DOI: 10.1002/aoc.3769

FULL PAPER



Copper immobilized on magnetite nanoparticles coated with ascorbic acid: An efficient and reusable catalyst for C—N and C—O cross-coupling reactions

Abdol R. Hajipour^{1,2} 🕞 | Maryam Check¹ | Zahra Khorsandi¹

¹Department of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran

² Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, Wisconsin 53706-1532, U.S.A.

Correspondence

Abdol R. Hajipour, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran. Email: haji@cc.iut.ac.ir

Funding Information

Isfahan University of Technology (IUT); Center of Excellence in Sensor and Green Chemistry Research

1 | INTRODUCTION

The performance organic reactions in water as the most inexpensive and versatile solvent is now of great interest.^[1] Moreover, water is regarded as one of the most suitable solvents from an environmental point of view due to lack of inflammable, explosive, mutagenic and carcinogenic properties; therefore, using it as a solvent in organic synthesis is very desirable for chemists.

Some of the most powerful organometallic transformations for the synthesis of various organic molecules are transition metal-catalyzed C—O and C—N cross-coupling reactions.^[2–8] The nitrogen-containing compounds and biphenyl ethers so obtained have many applications in agrochemical research, coordination and biological chemistry;^[9–11] in addition, these compounds have potential clinical applications as antitumor, antifungal and anti-inflammatory agents.^[12–16]

Principal methods for the synthesis of aniline derivatives are Ullmann,^[17–19] Chan–Lam^[20] and Buchwald– Hartwig^[21–23] cross-coupling reactions, and considerable efforts have been made to find new efficient and green

In a continuation of using magnetic nanoparticle (MNP)-supported catalysts, ascorbic acid (readily available, very safe and with strong affinity to MNPs) was used instead of the commonly used silica layer coating. This hybrid was used for immobilizing copper nanoparticles to produce Cu/ascorbic acid@MNPs catalyst. The catalyst was characterized and used in carbon–oxygen and carbon–nitrogen (various substrates) cross-coupling reactions in aqueous media and at room temperature with excellent product yields. Furthermore, the catalyst could be quickly and completely recovered using an external magnetic field and reused for six reaction cycles without significant change in catalytic activity.

KEYWORDS

ascorbic acid, C-N and C-O coupling, magnetic nanoparticles, room temperature conditions

catalytic systems and methodologies to improve these reactions. In this respect, various metal catalysts such as palladium,^[24] nickel^[25,26] and copper^[27–32] are employed along with a variety of coordinating ligands such as proazaphosphatranes,^[33,34] phosphanes,^[35–38] N-heterocyclic carbenes,^[39–41] chelating bisphosphanes^[42,43] and N- or O-heteroatom-functionalized ligands.^[44–49] Despite successful use of these catalysts and ligands which provide good results, they have some disadvantages such as cost, toxicity, non-recoverablity and sensitively to air and moisture. One way to overcome these problems is the immobilization of metal catalysts on various solid supports.

There are several accounts in the literature of the synthesis, characterization and applications of heterogeneous copper catalysts utilized in coupling reactions;^[50–53] however, most of the catalytic systems cause high metal contamination of the final products and require nitrogen atmosphere and prolonged reaction times. Therefore the development of new approaches taking into consideration short reaction time, minimum metal pollution of products, simple reaction conditions, easy isolation of products and catalysts, and

2 of 9 WILEY-Organometallic Chemistry

renewability of catalysts is highly desirable. Use of nano-supports for the generation heterogeneous copper catalysts, such as magnetic nanoparticles (MNPs), has attracted considerable interest due to their high activity and environmental acceptability^[54–57]; but the preparation of most reported catalysts seems rather laborious and time-consuming.

Currently, magnetic separation provides a very useful method for removing MNPs with an external magnet.^[58–64] Furthermore, MNP-supported catalysts also demonstrate high dispersion and reactivity with a high degree of chemical stability, but magnetostatic interactions between particles make them susceptible to agglomeration. In order to prevent this aggregation, the surface of the MNPs is usually modified with a suitable coating such as a silica layer.

Development of effective and practical catalytic methods, which have economic and 'greener' aspects, has been a topic of much interest in recent years. Learning from nature, employing biomolecules is highly favorable in chemical transformations. In the work reported herein, ascorbic acid (vitamin C) was found as a particularly useful molecule for coating of MNPs, since it is readily available, very safe and has a strong affinity to MNPs. Furthermore, the hydrocarbon tails containing hydroxyl groups which are obtained from reaction of ascorbic acid and MNPs can help to stabilize transition metal catalysts and also prevent them from aggregation.

