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Nanocrystalline Magnesium Oxide-Stabilized Palladium(0): An Efficient and Reusable Catalyst for Suzuki and Stille Cross-Coupling of Aryl Halides

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Abstract: A nanocrystalline magnesium oxide-stabilized palladium(0) catalyst is prepared by counterion stabilization of $PdCl_4^{2-}$ with nanocrystalline MgO followed by reduction. This ligand-free heterogeneous nanocrystalline MgO-stabilized nanopalladium [NAP–Mg–Pd(0)] catalyst using the basic MgO in place of basic ligands exhibits excellent activity in Suzuki and Stille cross-coupling of haloarenes (chloro, bromo and iodo) to afford the unsymmetrical biaryls. The catalyst is quantitatively recovered by simple filtration and reused for four cycles with almost consistent activity.

Keywords: nanocrystalline magnesium oxide; palladium(0); Stille cross-coupling; Suzuki cross-coupling

Introduction

The palladium-catalyzed Suzuki and Stille cross-coupling reactions represent two very well established methodologies[1,2] in modern organic synthesis to make C–C bonds. Most of the catalytic systems, mainly the combination of palladium salts with various phosphine ligands or N-heterocyclic carbene ligands, result in excellent yields with high efficiency. Despite the synthetic elegance and high turnover numbers, the non-reusability of the precious palladium precludes wide synthetic applications in the pharmaceutical industry. In view of the above, it is desirable to develop a ligand-free[3] and reusable catalytic system to dispense with the use of expensive and air-sensitive ligands. Earlier, we reported the effective Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes using Mg-Al layer hydroxides-supported nanopalladium catalyst.[3d] In an effort to develop a new heterogeneous system, we turned our attention towards the exploration of highly basic nanocrystalline magnesium oxide (NAP–MgO) as support. Recently we reported the enhanced activity of NAP–MgO[4] stabilized osmate, palladate, and tungstate systems in tandem dihydroxylation of alkenes, Heck vinylation, and *N*-oxidation over their homogeneous counterparts. Due to the high surface area and basicity of the nanocrystalline magnesium oxide support, these catalysts exhibit high activity. The presence of edge-corner and other defect sites allows the nanostructured MgO materials to possess a high concentration of reactive surface ions. The reactive sites on the surface of MgO are as follows:[5] 1) Mg^{2+} site, which is of the Lewis acid type, 2) O^{2-} site which is of the Lewis base type, 3) lattice bound and 4) isolated hydroxy groups and anionic and cationic vacancies. An edge or even more so, a corner O^{2-} anion is coordinatively unsaturated and is seeking Lewis acids to help stabilize and delocalize its negative charge. Conversely, an Mg^{2+} ion on an edge or corner is seeking Lewis bases to stabilize and delocalize its positive charge. Therefore, these coordinatively unsaturated O^{2-} and Mg^{2+} ions readily accept incoming reagents with Lewis acid or Lewis base character. Herein we report the Suzuki and Stille cross-coupling of a broad range of aryl halides with arylboronic acids and phenyltributyltin, respectively, in moderate to excellent yields using the ligand-free nanocrystalline MgO-stabilized palladium(0) catalyst.

Results and Discussion

Preparation of Nanocrystalline MgO-Stabilized Pd(0) Catalyst

The peculiar characteristics of the nanomaterials present an opportunity to prepare new and unusual materi-

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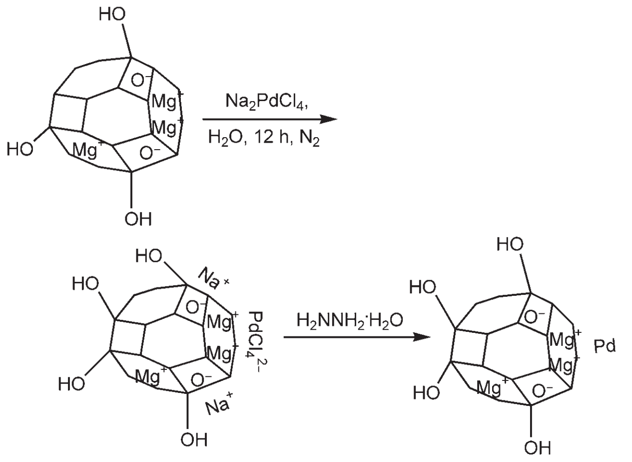

