Full paper

Applied
Organometallic
Chemistry

Received: 4 March 2016 Revised: 15 April 2016 Accepted: 18 April 2016

(wileyonlinelibrary.com) DOI 10.1002/aoc.3512

Palladium 2-mercapto-*N*-propylacetamide complex anchored onto MCM-41 as efficient and reusable nanocatalyst for Suzuki, Stille and Heck reactions and amination of aryl halides

Mohsen Nikoorazm*, Arash Ghorbani-Choghamarani, Nourolah Noori and Bahman Tahmasbi

A palladium 2-mercapto-*N*-propylacetamide complex supported on functionalized MCM-41 was prepared by a post-grafting method and considered as an efficient catalyst for C–C cross-coupling reactions between various aryl halides and sodium tetraphenylborate, phenylboronic acid, triphenyltin chloride or alkenes. Also, this catalyst shows good reactivity towards amination of aryl halides. This nanocatalyst was characterized using thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, inductively coupled plasma and transmission electron microscopy techniques. Further results indicated that the heterogeneous catalyst could be recovered easily and reused several times without any loss of its catalytic activity. Copyright © 2016 John Wiley & Sons, Ltd.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: MCM-41; palladium; heterogeneous; C–C coupling reaction; amination

Introduction

Homogeneous palladium catalysis has gained enormous relevance in various coupling reactions such as Heck, Stille, Sonogashira, Suzuki and Buchwald–Hartwig reactions.[1,2] Many products can be synthesized using this methodology for the first time or in a much more efficient way than before. This type of homogeneous catalysis provides high reaction rate and often affords high yields and selectivity.[3]

Anilines are important organic compounds, and commonly used for various applications, such as in the agrochemical, pharmaceutical, cosmetic, resin, dye and toiletry industries.[4–6] Traditionally, these compounds have been prepared by C–N bond formation, although ammonia is an attractive and low-cost nitrogen source for the industrial production of anilines.[7,8] The palladium-catalysed amination of aryl halides is a powerful and valuable tool for the construction of arylamines.[9–12] However, homogeneous catalysis has a number of drawbacks, in particular the lack of separation and reusability, which is a significant environmental and economic concern in large-scale synthesis.[13] These problems have to be overcome in the application of homogeneous Pd-catalysed coupling reactions in industry, which is still a challenge. The immobilization of homogeneous catalysts on various insoluble supports (especially porous materials with high surface areas) can lead to the simplification of catalyst recycling via filtration.[14–16] In general, various supports have been employed to fabricate heterogeneous Pd catalysts, such as carbon,[17] metal oxides,[18,19] ionic liquids,[20] molecular sieves (SBA-15 and MCM-41)[21–26] and polymers.[27] In this study, mesoporous MCM-41 has been considered as a very good support for a Pd complex. The reason for the use of mesoporous MCM-41 as a good support is that it possesses thermal, mechanical and chemical stability. It also has an extremely high surface area (1000 $m^2\ g^{-1}$), and large channels from 1.5 to 10 nm, ordered in a hexagonal array, and large pore volume, which allows for the easy diffusion of substrates to active sites.[28]

In the current paper, we report the synthesis of functionalized mesoporous MCM-41 by the immobilization of a Pd complex onto mesoporous MCM-41 silica, and successfully demonstrate its application as a heterogeneous catalyst for C–C coupling reactions and synthesis of anilines. Also, this catalytic system offers simplicity of operation, heterogeneous nature, excellent yields, short reaction times and simple work-up in cross-coupling reactions for the formation of carbon–carbon bonds and amination with aryl halides.

Experimental

Materials and Instrumentation

Analytical-grade cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS; 98%), sodium hydroxide (NaOH), aryl halides, sodium tetraphenylborate, phenylboronic acid, triphenyltin chloride and other materials were purchased from Aldrich, Merck or Fluka and used without further purification. The progress of all the reactions was monitored by TLC. Powder X-ray diffraction (XRD)

---

* *Correspondence to: M. Nikoorazm, Department of Chemistry, Ilam University, PO Box 69315516, Ilam, Iran. E-mail: e_nikoorazm@yahoo.com*

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

patterns of samples were recorded using a Philips X'pert diffractometer with monochromatized Cu Kα radiation under the conditions of 40 kV and 30 mA. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets with a VRTEX 70 FT-IR spectrometer (Bruker). Thermogravimetric analysis (TGA) of samples was conducted using a Shimadzu DTG-60 automatic thermal analyser in the temperature range 30–900 °C at a heating rate of 10 °C min^{-1} in air. Scanning electron microscopy (SEM) images were obtained with a VEGA TESCAN. The content of Pd was determined using inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer optima 8000). Transmission electron microscopy (TEM) images were obtained with a Philips CM10 microscope, working at 200 kV accelerating voltage.

General Procedure for Synthesis of MCM-41

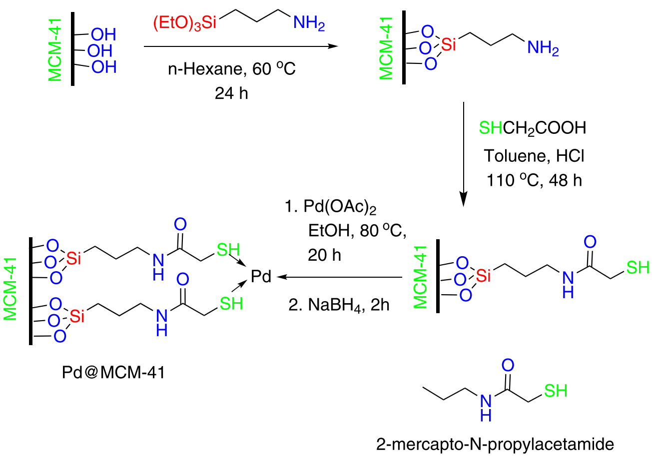
Nanosized MCM-41 was prepared using the sol–gel method with CTAB as the template, TEOS as the silicon source and sodium hydroxide as pH control agent. In a typical procedure, CTAB (2.74 mmol, 1 g) was added to a solution of deionized water (480 ml) and NaOH (2 M, 3.5 ml) at 80 °C. When the solution became homogeneous (after complete dissolution), TEOS (5 ml) was added dropwise to the solution under continuous stirring at 80 °C, and the obtained gel was aged under reflux for 2 h. The mixture was allowed to cool to room temperature and the resulting product was filtered and washed with distilled water. It was then subjected to Soxhlet extraction with ethanol for 24 h and dried in an oven at 60 °C. The obtained material was calcined at 550 °C in air for 5 h and is designated as MCM-41.

