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Mesoporous Organosilica Grafted Pd Catalyst (MOG-Pd) For Efficient Base Free and Phosphine Free Synthesis of Tertiary Butyl Esters *via* tertiary-Butoxycarbonylation of Boronic Acid Derivatives Without Using Carbon Monoxide

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Abstract

A mesoporous organosilica grafted palladium(II) catalyst was synthesized and characterized using various spectroscopic techniques. Its catalytic activity was evaluated for the synthesis of tertiary butyl esters *via* tert-butoxycarbonylation of boronic acid derivatives. The tertiary butyl esters were obtained directly from boronic acid pinacol esters and di-tert-butyl dicarbonate. The reaction was optimized by varying the bases, temperature and solvents. The catalyst was very stable and can be facilely recovered and reused six times without significant decrease in its activity and selectivity.

Keywords: Mesoporous organosilica, Palladium(II) complex, tertiary butyl esters, non CO process, phosphine free.

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Introduction

Esters are some of the most important compounds in organic synthesis and are used in production of bulk and fine chemicals, natural and pharmacological compounds.[1] Derivatives of aryl (heteroaryl) esters are important source of carboxylic acids.[2] Esterification reactions are also widely employed as a means of installing protecting groups.[3] Therefore, a tremendous number of approaches for ester synthesis have been developed. *tert*-butyl group is a very important protecting group for acids, alcohols, phenols and peptide synthesis,[4] because of their stability toward strong basic conditions like organolithium and organomagnesium compounds, its relative resistance to nucleophilic attack and its ready removal by acidolysis. *tert*-Butyl groups are one of the underused protecting groups, since they are sensitive toward strong acids and harsh formation conditions.[5] However, the high utility of tertiary esters, especially as protecting groups for the free carboxylic acid, calls for the continuous development towards their synthesis.[6] Although numerous protocols are reported in the literature, the formation of tertiary esters under mild conditions remains a persistent challenge.

Carbonylation chemistry has been the focus of extensive research in laboratory-scale organic syntheses, including industrial processes.[7] Because of the continuous progress in this area, its versatility and increasing elaboration as a synthetic tool has led to broader applications in the synthesis of a wide variety of simple carbonyl compounds to more complex organic molecules. Despite the fact that Pd-catalyzed carbonylative reactions are among the most studied, only a limited amount of work has been published regarding the formation of tertiary esters.[8] The obvious drawback in such reactions is the high sterical bulk of the incoming alcohol impeding its coordination to the metal centre.[9] The use of toxic gaseous carbon monoxide, phosphine and homogeneous Pd catalyst also stands as hindrances from the viewpoint of economical and sustainable chemistry.

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The above mentioned methods suffer from some major disadvantages; the difficulty in handling toxic, gaseous carbon monoxide, including its storage and transport, represents real problems. All these disadvantages reduce the overall utility of traditional carbonylation method. Many efforts to develop the method without the use of carbon monoxide are continuously in progress and many interesting reports have appeared in past few years. In all cases, the key to success is in knowing how a carbonyl group can be transferred by using substitutes for carbon monoxide.[10]

On the other hand, arylboronic acid derivatives are air and moisture stable, and are compatible with a broad range of common functional groups.[11] Since Suzuki first reported the palladium(0)-catalyzed crosscoupling reaction of aryl boronate derivatives,[12] the exciting breakthroughs have been achieved as an important C–C bond forming reaction extensively used in the synthesis of natural products and pharmaceutical compounds. Organoboron reagents are stable and easily obtained structure. So it is a powerful substrate as an alternative to the conventional organometallic building blocks. For these reasons, they have been widely applied in chemical syntheses.[13] In contrast, the relevant palladium(II)-catalyzed alkoxycarbonylation of organoboron compounds has remained far less explored. There exist only few reports on the methoxycarbonylation of vinyl and arylboron reagents.[14] Similarly, di-t-butyl dicarbonate or Boc_2 is inexpensive and widely known as a useful stable raw material for the protection of amines and amine derivatives. It is also an efficient *tert*-butoxycarbonylating agent for phenols and thiols and used in *tert*-butoxycarbonylation of alcohols, amides, lactams and carbamates.[15] But except Y. Wu et al, none before has reported the use of Boc_2 in alkoxycarbonylation reaction for the synthesis of tert-butyl esters from boronic acid or boronic acid pinacol esters as an alternative method of tert-butyloxycarbonylation reaction without carbon monoxide.[16] In this protocol *tert*-butyl esters

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are prepared directly from boronic acids or boronic acid pinacol esters and di-t-butyl dicarbonate.

In all the above mentioned procedures for *tert*-butoxycarbonylation reactions, the Pd catalysts used are homogeneous in nature. So the catalysts are not easily separable from reaction mixtures and they are non-recyclable. Our group reported quite a few heterogeneous and recyclable catalysts for carbonylation reaction[7d-h] and now we have focussed on tertiary butoxycarbonylation in a green pathway.

In this regard, ordered mesoporous silica materials have opened many new possibilities for applications in the field of heterogeneous catalysis, adsorption, and separation due to their large, well-defined pore sizes and high surface areas.[17] Organically functionalized mesoporous materials have attracted great attention in recent times due to their huge potential applications in gas storage, sensing, light-harvesting, catalysis, drug-delivery and so on.[18] Surface functionalization with catalytic homogeneous systems especially metal complexes has been widely applied in order to generate active sites onto these mesoporous silica material surfaces. The immobilization of catalytically active metal complexes onto the surfaces offer advantages of combination of high catalytic activity, selectivity and stability with easier separation of the catalysts from the reaction media thus making it a reusable and efficient system.[20] In this context, the amine group containing organic moiety, 3-aminopropyltriethoxysilane (3-APTES), has been first anchored on the surface of mesoporous silica *via* Si-O-Si bonds, taking advantage of the surface silanol groups. Then Schiff-base condensation between the amine group and aldehyde group of furfural lead to the formation of the coordinating ligand in the mesoporous matrix which then binds covalently with palladium(II) ions

Herein we report the synthesis and characterization of a newly synthesized mesoporous silica grafted Pd(II) catalyst and its catalytic applications towards tertiary

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butoxycarbonylation reaction in a green pathway under carbon monoxide free, base free and phosphine free conditions.

Experimental

Materials and Instruments

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. The reagents were supplied by Sigma-Aldrich chemicals Company, USA and Merck Co. The chemical analysis was done by the usual procedure. The purities of solvents and substrates were checked by gas chromatography. Liquid substrates were predistilled and dried with appropriate molecular sieves. Distillation and purification of the solvents and substrates were done by standard procedures.[20]

^{1}H NMR and ^{13}C spectra were recorded on a Bruker DPX-400 NMR spectrometer in pure deuterated solvents with TMS as internal standard at 400MHz and 100MHz respectively. FTIR spectra of the samples were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Nitrogen adsorption/desorption isotherms were obtained by using a Belsorp-HP instrument (Bel Japan Inc.) at 77 K. Prior to gas adsorption measurements, all samples were degassed for 4 h at 423 K. A Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric (TGA) analysis. Powder X-ray diffraction patterns of the pure functionalized materials were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current using a Cu tube ($\lambda = 0.15406$ nm) as the radiation source. TEM analysis was carried outby using a JEOL 2010 TEM operated at 200 kV. The metal content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

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Synthesis of catalyst

Preparation of mesoporous silica (A)

In a typical synthesis, 2.96 g of cetyltrimethylammonium bromide (CTAB) (8.14 mmol) and 1.5 g of Brij-35 ($C_{12}H_{25}(OC_2H_4)_{23}OH$, a polyether and aliphatic hydrocarbon chain surfactant) were dissolved in an acidic aqueous solution of tartaric acid (TA, 0.78 g in 60.00 g H_2O) under vigorous stirring at room temperature for 0.5 h. Then 3.50 g of tetraethylorthosilane (TEOS; 16.8 mmol) was added to the mixture under continuous stirring for 1 h. Tetramethylammonium hydroxide (TMAOH, 25% aqueous solution) was thereby added dropwise and the pH was maintained at approximately 11.0. The resulting mixture was aged overnight under stirring at room temperature and then heated at 353 K for 72 h without stirring. The solid product was then recovered by filtration, washed several times with water, and dried under vacuum in a lypholyzer. The resulting powder was calcined in the flow of air at 723 K for 8 h to remove all the organic surfactants.