Scheme 1. Preparation of nanocrystalline MgO-stabilized palladium catalyst.

als, wherein the highly reactive ions could be stabilized by forming adducts with the reactive-accepting surface sites on the MgO. In an effort to obtain counterionic stabilization of $PdCl_4^{2-}$ with the Mg^{2+} of the MgO, commercially available CM-MgO [surface area (SA) 30 m^2/g)], and aerogel prepared nanocrystalline MgO (NAP–MgO) (SA 600 m^2/g) were treated with Na_2PdCl_4 to afford CM–Mg–$PdCl_4$ and NAP–Mg–$PdCl_4$. NAP–Mg–$PdCl_4$ was further reduced with excess hydrazine hydrate to produce NAP–Mg–Pd(0). In the reaction with NAP–MgO, (SA 600 m^2/g) the entire amount of Na_2PdCl_4 used was consumed. On the other hand, a small amount ($< 0.3\%$) of palladate was detected in the treated samples of CM–MgO. During the preparation of the catalyst, which involves the reaction with Na_2PdCl_4, the Na^+ ion will interact with the O^{x-} sites/anionic vacancies and the $PdCl_4^{2-}$ will interact with the Mg^{2+} sites/cationic vacancies present on corners or edges of nanocrystalline MgO to form the catalyst as described in Scheme 1.

Characterization of NAP–Mg–Pd(0)

The NAP–Mg–Pd(0) catalyst developed was well characterized by FTIR, XRD, XPS, SEM-EDX, TEM and UV/Vis-DRS. During the preparation of this catalyst the surface of nanocrystalline MgO was hydroxylated as indicated by non-H-bonded OH groups at 3697 cm^{-1} in the FTIR spectra (Figure 1).

This is consistent with the reactive profile of NAP–MgO with water.[6] The surface of the nano-MgO is only hydroxylated to $Mg(OH)_n$, and it takes a longer time and heating to transform the bulk nano-MgO. The XRD of the NAP–Mg–$PdCl_4$ and NAP–Mg–Pd(0) samples also indicate the formation of $Mg(OH)_n$ during preparative protocol (Figure 2).[7]

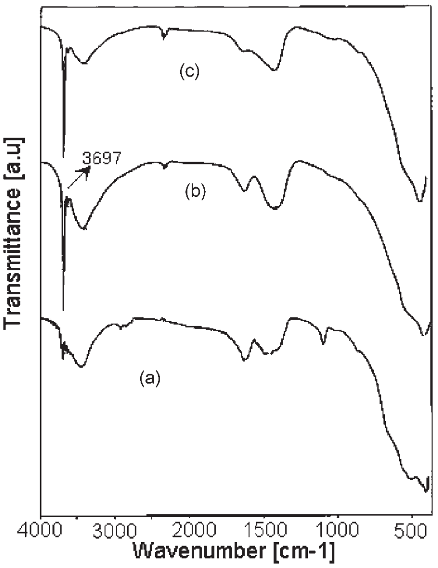

Figure 1. FTIR spectra of **a**) NAP–MgO, **b**) NAP–Mg–$PdCl_4$, and **c**) NAP–Mg–Pd(0).

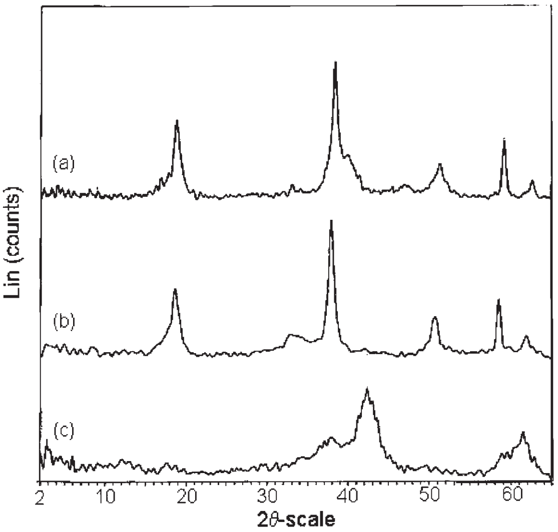

Figure 2. XRD of **a**) NAP–Mg–Pd(0), **b**) NAP–Mg–$PdCl_4$, and **c**) NAP–MgO.