Preparation of MCM-41 Coated by (3-Aminopropyl) triethoxysilane (APTES)

An amount of 1.0 g of the obtained MCM-41 was refluxed with APTES (1 g) in *n*-hexane (100 ml) under nitrogen atmosphere for 24 h. After the completion of the reaction, APTES-functionalized MCM-41 (APTES@MCM-41) was filtered as a white solid, washed with *n*-hexane and dried under vacuum (Scheme 1).

Preparation of APTES@MCM-41 Coated by 2-Mercaptoacetic acid

MCM-41@APTES (1 g) was first suspended in dry toluene (30 ml). Subsequently, 4 mmol of 2-mercaptoacetic acid, containing a few drops hydrochloric acid, was added dropwise and the reaction was heated at 110 °C under reflux conditions for 48 h. Then, the final product was filtered and washed several times with dry ethanol and dried at room temperature.



Scheme 1. Synthesis of Pd-MPA@MCM-41 catalyst.

Preparation of Heterogeneous Catalyst

The functionalized material (1 g) described above was mixed with $Pd(OAc)_2$ (0.5 g) in ethanol (20 ml) under reflux for 16 h. Subsequently, sodium borohydride (0.6 g) was added to this mixture and kept under reflux for 4 h (Scheme 1). Finally, the resulting black precipitate was filtered off and washed several times with ethanol to remove any unanchored metal ion and dried at room temperature to afford Pd-MPA@MCM-41.

Typical Procedure for Synthesis of Baryls

In a 5 ml round-bottom flask, a reaction mixture of aryl halide (1.0 mmol), $NaBPh_4$ (0.5 mmol) or Ph_3SnCl (0.5 mmol) or $PhB(OH)_2$ (1 mmol), K_2CO_3 (1.5 mmol), Pd-MPA@MCM-41 (10 mg, 1.7 mol%) and poly(ethylene glycol) (PEG; 2 ml) were stirred magnetically at 100 °C for the appropriate time (Table 1). The reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. Then, the catalyst was easily recovered by filtration and the filtrate was poured into water (10 ml) and extracted with diethyl ether (3 × 10 ml). The combined organic layers were dried over Na_2SO_4 (1.5 g), followed by the evaporation of the solvent, yielding the pure product.

Table 1. Optimization of various parameters for the reaction of iodobenzene with $NaBPh_4$ or $PhB(OH)_2$ or Ph_3SnCl catalysed by Pd-MPA@MCM41[a]

Entry	Catalyst (mol%)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%)[b]
1	1.7	PEG	—	100	1440	0
2	1.7	PEG	K_2CO_3	100	85	95
3	1.7	PEG	Na_2CO_3	100	85	90
4	1.7	PEG	$(Et)_3N$	100	85	80
5	1.7	PEG	KOH	100	85	35
6	1.7	PEG	$NaHCO_3$	100	85	Trace
7	1.7	PEG	$NaHSO_4$	100	85	Trace
8	1.7	DMSO	K_2CO_3	100	85	86
9	1.7	DMF	K_2CO_3	100	85	81
10	1.7	1,4-Dioxane	K_2CO_3	100	85	73
11	1.7	H_2O	K_2CO_3	100	85	58
12	1.7	PEG	K_2CO_3	80	85	58
13	1.7	PEG	K_2CO_3	60	85	Trace
14	1.7	PEG	K_2CO_3	40	85	0
15	1.7	PEG	K_2CO_3	r.t.	85	0
16	0	PEG	K_2CO_3	100	1440	0
17	2	PEG	K_2CO_3	100	85	96
18	1.3	PEG	K_2CO_3	100	85	83
19	0.8	PEG	K_2CO_3	100	85	Trace

[a] Reaction conditions: iodobenzene (1.0 mmol), base (1.5 mmol), 0.5 mmol of $NaBPh_4$ or 1 mmol of $PhB(OH)_2$ or 0.5 mmol of Ph_3SnCl and solvent (2 ml).

[b] Isolated yield.

Typical Procedure for Heck Reaction Catalysed by Pd-MPA@MCM-41

For the Heck coupling reaction, a reaction tube equipped with a magnetic stirring bar was charged with aryl halide (1 mmol), butyl acrylate (1.2 mmol), K_2CO_3 (3 mmol), Pd-MPA@MCM-41 (2.5 mol%) and 2 ml of dimethylformamide (DMF), and the obtained mixture was heated at 120 °C for the appropriate time. The progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was allowed to cool to room temperature. The catalyst was then removed by filtration, washed with acetonitrile (2 × 10 ml) and dried at 50 °C for reuse. The residual mixture was extracted with CH_2Cl_2 and the obtained organic layer was dried over Na_2SO_4.

General Procedure for Synthesis of Anilines

In a typical procedure, to a mixture of aryl halide (1 mmol) and ammonium hydroxide (28%, 1 ml, 0.003 mol), 1.7 mol% of Pd-MPA@MCM-41 was added and the reaction mixture was stirred at room temperature for an appropriate time. The progress of the reaction was followed by TLC. After the reaction was completed, the product was extracted with ethyl acetate (3 × 10 ml). The obtained extracts were dried with Na_2SO_4 followed by evaporation of the solvent which afforded the corresponding aniline with excellent yield.

Results and Discussion

We prepared and characterized Pd-MPA@MCM-41 as a highly efficient and reusable heterogeneous catalyst for Suzuki, Stille and Heck reactions and amination of aryl halides.