In continuation of our recent investigations of the application of heterogeneous catalytic systems in cross-coupling reactions,^[65–69] in this paper we report a new strategy for C–O and C–N cross-coupling reactions of aryl halides (including aryl chlorides) and aliphatic/aromatic amines and alcohols using the very safe, efficient and ecofriendly ascorbic acid which is tagged on an MNP scaffold-based copper (I) catalyst (Cu/ascorbic acid@MNPs).

2 | **RESULTS AND DISCUSSION**

The catalyst was prepared following a straightforward and green procedure. This is described in Scheme 1.

The produced catalyst, unsupported ascorbic acid and iron oxide MNPs were characterized using Fourier transform infrared (FT-IR) spectroscopy (Figure 1). In the spectra, the broad bands near 3442 and 558 cm⁻¹ in Figure 1(a) correspond to OH and Fe–O (stretch vibrations); the absorption bands at 577 cm⁻¹ are also attributed to Fe–O stretch vibrations which confirms the existence of Fe₃O₄ (Figure 1c).^[70] Moreover, the characteristic peaks in Figure 1(c) at around 1650 and 1000–1300 cm⁻¹ can be assigned to the C=O and C–O stretch vibrations, respectively, which relate to the ligand.

The field emission scanning electron microscopy (SEM) images in Figure 2 demonstrate the phase morphology of Cu/ascorbic acid@MNPs.

Transmission electron microscopy (TEM) images are shown in Figure 3, indicating that copper immobilized on the MNPs does not aggregate. It can be observed that the MNPs are spherical in shape and are completely monodispersed. All these observations also show that the opened-ring ascorbic acid is a good host and ligand for copper nanoparticles. The average size of the MNPs is about 8– 15 nm.

Figure 4 shows the magnetization curves of the catalyst. The saturation magnetization for Fe₃O₄ is equal to 69.4 emu g⁻¹ and the magnetization value of Cu/ascorbic acid@MNPs is 18.5 emu g⁻¹. This investigation proves the paramagnetic behavior of the catalyst. Due to the coating of MNPs with the organic compound, M_s is considerably lower than that of the bulk magnetite.

The Cu loading of the catalyst was measured using inductively coupled plasma (ICP) analysis and it was 3.12% (0.52 mmol g⁻¹). The crystalline structure of catalyst was investigated using X-ray diffraction (XRD). As shown in Figure 5, the characteristic peaks of Fe₃O₄ appear at $2\theta = 30^{\circ}$, 35° , 43° , 53° , 57° and 63° . For CuCl the most intense peak is seen at $2\theta = 28.45^{\circ}$, and two less intense peaks also appear at 47.44° and 56.27° .

The thermal stability of the catalyst was also evaluated using thermogravimetric analysis (TGA), and the thermogram is shown in Figure 6. According to this curve, the weight loss below 200 °C is 4% which corresponds to the removal of physically adsorbed water. The main weight loss in the second step is a result of removal of organic moieties. These results indicate that the catalyst has high thermal stability below 200 °C and can be attributed to the formation



SCHEME 1 Preparation of Cu/ascorbic acid@MNPs



FIGURE 1 FT-IR spectra of (a) MNPs, (b) ascorbic acid and (c) Cu/ ascorbic acid@MNPs



FIGURE 2 Field-emission SEM images of Cu/ascorbic acid@MNPs

of a stable copper complex. The degree of functionalization on the MNPs could be calculated from the weight loss between 200 and 800 $^{\circ}$ C of TGA and elemental analysis.

Applied Organometallic-Chemistry 200nm 100nm 60nm 40nm

3 of 9

FIGURE 3 TEM images of Cu/ascorbic acid@MNPs

The observed total weight loss for the catalyst is 45.1%; on the basis of this value, the amount of organic moieties is about 2.42 mmol g^{-1} of catalyst.

