Received: 18 October 2014

Revised: 26 November 2014

(wileyonlinelibrary.com) DOI 10.1002/aoc.3266

Accepted: 28 November 2014

Published online in Wiley Online Library

Cu(II)–Schiff base complex-functionalized magnetic Fe₃O₄ nanoparticles: a heterogeneous catalyst for various oxidation reactions

Arash Ghorbani-Choghamarani*, Zahra Darvishnejad and Masoomeh Norouzi

Cu(II)–Schiff base complex-functionalized magnetic Fe_3O_4 nanoparticles were prepared and characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy techniques. This compound acts as a highly active and selective catalyst for the oxidation of sulfides and thiols. These reactions can be carried out in ethanol or solvent-free conditions in the presence of hydrogen peroxide with complete selectivity and very high conversion under mild reaction conditions. The designed catalytic system prevents effectively the over-oxidation of sulfides to sulfones. Separation and recycling can also be easily done using a simple magnetic separation process. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: magnetic Fe₃O₄; nanoparticles; hydrogen peroxide; oxidation; thiol; sulfide

Introduction

In recent years, reactions catalysed by chiral salen-based transition metal complexes have become a matter of interest.^[1] Stable complexes are easily formed with most transition metal ions with different oxidation states. In many cases, metal–salen complexes have been immobilized on different materials, such as polymers^[2] or inorganic solids such as silica^[3] and zeolites.^[4] Interest in them is related to the fact that they perform highly selective processes in a multi-phase system, where the catalysts can be easily recovered.^[5]

In this regard, magnetic nanoparticle-supported catalysts have been efficiently employed as heterogeneous catalysts. The main advantage of a catalytic system based on magnetic nanoparticles is that the nanoparticles can be efficiently isolated from the product solution through a simple magnetic separation process after completion of the reactions.^[6] Additionally, magnetic nanoparticle-supported catalysts also show high dispersion and reactivity with a high degree of chemical stability. Because of these advantages of magnetic nanoparticles over other supporting materials, various catalysts and ligands have been immobilized on these particles.^[7]

So, magnetic catalytic systems have been introduced as very powerful, clean, recoverable supports for a variety of catalytic reactions. The use of nanoparticles as catalyst support has some disadvantages. One of them is their highly active surface which leads to the agglomeration of the catalyst particles. Coating the catalyst surface with an organic or an inorganic shell is an appropriate strategy to prevent agglomeration.^[8-12]

The selective oxidation of organic molecules is fundamentally vital in life sciences and immensely useful in industry.^[13] Selective oxidation of sulfides to sulfoxides and sulfones under adjusted reaction conditions is an important process in the decontamination of sulfur mustard (a chemical warfare agent)^[14–18] and in the production of organosulfurous compounds of medicinal importance.^[19]

The oxidation reaction of organic sulfides is also of potential use in the decontamination of toxic chemicals and facile electron transfer reactions.^[20,21] Metal–salen complexes (metal = Mn, Cr, Fe, Ru, Co, V and Ti) have been used extensively as efficient homogeneous catalysts for the selective oxidation of organic sulfides and sulfoxides.^[22–28]

Disulfides play interesting roles in both biological (DNA cleavage properties and stabilization of peptides in proteins) and chemical^[29] (protecting groups, vulcanizing agents, and oils for rubber and elastomers) processes. The easy interconversion between thiols and disulfides and the higher stability of the latter mean that disulfides are frequently used as a source for thiols.^[30]

Thiols are among the functional groups which can be easily over-oxidized; therefore, extensive studies have been carried out for their controlled oxidation with molecular oxygen,^[31] peroxide^[32] and metal oxidants.^[33] Methods using iodine/hydrogen iodide,^[34] bromine,^[35] potassium dichromate^[36] and potassium permanganate/copper(II) sulfate^[37] are also known for performing this oxidative transformation.^[38]

Here we report copper(II)-coordinated magnetic nanoparticles as a catalyst for the oxidation of a wide range of organic compounds in the presence of H_2O_2 . The magnetic catalyst could be readily separated from the reaction media by simple magnetic decantation, and could be reused without significant degradation in activity and to minimize environmental damage.

Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

^{*} Correspondence to: Arash Ghorbani-Choghamarani, Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran. E-mail: a. ghorbani@mail.ilam.ac.ir



Scheme 1. Synthesis of Fe_3O_4 -Schiff base of Cu(II).



Figure 1. FT-IR spectra of (a) Fe_3O_4 nanoparticles and (b) $Fe_3O_4\text{--Schiff}$ base of Cu(II).

Experimental

Materials

Chemicals and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and were used without further purification.

Instrumentation

The particle size and morphology were investigated using a JEOL JEM-2010 scanning electron microscopy (SEM) instrument, at an

accelerating voltage of 200 kV. FT-IR measurements were performed using KBr discs with a Thermo IR-100 infrared spectrometer (Nicolet). Thermogravimetric analysis (TGA) curves were recorded using a PL-STA 1500 device (Thermal Sciences).

Preparation of Magnetic Fe₃O₄ Nanoparticles

FeCl₃·6H₂O (5.838 g, 0.0216 mol) and FeCl₂·4H₂O (2.147 g, 0.0108 mol) were dissolved in 100 ml of deionized water in a three-necked flask (250 ml) under nitrogen atmosphere. Thereafter, under rapid mechanical stirring, 10 ml of NH₃ solution (32%) was added into the solution within 30 min. After being rapidly stirred for 30 min, the resultant black dispersion was heated to 80 °C for 30 min. The black precipitate formed was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 80 °C in vacuum.

Preparation of Schiff Base Complex of Metal Ions

The Schiff base was prepared as follows. To a solution of 3aminopropyl(triethoxy)silane (1 mmol, 0.176 g) in 25 ml of ethanol was added a solution of salicylaldehyde (1 mmol, 0.122 g) in ethanol (5 ml) at room temperature. The colour of the reaction solution changed to yellowish, due to imine formation. The

resulting Schiff base ligand, as a bright yellow precipitate, was separated by filtration. This yellow precipitate was collected and was washed with ethanol. The precipitate was dried under vacuum at room temperature. The crude product was recrystallized from ethanol to obtain the pure product.

The Schiff base complex of metal ions was prepared as follows. A solution of the corresponding Schiff base (2 mmol) in ethanol and anhydrous $Cu(NO_3)_2$ (0.178 g, 1 mmol) were mixed at room temperature and allowed to stand for 4 h. A colour change from yellow to light green was observed. Then the complex was filtered and was washed with a large excess of ethanol. The greenish blue precipitate was collected and dried under vacuum at room temperature. Then the product was purified by recrystallization from ethanol affording the pure Schiff base complex.

Preparation of Fe₃O₄-Schiff Base of Cu(II)

The copper(II) complex was prepared by adding an ethanol suspension of magnetic nanoparticles (2 g) to a vigorously stirred



Figure 2. TGA curves of (a) Fe₃O₄ and (b) Fe₃O₄–Schiff base of Cu(II).



Figure 3. SEM images of ${\rm Fe_3O_4-Schiff}$ base of Cu(II) at different magnifications.

Schiff complex of metal ions (1 mmol). The resulting mixture was refluxed for 4 h. The solvent was removed and the resulting solid was dried at 80 °C overnight. The FT-IR spectrum of the catalyst showed the expected bands, including a distinctive band due to C=N stretching.

Catalytic Oxidation of Organic Compounds

Oxidation of sulfides

Cu(II)–Schiff base complex-functionalized magnetic Fe₃O₄ nanoparticles (0.02 mmol) were added to sulfides (1 mmol) under solventfree conditions. Then the mixture was allowed to equilibrate at a reaction temperature of 40 °C. Then H₂O₂ (0.4 ml) added to the

Table 1.	Table 1. Optimization of the amount of Fe_3O_4 -Schiff base of $Cu(II)^a$					
Entry	Catalyst	Yield (%) ^b				
1	0	c				
2	0.005	42				
3	0.01	52				
4	0.015	65				
5	0.02	97				
6	0.03	97				
^a Reaction conditions: methylphenyl sulfide (1 mmol), H_2O_2 (0.4 ml, 1 mmol) and solvent free at 40 °C.						