Preparation of Amine Functionalized Mesoporous Silica (B):

Modification of the mesoporous silica material with 3-APTES has been done by stirring 0.1 g of the obtained silica material in previous step with 0.18 g of 3-APTES in dry ethanol at room temperature for 12 h under N_2 atmosphere.[21] The white solid aminopropylfunctionalized silica thus obtained was filtered, washed repeatedly with ethyl acetate and acetone, and finally dried in air.

Preparation of functionalized mesoporous silica ligand (C) and its Pd(II) complex (D)

The 3-APTES-functionalized silica was refluxed with the furfural dissolved in methanol (20 ml) for 24 h at 333 K. The obtained silica ligand (2 g) in methanol (20 mL) was reacted with 5 mL methanolic solution of $Pd(OAc)_2$ under constant stirring and then refluxed for 24 h. The colour of the complex changes from brown to deep brown. The polymer-

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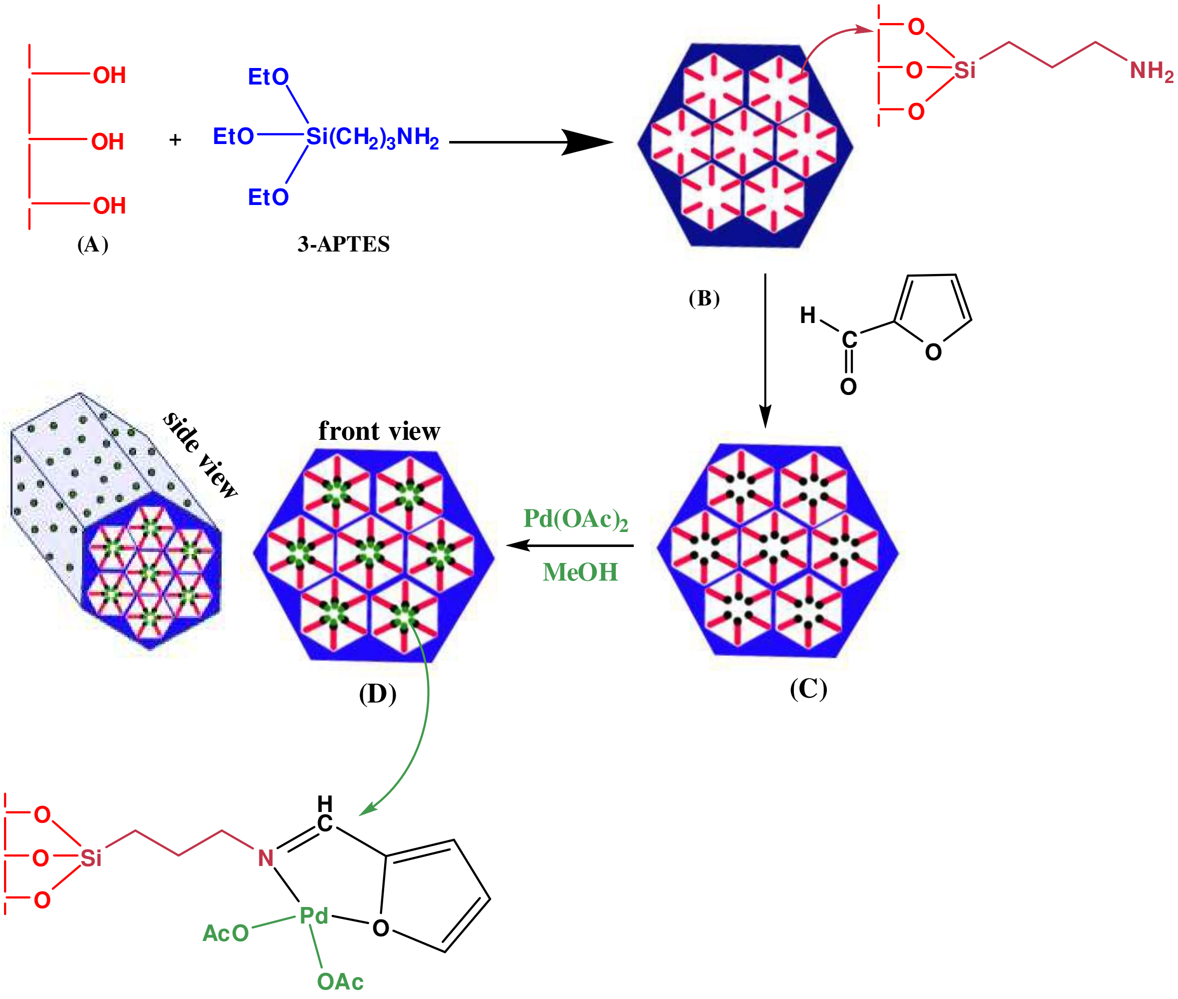
anchored metal complex obtained in this process was filtered and washed successively with acetic acid, methanol and finally dried under vacuum (Scheme 1).



Scheme 1 Synthesis of functionalized mesoporous silica grafted Pd(II) complex

General procedure for tert-butoxycarbonylation catalysed by MOG-Pd(II)

A dried round bottomed flask equipped with a magnetic stir bar was charged with 25 mg MOG-Pd(II) catalyst (6.44 x 10^{-3} mmol), 10 mol % DABCO, aryl(hetero) boronic acid pinacol esters (1 mmol) and di-tert-butyl dicarbonate (1.8 mmol). Anhydrous dioxane (2.0 mL) was added to the reaction flask and the mixture was charged with argon gas three times.

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The reaction mixture was then stirred at 80℃ under argon gas 12h. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was washed with brine solution (3 × 5 mL) and extracted with ethyl acetate (3 × 5 mL). It was then dried over Na_2SO_4 and then evaporated in vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate as the eluent to afford the corresponding tertiary butyl esters. The products were characterized by ^1H NMR and ^{13}C NMR.

Results and Discussion

Characterization of the catalyst

The attachment of metal onto the mesoporous support was confirmed by comparison of the FT-IR spectra (Fig. 1) of the support before and after loading with Pd, both in the mid-IR (4,000–400 cm^{-1}) region. FTIR spectra of both MOG (Fig. 1a) and MOG-Pd (Fig.2a) materials reveal bands at around 1087 cm^{-1} which is due to Si-O-Si linkages of the silica network. From Fig. 1a, it is evident that the peak at 1645 cm^{-1} is for C=N. For the Pd anchored mesoporous material the C=N stretching frequency is shifted to lower wavelength at 1628 cm^{-1} indicating the C=N bond is coordinated to Pd through the lone pair of electrons of nitrogen.[22]