The covalent anchoring of ligand and metal was confirmed using X-ray photoelectron spectroscopy (XPS). The peaks at 284.5 and 933 eV are attributed to C and Cu(I). The peaks corresponding to oxygen, carbon, nitrogen, iron



FIGURE 4 Room temperature magnetization curves of Cu/ascorbic acid@MNPs



FIGURE 5 XRD pattern of Cu/ascorbic acid@MNPs catalyst



FIGURE 6 TGA curve of Cu/ascorbic acid@MNPs

and copper are clearly observed in the XPS elemental survey of the catalyst (supporting information S1).

The catalytic activity of Cu/ascorbic acid@MNPs was investigated in C–N and C–O cross-coupling reactions. Initially, the reaction of iodobenzene and aniline was selected as a model reaction (Table 1). The activity of the catalyst was studied with variation of several factors including base, solvent, temperature and catalyst loading. Among the various bases, KOH is found to be the most effective base. Then, the same reaction was carried out in different solvents. According to the optimization results and the essential goal of green chemistry, water is the best one. The effects of the amount of catalyst and reaction temperature on the model reaction were also explored. The best result is obtained using 5 mg of catalyst (0.002 mol% Cu) at room temperature.

With the optimized conditions in hand, the substrate scope of the amination of aryl halides was studied (Table 2). The results indicate that a wide range of activated and inactivated aryl iodides, bromides and even chlorides work well. In principle, regardless of the exact mechanism of the reaction, catalytic activity in nanocatalysis is determined by the size of the nanoparticles. The smaller the nanoparticles are, the more effective the catalytic activity. The high activities of Cu/ascorbic acid@MNPs can be related to the good dispersion and small size of the copper nanoparticles.

To extend the substrate scope, the reactions of benzylamine and various aryl halides were also investigated under same conditions, the desired products being formed in good to excellent yields (Table 3).

Also, *N*-arylation of aryl halides with imidazole is also effective and can provide high yields of coupling products (Table 4). The scope and generality of the reaction was also evaluated by employing various aryl halides and butylamine and 1,2- and 1,3-diamines. The results are summarized in Table 5. The reaction of aryl bromide and iodide with various 1,2- and 1,3-diamines and butylamine can be performed using our catalyst (Table 5).

In continuation, the scope of the process was explored in C–O coupling reaction using phenol (Table 6). Phenol is found to be reactive with iodo- and bromobenzene and produces the desired products in considerable yields.

Gratifyingly, this heterogeneous catalyst system exhibits high activity in C—O (Table 6).and multiple C—N coupling reactions including anilines (Table 2) benzylamine (Table 3) imidazole (Table 4).and aliphatic amines (Table 5) as substrates, which provide moderate to excellent yields of corresponding products.

A diversity of aryl iodides, bromides and chlorides containing electron-donating and electron-withdrawing substituents react efficiently with amines and phenols at room temperature without protection of inert atmosphere. The experimental results show that the electronic properties of the substituents on the aromatic rings of the starting materials have no significant effect on the reaction; however, aryl iodides are found to be more reactive than aryl bromides and aryl chlorides. Among aryl halides, aryl chlorides are ideal substrates for coupling reactions because they are inexpensive and widely available in comparison to their bromide or iodide counterparts. The first step in catalytic coupling reactions (oxidative addition) disfavors aryl chloride substrates because of the high strength of the C-Cl bond. Most reported methods require high loadings of palladium or copper catalyst and harsh reaction

TABLE 1 Optimization of reaction conditions^a

ĺ	+ H ₂ N		u/AA@MNI base, solve	Ps mt □	
Entry	Catalyst (mg)	Base	Solvent	<i>T</i> (°C)/ <i>t</i> (h)	Yield (%) ^b
1	5	КОН	DMF	120/2	98
2	5	KOH	DMF	80/3	95
3	5	КОН	H_2O	80/3	90
4	5	K_3PO_4	H_2O	80/3	73
5	5	K_2CO_3	H_2O	80/3	71
6	5	KOH	H_2O	60/4	90
7	5	КОН	H_2O	r.t./6	96
8	5	K_2CO_3	H_2O	r.t./6	65
9	5	None	H_2O	r.t./6	Trace
10	1	KOH	H_2O	r.t./6	62
11	10	КОН	H_2O	r.t./6	98
12	5	KOH	PEG	r.t./8	82
13	5	КОН	DMSO	r.t./6	49
14	5	КОН	None	r.t./6	34

^aReaction conditions: iodobenzene (1 mmol), aniline (1 mmol), catalyst (5 mg = 0.002 mol% Cu), KOH (3 mmol), H₂O (1.5 ml).