^cReaction proceeds in the absence of the catalyst.



Scheme 2. Oxidation of sulfides to the corresponding sulfoxides using H_2O_2 catalyzed by Fe_3O_4-Cu(II)-Schiff base complex.

mixture with stirring. The conversion and selectivity were determined using TLC analysis.

Oxidation of thiols

Cu(II)–Schiff base complex-functionalized magnetic Fe₃O₄ nanoparticles (0.01 mmol) were suspended in a solution of a thiol (1 mmol) in ethanol (5 ml). Then H₂O₂ (0.4 ml) added to the reaction mixture .The mixture was stirred at room temperature to achieve pure products.

Results and Discussion

Characterization of Cu(II)–Schiff Base Complex-functionalized Magnetic Fe_3O_4 Nanoparticles

Scheme 1 shows the preparation route of the functionalized Fe_3O_4 nanoparticles. In this scheme, the most probable modes for coordination of Cu to imine-modified magnetic nanoparticles are shown. First, imines are typically prepared by the condensation of primary

Table 2. Oxidation of sulfides to corresponding sulfoxides using Fe_3O_4 -Cu(II)-Schiff base complex ^a						
Entry	Substrate	Product	Time (min)	Yield (%) ^b	M.p. (°C)	Ref.
1	1a	2a	60	98	Oil	[14]
2	1b	2b	35	99	Solid (white)	[14]
3	1c	2c	45	90	Oil	[14]
4	1d	2d	1440	48	66–69	[14]
5	1e	2e	45	90	Oil	[14]
6	1f	2f	20	96	Oil	
7	1g	2g	180	99	127–129	[14]
8	1h	2h	60	93	Oil	[15]
9	1i	2i	45	96	Oil	[15]
10	1j	2j	10	90	Oil	[14]
11	1k	2k	10	97	Oil	[16]

 a Sulfide/Fe $_3O_4-$ Schiff base of Cu(ll)/H $_2O_2$ (1 mmol/0.02 g/0.4 ml). b Isolated yields.



Scheme 3. Oxidative coupling of thiols to the corresponding disulfides using H_2O_2 catalyzed by Fe_3O_4 -Cu(II)-Schiff base complex.

amines and aldehydes. Then, the copper(II) complex is reacted with the magnetic nanoparticles to obtain the amine-modified magnetic nanoparticles. The prepared catalyst was characterized using FT-IR spectroscopy, TGA and SEM.

FT-IR spectra of the Fe₃O₄ nanoparticles and Fe₃O₄–Schiff base of Cu(II) are shown in Figs 1(a) and (b), respectively. The strong absorption at 580 cm⁻¹ is characteristic of the Fe–O stretching vibration but for Fe₃O₄ nanoparticles is at 572 cm⁻¹ as a blue shift, due to the size reduction. The broad feature at 3500–3000 cm⁻¹ for magnetic nanoparticles corresponds to the absorption of –OH stretching of hydroxyl groups. In the spectrum of Fe₃O₄–Schiff base of Cu(II) in Fig. 1(b), the band appearing at 1620 cm⁻¹ is due to imine (mainly ascribed to the C=N stretching band). The spectra display a number of absorption peaks ascribed to 3-aminopropyl(triethoxy)silane. The absorptions at around 1111 and 1001 cm⁻¹ correspond to Si–O stretching vibration. The FT-IR spectra have a broad band at 3394 cm⁻¹, representing bonded –NH₂ groups. The band observed at about 2854–2922 cm⁻¹ can be assigned to the aliphatic C–H group.

