all catalytic oxidation reactions of olefins were carried out at this temperature. The activity of the polymer anchored Cu(II) catalyst in the oxidation of styrene was also evaluated using three different molar ratios of styrene to TBHP (Table 1, Entries 2 and 9-10). The conversion of styrene was increased from 68% to 96% on increasing the styrene: TBHP ratio from 1:1 to 1:2. On further increasing this ratio to 1:3, the conversion was hardly affected. From the results, it was suggested that 1:2 ratio



Scheme 1. Synthesis of polymer anchored copper(II) catalyst.



Fig. 1. FE SEM image of polymer anchored ligand (3) (1A) and polymer anchored Cu(II) catalyst (1B).

of styrene to TBHP is sufficient for the good conversion of styrene. In order to show the effect of polymer anchored copper complex in the oxidation reaction, a blank experiment (Table 1, Entry 11) in the presence of oxidant and using the same experimental conditions in the absence of the catalyst was also investigated in the oxidation of styrene. The obtained results showed that TBHP has poor ability to oxidize the styrene.

The above optimized reaction conditions could be applied to the oxidation reactions of other olefins by polymer anchored Cu(II)

catalyst and the results are shown in Table 2. This catalyst efficiently converts olefins to their corresponding allylic products with TBHP in aqueous medium. In the oxidation of cyclohexene, allylic products 2-cyclohexene-1-one and 2-cyclohexene-1-ol were obtained. Substituted styrene produced selectively corresponding aldehydes. Acetophenone was detected in the oxidation of α -methyl styrene as major product. *trans*-Stilbene was also oxidized by this heterogeneous catalyst in high yields. *trans*-Stilbene gives benzaldehyde as major product with benzil. This catalytic system shows a good activity in the case of α -pinene. In



Fig. 2. EDAX data of polymer anchored ligand (3) (A) and polymer anchored Cu(II) catalyst (B).

Table 1

Oxidation of styrene using different oxidants catalyzed by polymer anchored Cu(II) catalyst.^a

Entry	Oxidant	Temperature	Conversion (%) ^b	Selectivity(%) ^b		TOF
				Benzaldehyde	Styrene oxide	(h ⁻¹) ^c
1	None	60 °C	0	0	0	-
2	TBHP	60 °C	96	88	9	57.14
3	H_2O_2	60 °C	41	83	15	24.40
4	PhIO	60 °C	17	59	36	10.12
5	NaIO ₄	60 °C	35	43	55	20.83
6	KHSO ₅	60 °C	29	54	43	17.26
7	TBHP	50 °C	57	86	13	33.93
8	TBHP	70 °C	96	75	21	57.14
9 ^d	TBHP	60 °C	68	82	17	40.48
10 ^e	TBHP	60 °C	97	90	9	57.74
11f	TRHD	60 °C	8	74	25	

^a Reaction conditions: catalyst (0.03 g, 1.05×10^{-2} mmol), styrene (5 mmol), water (5 mL), oxidant (10 mmol), time (8 h).

^b Determined by GC.

 $^{\rm c}$ Turn over frequency (TOF): moles of substrate converted/mol of Cu/h. Loading of Cu = 0.035 mol%.

^d mmol ratio of styrene and TBHP = 1:1.

^e mmol ratio of styrene and TBHP=1:3.

^f Reaction carried out without catalyst.

the oxidation of α -pinene, the major products were verbenone and verbenol.

Further we have compared the activity of the polymer anchored copper(II) catalyst in the oxidation reaction with the other reported catalysts [33–36] (Table 3). The results show that our catalyst is superior to the reported catalysts in terms of reaction time, reaction temperature, and conversion and in the present system; the reaction is conducted in environmental friendly water.