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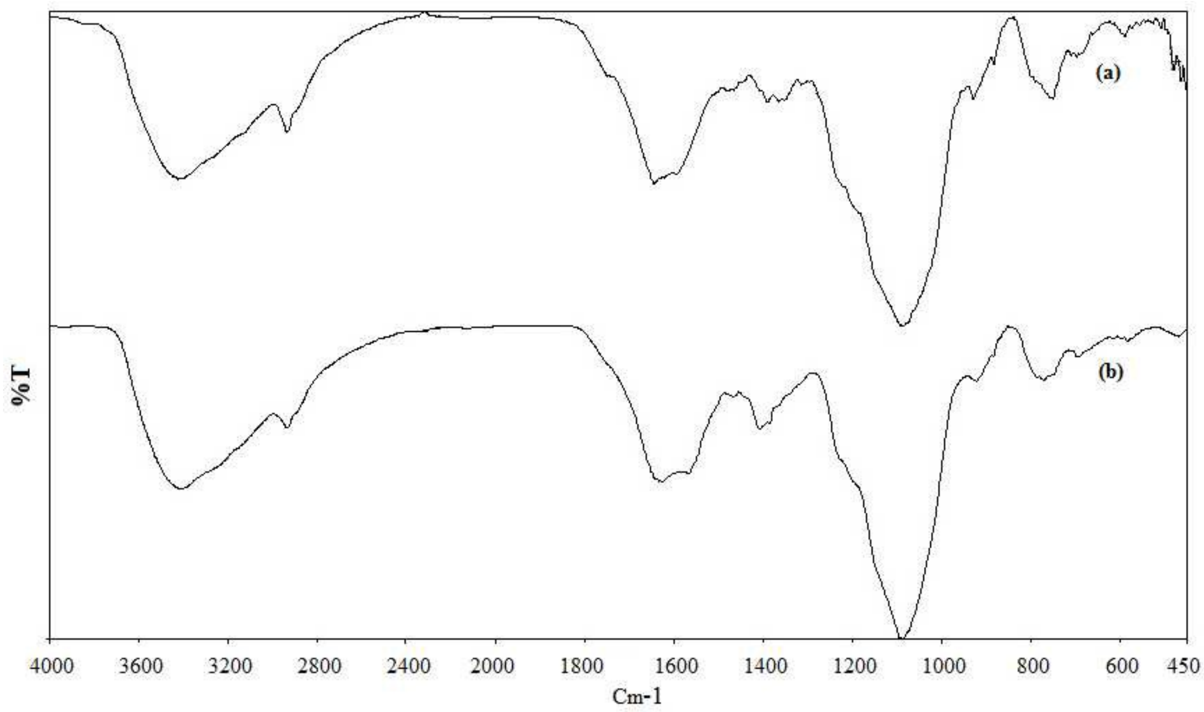

Fig. 1. FT-IR spectra of mesoporous silica (a) and grafted Pd(II) catalyst (b).

The electronic spectra (Fig. 2) of the polymer-supported metal complex were recorded in diffuse reflectance spectrum mode as $MgCO_3/BaSO_4$ disks. The present MOG material and MOG-Pd(II) complex shows a showed bands at 250-260 and 310-360 nm due to $\pi \rightarrow \pi^*$ and LMCT transitions. A broad band appears in the region 575-750 nm in MOG-Pd(II) complex due to d-d transitions.[23]

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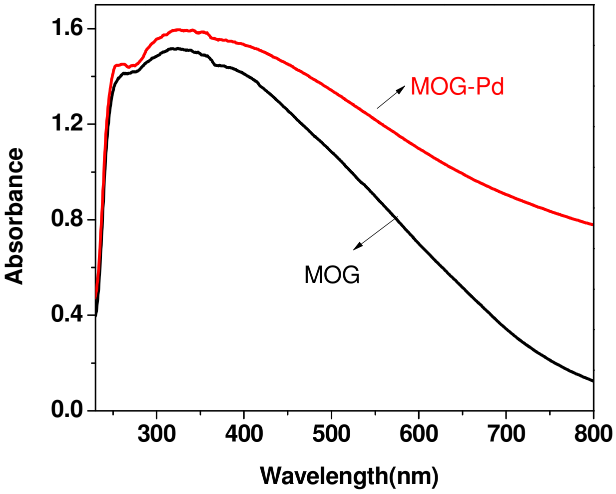

Fig. 2. DRS-UV vis spectra of MOG-Pd(II) complex

Thermal stability of complex was investigated using TGA over a temperature range of 0-700 ^{0}C. TGA curve of mesoporous silica grafted Pd(II) complex is shown in Fig. 3. The initial sharp weight loss up to 150 °C may be due to the pore occupancy by solvent molecules and moistures. A maximum weight loss has been observed from 300 °C to 700 °C and this could be attributed to the loss of the organic fragments from MOG-Pd.[24]

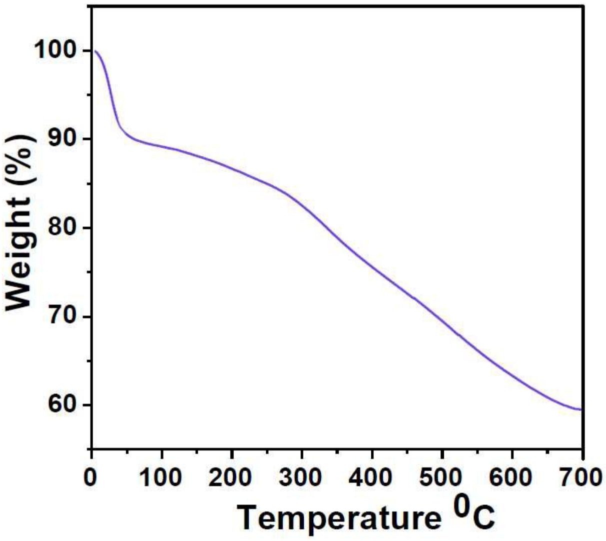

Fig. 3. TGA curve mesoporous organosilica grafted Pd(II) catalys

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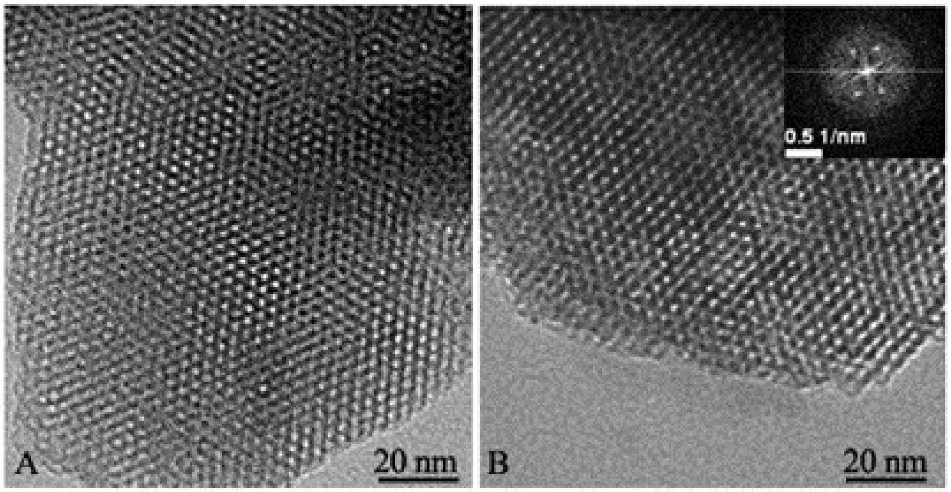
The mesoporous organosilica grafted Pd(II) catalyst was also characterized by HR-TEM analysis (Fig. 4). The presence of 2D-hexagonal mesophase and hexagonal arrangement of the pore channels are clearly observed and are shown in Fig. 4. Low electron density spots (pores) are present throughout the specimen and they are arranged in a honeycomb-like hexagonal array. FFT pattern shown in the inset of Fig. 4(B) further confirmed the hexagonal arrangement of the pores. This result suggests that the ordered arrangement of the porous framework of MOG-Pd remains unperturbed after palladium loading on MOG.[24] Further, atomic absorption spectroscopy (AAS) analysis revealed loading of 2.74 wt% Pd in MOG-Pd. The EDX image of MOG-Pd complex (Fig. 4c) confirms the presence of the respective atoms: C, N, O, Si and Pd. The TEM image of the reused catalyst is provided in Fig. S2 (supporting information).