The X-ray photoelectron spectroscopic (XPS) investigation of the NAP–Mg–Pd(0) at the Pd 3d level shows a $3d_{5/2}$ line at 335.02 eV, which clearly indicates that the metal is in the zero oxidation state.[8] The SEM-EDX (scanning electron microscopy-energy dispersive X-ray analysis) of NAP–Mg–Pd(0) shows the presence of palladium (10.57%) in the sample. The TEM image of the NAP–Mg–Pd(0) catalyst shows the average size of the nanopalladium particles in the range of 30–40 nm. The complete reduction of palladium in NAP–Mg–Pd(0) was further confirmed by diffuse-reflectance UV/Vis spectra, in which the peak at 290 nm

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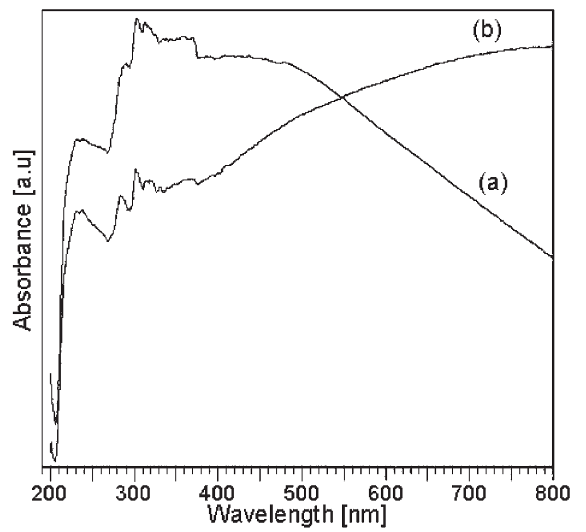


Figure 3. Diffuse-reflectance UV/Vis spectra of **a**) NAP–Mg–$PdCl_4^{2-}$ and **b**) NAP–Mg–Pd(0).

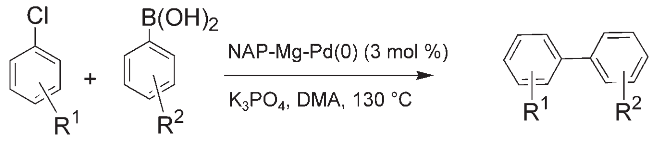
corresponding to $PdCl_4^{2-}$ disappeared on reduction (Figure 3).[3d]

Catalytic Suzuki Coupling of Chloroarenes

A variety of chloroarenes reacted in the presence of 3 mol % of NAP–Mg–Pd(0) catalyst with different arylboronic acids in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB, 20 mol %) at 130 °C in dimethylacetamide (DMA) solvent for 2–6 h to afford the corresponding cross-coupling product in moderate to excellent yields. The results are summarized in Table 1.

The presence of electron-withdrawing or electron-donating group in the chloroarene system significantly influences the reaction rate. The chloroarenes with electron-withdrawing group gave excellent yields, whereas

Table 1. Suzuki coupling reactions of chloroarenes with NAP–Mg–Pd(0) catalysts.[a]