TABLE 2 C-N reaction of various aryl halides with aniline^a

^bGC yield.

R +	H ₂ N	Cu/AA@MNPs (5 mg) KOH, H ₂ O, r.t.	R
Entry	Х	R	Yield (%) ^b
1	Ι	Н	96
2	Ι	4-OMe	95
3	Br	Н	90
4	Br	4-OMe	83
5	Br	4-NO ₂	76
6	Br	2-NO ₂	78
7	Br	4-Cho	71
8	Br	4-COMe	76
9	Br	4-Br	94
10	Cl	Н	52
11	Cl	4-NO ₂	61
12	Cl	4-COMe	49

^aReaction conditions: aryl halide (1 mmol), aniline (1.5 mmol), KOH (3 equiv.), water (3 ml) and room temperature for 6 h.

^bIsolated yield.

TABLE 3 C-N reaction of various aryl halides with benzylamine^a

pplied

Organometallic Chemistry 5 of 9

R	H ₂ N +	Cu/AA@MNPs (5 mg) KOH, H ₂ O, r.t.	R R R R R R R R R R R R R R R R R R R
Entry	Х	R	Yield (%) ^b
1	Ι	Н	97
2	Ι	4-OMe	93
3	Br	Н	87
4	Br	4-OMe	84
5	Br	4-NO ₂	89
6	Br	2-NO ₂	92
7	Br	4-Br	89
8	Br	4-Cho	41
9	Br	4-COMe	94
10	Cl	Н	67
11	Cl	4-NO ₂	51
12	Cl	4-COMe	43

^aReaction conditions: aryl halide (1 mmol), benzylamine (1.5 mmol), KOH (3 equiv.), water (3 ml) and room temperature for 6 h. ^bIsolated yield.

TABLE 4 C-N reaction of various aryl halides with imidazole^a

R +		u/AA@MNPs (5 mg) KOH, H ₂ O, r.t.	N.ZN
Entry	X	Aryl halide	Yield (%) ^b
1	Ι	Н	97
2	Ι	4-OMe	92
3	Br	Н	71
4	Br	4-OMe	68
5	Br	4-NO ₂	75
6	Br	2-NO ₂	83
7	Br	4-Br	77
8	Br	4-Cho	66
9	Cl	Н	59
10	Cl	4-COMe	40

^aReaction conditions: aryl halide (1 mmol), imidazole (1.5 mmol), KOH (3 equiv.), water (3 ml) and room temperature for 6 h.

^bIsolated yield.

conditions. Herein, C–N coupling of the less reactive aryl chlorides gives good yields as evidenced from the results in Tables 2–4.

In general, for the catalytic cycle of the C-N crosscoupling reaction using Cu/ascorbic acid@MNPs, the

TABLE 5 C-N reaction of aryl halides with aliphatic amines^a

R	+ NH ₂ -R	Cu/AA@MNPs (5 mg) KOH, H ₂ O, r.t.	R NHR
Entry	X	Alkylamine	Yield (%) ^b
1	Ι	H ₂ N	92
2	Ι	H ₂ N ^{NH} 2	93
3	Ι	H_2N NH_2	93
4	Br	H ₂ N	90
5	Br	H ₂ N NH ₂	84
6	Br	$H_2N^{NH_2}$	88

^aReaction conditions: aryl halide (1 mmol), aliphatic amine (1.5 mmol), KOH (3 equiv.), water (3 ml) and room temperature for 6 h. ^bIsolated yield.

TABLE 6 C-O reaction of various aryl halides with phenol^a

R +	HO	Cu/AA@MNPs (5 mg) KOH, H₂O, r.t.	
Entry	Х	R	Yield (%) ^b
1	Ι	Н	97
2	Ι	4-OMe	94
3	Br	Н	81
4	Br	4-OMe	94
5	Br	4-NO ₂	91
6	Br	2-NO ₂	95
7	Br	4-Br	81
8	Br	4-Cho	93
9	Br	4-COMe	67

^aReaction conditions: aryl halide (1 mmol), phenol (1.5 mmol), KOH (3 equiv.), water (3 ml) and room temperature for 12 h.

^bIsolated yield.

reaction may occur via oxidative addition and then reductive elimination providing the C–N cross-coupled product followed by removal of hydrogen halide with base.