X-ray Diffraction

Figure 1 shows low-angle XRD patterns of calcined MCM-41 and Pd-MPA@MCM-41. The XRD pattern of MCM-41 shows a typical three-peak pattern with a very strong reflection at $2\theta = 2.21°$ due to the d_{100} plane and also two other weaker reflections at $2\theta = 3.63°$ and 4.23°, due to higher order d_{110} and d_{200} planes, respectively, indicating the formation of a well-ordered mesoporous material with hexagonal symmetry. The XRD pattern of Pd-MPA@MCM-41 exhibits three reflections in the region of $2\theta = 2$–4.60°. Also, this sample shows the same pattern indicating that the structure of the MCM-41 is well retained. The comparison study of XRD patterns of MCM-41 and Pd-MPA@MCM-41 shows that after grafting of Pd through complex formation into MCM-41, the d_{110} and d_{200} reflections with weaker intensities are observed. In order to observe the peaks associated with the palladium nanoparticles, the wide-angle XRD pattern of Pd-MPA@MCM-41 was recorded. Figure 1 shows three peaks at 40.12°, 46.16° and 68.14° corresponding to (111), (200) and (220) lattice planes of the palladium nanoparticles.[29]

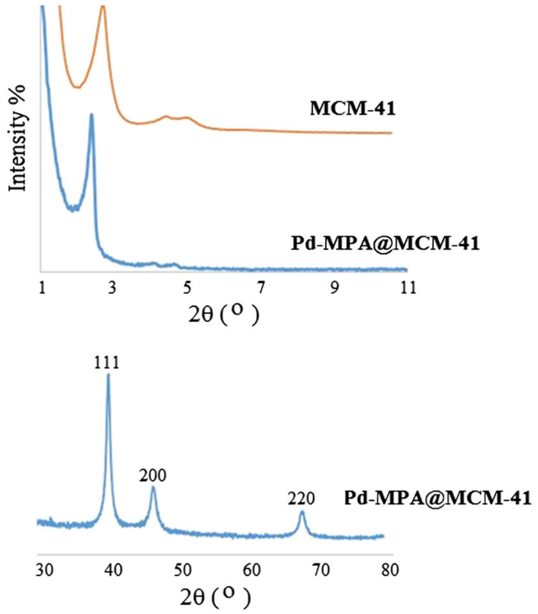


Figure 1. Low-angle powder XRD patterns of calcined MCM-41 and Pd-MPA@MCM-41 (top). Wide-angle powder XRD pattern of Pd-MPA@MCM-41 (bottom).

FT-IR Spectroscopy

Figure 2 shows the FT-IR spectra of MCM-41, MCM-41-nPr-NH_2, MCM-41-MPA, Pd-MPA@MCM-41 and recovered Pd-MPA@MCM41 in the range 400–4000 cm^{-1}. Figure 2(a) is the spectrum of MCM-41, which shows a band at 463 cm^{-1} which is attributed to the Si–O bending vibration. The band at 1100–1200 cm^{-1} is due to Si–O–Si asymmetric stretching and the band at 3000–3600 cm^{-1} can be attributed to the silanol OH groups. MCM-41-nPr-NH_2 spectrum (Fig. 2(b)) is confirmed by C–H stretching vibration at 2959 cm^{-1}, and two bands belonging to N–H group appear at 1650 and 1468 cm^{-1}. In Fig. 2(c) (MCM-41-MPA spectrum) it is clear that the band at 1640 cm^{-1} evidences the presence of the C–O bond, which is assigned to the stretching vibration of C–O in amide,

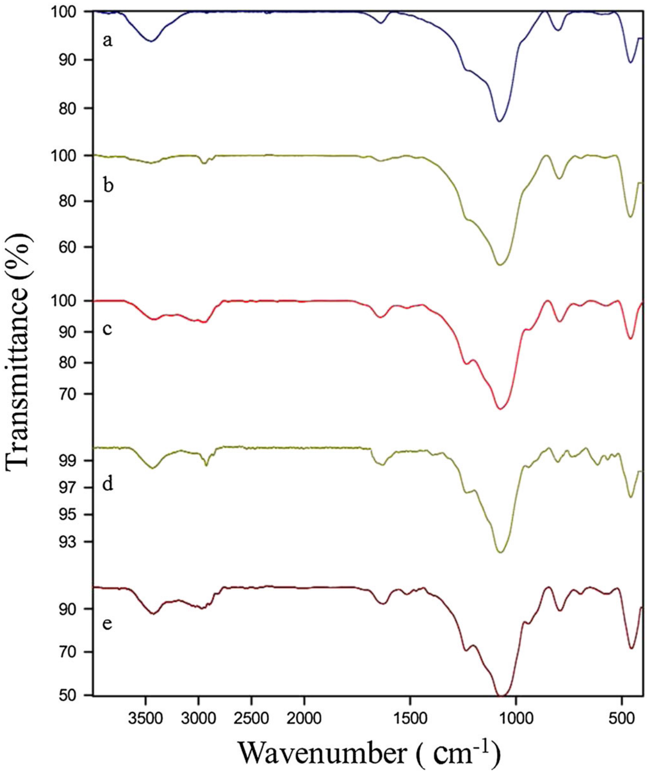


Figure 2. FT-IR spectra: (a) MCM-41; (b) MCM-41-nPr-NH_2; (c) MCM-41-MPA; (d) Pd-MPA@MCM-41; (e) recovered Pd-MPA@MCM-41.

and the band centred at 3440 cm^{-1} is assignable to (N–H) stretching vibration band. Figure 2(d) shows the complexion of Pd ions with MCM-41-MPA. The spectrum of recycled Pd-MPA@-MCM-41 (Fig. 2(e)) indicates that the catalyst is stable during the C–C coupling reaction.

SEM/EDS Analysis

As depicted in Fig. 3, the SEM images of MCM-41 and Pd-MPA@-MCM-41 samples (Figs 3(a) and (b), respectively) reveal that these materials have been formed with a spherical structure. The SEM image of Pd-MPA@MCM-41 (Fig. 3(b)) confirms that the catalyst is made up of uniform nanometre-sized particles, and also no significant changes in the surface morphology occur upon the insertion of the Pd complex onto MCM-41 The EDS analysis of Pd-MPA@-MCM-41 (Fig. 3(c)) indicates that Pd particles are well dispersed onto the MCM-41 surface, which agrees well with the XRD pattern. Also, in order to estimate the exact amount of Pd loaded on the mesoporous catalyst, ICP-OES analysis was performed, from which the amount is found to be 1.69×10^{-3} mol g^{-1}.

TEM Analysis

Figure 4 shows TEM images of MCM-41 and Pd-MPA@MCM-41. As shown in Fig. 4(a), the TEM image of MCM-41 indicates well-ordered hexagonal arrays of mesoporous arrangement and long-range mesoporous architecture (100 nm). Also, the catalyst sample exhibits a similar type of array of regular hexagonal arrangement, as shown in Fig. 4(b). Therefore, it can be concluded that both of the samples have a similar type of morphology.