Entry	Chloroarene	Arylboronic acid	Isolated yield [%]
1	p-NO_2-C_6H_4-Cl	C_6H_5-$B(OH)_2$	90, 85[b]
2	p-CN-C_6H_4-Cl	C_6H_5-$B(OH)_2$	85
3	p-CH_3CO-C_6H_4-Cl	C_6H_5-$B(OH)_2$	80
4	C_6H_5-Cl	C_6H_5-$B(OH)_2$	65
5	C_6H_5-Cl	p-MeO-C_6H_4-$B(OH)_2$	78
6	C_6H_5-Cl	p-Me-C_6H_4-$B(OH)_2$	65
7	C_6H_5-Cl	m-NO_2-C_6H_4-$B(OH)_2$	45
8	C_6H_5-Cl	p-F-C_6H_4-$B(OH)_2$	51
9	p-Me-C_6H_4-Cl	C_6H_5-$B(OH)_2$	58
10	p-MeO-C_6H_4-Cl	C_6H_5-$B(OH)_2$	45

[a] Chloroarene (1 mmol), arylboronic acid (1.5 mmol), NAP-Mg-Pd(0) (3 mol %), K_3PO_4 (3 mmol), and TBAB (0.2 mmol) heated at 130 °C for 2 – 6 h under argon. All reactions were carried out in DMA (2 mL) solvent.

[b] Yield after 5th cycle.

Table 2. Suzuki coupling of bromo- and iodoarenes with NAP–Mg–Pd(0) catalysts.[a]

Entry	Haloarene	Arylboronic acid	Isolated yield [%]
1	C_6H_5-I	C_6H_5-B(OH)$_2$	95, 92[b], 90[c], 88[d], 85[e], 40[f]
2	C_6H_5-I	*p*-MeO-C_6H_4-B(OH)$_2$	98
3	C_6H_5-I	*p*-Me-C_6H_4-B(OH)$_2$	97
4	C_6H_5-I	*p*-F-C_6H_4-B(OH)$_2$	95
5	*p*-NO$_2$-C_6H_4-I	C_6H_5-B(OH)$_2$	98
6	*p*-MeO-C_6H_4-I	C_6H_5-B(OH)$_2$	90
7	*o*-Me-C_6H_4-I	C_6H_5-B(OH)$_2$	92
8	*p*-Me-C_6H_4-Br	C_6H_5-B(OH)$_2$	95
9	C_6H_5-Br	C_6H_5-B(OH)$_2$	92
10	*p*-NO$_2$-C_6H_4-Br	C_6H_5-B(OH)$_2$	95
11	*p*-MeO-C_6H_4-Br	C_6H_5-B(OH)$_2$	90

[a] Haloarene (1.0 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), water (1 mL), NAP-Mg-Pd(0) (0.5 mol %) stirred at room tempareture for 5 – 6 h.

[b] Yield after 5th cycle.

[c] NAP-Mg-Pd(0) (0.1 mol %), reaction time 24 h.

[d] NAP-Mg-Pd(0) (0.01 mol %), reaction time: 40 h.

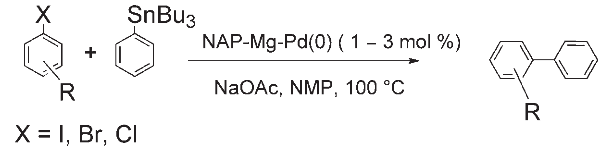
[e] NAP-Mg-PdCl$_4$ (0.5 mol %).

[f] Na$_2$PdCl$_4$ (0.5 mol %) reaction time 24 h.

the electron-rich chloroarenes led to moderate yields. Conversely, arylboronic acids with electron-donating groups afforded higher yields than those with electron-withdrawing groups. The catalyst was reused for four times (Table 1, entry 1). It was interesting to find out that this NAP–Mg–Pd(0) catalyst can efficiently promote the coupling of a variety of iodo- and bromoarenes with different arylboronic acids at room temperature in aqueous medium with only 0.5 mol % loading without any additive. The results are summarized in Table 2.

