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Graphical Abstract

Polymer Supported Pd Catalyzed Carbonylation of Aryl Bromides for the Synthesis of Aryl esters and amides

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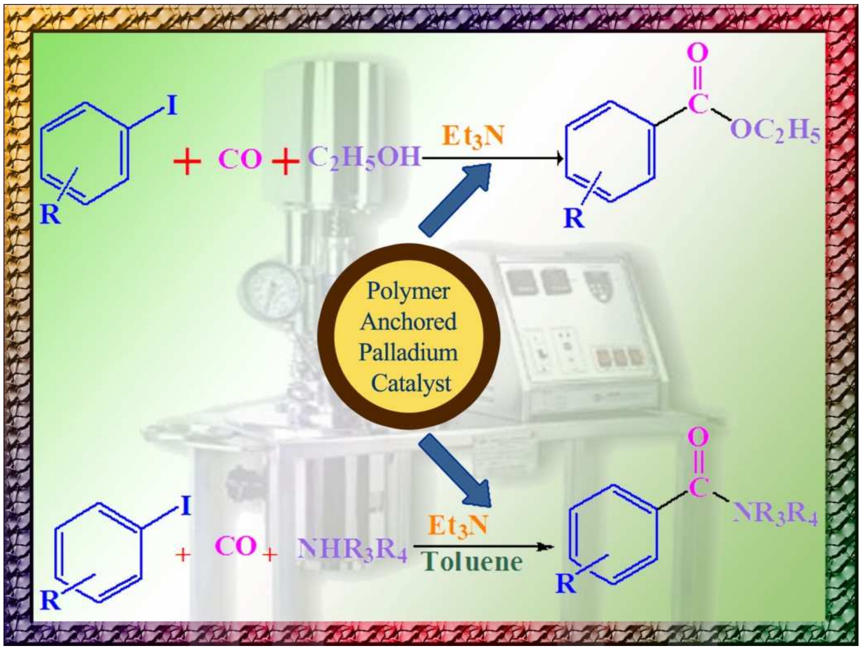
‡These authors contributed equally to this manuscript.

A new polymer anchored Pd(II) Schiff base catalyst has been synthesized for the evaluation of alkoxycrbonylation and aminocarbonylation reactions of various substituted aryl bromides with alcohols and amines.



Polymer Supported Pd Catalyzed Carbonylation of Aryl Bromides for the Synthesis of Aryl esters and amides

S. M. Islam,* Kajari Ghosh, Anupam Singha Roy[‡], Rostam Ali Molla[‡]

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Abstract

A polymer-anchored palladium(II) catalyst was synthesized and characterized using various spectroscopic techniques. Its catalytic activity was evaluated for the alkoxycrbonylation and aminocarbonylation reactions. These carabonylation reactions were carried out for various substituted aryl bromides using alcohols and amines. Both the reactions were optimized by varying the bases, temperature and solvents. These experiments were carried out under high CO pressure. The catalyst was very stable and can be facilely recovered and reused six times without significant decrease in its activity and selectivity.

Keywords: Polymer anchored, Palladium(II) complex, Alkoxycarbonylation, Aminocarbonylation, Carbon monoxide.

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Introduction

Carbonylation processes using carbon monoxide (CO) as a C_1 building block have proven to be a powerful tool to construct important scaffolds in natural products, pharmaceuticals, agrochemicals, and functional materials.[1-2] Over the past few decades, extensive efforts have been made to develop transition-metal catalyzed carbonylation of organic halides[3-5] or organic pseudohalide[6-7] for the synthesis of carboxylic acids, esters, amides, and so on.

Carbonylation of aryl halides with alcohols or amines catalyzed by palladium complexes is a convergent and direct route for the synthesis of aromatic esters and amides.[8] Aromatic esters are important building blocks for various pharmaceuticals and agrochemicals.[9] Traditionally, these esters were synthesized via reaction of the carboxylic acid with alcohols.[10] Carbonylation of the aryl halides in the presence of an alcohol is an attractive alternative method that tolerates a wide range of substrates, thus demonstrating a great advantage for the synthesis of substituted aromatic esters and its derivatives.[11-13] In this regard, various palladium-based catalytic systems have been explored for alkoxycarbonylation reaction.[14-18]