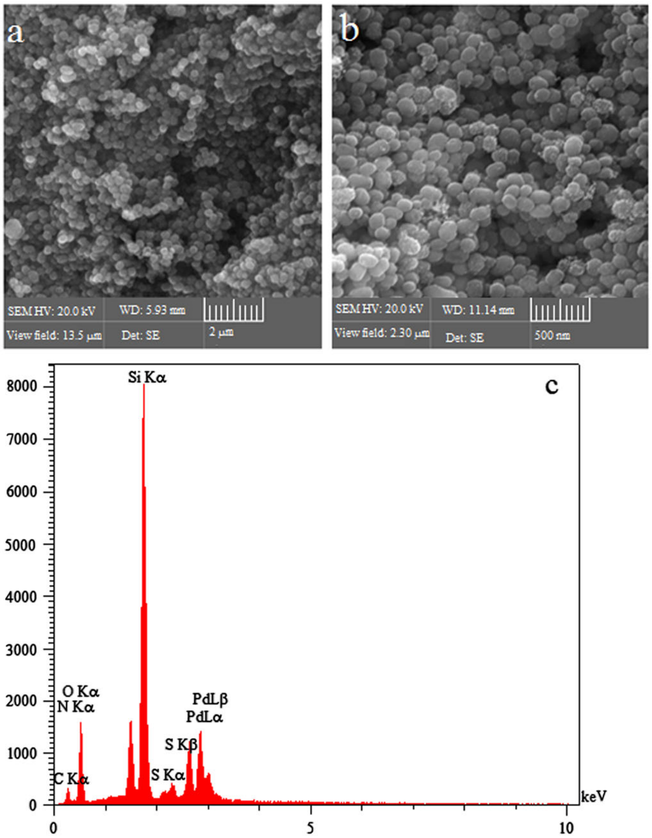


Figure 3. SEM images of (a) MCM-41 and (b) Pd-MPA@MCM-41. (c) EDS pattern of Pd-MPA@MCM-41.

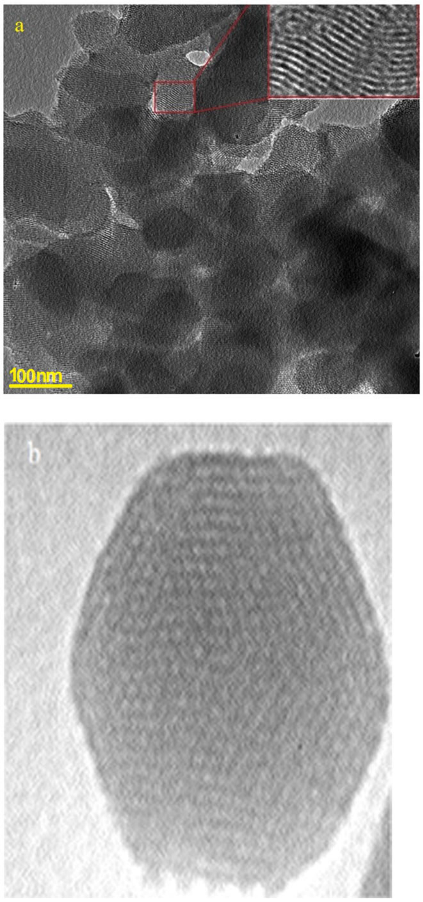


Figure 4. TEM images of (a) parent MCM-41 and (b) synthesized Pd-MPA@MCM-41 catalyst.

Thermogravimetric Analysis

TGA curves of MCM-41 and PdMPA@MCM-41 are presented in Fig. 5. The TGA curve of calcined MCM-41 shows a weight loss of about 6% between room temperature and 100 °C attributed to the loss of physically adsorbed water. The TGA curve of Pd-MPA@-MCM-41 catalyst shows a three-step weight loss. The first step of weight loss (about 3%) appearing at 25–100 °C seems to be due to the removal of adsorbed water; the second weight loss appears in the range 250–350 °C (10%) mainly related to the decomposition

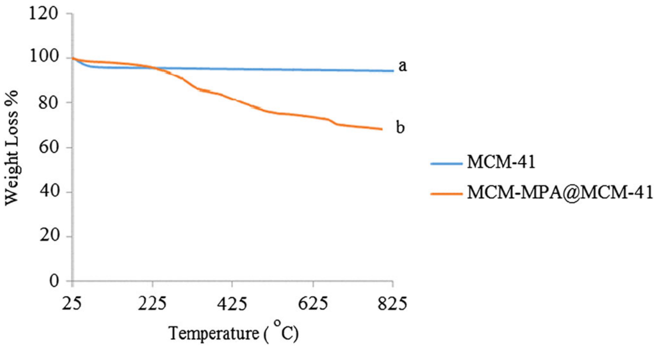


Figure 5. TGA curves of (a) MCM-41 and (b) Pd-MPA@MCM-41.

of the organically modified moieties on MCM-41; and the third weight loss (about 5%) appears at above 600 °C as a result of the condensation of the silanol groups.

Catalytic Results

After confirming the exact characteristics of Pd-MPA@MCM-41, the catalytic activity of this mesoporous compound was explored in C–C cross-coupling reactions of various aryl halides with different phenylating agents. Initially, in order to optimize the reaction conditions, iodobenzene as an example of a non-activated aryl iodide was selected as a model substrate for the coupling reaction with sodium tetraphenylborate or phenylboronic acid or triphenyltin chloride as coupling partner in the presence of a catalytic amount of Pd-MPA@MCM-41 and various types of bases and solvents at different temperatures (Table 1).

Because the desired cross-coupling product is not obtained in any noticeable amounts in the absence of base, the effect of bases on the outcome of the reaction is significant (Table 1, entry 1). Table 1 shows that among the various studied bases, K_2CO_3 is more effective for this coupling reaction. Therefore, we chose K_2CO_3 as the base in all of the coupling reactions (Table 1, entry 2).

Subsequently, the effect of various solvents on the outcome of the C–C coupling reaction was investigated (Table 1). The reaction rate is greatly affected by the kind of applied solvent. Among the commonly used solvents such as dimethylsulfoxide (DMSO), PEG, DMF 1,4-dioxane and water, the best result is obtained for PEG in terms of the conversion and product selectivity (Table 1, entry 2). Moreover, PEG solvent has an important advantage, which makes it a unique solvent: its water solubility makes product extraction and purification very easy.