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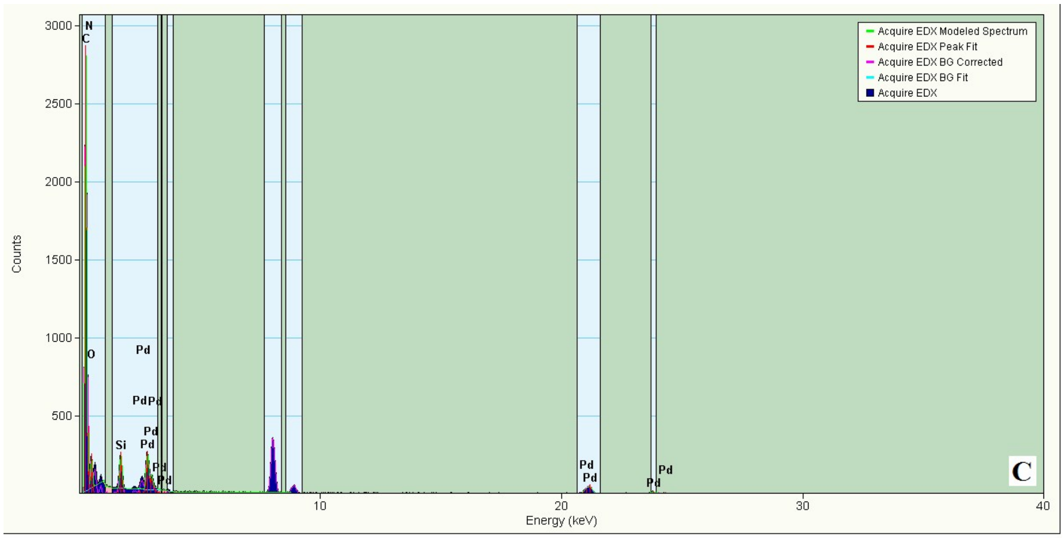

Fig. 4. HR-TEM (a-b) and EDX (c) images of mesoporous organosilica grafted Pd(II) catalyst

The powder X-ray diffraction patterns for the MOG and MOG-Pd complex are shown in Fig. 5. Fig. 5(a) is highly ordered, showing three strong diffraction peaks for the 100, 110, and 200 planes of the 2D-hexagonal mesophase.[25] MOG exhibits a single intense peak with maxima at a 2θ value of 2.28, indicating presence of mesophase in the sample. After loading with Pd, intensity of the peak was reduced and it shifted towards high angle, having a 2θ value of 2.42. The d spacing for MOG and MOG-Pd are 3.70 nm and 3.58 nm respectively indicating the retaintion of mesophase both before and after loading with Pd. The XRD pattern of the reused catalyst (Fig S1, supporting information) is almost similar to the fresh MOG-Pd(II) catalyst

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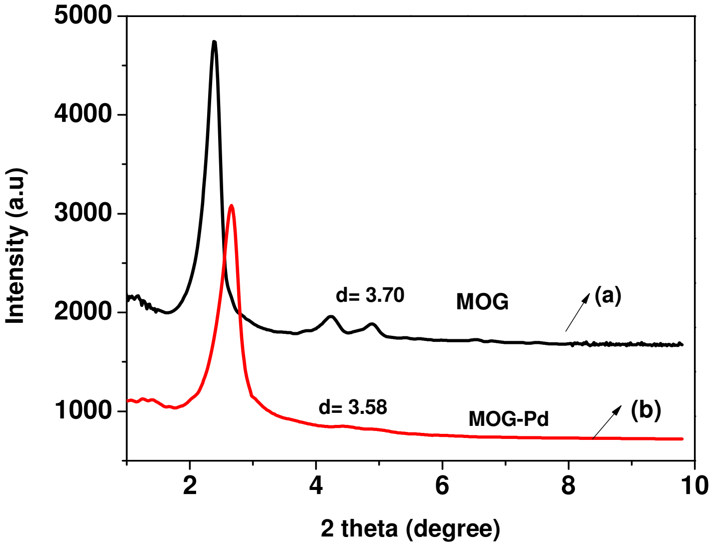

Fig. 5. XRD curve of MOG and MOG-Pd(II) catalyst

The N_2 adsorption-desorption isotherms at 77 K of the MOG-Pd material reveals typical type IV isotherms which suggests the presence of a mesoporous network (Fig. 6). The BET surface area and pore width for the amine functionalized mesoporous silica material are 881 m^2g^{-1} and 3.2 nm respectively, whereas the corresponding values for sample MOG-Pd have decreased to 156 m^2g^{-1} and 2.6 nm respectively. This decreased in pore width surely due to the Pd loading at the inner pores of mesoporous silica. A considerable decrease in the BET surface area suggests that Pd-centers have been anchored on the surfaces.[26]

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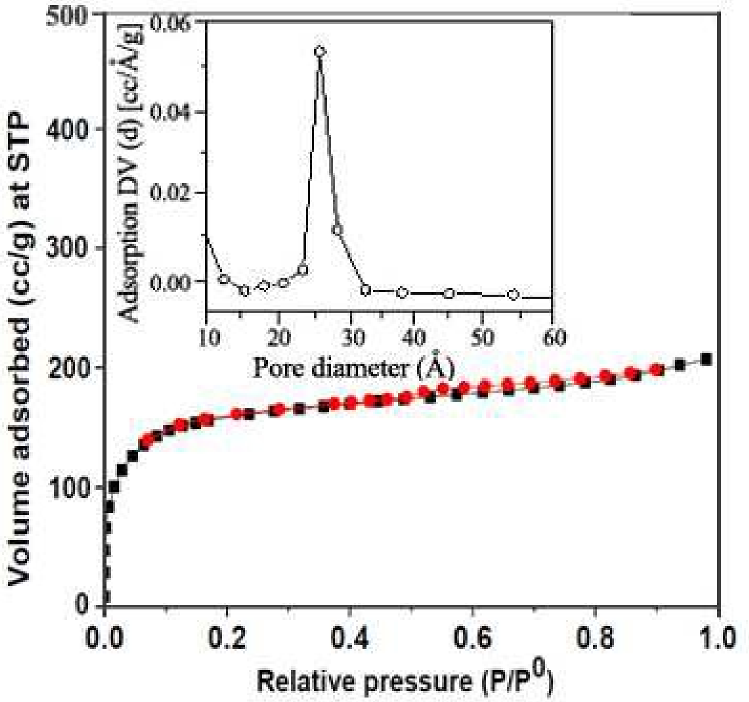

Fig. 6. N_2 adsorption-desorption of MOG-Pd(II) catalyst

Catalytic activity

As we have seen and reported several supported[27] palladium catalyst that exhibit high catalytic activity in the field of carbonylation reactions using carbon monoxide, we decided to investigate the catalytic activity of the MOG-Pd catalyst to preparare tertiary butyl esters *via* carbonylation reaction without using carbon monoxide.