TGA was performed and the profiles obtained are exhibited in Fig. 2. The profile of magnetic nanoparticles shows a very small weight loss at about 126 °C owing to the removal of physically adsorbed solvent and surface hydroxyl groups (Fig. 2(a)). In addition, there is a weight loss of about 2.5% for the magnetic nanoparticles in the temperature range between 260 and 355 °C which may be associated with the thermal crystal phase transformation from Fe₃O₄ to γ -Fe₂O₃.

The TGA curve of Fe₃O₄–Schiff base of Cu(II) (Fig. 2(b)) initially shows a very similar weight loss of 4.54% between 80 and 110 °C, which corresponds to removal of water molecules. Fe₃O₄–Schiff base of Cu(II) shows a weight loss of 21.56% between 110 and 480 °C which is similar to the decomposition of organic chemicals.

SEM images of the Fe₃O₄–Cu(II)–Schiff base complex at different magnifications are shown in Fig. 3. Fe₃O₄–Schiff base of Cu(II) exhibits a cluster of aggregated spherical particles with an average size larger than 70–80 nm in diameter. The surface morphology of the supported Schiff base complex of Cu(II) is practically identical to that of supported molecular sieves and is composed of relatively

well-formed, spherical particles having rather uniform coating of organic layers.

Application of Fe_3O_4 -Cu(II)-Schiff Base Complex in Oxidation Reaction

We investigated the catalytic activity of Fe_3O_4 -Schiff base of Cu(II) for oxidation of organic substrates such as sulfides and thiols. First, the reaction parameters such as catalyst amount, kind of solvent and effect of temperature were optimized in the oxidation reaction of sulfides to sulfoxides.

In order to optimize the catalyst amount, various quantities of catalyst were used in the oxidation of methylphenyl sulfide (1 mmol) with H_2O_2 (0.4 ml). For oxidation of methylphenyl sulfide in the absence of catalyst, no formation of product occurs after 60 min (Table 1, entry 1). To improve the yield and optimize the reaction conditions, the same reaction was carried out in the presence of a catalytic amount of Fe₃O₄–Cu(II)–Schiff base complex under similar conditions. Surprisingly, a significant improvement is observed and the yield of methylphenyl sulfoxide is markedly increased to 42% after stirring; the mixture was stirred for only 60 min (Table 1, entry 2). An increase in the quantity of Fe₃O₄–Schiff base of Cu(II) from 0.005 to 0.02 g increases the product yield slightly from 42 to 97% (Table 1, entry 5). Using more than 0.02 g of Fe₃O₄–Schiff base of Cu(II) has less effect on the yield and time of the reaction.

Table 3. Oxidation of thiols to corresponding disulfides using Cu(II)–Schiff base complex-functionalized magnetic Fe_3O_4 nanoparticles ^a						
Entry	Substrate	Product	Time (min)	Yield (%) ^b	M.p. (°C)	Ref.
1	3a	4a	95	99	174–176	[39]
2	3b	4b	10	99	36–38	[38]
3	3c	4c	60	99	56	[39]
4	3d	4d	5	99	161–165	
5	3e	4e	10	53	87–91	[39]
6	3f	4f	10	93.4	Oil	[40]
7	3g	4g	120	98	86–90	[38]
8	3h	4h	10	99	87–89	[40]
9	3i	4i	10	92	Oil	[38]
10	Зј	4j	120	99	278–284	
11	3k	4k	120	99	134–136	[38]

 a Thiol/ Fe $_{3}O_{4}$ -Schiff base of Cu(II)/ H $_{2}O_{2}$ (1 mmol/ 0.01 g/ 0.4 ml). b Isolated yields.