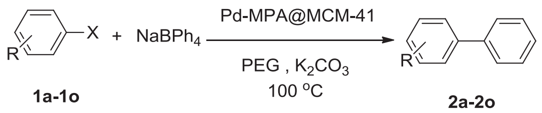
The effect of temperature on the activity of Pd-MPA@MCM-41 was investigated in the range 25–100 °C and it is found that the reaction temperature has a great effect on the outcome of the reaction. Table 1 shows that the reaction is very slow or even that there is no reaction below 60 °C (Table 1, entries 13–15), while the product conversion increases on increasing temperature above 60 °C. The reaction can proceed completely at 100 °C (Table 1, entry 2).

Also, we investigated the effects of the amount of catalyst in the coupling reaction. As evident from Table 1, the yield of product increases with increasing catalyst amount. The reaction is complete within 85 min with excellent conversion and high yield using 1.7 mol% of catalyst (Table 1, entry 2). When the amount of catalyst decreases to 0.8 mol%, a trace formation of biphenyl product is obtained (Table 1, entry 19). However, when a higher amount of catalyst (2 to 3 mol%) is used, the catalyst still functions fairly well, but the conversion is slightly increased (Table 1, entry 18).

Under the obtained optimized conditions, we examined the general applicability of Pd-MPA@MCM-41 with various aryl halides. As evident from Tables 2–4, a wide range of aryl halides containing electron-withdrawing or electron-donating groups are efficiently coupled with phenylating agents to produce the corresponding biaryl product in excellent isolated yield. The results including reaction time, product yield, melting point, turnover number (TON) and turnover frequency (TOF) are summarized in Tables 2–4.

As is obvious from Tables 2–4, in all cases excellent isolated yields (>90%) are obtained, regardless of the nature of the substituent present on the aryl halides (electron-withdrawing or electron-donating groups), which confirms the reliability of these synthetic methods. Upon comparing the results in Tables 2–4, the electronic effect of substrates is obvious. Aryl halides containing electron-withdrawing substituents give lower reaction times compared to those containing electron-donating substituents. Also aryl chlorides

Table 2. Coupling of various aryl halides with $NaBPh_4$ in presence catalyst[a]



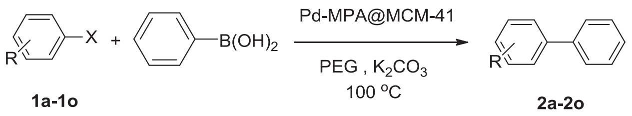
Entry	Aryl halide	Product	Time (h)	Yield (%)[b]	M.p. (°C)	TON	TOF (h^{-1})
1	Iodobenzene	**2a**	1.4	95	67–68[30]	55.88	39.9
2	4-Iodoanisole	**2b**	1.1	95	80–82[30]	55.88	50.80
3	4-Iodotoluene	**2c**	0.33	97	42–44[33]	57.05	172.90
4	4-Bromonitrobenzene	**2d**	1.5	93	111–113[30]	54.70	36.47
5	4-Iodoaniline	**2e**	2.5	94	53–54[33]	55.29	22.11
6	4-Bromobenzonitrile	**2f**	1	97	85–86[30]	57.05	57.05
7	Bromobenzene	**2 g**	1.66	94	69[30]	55.29	33.30
8	1-Bromonaphthalene	**2 h**	11	92[c]	Oil[30]	36.8	3.34
9	4-Bromoaniline	**2i**	4.5	92	52–54[33]	54.11	12.02
10	4-Bromobenzyl alcohol	**2j**	5.25	90	93–94[32]	52.94	10.08
11	4-Bromobenzaldehyde	**2 k**	0.3	91	56–58[30]	53.52	162.2
12	4-Bromophenol	**2 l**	0.33	92	162–164[30]	54.11	163.96
13	4-Bromotoluene	**2 m**	0.5	96	42–44[33]	56.47	112.94
14	4-Bromochlorobenzene	**2n**	1	97	71–73[33]	57.05	57.05
15	4-Bromobenzoic acid	**2o**	2	95	228–230[33]	55.88	27.94

[a] Reaction conditions: 1 mmol of aryl halide,0.5 mmol of sodium tetraphenylborate, 1.5 mmol of K_2CO_3 and (1.7 mol%) of catalyst in 2 ml of PEG solvent at 100 °C.

[b] Isolated yield.

[c] Amount of catalyst used was 2.5 mol%.

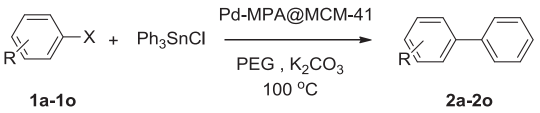
Table 3. Coupling of various aryl halides with $PhB(OH)_2$ in presence catalyst[a]



Entry	Aryl halide	Product	Time (h)	Yield (%)[b]	M.p. (°C)	TON	TOF (h^{-1})
1	Iodobenzene	**2a**	2	95	67–68[30]	55.88	27.94
2	4-Iodoanisole	**2b**	1.7	95	80–82[31]	55.88	32.87
3	4-Iodotoluene	**2c**	1	94	42–44[33]	55.29	55.29
4	4-Bromonitrobenzene	**2d**	1.45	93	111–113[30]	54.70	37.72
5	4-Iodoaniline	**2e**	3	95	53–54[33]	55.88	18.62
6	4-Bromobenzonitrile	**2f**	1.3	97	85–86[30]	57.05	43.89
7	Bromobenzene	**2 g**	2.2	94	69[30]	55.29	25.13
8	1-Bromonaphthalene	**2 h**	12	97[c]	Oil[30]	38.8	3.23
9	4-Bromoaniline	**2i**	5.1	91	52–54[33]	53.52	10.49
10	4-Bromobenzyl alcohol	**2j**	6	94	93–94[32]	55.29	9.21
11	4-Bromobenzaldehyde	**2 k**	0.75	93	56–58[30]	54.70	72.94
12	4-Bromophenol	**2 l**	0.75	94	162–164[30]	55.29	73.72
13	4-Bromotoluene	**2 m**	1	95	42–44[33]	55.88	55.88
14	4-Bromochlorobenzene	**2n**	1.5	96	71–73[33]	56.47	37.64
15	4-Bromobenzoic acid	**2o**	2.5	95	228–230[33]	55.88	22.35

[a] Reaction conditions: 1 mmol of aryl halide,1 mmol of phenylboronic acid, 1.5 mmol of K_2CO_3 and (1.7 mol %) of catalyst in 2 ml of PEG solvent at 100 °C.
[b] Isolated yield.
[c] Amount of catalyst used was 2.5 mol%.