Besides the above catalytic studies, we have also investigated the epoxidation reaction of cyclooctene using polymer anchored copper catalyst. Thus the epoxidation of cyclooctene catalyzed by polymer anchored copper catalyst was first optimized and the results are summarized in Table 4. The catalyst is very effective for the epoxidation of cyclooctene in water with TBHP as the oxidant. The oxidation of cyclooctene proceeded smoothly at 60 °C yielding to 92% conversion within 8 h with 10 mmol of TBHP. The corresponding diol was formed as a by-product. Among the screening of various solvents, it appears that water is the best choice as compared to the others because it is polar and has high dielectric constant. We investigated the ability of various oxidants like TBHP, NaIO₄, PhIO and NaOCI (Table 4, Entries 1–4). Among them TBHP was more effective

Table 2

Olefins oxidation using TBHP catalyzed by polymer anchored Cu(II) catalyst.^a

Entry	y Substrate	Conversion(%) ^b	Product (selectivity %)	TOF (h^{-1})
1	Cyclohexene	83	2-Cyclohexene-1-one (64) 2-cyclohexene-1-ol (29) Cyclohexene epoxide (7)	49.40
2	trans-Stilbene	67	Benzaldehyde (78) Benzil (16) <i>trans</i> -Stilbene oxide (6)	39.88)
3	α -Pinene	48	Verbenol (32) Verbenone (55) α -pinene oxide (13)	28.57
4	4-Methylstyrene	84	4-Methyl benzaldehyde (84) 4-Methylstyrene epoxide (16)	50.00
5	4-Chlorostyrene	85	4-Chloro benzaldehyde (86) 4-Chlorostyrene epoxide (14)	50.59
6	4-Nitrostyrene	82	4-Nitro benzaldehyde (83) 4-Nitro styrene oxide (17)	48.81
7	α -Methyl styrene	79	Acetophenone (100)	47.02

 a Reaction conditions: catalyst (0.03 g, 1.05×10^{-2} mmol), substrate (5 mmol), water (5 mL), TBHP (10 mmol), time (8 h).

^b Determined by GC.

Table 3

Oxidation of styrene with TBHP catalyzed by a variety of catalysts.

Catalyst	Reaction condition	Conversion (%)	Reference
Polymer anchored Cu(II) catalyst	Water, 60 °C, 8 h	96	This study
CuCl ₁₆ Pc-MCM-41	ACN, 40 °C, 8 h	47	28
$[Cu(2,2-bipy)(H2btec)]\alpha$	1,2-Dichloroethane, 75 °C, 24 h	23.7	29
HMS-Cu-I	ACN, 60 °C, 12 h	89.4	30
$\begin{array}{l} [Cu_2L(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3) \\ (\mu_{1,1,1}\text{-}N_3)]/\ silica \end{array}$	ACN, 60 °C, 24 h	88	31

compared to others oxidants. Experiments were also carried out to determine the effects of substrate to oxidant molar ratios on conversion. For these experiments, cyclooctene and catalyst amounts were held constant in water at 60 °C while the relative amounts of TBHP were varied. As shown in Fig. 3, the conversion increases with TBHP concentration and 1: 2 molar ratio of cyclooctene to TBHP was optimal for the epoxidation reaction. Mechanistic pathway for the formation of epoxide can be explained by the similar type mechanism [37]. Here, peroxide replaced chloride from the metal complex and formed peroxy linked copper complex. This peroxy linked copper complex reacts with alkenes and formed an active intermediate. Then peroxide attacked the active metal site and released epoxide.

Several excellent catalysts for the oxidation of alcohols to the corresponding aldehydes or ketones have been reported; most of them required organic solvents and addition of base, which violate the requirements of the "green chemistry". Water is the most ideal solvent because it is not only a green solvent but also can avoid the hazards associated with the use of oxidizable organic solvents. Base-free systems are also highly desired in that the presence of base probably leads to the unwanted by-products. In line with the requirements of "green chemistry", we chose water as a reaction medium to conduct the oxidation of alcohols in the absence of base.