Amides are also important chemicals that exist in pharmaceuticals, natural products, and many functional materials.[19-20] Arylacetamides have gained considerable attention because of their pharmacological and biological activities.[21] Some heterocyclic amides are potential CNS (central nervous system)-active compounds.[22] Among the methods documented for the preparation of amides, most of them require harsh conditions (>150 ^{0}C) or multistep operations.[23-27] Alternatively, transition-metal catalyzed aminocarbonylation has emerged as an efficient strategy toward such types of compounds.[28] Aminocarbonylation is a constructive method for the direct synthesis of aromatic amides via coupling of aryl, heteroaryl, or alkynyl halides with primary/secondary amines.[9]

Literature reports reveal that alkoxycarbonylation and aminocarbonylation have been well explored by using a variety of homogeneous Pd complexes using various air and moisture-sensitive N/P-containing ligands.[29-35] But the recovery and recycling of the homogeneous palladium catalyst is a challenging task. To get rid of these serious issues, some heterogeneous catalysts have been reported.[36] However, these methods require prolonged reaction time, exotic reaction condition and the important issue is that most of these reported methods used phosphine containing complex which is toxic in nature. On the other hand most of the alkoxy and amino carbonylations used aryl iodides as the choice of substrate, and quantitative yields were reported.[37, 9] Therefore, developing a simple and versatile method for the preparation of aryl esters and amides from less expensive aryl bromides catalyzed by heterogeneous palladium catalyst under phosphine free condition is still a matter of interest in organic synthesis.

Herein we report the synthesis and characterization of a newly synthesized polymer anchored palladium(II) Schiff base complex and its catalytic applications towards alkoxycarbonylation and aminocarbonylation reactions of aryl bromides under the phosphine free conditions.

Experimental

Materials and Instruments

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. Chloromethylated polystyrene was supplied by Sigma-Aldrich chemicals Company, USA. Other reagents were obtained from Merck Co. The chemical analysis was done by the usual procedure. The purity of solvents and substrates were checked by gas chromatography. Carbon monoxide (99.9%) purchased from IOL Bombay and palladium acetate from Arora Matthey, India, were used as received. Liquid substrates were predistilled and dried using appropriate molecular sieves. Distillation and purification of the solvents and substrates were done by standard procedures.[38]

^{1}H NMR spectra were recorded on a Bruker DPX-400 NMR spectrometer in pure deuterated solvents with TMS as internal standard. A Perkin-Elmer 2400 C elemental analyzer was used to collect micro-analytical data (C, H and N). FTIR spectra of the samples were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. A Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric (TGA) analysis. The morphology of the functionalized polystyrene and complex was analyzed using a scanning electron microscope (SEM)(ZEISS EVO40, England) equipped with EDAX facility. The metal content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