Table 4. Coupling of various aryl halides with Ph_3SnCl in presence catalyst



Entry	Aryl halide	Product	Time (h)	Yield [b] %	Mp (°C)	TON	TOF (h^{-1})
1	Iodobenzene	**2a**	1.8	96	67–68[30]	56.47	31.37
2	4-Iodoanisole	**2b**	1.5	94	80–82[31]	55.29	36.86
3	4-Iodotoluene	**2c**	0.4	95	42–44[33]	55.88	139.70
4	4-Bromonitrobenzene	**2d**	1.5	92	111–113[30]	54.11	36.07
5	4-Iodoaniline	**2e**	2.7	96	53–54[33]	56.47	20.91
6	4-Bromobenzonitrile	**2f**	1.1	95	85–86[30]	55.88	50.80
7	Bromobenzene	**2 g**	1.9	94	69[30]	55.29	29.10
8	1-Bromonaphthalene	**2 h**	12	94[c]	Oil[30]	37.6	3.13
9	4-Bromoaniline	**2i**	4.7	92	52–54[33]	54.11	11.51
10	4-Bromobenzyl alcohol	**2j**	5.5	93	93–94[32]	54.70	9.94
11	4-Bromobenzaldehyde	**2 k**	0.5	93	56–58[30]	54.70	109.41
12	4-Bromophenol	**2 l**	0.7	94	162–164[30]	55.29	78.99
13	4-Bromotoluene	**2 m**	0.6	97	42–44[33]	57.05	95.09
14	4-Bromochlorobenzene	**2n**	1.2	95	71–73[33]	55.88	46.56
15	4-Bromobenzoic acid	**2o**	2.2	96	228–230[33]	56.47	25.66

[a] Reaction conditions: 1 mmol of aryl halide,0.5 mmol of triphenyltin chloride, 1.5 mmol of K_2CO_3 and (1.7 mol%) of catalyst in 2 ml of PEG solvent at 100 °C.
[b] Isolated yield.
[c] Amount of catalyst used was 2.5 mol%.

are coupled with phenylating reagents to afford the corresponding product in excellent yields (Table 2–4, entries 14, 16–18). This clearly shows the efficiency of the present catalytic system.

In order to explore more reactions of the described catalyst, the Heck reaction was selected as another C–C cross-coupling reaction. Initially, we optimized the reaction conditions and investigated the effect of the amount of catalyst, solvent, base and temperature on the coupling reaction between iodobenzene and butyl acrylate as a model reaction in DMF as solvent in the presence of K_2CO_3 as base with a catalyst loading of 2.5 mol%

Table 5. Optimization of reaction conditions for C C coupling reaction of iodobenzene with butyl acrylate for 40 min

Entry	Catalyst (mol%)	Solvent	Base	Temperature (°C)	Yield (%)[a]
1	—	DMF	K_2CO_3	120	—[b]
2	1.49	DMF	K_2CO_3	120	50
3	1.66	DMF	K_2CO_3	120	85
4	2.5	DMF	K_2CO_3	120	98
5	2.5	PEG	K_2CO_3	120	50
6	2.5	DMSO	K_2CO_3	120	75
7	2.5	DMF	Na_2CO_3	120	60
8	2.5	DMF	Et_3N	120	75
9	2.5	DMF	KOH	120	30
10	2.5	DMF	K_2CO_3	100	40
11	2.5	DMF	K_2CO_3	80	25

[a] Isolated yield.
[b] No reaction after 24 h.

of Pd at 120 °C. To study the influence of the catalyst, the model reaction was carried out in the absence of the catalyst. No conversion is seen even when the reaction lasts for 24 h (Table 5, entry 1). However, when a similar reaction is conducted in the presence of catalyst (Pd-MPA@MCM-41, 2.5 mol%), the reaction is completed within 40 min with an excellent conversion and a high yield (98%) (Table 5, entry 4).

In the next step, several solvent systems were assessed. Among the studied solvents, the use of DMF givea acceptable conversion (98%) and, as a result, this solvent was chosen as the preferred solvent in terms of yield (Table 5, entry 4). After optimization of the catalyst amount and solvent, various bases such as Et_3N, KOH, K_2CO_3 and Na_2CO_3 were also screened for their effect on the model reaction (Table 5, entries 4, 7–9). A superior yield and a shorter reaction time are obtained when K_2CO_3 is employed as base (Table 5, entry 4).

As evident from Table 5, the coupling reaction yields are likely to change in response to temperature changes in the presence of 2.5 mol% of catalyst (Table 5, entries 4, 10 and 11). An obvious improvement in the conversion (98%) is obtained for reaction at 120 °C after 40 min (Table 5, entry 4). To study the generality of this Heck cross-coupling reaction, under the optimized conditions (Table 6) we examined the reaction of *n*-butyl acrylate with a wide array of aromatic aryl halides.

Table 7 summarizes the catalytic activity of the described Pd-MPA@MCM-41 heterogeneous catalyst that was examined through reaction of aryl halides with aqueous ammonia for the synthesis of aniline derivatives under various conditions.

At first, we selected iodobenzene as an example of a non-activated aryl halide with aqueous ammonia as a model reaction in the absence of base with a catalytic loading of 1.7 mol% of Pd at room temperature. Influences of various parameters were examined to find the best possible combination. Parameters such as amount of catalyst, solvent and base were screened using the same model reaction (Table 7).

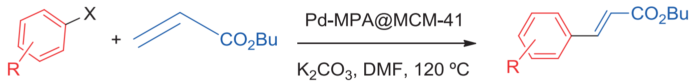
To investigate the influence amount of catalyst, systematic studies were done in the presence of different amounts of the catalyst

Table 7. Optimization of amination of aryl halides[a]

Entry	Solvent	Base	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	—	—	1.7	3.5	97
2	—	—	1.36	5.75	85
3	—	—	0.85	8	75
4	PEG	—	1.7	24	50
5	DMF	—	1.7	24	65
6	EtOH	—	1.7	24	77
7	DMSO	—	1.7	24	70
8	1,4-Dioxane	—	1.7	80	45
9	—	$(Et)_3N$	1.7	15	90
10	—	Na_2CO_3	1.7	12	80
11	—	K_2CO_3	1.7	7	88
12		KOH	1.7	22	70

[a] Reaction conditions: iodobenzene (1 mmol), aqueous ammonia (1 ml) at room temperature.
[b] Isolated yield.