The separation and reusability of noble metal catalysts are trends of the catalysis industry and green chemistry, not only for lowering costs, but also for avoiding pollution. To gain an insight into this issue, catalyst reusability experiments in the reaction of iodobenzene with aniline were carried out. After each cycle, the recovered catalyst was washed with diethyl ether and ethanol to remove any organic materials and acidic solution. The recovery of our catalyst can be easily achieved using a magnetic bar and the catalyst was successfully reused at least six times without any significant loss of activity (Table 7). The recovered catalyst was analyzed using FT-IR spectroscopy and no marked changes are observed in the catalyst structure (Figure 7).

Leaching of metal ions is a serious problem for supported metal catalysts and prevents catalyst separation and recycling. To this end, the reaction between iodobenzene and aniline was carried out simultaneously in two different vessels under exactly the same conditions. In each case, the reaction progress was monitored using GC. After 2 h the catalyst was separated from one of these vessels using a magnetic bar, while the other remained unchanged. Thereafter, both of the reactions were continued under the same conditions. After another 2 h, both the reactions were stopped and their completion was again examined using GC. The results showed that the reaction in the absence of the catalyst no longer proceeded, while completion of the reaction in the other vessel was improved. This observation confirmed that no leaching was occurring in the reaction medium during the

TABLE 7 Reusability of catalyst

Run	Yield (%) ^a	Run	Yield (%) ^a
1	96	4	81
2	95	5	75
3	87	6	73

^aIsolated yield.



FIGURE 7 FT-IR spectra of fresh catalyst and catalyst recovered after six runs

process. The copper content of the recovered catalyst was also determined after reaction using ICP analysis and the results showed that only a very small amount (about 1%) of copper metal was removed from the catalyst. In fact, the leaching phenomenon that often is seen in heterogeneous catalytic systems does not occur here, perhaps because of the specific nature of the ligand. Therefore, it is concluded that the ascorbic acid-modified MNP support plays an essential stabilizing role for the supported catalyst in these coupling reactions. It should be noted that, to the best of our knowledge, this is the first demonstration of the combination of copper(I) chloride nanoparticles onto MNPs coated with ascorbic acid to generate an efficient and recyclable green catalytic system.

3 | CONCLUSIONS

We have demonstrated the synthesis of a new and powerful magnetic nanocatalyst which was employed in C–N and C–O coupling reactions in aqueous media and at room temperature. Excellent yields were achieved in relatively short reaction times for a wide range of iodo-, bromo- and chloro-arenes bearing both electron-donating and electron-withdrawing groups. Marked advantages, such as palladium- and phosphorus-free catalyst, the use of an ecofriendly support and green solvent, provide the method with great benefits in terms of safety, economy and sustainability.

4 | EXPERIMENTAL

4.1 | General

¹H NMR and ¹³C NMR spectra were obtained with a Bruker Avance 400 MHz spectrometer in CDCl₃. FT-IR spectra were recorded with a Jasco 680 (Japan) spectrophotometer using KBr pellets. The saturation magnetization (M_s) of the samples was measured with a vibrating sample magnetometer (Megh-natis Daghigh Kavir Co). XRD patterns were measured with a Philips X'pert powder X-ray diffractometer. The samples were scanned in the 2θ range of 0–100°. The metal content of the complex was measured using ICP analysis (Varian Vista-mpx). The TGA curve was obtained with a heating rate of 10 °C min⁻¹ using an STA503 win TA (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany). SEM images were obtained using a Philips XL20 microscope. TEM images were obtained using an EM208S microscope with an accelerating voltage of 100 kV.

4.2 | Catalyst preparation

The MNPs were prepared according to the literature^[71] based on precipitation of magnetite nanoparticles from a

Applied WILEY-Organometallic-7 of 9 Chemistry

mixture of iron(III) chloride and iron(II) sulfate by ammonia (25% solution in water). The MNP suspended in deionized water were reacted with 3 g of ascorbic acid. After mixing for 25 min, the black precipitates were collected with the help of a magnet. The collected ascorbic acid@MNPs were washed repeatedly with ethanol and dried under vacuum conditions for 7 h at 60 °C. Next, CuCl (1 g) was added to a water solution of ascorbic acid@MNPs and stirred for 5 h. The resulting hybrid was collected using an external permanent magnet and washed with ethanol (3 × 10 ml) to remove the unreacted CuCl, and finally dried under air (89% yield upon Cu consumption determined by ICP analysis).