Figure 4. Reuse of the nanocatalyst in the oxidation of 4-methylthiophenol to 1,2-di-*p*-tolyldisulfane.

procedures							
Entry	Substrate	Catalyst	Time (min)	Yield (%) ^a	Ref.		
1	Methylphenyl sulfide	Fe ₃ O ₄ -Cu(II)-Schiff base complex/H ₂ O ₂	60	98	This work		
2	Methylphenyl sulfide	Thiourea dioxide/TBHP	210	93	[42]		
3	Methylphenyl sulfide	Alumina-supported nanoruthenium/H ₂ O ₂	120	92	[28]		
4	Methylphenyl sulfide	2NaBO ₃ ·4H ₂ O(I)/KBr	120	57	[43]		
5	Methylphenyl sulfide	Clay-supported ceric ammonium nitrate (CAN)/O ₂	300	35	[44]		
6	Methylphenyl sulfide	SiO ₂ -W ₂ -Py/H ₂ O ₂	150	90	[45]		
7	4-Methylbenzenethiol	Fe ₃ O ₄ -Cu(II)-Schiff base complex/H ₂ O ₂	10	99	This work		
8	4-Methylbenzenethiol	Nal/H ₂ O ₂	30	99	[37]		
9	4-Methylbenzenethiol	$Fe(NO_3)_3 \cdot 9H_2O/Fe(HSO_4)_3$	40	85	[45]		
10	4-Methylbenzenethiol	$(CH_3)_4 N^+ CrO_3 F^-$	75	82	[46]		
11	4-Methylbenzenethiol	Fe(TPP)CI/UHP	10	91	[47]		
12	4-Methylbenzenethiol	$(C_2H_5)_3NH^+[CrO_3F]^-$	115	84	[48]		
^a lsolated yield.							

Table 4. Comparison of Fe₃O₄-Schiff base of Cu(II)/H₂O₂ for oxidation of methylphenyl sulfide and 4-methylbenzenethiol with previously reported procedures

In order to optimize reaction conditions, methylphenyl sulfide was subjected to oxidation in various solvents but the reaction did not complete after 24 h under these conditions. Eventually, we decided to carry out the oxidation reaction in the absence of solvent (i.e. solvent-free conditions) for all reactions. Interestingly we observe that the oxidation reaction of methylphenyl sulfide completes within 60 min in 97% yield.

In the next step, the influence of temperature on methylphenyl sulfide conversion and product selectivity in the presence Fe₃O₄– Schiff base of Cu(II) (0.02 g) was examined. When the reaction temperature is increased gradually from room temperature to 40 °C, the yield of the reaction increases from 0 to 97% in 60 min.

Oxidation of Sulfides to Sulfoxides

After optimization of the reaction parameters, the wider applicability of the catalyst was tested for oxidation of a variety of substituted aromatic and aliphatic sulfides (Scheme 2). The results are summarized in Table 2. We used several sulfides as substrates for oxidation and obtained corresponding sulfoxides without by-products such as sulfones.

Oxidation of Thiols to Disulfides

In order to investigate and develop the scope and limitation of this oxidizing system we decided to examine the oxidative coupling of thiols to corresponding disulfides (Scheme 3). Oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature with H_2O_2 . Thiols are easily oxidized to produce disulfides in ethanol solvent (Table 3). After reaction completion, the product is extracted by simple filtration and dichloromethane is removed by evaporation.

Reuse of Cu(II)–Schiff Base Complex-functionalized Magnetic Fe₃O₄ Nanoparticles

Subsequently, the recyclability of the Fe₃O₄–Schiff base of Cu(II) was investigated for the oxidation of 4-methylthiophenol to 1,2-di-*p*-tolyldisulfane. The catalytic system could be reused directly for the next cycle after full extraction of the product with 5 ml of CH₂Cl₂ per extraction and drying in vacuum. The results shown in Fig. 4 demonstrate that this oxidative system is readily recyclable for ten runs without any significant loss of catalytic activity.

In order to investigate the efficiency of this procedure in comparison with known methods reported in the literature, the results for the preparation of (methylsulfinyl)benzene (Table 4, entries 1–6) and 1,2-di-*p*-tolyldisulfane (entries 7–12), as representative examples, are compared with the best of well-known data from the literature.