Table 6. Coupling of aryl halides with butyl acrylate (Heck reaction) in the presence of catalytic amounts of Pd-MPA@MCM41[a]



1a-1i **2a-2i**

Entry	Aryl halide	Product	Time (h)	Yield %	Mp (°C)	TON	TOF (h^{-1})
1	Iodobenzene	**4a**	1	98	Oil[36]	39.2	39.2
2	4-Iodotoluene	**4b**	1.15	96	Oil[34]	38.4	33.39
3	4-Iodoanisole	**4c**	1.5	94	Oil[36]	37.6	25.06
4	2-Iodoanisole	**4d**	5	94	Oil[37]	37.6	7.52
5	2-Iodoanisole	**4e**	4.75	97	Oil[38]	38.8	8.16
6	Bromobenzene	**4f**	1.75	95	Oil[34]	38	21.71
7	3-bromopyridine	**4 g**	0.5	96	Oil[34]	38.4	76.8
8	4-Bromochlorobenzene	**4 h**	3	97	Oil[34]	38.8	12.93
9	4-Bromobenzonitrile	**4i**	1.25	98	39–42[34]	39.2	31.36
10	Chlorobenzene	**4j**	2.5	96	Oil[37]	38.4	15.36
11	4-Bromonitrobenzene	**4 k**	1.3	97	58–63[35]	38.8	29.84
12	4-Chlorobenzonitrile	**4 l**	12	92	39–42[34]	36.8	3.06

[a] Reaction conditions: aryl halide (1 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (3 mmol), Pd-MPA@MCM-41 (2.5 mol%) and DMF (2 ml), 120 °C.

Table 8. Amination of aryl halides in presence of Pd-MPA@MCM-41 using aqueous ammonia[a]

1a-1j **2a-2j**

Entry	Aryl halide	Product	Time (h)	Yield (%)[b]	M.p. (°C)	TON	TOF (h^{-1})
1	Iodobenzene	**2a**	3.5	96	Oil[7]	56.47	16.13
2	Bromobenzene	**2b**	3.75	93	Oil[7]	54.70	14.58
3	4-Bromochlorobenzene	**2c**	7	95	68–70[39]	55.88	7.98
4	4-Iodotoluene	**2d**	4	94	43–44[7]	55.29	13.82
5	4-Iodoanisole	**2e**	5.5	95	57–58[39]	55.88	10.16
6	2-Bromonaphthalene	**2f**	18	93	47–49[7]	54.70	3.03
7	4-Bromonitrobenzene	**2 g**	3	98	146–148[39]	57.69	19.23
8	2-Bromopyridine	**2 h**	7	96	56–58[5]	56.47	8.06
9	4-Bromophenol	**2i**	12	94	186–190[40–42]	55.29	4.60
10	4-Bromobenzonitrile	**2j**	2.5	97	87–88[39]	57.05	22.82

[a] Reaction conditions: aryl halide (1 mmol), aqueous ammonia (1 ml) and catalyst (10 mg, 1.7 mol%) at room temperature.
[b] Isolated yield.

from 0.85 to 1.7 mol% at room temperature under solvent-free conditions (Table 7, entries 1–3). The findings reveal that with increasing catalyst concentration a general increasing trend is seen in isolated yields of products. Therefore, the best yield is obtained in the presence of 1.7 mol% of Pd (Table 7, entry 3).

To find the best reaction conditions, the effects of various solvents, such as DMF, PEG, EtOH, DMSO and 1,4-dioxane, were investigated (Table 7, entries 4–8). Under solvent conditions the reaction is not complete after 24 h. Finally, we carried out the amination of aryl halides in the absence of solvent for all reactions (solvent-free conditions) (Table 7, entry 1).

Then, after optimizing the amount of catalyst and solvent, we explored the effects of bases on the model reaction in solvent-free conditions in order to find the appropriate base. Various inorganic and organic bases including Et_3N, Na_2CO_3, K_2CO_3 and KOH were examined (Table 7, entries 9–12). As evident from Table 7, the reaction was performed in neat conditions in terms of short reaction time and high yield (Table 7, entry 1).

With the optimized reaction conditions in hand, a series of various electron-rich and electron-poor aryl iodides or bromides were reacted with aqueous ammonia to synthesize the corresponding aniline derivatives. The findings are summarized in Table 8.

Reusability of Catalyst

From practical and industrial points of view, catalyst recyclability is highly desirable. To investigate this issue, catalytic reusability of Pd-MPA@MCM-41 was examined under the optimized reaction conditions in the model reaction (Fig. 6). After completion of the reaction, the catalyst was collected by centrifugation and washed with acetonitrile several times. Then, the catalyst was dried at 50 °C and reused for the next run. After the eighth reaction run, the yield of product is decreased from 95 to 88%. This decrease in the product yield may be due to the weight loss of catalyst in the operation for recovery and/or deactivation of the catalyst. Therefore, the Pd-MPA@MCM-41 catalyst shows excellent reusability, and no significant loss of selectivity and activity is found even after eight subsequent runs.

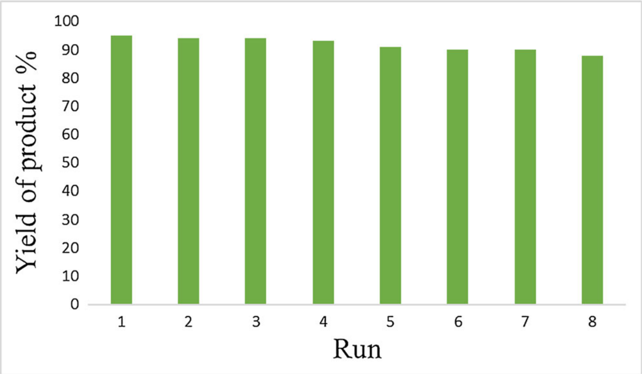


Figure 6. Reusability of Pd-MPA@MCM-41.

In order to show the activity of the catalyst on a large scale for industrial applications, the coupling of iodobenzene (10 g, 49 mmol) with $PhB(OH)_2$ (6 g, 49 mmol) under optimized condition was performed. A yield of 96% of biphenyl is obtained in 135 min. Also, in order to examine the reusability of catalyst on a large scale, after completion of reaction, the catalyst was recovered and reused again. In this stage 94% of product is obtained after 145 min, which clearly demonstrates the practical recyclability of this catalyst on a large scale.