4.3 | General procedure for coupling of aryl halides with amines

In a round-bottomed flask equipped with a magnetic stirrer, aryl halide (1 mmol), amine (1.5 mmol), catalyst (5 mg, 0.002 mol% Cu) and KOH (3 mmol) were stirred in water (3 ml) under air atmosphere at room temperature for 6 h. The progress of the reaction was monitored by TLC (eluent: *n*-hexane–ethyl acetate, 5:1) and GC. After completion of the reaction, CH_2Cl_2 (15 ml) was added and the catalyst was separated using an external magnet. The organic layer was washed with water (3 × 10 ml) and dried over anhydrous MgSO₄. The product was isolated by column chromatography (*n*-hexane–ethyl acetate, 5:1) to afford the corresponding products. The described procedure was applied for all of the amination reactions studied in the work reported in this paper.

4.4 | General procedure for coupling of aryl halides with phenol

In a round-bottomed flask equipped with a magnetic stirrer, aryl halide (1 mmol), phenol (1 mmol), catalyst (5 mg, 0.002 mol% Cu) and KOH (3 mmol) were stirred in water (3 ml) under air atmosphere at room temperature for 12 h. The progress of the reaction was monitored by TLC (eluent: *n*-hexane–ethyl acetate, 5:1) and GC. After completion of the reaction, CH₂Cl₂ (15 ml) was added and the catalyst was separated using an external magnet. The organic layer was washed with water (3 × 10 ml) and dried over anhydrous MgSO₄. The product was isolated by column chromatography (*n*-hexane–ethyl acetate, 5:1) to afford the corresponding products.

The products were characterized by comparing their physical properties, melting points, and FT-IR, ¹H NMR and ¹³C NMR spectra with those found in the literature.^[72–76]

8 of 9 WILEY-Organometallic Chemistry

ACKNOWLEDGMENTS

Financial support from Isfahan University of Technology (IUT), Iran is appreciated. Additional financial support from the Center of Excellence in Sensor and Green Chemistry Research (IUT) is gratefully acknowledged.

REFERENCES

- [1] M. O. Simon, C. J. Li, Chem. Soc. Rev. 2012, 41, 1415.
- [2] Q. Shelby, N. Kataoka, G. Mann, J. F. Hartwig, J. Am. Chem. Soc. 2000, 122, 10718.
- [3] E. Sperotto, G. Klink, J. G. Vries, G. Koten, J. Org. Chem. 2008, 73, 5625.
- [4] B. Sreedhar, R. Arundhathi, P. L. Reddy, M. L. Kantam, J. Org. Chem. 2009, 74, 7951.
- [5] L. Rout, T. K. Sen, T. Punniyamurthy, Angew. Chem. Int. Ed. 2007, 46, 5583.
- [6] A. Correa, M. Carril, C. Bolm, Angew. Chem. Int. Ed. 2008, 47, 2880.
- [7] S. Jammi, P. Barua, L. Rout, P. Saha, T. Punniyamurthy, *Tetrahe*dron Lett. 2008, 49, 1484.
- [8] S. A. Agawane, J. M. Nagarkar, Tetrahedron Lett. 2011, 52, 5220.
- [9] C. Kibayashi, Chem. Pharm. Bull. 2005, 53, 1375.
- [10] J. H. Cheng, K. Kamiya, I. Kodama, *Cardiovasc. Drug Rev.* 2001, 19, 152.
- [11] C. Sanchez, C. Mendez, J. A. Salas, Nat. Prod. Rep. 2006, 23, 1007.
- [12] J. B. Buckingham, *Dictionary of Natural Products*, CRC Press, Boca Raton, FL **1994** 1.
- [13] P. N. Craig, *Comprehensive Medicinal Chemistry*, Pergamon Press, New York **1991** 83.
- [14] C. Fischer, B. Koenig, J. Org. Chem. 2011, 7, 59.
- [15] A. Gangjee, Y. Zeng, T. Talreja, J. J. McGuire, R. L. Kisliuk, S. F. Queener, J. Med. Chem. 2007, 50, 3046.
- [16] N. Jarkas, J. McConathy, R. J. Voll, M. M. Goodman, J. Med. Chem. 2005, 48, 4254.
- [17] H. Zhang, Q. Cai, D. W. Ma, J. Org. Chem. 2005, 70, 5164.
- [18] F. Y. Kwong, A. Klapars, S. L. Buchwald, Org. Lett. 2002, 4, 581.
- [19] D. S. Jiang, H. Fu, Y. Y. Jiang, Y. F. Zhao, J. Org. Chem. 2007, 72, 672.
- [20] T. D. Quach, R. A. Batey, Org. Lett. 2003, 5, 4397.
- [21] J. F. Hartwig, Angew. Chem. Int. Ed. 1998, 37, 2046.
- [22] S. L. Buchwald, C. Mauger, G. Mignani, U. Scholz, Adv. Synth. Catal. 2006, 348, 23.
- [23] A. R. Muci, S. L. Buchwald, Top. Curr. Chem. 2002, 219, 131.
- [24] N. R. Guha, A. K. Shil, D. Sharma, P. Das, *Tetrahedron Lett.* 2012, 53, 5318.
- [25] C. Y. Gao, X. Cao, L. M. Yang, Org. Biomol. Chem. 2009, 7, 3922.
- [26] S. Nagao, T. Matsumoto, Y. Koga, K. Matsubara, *Chem. Lett.* 2011, 40, 1036.
- [27] F. Chen, N. Liu, E. Ji, B. Dai, RSC Adv. 2015, 5, 51512.