We examined the catalytic activity of the polymer anchored Cu(II) catalyst for the oxidation of benzyl alcohol by varying the various reaction conditions. The effect of the amount of TBHP on the oxidation of benzyl alcohol into benzaldehyde was studied and the results are shown in Table 5. The percent conversion of benzyl alcohol into benzaldehyde is dependent upon TBHP up to a considerable amount. The amount of TBHP was varied in terms of benzyl alcohol to TBHP molar ratios. Benzyl alcohol to TBHP molar ratio of 1:1 resulted in 61% conversion when the amount of catalyst was 0.050 g, temperature was 50 °C and reaction time was 6 h. When benzyl alcohol to TBHP molar ratio was raised to 1:2, the conversion was increased to 95% under all other similar conditions. However, the conversion was found almost constant when benzyl alcohol to TBHP molar ratio was further increased up to 1:3. Therefore 1:2 molar ratio of benzyl alcohol and TBHP was found to be optimum. The results for the oxidation of benzyl alcohol in the presence of different amounts of catalyst were

Table 4

Effect of various oxidants and solvents on epoxidation of cyclooctene using polymer anchored Cu(II) catalyst.^a

Entry	Oxidant	Solvent	Temperature (°C)	Conversion $(\%)^{b}$	$TOF(h^{-1})$
1	TBHP	H ₂ 0	60	92	54.76
2	NaIO ₄	H_2O	60	49	29.17
3	PhIO	H_2O	60	27	16.07
4	NaOCl	H_2O	60	34	20.24
5	TBHP	Toluene	60	56	33.33
6	TBHP	MeOH	60	65	38.69
7	TBHP	CH_2Cl_2	60	45	26.79
8	TBHP	H_2O	50	78	46.43
9	TBHP	H_2O	40	43	25.59

^a Reaction conditions: catalyst (0.03 g, 1.05×10^{-2} mmol), cyclooctene (5 mmol), solvent (5 mL), oxidant (10 mmol), time (8 h).

^b Determined by GC.



Fig. 3. Influence of the amount of TBHP on epoxidation of cyclooctene. Reaction condition: [cyclooctene] = 5 mmol, TBHP (10 mmol), water (10 ml), temperature (60 °C).

presented in Fig. 4. All the tests were conducted with 5 mmol substrate, 10 mmol TBHP and at 50 °C in 5 mL water under base free condition. 0.02 g polymer anchored catalyst afforded a conversion of 27% within 6 h. No by-products such as benzoic acid were detected under this reaction conditions. When the amount of the catalyst increased up to 0.040 g, the conversion had an apparent increase and a 78% conversion was achieved. But in this condition, a little amount of benzoic acid was detected. A further increase in catalyst amount up to 0.05 g

Table 5			
Oxidation of aromatic alcohols with TBHF	catalyzed polymer a	anchored Cu(II)	catalyst. ^a

Entry	Aromatic alcohol	Conversion (%) ^b	Product selectivity $(\%)^{b}$	TOF (h ⁻ 1)
1 ^c	Benzyl alcohol	61	Benzaldehyde (92)	29.05
2 ^d	Benzyl alcohol	95	Benzoic acid (8) Benzaldehyde (96) Benzoic acid (4)	45.24
3 ^e	Benzyl alcohol	96	Benzaldehyde (71)	45.71
4 ^f	Benzyl alcohol	54	Benzoic acid (29) Benzaldehyde (87) Benzoic acid (13)	25.71
5 ^g	Benzyl alcohol	96	Benzaldehyde (75) Benzoic acid (25)	45.71
6	4-Methoxybenzyl alcohol	84	4-Methoxy benzaldehyde (84)	40.00
			4-Methoxy benzoic acid (16)	
7	4-Methylbenzyl	83	4-Methyl benzaldehyde	39.52
	aconor		(88) 4-Methyl benzoic acid (12)	
8	4-Nitrobenzyl alcohol	80	4-Nitro benzaldehyde (87)	38.09
9	4-Chlorobenzyl alcohol	89	4-Nitro Denzoic acid (13) 4-Chloro benzaldehyde (88)	42.38
10	4-Cynobenzyl alcohol	87	4-Chloro benzoic acid (12) 4-Cyno benzaldehyde (89)	41.43
11	1-Phenyl ethanol	74	4-Cyno benzoic acid (11) Acetophenone (100)	35.24

^a Reaction condition: aromatic alcohol (5 mmol), TBHP (10 mmol), water (5 mL), catalyst (50 mg, 1.75×10^{-2} mmol), temperature (50 °C), time (6 h).