Conclusions

In this work, briefly, we have prepared a palladium complex supported on MCM-41 and carefully characterized its structure using FT-IR, SEM, EDS, TEM, XRD, ICP and TGA techniques. Pd-MPA@-MCM-41 has been used for the cross-coupling reaction of aryl halides with phenylating agents and alkenes; also amination of aryl halides was performed in the presence of this catalyst. This simple reported procedure offers several significant advantages such as isolation of highly pure products in excellent yields, good reaction times, simple product separation procedure, reusability of the catalyst and environmentally benign C–C bond formation and amination procedure.

Acknowledgement

This work was supported by the research facilities of Ilam University, Ilam, Iran.

References

[1] N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609.
[2] A. Molnar, *Chem. Rev.* **2011**, *111*, 2251.
[3] L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133.
[4] H. Yuzawa, H. Yoshida, *Chem. Commun.* **2010**, *46*, 8854.
[5] B. Yang, L. Liao, Y. Zeng, X. Zhu, Y. Wan, *Catal. Commun.* **2014**, *45*, 100.
[6] X. Yang, Q. Guan, W. Li, *J. Environ. Manag.* **2011**, *92*, 2939.
[7] F. Havasi, A. Ghorbani-Choghamarani, F. Nikpour, *New J. Chem.* **2015**, *39*, 6504.
[8] J. Chen, T. Yuan, W. Hao, M. Cai, *Tetrahedron Lett.* **2011**, *52*, 3710.
[9] S. Rostamnia, X. Liu, D. Zheng, *J. Colloid Interface Sci.* **2014**, *432*, 86.
[10] M. Esmaeilpour, A. R. Sardarian, J. Javidi, *J. Organometal. Chem.* **2014**, *749*, 233.
[11] S. J. Sabounchei, M. Ahmadi, Z. Nasri, E. Shams, M. Panahimehr, *Tetrahedron Lett.* **2013**, *54*, 4656.
[12] Y. Q. Tang, J. M. Lu, L. X. Shao, *J. Organometal. Chem.* **2011**, *696*, 3741.
[13] M. R. Maurya, A. K. Chandrakar, S. Chand, *J. Mol. Catal. A* **2007**, *263*, 227.
[14] A. Orejon, A. M. Masdeu-Bulto, P. Salagre, S. Castillon, C. Claver, A. Padilla, B. Almena, F. Luis Serrano, *Ind. Eng. Chem. Res.* **2008**, *47*, 8032.
[15] P. McMorn, G. J. Hutchings, *Chem. Soc. Rev.* **2004**, *33*, 108.
[16] Y. S. Fu, S. J. Yu, *Angew. Chem. Int. Ed.* **2001**, *40*, 437.
[17] L. Zhang, C. Feng, S. Gao, Z. Wang, C. Wang, *Catal. Commun.* **2015**, *61*, 21.
[18] M. Jin, J. N. Park, J. K. Shon, J. H. Kim, Z. Li, Y. K. Park, J. M. Kim, *Catal. Today* **2012**, *185*, 183.
[19] L. M. Neal, M. L. Everett, G. B. Hoflund, H. E. Hagelin-Weaver, *J. Mol. Catal. A* **2011**, *335*, 210.
[20] S. Ghosh, R. Dey, S. Ahammed, B. C. Ranu, *Clean Techn. Environ. Policy* **2014**, *16*, 1767.
[21] S. M. Sarkar, M. L. Rahman, M. M. Yusoff, *RSC Adv.* **2015**, *5*, 1295.
[22] H. Veisi, D. Kordestani, A. R. Faraji, *J. Porous Mater.* **2014**, *21*, 141.
[23] F. Zhang, C. Zhang, Y. Deng, L. Xu, H. Qiu, G. Lai, J. Jiang, *Acta Chim. Sinica* **2010**, *68*, 443.
[24] J. Jiang, P. Wang, M. Cai, *J. Chem. Res.* **2014**, *4*, 218.
[25] H. Zhao, G. Zheng, W. Hao, M. Cai, *J. Organometal. Chem.* **2010**, *24*, 92.
[26] H. Zhao, G. Zheng, S. Sheng, M. Cai, *Catal. Commun.* **2009**, *11*, 158.
[27] Z. Dong, Z. Ye, *Appl. Catal. A* **2015**, *489*, 61.
[28] A. M. Akondi, R. Trivedi, B. Sreedhar, M. L. Kantam, S. Bhargava, *Catal. Today* **2012**, *198*, 35.
[29] S. Navaladian, B. Viswanathan, T. K. Varadarajan, R. P. Viswanath, *Nanoscale Res. Lett.* **2009**, *4*, 181.
[30] L. Bai, J. X. Wang, *Adv. Synth. Catal.* **2008**, *350*, 315.
[31] D. Zim, A. S. Gruber, G. Ebeling, J. Dupont, A. L. Monteir, *Org. Lett.* **2000**, *2*, 2881.
[32] A. Modak, T. Naveen, D. Maiti, *Chem. Commun.* **2013**, *49*, 252.
[33] Z. Du, W. Zhou, F. Wang, J. X. Wang, *Tetrahedron* **2011**, *67*, 4914.
[34] N. Iranpoor, H. Firouzabadi, A. Tarassoli, M. Fereidoonnezhad, *Tetrahedron Lett.* **2010**, *66*, 2415–21.
[35] O. Aksın, H. Turkmen, L. Artok, B. Cetinkaya, C. Ni, O. Buyukgungor, E. Ozka, *J. Organometal. Chem.* **2006**, *691*, 3027.
[36] T. Chen, J. Gao, M. Shi, *Tetrahedron Lett.* **2006**, *62*, 6289.
[37] Q. Xu, W. L. Duan, Z. Y. Lei, Z. B. Zhu, M. Shi, *Tetrahedron Lett.* **2005**, *61*, 11225.
[38] Y. P. Wang, H. M. Lee, *J. Organometal. Chem.* **2015**, *791*, 90.
[39] K. G. Thakur, K. S. Srinivas, K. Chiranjeevi, G. Sekar, *Green Chem.* **2011**, *13*, 2326.
[40] http://www.chemspider.com/Chemical-Structure.392.html
[41] G. Quartarone, L. Ronchin, A. Tosetto, A. Vavasori, *Appl. Catal. A* **2014**, *475*, 169.
[42] P. Guo, L. Tang, J. Tang, G. Zeng, B. Huang, H. Dong, Y. Zhang, Y. Zhou, Y. Deng, L. Ma, S. Tan, *J. Colloid Interface Sci.* **2016**, *469*, 78.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.