- [28] N. Evano, N. Blanchard, M. Toumi, Chem. Rev. 2008, 108, 3054.
- [29] P. L. Reddy, R. Arundhathi, D. S. Rawat, RSC Adv. 2015, 5, 92121.
- [30] M. Nasrollahzadeh, A. R. Vartooni, A. Ehsani, M. Moghadam, J. Mol. Catal. A 2014, 387, 123.
- [31] R. Mostafalu, B. Kaboudin, F. Kazemi, T. Yokomatsu, *RSC Adv.* **2014**, *4*, 49273.
- [32] K. Shimizu, K. Shimura, M. Nishimura, A. Satsuma, RSC Adv. 2011, 1, 1310.
- [33] S. Urgaonkar, J. H. Xu, J. G. Verkade, J. Org. Chem. 2003, 68, 8416.
- [34] C. V. Reddy, J. V. Kingston, J. G. Verkade, J. Org. Chem. 2008, 73, 3047.
- [35] D. S. Surry, S. L. Buchwald, Angew. Chem. Int. Ed. 2008, 47, 6338.
- [36] T. Yamamoto, M. Nishiyama, Y. Koie, *Tetrahedron Lett.* **1998**, *39*, 2367.
- [37] A. Tewari, M. Hein, A. Zapf, M. Beller, *Tetrahedron* 2005, 61, 9705.
- [38] L. L. Hill, L. R. Moore, R. C. Huang, R. Craciun, A. J. Vincent, D. A. Dixon, J. Chou, C. J. Woltermann, K. H. Shaughnessy, J. Org. Chem. 2006, 71, 5117.
- [39] N. Marion, O. Navarro, J. G. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, J. Am. Chem. Soc. 2006, 128, 4101.
- [40] O. Navarro, N. Marion, J. G. Mei, S. P. Nolan, *Chem. Eur. J.* 2006, 12, 5142.
- [41] M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O. Brien, M. Sayah, C. Valente, *Chem. – Eur. J.* 2008, 14, 2443.
- [42] J. F. Hartwig, Acc. Chem. Res. 2008, 41, 1534.
- [43] Q. Shen, T. Ogata, J. F. Hartwig, J. Am. Chem. Soc. 2008, 130, 6586.
- [44] X. Xie, T. Y. Zhang, Z. Zhang, J. Org. Chem. 2006, 71, 6522.
- [45] R. A. Singer, M. L. Dore, J. E. Sieser, M. A. Berliner, *Tetrahedron Lett.* 2006, 47, 3727.
- [46] L. Ackermann, R. Born, Angew. Chem. Int. Ed. 2005, 44, 2444.
- [47] L. Ackermann, J. H. Spatz, C. J. Gschrei, R. Born, A. Althammer, *Angew. Chem. Int. Ed.* **2006**, 45, 7627.
- [48] Q. Dai, W. Z. Gao, D. Liu, L. M. Kapes, X. M. Zhang, J. Org. Chem. 2006, 71, 3928.
- [49] C. M. So, Z. Zhou, C. P. Lau, Y. F. Kwong, Angew. Chem. Int. Ed. 2008, 47, 6402.
- [50] F. Nadora, M. A. Volpeb, F. Alonsoc, A. Feldhoffd, A. Kirschninge, G. Radivoya, *Appl. Catal. A* 2013, 455, 39.
- [51] A. G. Choghamarani, M. Norouzi, J. Mol. Catal. A 2014, 395, 172.
- [52] M. Mirabedini, E. Motamedi, M. Z. Kassaee, *Chin. Chem. Lett.* 2015, 26, 1085.
- [53] S. A. Sarode, J. M. Bhojane, J. M. Nagarkar, *Tetrahedron Lett.* 2015, 56, 206.
- [54] F. Nemati, A. Elhampour, H. Farrokhi, M. B. Natanzi, *Catal. Commun.* 2015, 66, 15.
- [55] F. Matloubi, S. E. Ayati, RSC Adv. 2015, 5, 3894.