The reaction between 3 pyridineboronic acid pinacol ester (A) and di tertiary butyl di carbonate (B) in argon atmosphere was chosen as the model reaction (Scheme 2). The effect of base, solvent, temperature and reaction atmosphere was monitored for the reaction. DABCO (1,4-diazabicyclo[2.2.2]octane) was used as a green, efficient and inexpensive reagent to activate and stabilize the palladium complex instead of phosphine which is expensive, air-sensitive and is not easily separable from products.[28]

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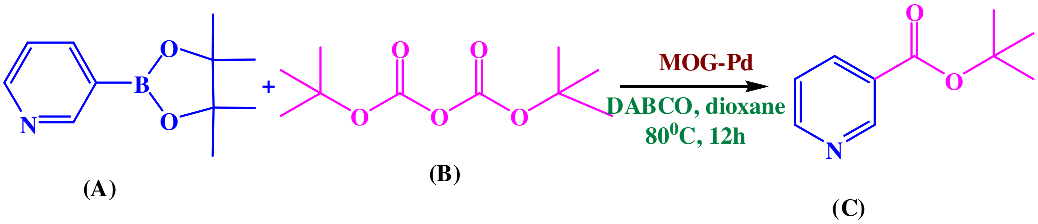

Scheme 2: Model reaction for tertiary butoxycarbonylation reaction

As bases play a very important role in a chemical reaction, so the first thing we studied after choosing the model reaction was the effect of bases. In most cases, the addition of a base increases the product yield.[29] The influence of various bases was studied for this butoxycarbonylation reaction. Na_2CO_3 gave a very good amount of tert-butoxy carbonylative product. Even K_2CO_3 and K_3PO_4 gave moderate amount of yield. KOAc and CsF were not very effective as bases and tBuOK did not furnish any carbonylative product. The most interesting point that was noted for this carbonylation reaction was that the reaction proceeded best in the absence of a base. This could be due to the oxidative addition of the Pd catalyst into di-tbutyl dicarbonate leading to the formation of an equivalent of tertiary butoxide, which may be serving as the base for the whole process.[30] The decreased yields with external bases added (especially strong bases) could be due to the fact that di-tertiary-butyl dicarbonate decomposes at high temperatures and in presence of strong base.[31] When no base was used in the reaction 96% carbonylative product was obtained.

Table 1: Effect of bases on MOG-Pd catalyzed tertiary butoxy carbonylation reaction

Entry	Base	Yield of isolated product (%)
1	Na_2CO_3	87

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2	K_2CO_3	70
3	KOAc	45
4	K_3PO_4	73
5	CsF	45
6.	t-BuOK	trace
7.	No base	96

Reaction conditions: 1mmol A, 1.8 mmol B, 25mg (6.44×10^{-3} mmol) MOG-Pd(II) catalyst, 10 mol % DABCO, 2 ml dioxane, 80 ^{0}C, 12 h, 2.2 mmol base.

The next important parameter that was optimized for the reaction was the effect of solvent. Solvents were found to have significant effects on the tertiary butoxycarbonylation reaction. Solvents like dioxane, DMF, toluene and DME were screened (Table 2). It was observed that the reaction proceeded well with moderately polar aprotic solvent and thus dioxane provided the best outcome (96%) at 80 ^{0}C (Table 2, entry 1).

Table 2: Effect of solvent on MOG-Pd catalyzed tertiary butoxy carbonylation reaction

Entry	Solvent	Yield of isolated product (%)
1.	dioxane	96
2.	DMF	4
3.	toluene	66
4.	DME	62

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Reaction conditions: 1 mmol A, 1.8 mmol B, 25 mg (6.44 x 10^{-3} mmol) MOG-Pd(II) catalyst, 10 mol % DABCO, 2 ml solvent, 80 ^{0}C, 12 h.

The reaction temperature was also varied to obtain the best yield of the tert butoxycarbonylative product. The reaction was conducted with a wide range of temperature varying from 60 ^{0}C to 120 ^{0}C. It was observed that the temperature of 80 ^{0}C served as the best reaction temperature giving an isolated product yield of 96%. Raising the temperature above 80 ^{0}C and upto 100 ^{0}C did not affect the product yield much. Above 100 ^{0}C, the desired ester yield started to decrease. This may be probably due to the decomposition of the di tertiary butyl dicarbonate.[32] Thus 80 ^{0}C was chosen as the optimized reaction temperature (Fig. 7).

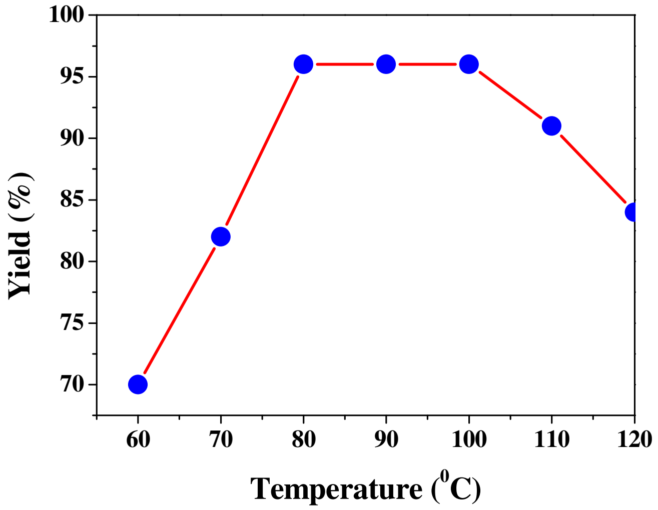

Fig. 7. Effect of temperature on MOG-Pd catalyzed tertiary butoxy carbonylation reaction

After optimizing the reaction temperature, another important parameter that was taken into account was reaction time. The best result was obtained when the reaction was carried out for 12 hrs (Fig S3, supporting information).

The amount of catalyst was also varied for tertiary butoxycarbonylation reaction. It was found that maximum yield was obtained when 25mg (6.44 x 10^{-3} mmol) of the MOG-Pd catalyst was used in the reaction (Fig S4, supporting information).

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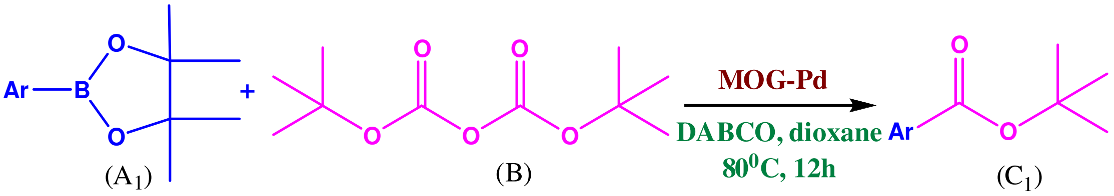
The reaction was also performed under oxygen atmosphere, but the product yield (80%) was less than that obtained by using argon atmosphere (96%).

After optimizing various reaction parameters, a range of pyridine boronic acid pinacol esters were explored to extend the reaction scope. Both electron donating and withdrawing pyridine boronic acid pinacol esters were converted to their corresponding products in good to excellent yields (Table 3, entries 1-15). A wide range of functional groups like nitrile, ether, ester, alkyl, vinyl, amino and naphthyl were found to be compatible with the present reaction conditions. The position of boronic acid pinacol esters of pyridine showed a prominent change in the yield of the tertiary butyl ester products (Table 3, entry 1-3). Tert-butyl isonicotinate furnished a low yield of the desired product (Table 3, entry 3) while tert-butyl nicotinate gave excellent yield of the product (Table 3, entry 2) and ter-butyl picolinate also gave a moderate yield of the desired product (Table 3, entry 1). For the nitrile substituted pinacol esters a moderate yield of the ester product was obtained (Table 3, entries 4 and 5). *tert*-butyl 5-ethoxynicotinate and *tert*-butyl 6-(benzyloxy)nicotinate gave excellent yields of the respective ester products (Table 3, entries 6 and 7). The other functional groups like esters, vinyl, amino and naphthyl produced moderate yields. The position of these functional groups did not have any pronounced effect on the product yield (Table 3, entries 8-15).