Screening of different solvents for the Suzuki coupling of *p*-Me-C_6H_4-Br and PhB(OH)$_2$ revealed that water (GC yield: 98%) is an excellent solvent for this reaction although methanol (95%), 2-propanol (97%) and toluene (95%) were also equally effective, but the yields with acetonitrile (20%) and DMF (15%) were poor. Among the different bases screened[9] K_2CO_3, KF, and NaOH were found to be of almost equal activity. Here we performed all the reactions with 0.5 mol % of Pd catalyst but we can also use 0.1 or 0.01 mol % of catalyst with longer reaction times (Table 2, entry 1). NAP–Mg–PdCl$_4$ also catalyzed the reaction, but less effectively than NAP–Mg–Pd(0) (Table 2, entry 1). The used NAP–Mg–PdCl$_4$ catalyst in XPS did not show any signal for Pd(0) and the reaction after 5 h virtually stops without any improvement in yield even on prolonged stirring (24 h). These facts suggest that NAP–Mg–Pd(0) is more active than the NAP–Mg–PdCl$_4$ probably due to the presence of nanopalladium particles having higher electron density prompted by strong interaction with basic nano-MgO support, which in turn facilitates the oxidative addition of the haloarenes and subsequently enhancing the coupling reaction. The NAP–Mg–Pd(0) also differs from

Table 3. Stille coupling of haloarenes with NAP–Mg–Pd(0) catalyst.[a]



Entry	Haloarene	Reaction time [h]	Isolated yield [%]
1	C_6H_5-I	2	95
2	*p*-MeO-C_6H_4-I	2.5	92
3	*p*-Me-C_6H_4-I	2.5	92, 90[b]
4	C_6H_5-Br	3	90
5	*p*-MeO-C_6H_4-Br	4	88
6	*p*-NO_2-C_6H_4-Cl	8	92
7	*p*-CN-C_6H_4-Cl	8	90
8	C_6H_5-Cl	12	85, 84[b]
9	*p*-MeO-C_6H_4-Cl	18	70

[a] Reaction conditions: haloarene (1.0 mmol), phenyltributyltin (1.5 mmol), NaOAc (2.0 mmol), NAP-Mg-Pd(0) (1 – 3 mol %), NMP (2 mL), 130 °C.

[b] Yield after 5th cycle.

the classical systems like Pd(OAc)$_2$ and other simple palladium(II) salts in its easy recovery by simple filtration and showing consistent activity for five cycles. Moreover these simple salts,[3h] Pd(OAc)$_2$ and PdCl$_2$·(SEt)$_2$ required 62–96 h for the completion of reaction (bromoarenes) at room temperature compared to the NAP–Mg–Pd(0) requiring only 5–6 h.

Catalytic Stille Coupling of Haloarenes with Phenyltributyltin

Impressed with the results for the Suzuki coupling reaction, we further tried to extend the scope of the NAP–Mg–Pd(0) catalyst in another important C–C bond forming reaction, namely Stille cross-coupling of haloarenes with phenyltributyltin.

Under our optimized conditions, iodo- and bromoarenes afforded the corresponding unsymmetrical biaryls in excellent yields in presence of 1 mol % of the catalyst (Table 3). However, the coupling of chloroarenes with phenyltributyltin took a much longer reaction time despite using high catalyst loading (3 mol %). As in the Suzuki reactions, chloroarenes bearing electron-withdrawing groups gave greater yields than the chloroarenes with electron-donating groups (Table 3, entries 6–9).

Heterogeneity and Reusability of the Catalyst

The heterogeneity of the catalyst is also evaluated to study whether the reaction using solid Pd catalysts occurred on the solid surface[3d, f,g] or were catalyzed by Pd species in the liquid phase.[10] To address this issue, we conducted two separate experiments with 4-nitrochlorobenzene and phenylboronic acid. In the first experiment, the reaction was terminated after 1 h, and the conversion was found to be 55%. At this juncture, the catalyst was separated from the reaction mixture at the reaction temperature and the reaction was continued with the filtrate for an additional 5 h. In the second experiment, the reaction was terminated after 2 h at 82% conversion and the catalyst was removed. The reaction was continued with the filtrate for an additional 5 h. In both the cases, the conversion remained almost unchanged. Palladium was not detected in the filtrate in both the experiments by ICP-AES. These studies demonstrate that the palladium bound to nanocrystalline MgO during the reaction is only active and the reaction proceeds on the heterogeneous surface. Furthermore, we checked the recyclability of the catalyst and almost consistent activity was noticed even after five cycles in all reactions (Table 1, entry 1; Table 2, entry 1; Table 3, entries 3, 8).