HAJIPOUR ET AL

- [56] J. Yu, Y. Luan, T. Qi, J. Hou, W. Dong, M. Yang, G. Wang, RSC Adv. 2014, 4, 55028.
- [57] W. He, H. Zhao, R. Yao, M. Cai, RSC Adv. 2014, 4, 50285.
- [58] S. Sobhani, M. S. Ghasemzadeh, M. Honarmand, F. Zarifi, RSC Adv. 2014, 4, 44166.
- [59] M. Esmaeilpour, J. Javidi, J. Chin. Chem. Soc. 2015, 62, 614.
- [60] R. S. Shelkar, S. H. Gund, J. M. Nagarkar, RSC Adv. 2014, 4, 53387.
- [61] C. Hui, J. Shen, L. Tian, H. Bao, C. Li, Nanoscale 2011, 3, 701.
- [62] S. Zheng, Y. Wang, C. Zhang, J. Liu, C. Xia, *Appl. Organometal. Chem.* 2014, 28, 48.
- [63] M. Ghotbinejad, A. R. Khosropour, I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, J. Mol. Catal A 2014, 385, 78.
- [64] M. Kooti, M. Afshar, Mater. Res. Bull. 2012, 47, 3473.
- [65] A. R. Hajipour, Z. Khorsandi, H. Karimi, Appl. Organometal. Chem. 2015, 29, 805.
- [66] A. R. Hajipour, Z. Khorsandi, Appl. Organometal. Chem. 2016, 30, 256.
- [67] A. R. Hajipour, E. Boostani, F. Mohammadsaleh, *RSC Adv.* 2015, 5, 94369.
- [68] A. R. Hajipour, E. Boostani, F. Mohammadsaleh, *RSC Adv.* 2015, 5, 24742.
- [69] A. R. Hajipour, G. Azizi, Green Chem. 2013, 15, 1030.
- [70] E. Rafiee, A. Ataei, S. Nadri, M. Joshaghani, S. Eavani, *Inorg. Chim. Acta* 2014, 409, 302.

[71] R. Rahimi, A. Maleki, S. Maleki, A. Morsali, M. J. Rahimi, Solid State Sci. 2014, 28, 9.

9 of 9

rganometallic

- [72] B. Yang, Z. Mao, X. Zhu, Y. Wan, Catal. Commun. 2015, 60, 92.
- [73] H. Maheswaran, G. G. Krishna, K. L. Prasanth, V. Srinivas, G. K. Chaitanya, K. Bhanuprakash, *Tetrahedron* 2008, 64, 2471.
- [74] Y. Huang, J. Gao, H. Ma, H. Miao, J. Xu, *Tetrahedron Lett.* 2008, 49, 948.
- [75] A. R. Hajipour, F. Dordahan, F. Rafiee, M. Mahdavi, Appl. Organometal. Chem. 2014, 28, 809.
- [76] R. Arundhathi, D. Damodara, P. R. Likhar, M. L. Kantam, P. Saravanan, T. Magdaleno, S. H. Kwonc, *Adv. Synth. Catal.* 2011, 353, 1591.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Hajipour AR, Check M, Khorsandi Z. Copper immobilized on magnetite nanoparticles coated with ascorbic acid: An efficient and reusable catalyst for C–N and C–O crosscoupling reactions. *Appl Organometal Chem*. 2017;e3769. https://doi.org/10.1002/aoc.3769