^b Determined by GC.

^c Benzyl alcohol: $H_2O_2 = 1:1$.

^d Benzyl alcohol: $H_2O_2 = 1:2$, temperature (50 °C).

^e Benzyl alcohol:H₂O₂=1:3.
 ^f Temperature (40 °C).

^g Temperature (60 °C).



Fig. 4. Effect of amount of catalyst on oxidation reaction of benzyl alcohol catalyzed by polymer anchored Cu(II) catalyst. Reaction condition: [benzyl alcohol]=5 mmol, TBHP (10 mmol), water (10 ml), temperature (50 °C).

led to an increase in the conversion (95%). However, when the catalyst amount continuously increased up to 0.060 g and 0.070 g, the conversion remains almost constant but the selectivity of benzalde-hyde reduces. These findings indicate that the oxidation of benzyl al-cohol is highly dependent on the amount of the solid catalyst. The influence of temperature on the oxidation of benzyl alcohol was investigated by performing the reaction at a temperature range from 40 to 60 °C with all other parameters fixed. The results are given in Table 5 which reveals that the conversion is dependent on temperature. 54%, 95% and 96% conversion was recorded corresponding to 40, 50 and 60 °C. Therefore, 50 °C was selected as the optimum temperature. At lower temperature, the conversion of benzyl alcohol into benzaldehyde was considerably decreased.

In order to study the further catalytic activity of the catalyst for the oxidation of aromatic alcohols, a series of benzylic alcohols were used. Substituted benzyl alcohols are also oxidized to corresponding aldehydes. In all above cases trace amount of acids were observed. On the otherhand, 1-phenyl ethanol is selectively converted to acetophenone on oxidation with this catalyst.

For any supported catalyst, it is important to know its ease of separation and possible reuse. For the recycling study, oxidation reactions of styrene, cyclooctene and benzyl alcohol were performed maintaining the above reaction conditions using the recovered catalyst. Each time after completion of the reaction catalyst was recovered by simple filtration, washed thoroughly with acetone, dried under vacuum and reused under the same reaction conditions as for the initial run. The recycling efficiency of the catalyst up to five successive runs is shown in Fig. 5. From the results, it is seen that the catalyst retained its high catalytic activity in these five repeating cycles.

To check the leaching of metal into the solution during the reaction, styrene oxidation reaction was carried out under the optimum reaction conditions. The reaction is stopped after the reaction proceeds 6 h. The separated filtrate is allowed to react for another 4 h under the same reaction conditions, but no further increment in conversion is observed in gas chromatographic analyses. The UV–vis spectroscopy was also used to determine the stability of these heterogeneous catalysts. The UV–vis spectra of the reaction solution, at the first run, do not show any absorption peaks characteristic of copper metal, indicating that the leaching of metal does not take place during the course of the oxidation reaction. These results suggest that this catalyst is heterogeneous in nature.



Fig. 5. Recycling efficiency for the oxidation of styrene, cyclooctene and benzyl alcohol with polymer anchored Cu(II) catalyst.

Polymer anchored copper complex has been prepared and used for the catalytic oxidation of olefins and aromatic alcohols with TBHP in aqueous medium. This catalyst shows good catalytic activities toward a wide variety of olefins and excellent yields of allylic oxidation products are obtained in aqueous medium. The procedure in this work offers several advantages for the oxidation of alkenes such as low loading of catalyst, mild conditions in aqueous medium, and high yields, which make it a useful and attractive methodology for organic synthesis. Using this catalyst, cyclooctene converted to epoxide and aromatic alcohols oxidized to corresponding aldehydes. Leaching test indicates that the catalytic reaction is mainly heterogeneous in nature. The simple workup procedure for the recycle of catalyst is also beneficial to this method. Further applications of this catalyst to other transformations are currently under investigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.07.002.

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added. After the reaction, the organic products were separated from the reaction mixture by extraction with dichloromethane (5 mL×2). The combined organic portions were dried and concentrated. Product analysis was performed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector using cyclohexanone as internal standard. All reaction products were identified by using Trace DSQ II GC-MS.

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