Table 3- MOG-Pd(II) Catalyzed tert-Butyloxycarbonylation Reactions of Various Pyridine Boronic Acid Pinacol Esters with Di-tert-butyl Dicarbonate[a]



Entry	Ar	Product	Isolated Yield (%)

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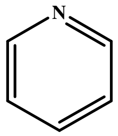
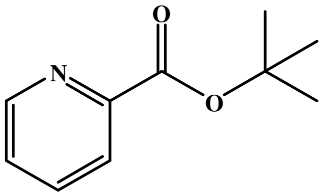
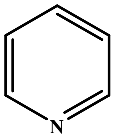
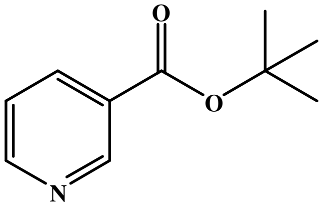
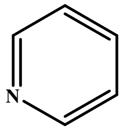
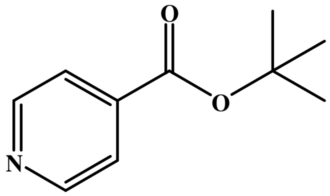
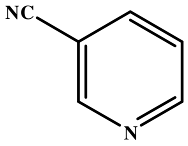
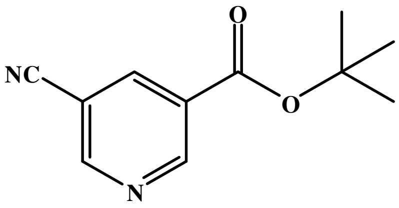
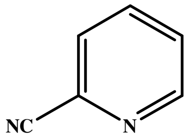
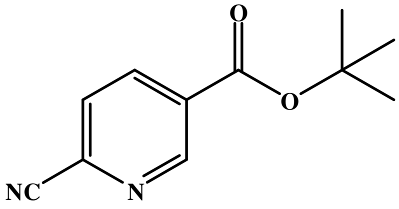
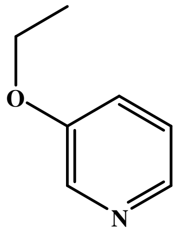
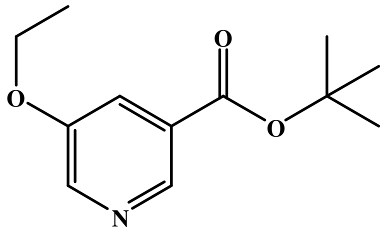
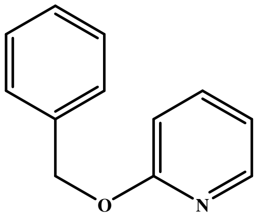
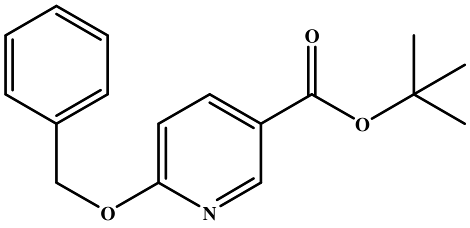
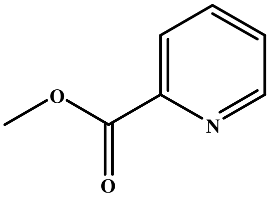
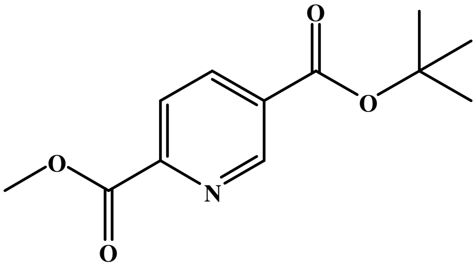
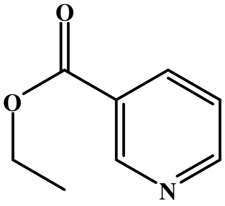
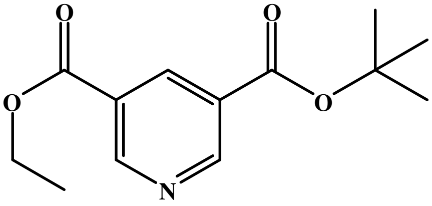
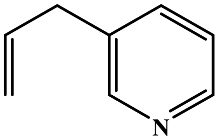
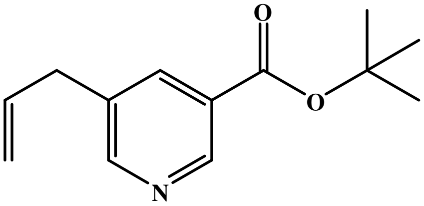
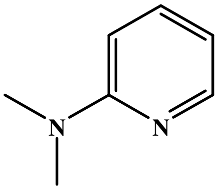
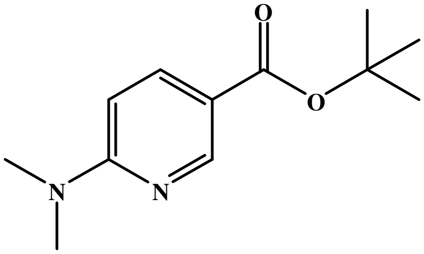
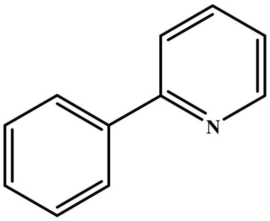
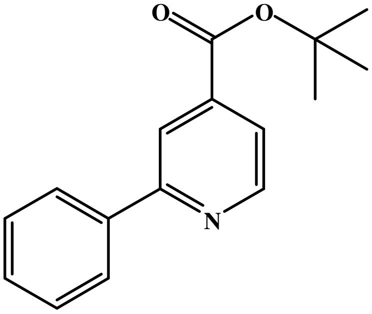
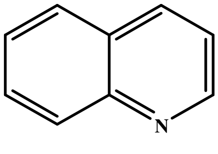
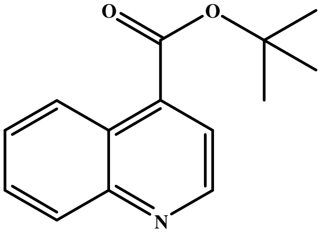
1			72
2			96
3			48
4			52
5			57
6			91
7			98

View Article Online
DOI: 10.1039/C4GC02443E

8			52
9			62
10			62
11			54
12			58
13			60

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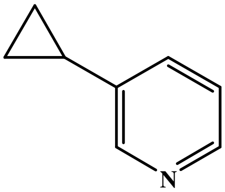
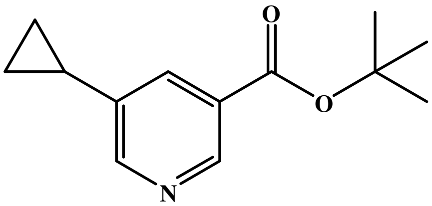
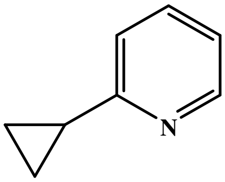
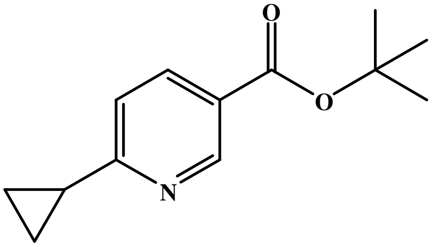
14			70
15			55

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[a] Reaction conditions: 1mmol A_1, 1.8 mmol B, 25mg (6.44 x 10^{-3} mmol) MOG-Pd(II) catalyst, 10 mol % DABCO, 2 ml dioxane, 80 ^{0}C, 12 h. The products were characterized by ^{1}H NMR and ^{13}C NMR.

We also investigated a variety of substituted phenyl boronic acid pinacol esters after the successful product yield of the tert-butyl esters from pyridine boronic acid pinacol esters. The substituted phenyl boronic acid pinacol esters furnished good to excellent yields of the respective tertiary butyl ester products. The results are summarized in Table 4. Both electron rich and electron deficient systems proved reactive towards the catalytic system, and the desired tert-butyl ester products were obtained in yields ranging from 66% to 89% (Table 4, entries 1-9). 4-biphenyl and 2-naphthyl boronic acid pinacol esters furnished excellent yields of the corresponding esters (Table 4, entries 10 and 12) while 1-naphthyl and 2-thiophenyl boronic acid pinacol esters gave quite good yields of the respective products (Table 4, entries 11 and 13).