Conclusions

Fe₃O₄–Schiff base of Cu(II) can function as a heterogeneous oxidation catalyst with H_2O_2 for oxidation of organic compounds. The large surface area of the magnetic nanoparticles makes Fe₃O₄–Schiff base of Cu(II) a good catalyst. Due to its operational simplicity, generality and efficacy, this material is applicable to the oxidation of a variety of organic compounds. It is important to mention that the morphology of Fe₃O₄–Schiff base of Cu(II) does not change after is use in oxidation reactions which is a key factor for its reusable property. The main advantage of a catalytic system based on magnetic nanoparticles is that it can be efficiently isolated from the product solution through a simple magnetic separation process after completion of the reactions.

References

- [1] V. Ayala, A. Corma, M. Iglesias, F. Sánchez, J. Mol. Catal. A 2004, 221, 201.
- [2] P. Piaggio, P. McHorn, D. Murphy, D. Bethell, P. C. Bulman Page, F. E. Hancock, C. Sly, O. J. Kerton, G. J. Hutchings, J. Chem. Soc. Perkin Trans. 2 2000, 2008.
- [3] L. Canali, E. Cowan, H. Deleuze, C. L. Gibson, D. C. Sherrington, J. Chem. Soc. Perkin Trans. 1 2000, 2055.
- [4] E. F. Murphy, L. Schmid, T. Bürgi, M. Maciejewski, A. Baiker, D. Günther, M. Schneider, *Chem. Mater.* 2001, 13, 1296.
- [5] E. Möllmann, P. Tomlinson, W. F. Hölderich, J. Mol. Catal. 2003, 206, 253.
- [6] M. Kooti, M. Afshar, *Mater. Res. Bull.* **2012**, *47*, 3473.
- [7] G. Chouhan, D. Wang, H. Alper, Chem. Commun. 2007, 4809.
- [8] H. Yoon, S. Ko, J. Jang, Chem. Commun. 2007, 1468.
- [9] H. H. Yang, S. Q. Zhang, X. L. Chen, Z. X. Zhuang, J. G. Xu, X. R. Wang, Anal. Chem. 2004, 76, 1316.
- [10] D. Lee, J. Lee, H. Lee, S. Jin, T. Hyeon, B. M. Kim, Adv. Synth. Catal. 2006, 348, 41.
- [11] C. Ó. Dálaigh, S. A. Corr, Y. Gun'ko, S. J. Connon, Angew. Chem. Int. Ed. 2007, 46, 4329.
- [12] M. Sheykhan, L. Ma'mani, A. Ebrahimi, A. Heydari, J. Mol. Catal. A 2011, 335, 253.
- [13] A. Rezaeifard, M. Jafarpour, H. Raissi, E. Ghiamati, A. Tootoonchi, Polyhedron 2011, 30, 592.