Conclusion

In summary, we used a counterion stabilization technique for the development of a recoverable and reusable ligand-free nanocrystalline MgO-stabilized palladium(0) catalyst and successfully employed the catalyst in the Suzuki and Stille cross-couplings of haloarenes. Moreover, the catalyst was recovered by simple filtration and reused for several cycles with almost consistent activity. The simple procedure, easy recovery and reusable catalytic systems are expected to contribute to the development of benign chemical processes and products.

Experimental Section

General Remarks

FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded on Bruker (300 MHz) and Varian Gemini 200 MHz spectrophotometer

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using $CDCl_3$ as solvent and TMS as the internal standard. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscope (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Diffuse reflectance UV/Vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV-VIS spectrometer in the range 200 to 800 nm with a scan speed 400 nm per minute. GC analysis was performed using Shimadzu GC-2010 and ZB-5 capillary column. All known compounds were characterized by comparing their physical data with those in the literature. Solvents used for experiments were dried and distilled according to literature procedures. All the reactants were commercially available and used without purification. NAP–MgO (commercial name: NanoActive™ Magnesium Oxide Plus, Specific surface area (BET) $\geq 600\ m^2/g$) was purchased from NanoScaleMaterials, Inc. (Manhattan, USA).

Preparation of Nanocrystalline MgO Stabilized Palladium Catalyst

NAP–Mg–$PdCl_4$: NAP–MgO (BET 600 m^2/g, 1 g) was treated with Na_2PdCl_4 (294 mg, 1 mmol) dissolved in 100 mL decarbonated water with stirring for 12 h under a nitrogen atmosphere to afford the brown colored NAP–Mg–$PdCl_4$. Then the catalyst was filtered, and washed with deionized water, acetone, and dried.

NAP–Mg–Pd(0): NAP–Mg–$PdCl_4$ (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in 20 mL dry ethanol for 3 h under a nitrogen atmosphere to get the black-colored, air-stable NAP–Mg–Pd(0) (Pd 0.99 mmol/g).

Experimental Procedure for Suzuki Coupling of Chloroarenes

In an oven-dried, 10-mL, round-bottom flask were charged chloroarene (1 mmol), phenylboronic acid (1.5 mmol), K_3PO_4 (3 mmol), NAP–Mg–Pd(0) (3 mol %), TBAB (0.2 mmol) and dimethylacetamide (2 mL) and stirred at 130 °C under an N_2 atmosphere and the reaction was monitored by TLC. After the completion of the reaction as judged by TLC, the catalyst was filtered and reused. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was chromatographed on silica gel using hexane/ethyl acetate (10:1) as an eluent to afford the pure product. NMR and mass spectrometry were used to identify the purity of the products.

Experimental Procedure for Room Temperature Suzuki Coupling of Iodo- and Bromoarenes

In an oven-dried, 10-mL, round-bottom flask were charged aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), NAP–Mg–Pd(0) (0.5 mol %), and water (1 mL) and stirred at room temperature and reaction was monitored by TLC. After the completion of the reaction as judged by TLC, the catalyst was filtered and reused. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated to afford the crude product. The crude reaction mixture was chromatographed on silica gel using hexane/ethyl acetate (10:1) as an eluent to afford the pure product.

Experimental Procedure for Stille Coupling of Haloarenes

In an oven-dried, 10-mL, round-bottom flask were charged haloarene (1 mmol), phenyltributyltin (1.5 mmol), NaOAc (2 mmol), NAP–Mg–Pd(0) (1–3 mol %), and NMP (2 mL) and stirred at 100 °C under an N_2 atmosphere and reaction was monitored by TLC. After the completion of the reaction as judged by TLC, the catalyst was filtered and reused. The filtrate was diluted with ethyl acetate and washed with saturated aqueous NaCl solution. The organic layers were combined and dried with Na_2SO_4 and concentrated to get the crude product. The crude reaction mixture was chromatographed on silica gel using hexane/ethyl acetate (10:1) as an eluent to afford the pure product.

Acknowledgements

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