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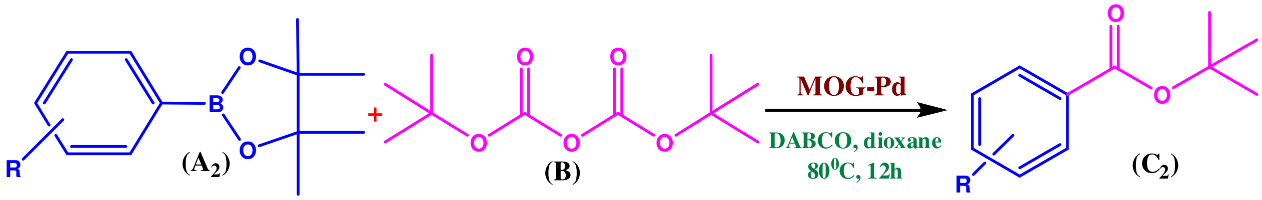
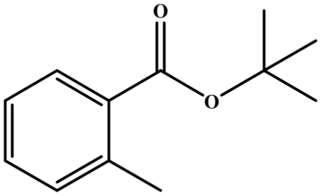
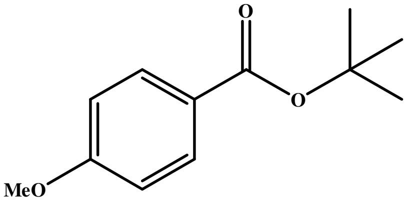
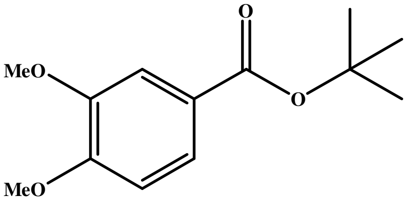
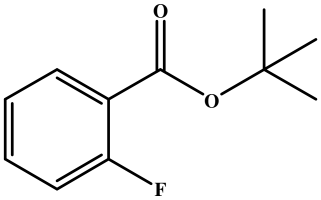
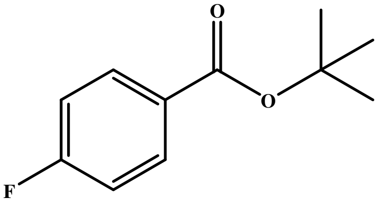
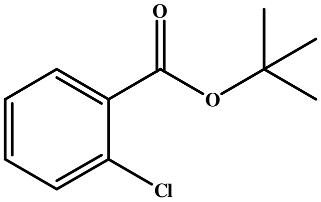
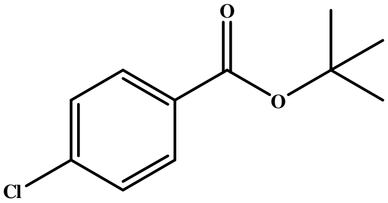
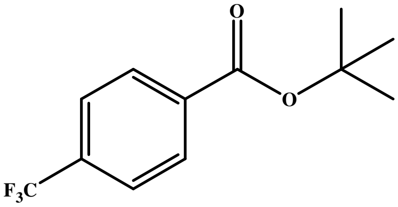
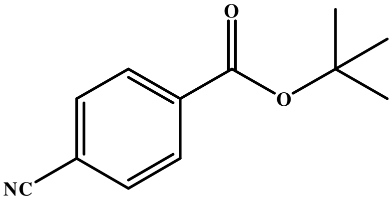
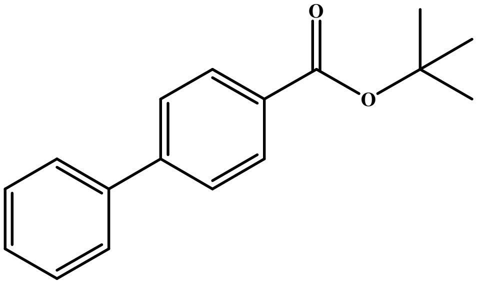
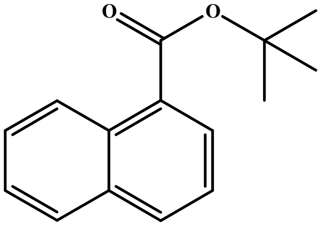
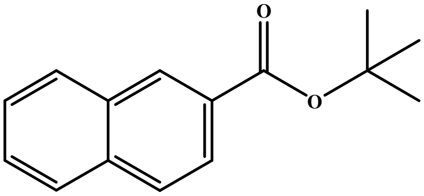
DOI: 10.1039/C4GC02443E

Table 4-MOG-Pd(II) Catalyzed tert-Butyloxycarbonylation Reactions of Various Boronic Acid Pinacol Esters with Di-tert-butyl Dicarbonate[a]

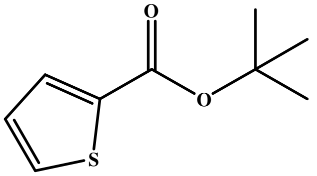


Entry	R	Product	Isolated Yield (%)
1	2-Me		84
2	4-OMe		89
3	3,4-di-OMe		86
4	2-F		72
5	4-F		79

View Article Online
DOI: 10.1039/C4GC02443E

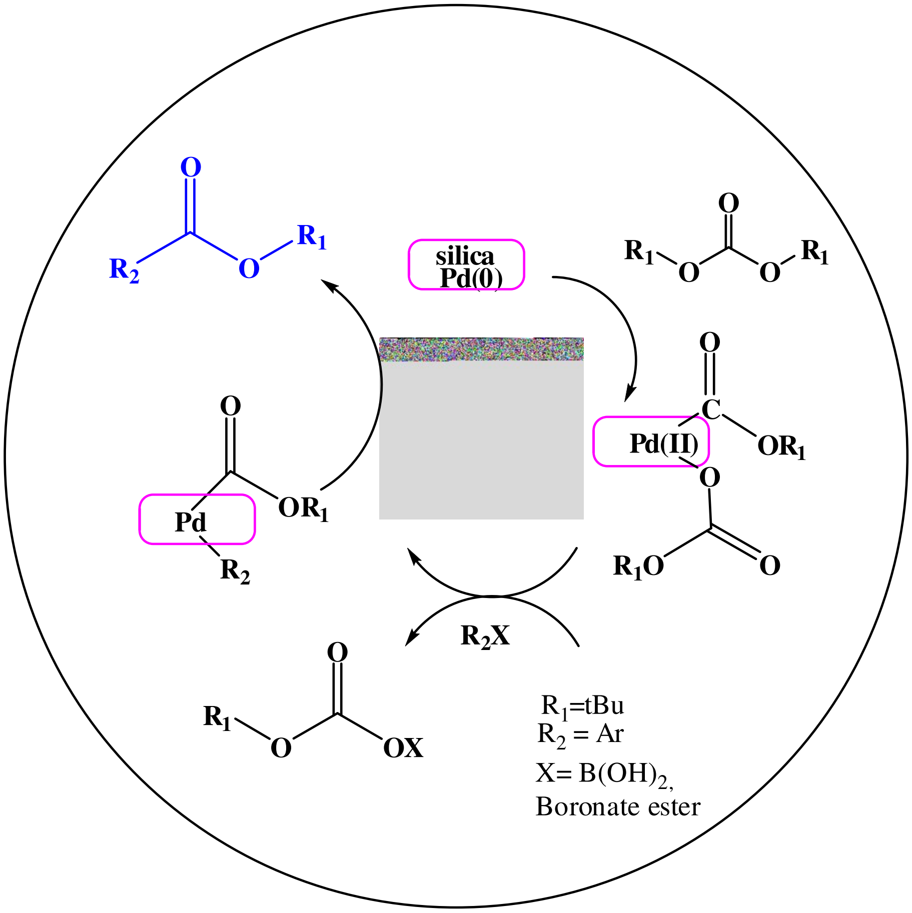
6	**2-Cl**		**66**
7	**4-Cl**		**76**
8	**4-CF_3**		**81**
9	**4-CN**		**81**
10	**4-biphenyl**		**93**
11	**1-napthyl**		**70**
12	**2-napthyl**		**90**

View Article Online
DOI: 10.1039/C4GC02443E

13	**2-thiophenyl**		**62**

[a] Reaction conditions: 1mmol A_2, 1.8 mmol B, 25mg (6.44 x 10^{-3} mmol) MOG-Pd(II) catalyst, 10 mol % DABCO, 2 ml solvent, 80 ^{0}C, 12 h. The products were characterized by ^{1}H and ^{13}C NMR.