- [14] G. W. Wagner, Y. C. Yang, Ind. Eng. Chem. Res. 2002, 41, 1925.
- [15] Y. C. Yang, L. L. Szafraniee, W. T. Beaudry, D. K. Rohrbaugh, J. Am. Chem. Soc. 1990, 112, 6621.
- [16] Y. C. Yang, L. L. Szafraniee, W. T. Beaudry, J. Org. Chem. 1993, 58, 6964.
- [17] Y. C. Yang, J. A. Baker, J. R. Ward, Chem. Rev. 1992, 92, 1729.
- [18] E. Raber, R. McGuire, J. Hazard. Mater. **2002**, *93*, 339.
- [19] S. Caron, R. W. Dugger, S. G. Roggeri, J. A. Ragan, D. H. B. Ripin, Chem. Rev. 2006, 106, 2943.
- [20] S. Balakumar, P. Thanasekaran, E. Rajkumar, K. John Adaikalasamy, S. Rajagopal, R. Ramaraj, T. Rajendran, B. Manimaran, K. L. Lu, Org. Biomol. Chem. 2006, 4, 352.
- [21] E. Rajkumar, S. Rajagopal, Photochem. Photobiol. Sci. 2008, 7, 1407.
- [22] A. Chellamani, P. Kulanthaipandi, S. Rajagopal, *J. Org. Chem.* **1999**, *64*, 2232.
- [23] R. Sevvel, S. Rajagopal, C. Srinivasan, N. M. I. Alhaji, A. Chellamani, J. Org. Chem. 2000, 65, 3334.
- [24] V. K. Sivasubramanian, M. Ganesan, S. Rajagopal, R. Ramaraj, J. Org. Chem. 2002, 67, 1506.
- [25] N. S. Venkataramanan, S. Premsingh, S. Rajagopal, K. Pitchumani, J. Org. Chem. 2003, 68, 7460.
- [26] N. S. Venkatramanan, G. Kuppuraj, S. Rajagopal, Coord. Chem. Rev. 2005, 249, 1249.
- [27] M. I. Jeyaseeli, S. Rajagopal, J. Mol. Catal. A 2009, 309, 103.
- [28] P. Veerakumar, Z. Lu, M. Velayudham, K. L. Lu, S. Rajagopal, J. Mol. Catal. A 2010, 332, 128.
- [29] B. D. Palmer, G. W. Newcastle, A. M. Thompson, M. Boyd, H. D. H. Showalter, A. D. Sercel, D. W. Fry, A. J. Kraker, W. A. Dennyyrosine, J. Med. Chem. 1995, 38, 58.

- [30] J. L. Ruano, A. Parra, J. Alemán, Green Chem. 2008, 10, 706.
- [31] M. Arisawa, C. Sugata, M. Yamaguchi, *Tetrahedron Lett.* 2005, 46, 6907.
- [32] V. Kesavan, D. Bonnet-Delpon, J. P. Bégué, Synthesis 2000, 2, 223.
- [33] T. J. Wallace, J. Org. Chem. **1966**, 31, 1217.
- [34] A. McKillop, D. Koyuncu, Tetrahedron Lett. 1990, 31, 5007.
- [35] J. B. Arterburn, M. C. Perry, S. L. Nelson, B. R. Dible, M. S. Holguin, J. Am. Chem. Soc. 1997, 119, 9309.
- [36] D. I. Relyea, P. O. Tawney, A. R. Williams, J. Org. Chem. 1962, 27, 477.
- [37] M. Kirihara, Y. Asai, S. Ogawa, T. Noguchi, A. Hatano, Y. Hiraib, *Synthesis* 2007, 21, 3286.
- [38] M. H. Ali, M. McDermott, Tetrahedron Lett. 2002, 43, 6271.
- [39] S. Patel, B. K. Mishra, *Tetrahedron Lett.* **2004**, 45, 32.
- [40] A. Shaabani, D. J. Lee, Tetrahedron Lett. 2001, 42, 5833.
- [41] S. Kumar, S. Verma, S. L. Jain, B. Sain, Tetrahedron Lett. 2011, 52, 3393.
- [42] D. Habibi, M. A. Zolfigol, M. Safaiee, A. Shamsian, A. Ghorbani-Choghamarani, *Catal. Commun.* **2009**, *10*, 1257.
- [43] A. Dhakshinamoorthy, K. Pitchumani, *Catal. Commun.* **2009**, *10*, 872.
- [44] S. Xian-Ying, W. Jun-Fa, J. Mol. Catal. A 2008, 280, 142.
- [45] F. Shirini, M. A. Zolfigol, A. R. Abri, Chin. Chem. Lett. 2008, 19, 51.
- [46] H. Imanieh, S. Ghamami, M. K. Mohammadi, A. Jangjoo, Russ. J. Gen. Chem. 2007, 77, 282.
- [47] B. Karami, M. Montazerozohori, M. Moghadam, M. H. Habibi, *Turk. J. Chem.* 2005, 29, 539.
- [48] S. Ghammamy, M. K. Mohammadi, A. H. Joshaghani, Maced. J. Chem. Chem. Eng. 2008, 27, 117.