Although the exact reaction sequence was not determined, based on former mechanistic studies of palladium-catalyzed reactions,[16, 28, 33] a probable reaction pathway is given in Scheme 3.



Scheme 3: Proposed reaction mechanism for tertiary butyl ester synthesis

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Test for heterogeneity

The leaching of palladium from polymer anchored palladium(II) complex was confirmed by carrying out analysis of the used catalyst (EDX, IR) as well as the product mixtures (AAS, UV-vis). Analysis of the used catalyst did not show appreciable loss in the palladium content as compared to the fresh catalyst. IR spectrum of the recycled catalyst was quite similar to that of fresh sample indicating the heterogeneous nature of this complex. Analysis of the product mixtures showed that if any palladium was present it was below the detection limit. The UV-vis spectroscopy was also used to determine the stability of this catalyst. The UV-vis spectra of the reaction solution, at the first run, did not show any absorption peaks characteristic of palladium metal, which indicates that the leaching of metal did not take place during the course of the reaction. The metal content of the recycled catalyst was determined with the help of AAS and it was found that palladium content of the recycled catalyst remained almost unaltered. These observations strongly suggest that the present catalyst is truly heterogeneous in nature.

Heterogeneity test for the tertiary butoxycarbonylation of 3 pyridineboronic acid pinacol ester and di tert- butyl di carbonate in argon atmosphere was carried out at 80 ^{0}C using MOG-Pd catalyst. Then after 6 h, the MOG-Pd complex catalyst was filtered off and was allowed to react further. We found that no further reaction occurred after this hot filtration procedure; hence, this experimental finding suggests there is no palladium leaching from the MOG-Pd complex during the progress of a reaction. In addition, to reconfirm this observation, AAS analysis of the reaction mixture was carried out after 6 and 12 h, which revealed a below detectable level (below 0.01 ppm) of palladium in solution.

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To ascertain if the reactions are truly heterogeneous we have also performed the three-phase test[34] for tert-butoxy carbonylation reaction. The three-phase test, developed by Rebek et al[35], is used to detect the presence of catalytically active homogeneous metal species in the reaction medium. In this test, one of the substrates is anchored to a solid support and can only react if a soluble catalytic Pd source is present. In our present study, 4-CHO substituted pyridine boronic acid pinacol ester was funtionalized to aminopropylfunctionalized silica and used in the three-phase test. The reaction mixture of 25 mg MOG-Pd(II) catalyst, 10 mol % DABCO, 3-pyridine boronic acid pinacol ester (1 mmol), di-tert-butyl dicarbonate (1.8 mmol), anhydrous dioxane (2.0 mL) was added to the reaction flask and the mixture was stirred at 80 ^{0}C under argon gas 12h. Resulting mixture was then cooled to room temperature, extracted with ethyl acetate. The combined organic layer was washed with water and brine solution. Then the combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The extracted product was analyzed by ^{1}H NMR which showed the compound was 3-pyridine tertiary butyl ester. The obtained residue was refluxed with 2M HCl and the solution was extracted with diethyl ether. The obtained 4-CHO pyridine boronic acid pinacol ester product confirms that it did not take part in the tertiarybutoxy carbonylation reaction. If any Pd leached to the solution, then anchored 4-CHO pyridine boronic acid pinacol ester would take part in the tertiarybutoxy carbonylation reaction. But this did not occur with MOG-Pd(II) catalyst here. Thus, this three-phase test provides further evidence that the reaction is truly heterogeneous in nature and there is no leaching of palladium during the course of reaction.

Recycling of catalyst

The catalyst remains insoluble in the present reaction conditions and hence can be easily separated by simple filtration followed by washing. The catalyst was washed with ethyl

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acetate and acetone and dried at 100 ^{0}C. *tert*-butoxycarbonylation reaction was carried out with the recycled catalyst under the optimized reaction conditions. The catalyst was recycled in order to test its activity as well as stability. After each run, AAS of the catalyst was performed and it was found that palladium content remained almost unchanged. The obtained results are presented in Fig. 8. As seen from Fig. 8, the catalyst did not show any appreciable change in its activity which indicates that the catalyst is stable and can be regenerated for repeated use.

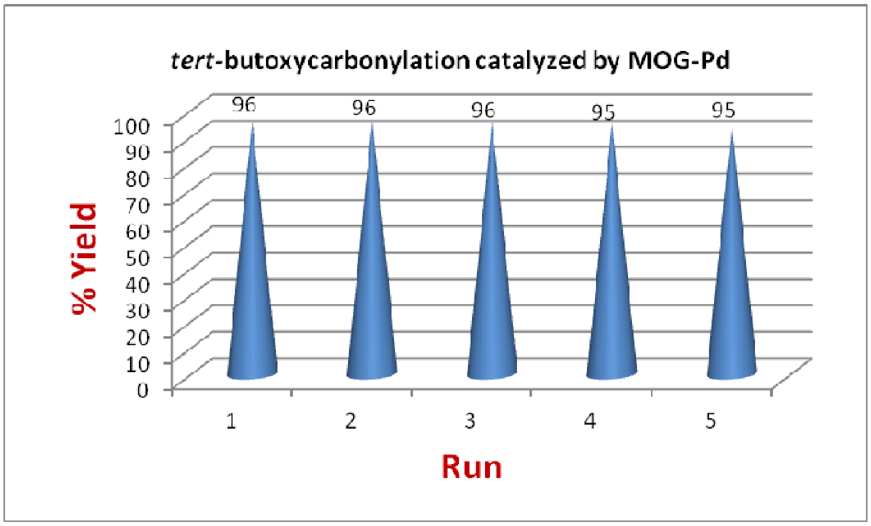

Fig. 8. Recycling efficiency of the MOG-Pd complex for the tertiary butoxy carbonylation reaction.

Conclusions

A mesoporous silica grafted palladium complex was prepared and characterized. The complex was an active and reusable catalyst for the tert butoxycarbonylation reaction of boronic acid derivatives with di-tert-butyl dicarbonate under base, CO and phosphine free conditions. The catalyst is stable and recyclable under the used reaction conditions. This heterogeneous catalyst shows no significant loss of activity in recycling experiments. The active sites do not leach out from the support and thus can be reused without appreciable loss

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of activity, indicating effective anchoring. The reusability of this catalyst is high without significant decrease in its initial activity.

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Graphical Abstract

Mesoporous Organosilica Grafted Pd Catalyst (MOG-Pd) For Efficient Base Free and Phosphine Free Synthesis of Tertiary Butyl Esters Via tertiary-Butoxycarbonylation Of Boronic Acid Derivatives Without Using Carbon Monoxide

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A mesoporous organosilica grafted Pd catalyst (MOG-Pd) has been synthesized and well characterized. This catalyst is highly efficient in *tert*-butoxycarbonylation under base free, phosphine free and carbon monoxide free condition and can be reused atleast six times.