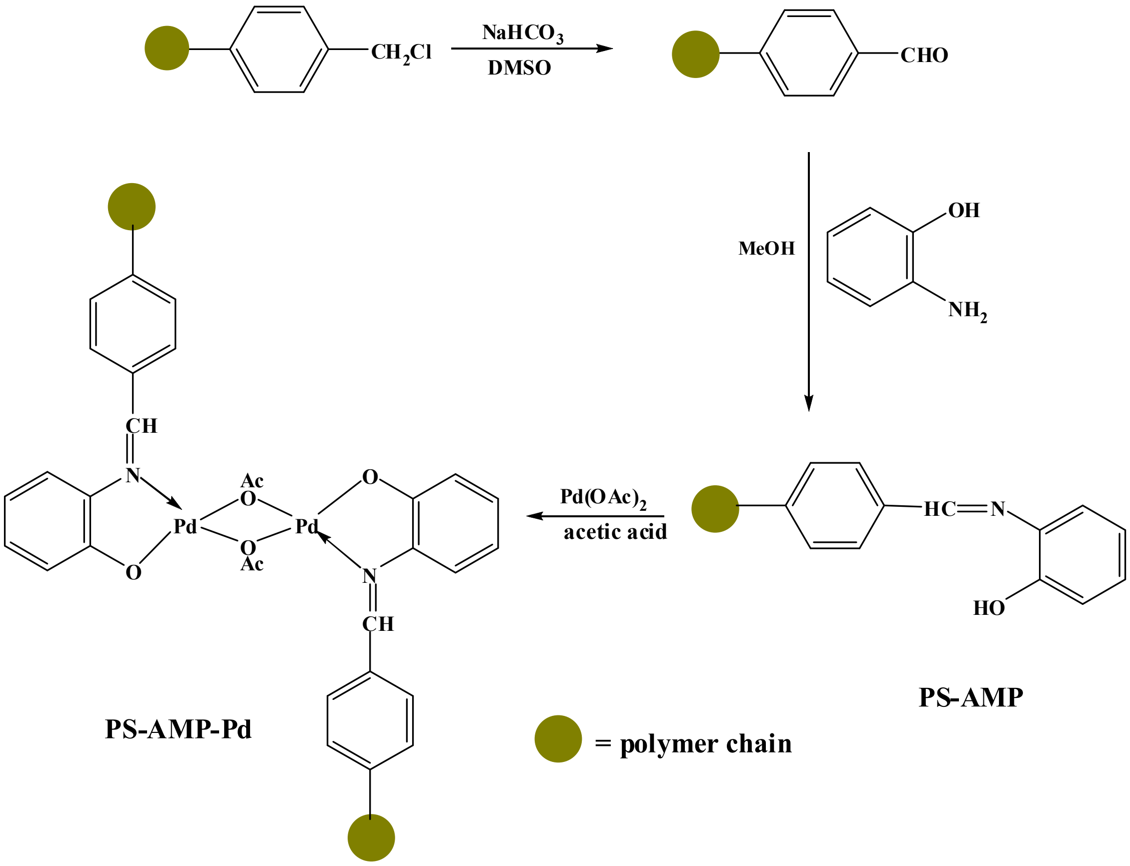
Synthesis of catalyst

Preparation of polymer-bound ligand

Polymer anchored ligand was readily prepared in two steps. Firstly, Chloromethylated (5.5 mmol Cl/g of resin) polystyrene (PS-CH_2Cl) was converted into PS-CHO according to literature.[39] 2-amino phenol was added (1:1 molar ratio) with polymer aldehyde in methanol solvent with stirring for 24 h under reflux condition to prepare the yellow Schiff base compound. The mixture was cooled to room temperature and then filtered. The residue was washed with ethanol until the filtrate became colorless and was dried under vacuum.

Preparation of polymer-bound Pd(II) complex

The polymer-anchored Schiff base ligand (2 g) in acetic acid (20 mL) was placed in a round bottom flask. 5 mL acetic acid (17.4 molar) solution (2%, w/v) of $Pd(OAc)_2$ were added with constant stirring and then refluxed for 24 h. The colour of the complex changed from yellow to deep brown. The polymer-anchored metal complex obtained by this process, was filtered and washed successively with acetic acid, methanol and finally dried under vacuum.



Scheme 1 Synthesis of polymer anchored Pd(II) complex

General procedure for Alkoxycarbonylation reaction catalysed by PS-AMP-Pd

To a 50 mL autoclave, aryl bromide (1 mmol), alcohol (5 mL), PS-AMP-Pd (4 x 10^{-4} mmol), and Et$_3$N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 1 atm of CO, and heated at 70 ^{0}C for 3 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was carefully vented, and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2×10 mL) to remove any traces of the product and catalyst if present. The catalyst was filtered, and the reaction mixture was evaporated under vacuum.

The obtained residue was purified by column chromatography (silica gel, 100-200 mesh; petroleum ether/ethyl acetate, 95:05) to afford the desired product.

General experimental procedure for Aminocarbonylation reaction

To a 50 mL high pressure autoclave, aryl bromide (1 mmol), amine (2 mmol), PS-AMP-Pd (4 x 10^{-4} mmol), toluene (10 mL), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 3 atm of CO and heated at 100 °C for 8 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 × 10 mL) to remove any traces of the product and catalyst if present. The catalyst was filtered, and the reaction mixture was evaporated under vacuum. The residue obtained was purified by column chromatography to afford the desired product.

Results and Discussion

Characterization of the polymer anchored Pd catalyst

Due to the insolubilities of the polymer-supported metal complex in all common organic solvents, its structural investigation was limited to their physicochemical properties, chemical analysis, SEM, TGA, FTIR and UV-Vis spectral data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported palladium catalyst. The palladium content of the polymer-supported catalysts was estimated by atomic absorption spectrometer and it suggests 8.79 wt% Pd in the catalyst.

Table 1 Chemical composition of polymer anchored ligand and polymer supported catalyst

Compound	colour	C%	H%	Cl %	N%	metal%
PS-AMP	yellow	75.50	5.96	5.89	2.32	-
PS-AMP-Pd	brown	68.11	5.34	4.09	2.37	8.79

The attachment of metal onto the support was confirmed by comparison of the FT-IR spectra (Fig. 1) of the polymers before and after loading with metals, both in the mid-IR (4000–400 cm^{-1}) region. The IR spectrum of pure chloromethylated polystyrene has an absorption band at 1261 cm^{-1} due to the C–Cl group, which was weak in the ligand and in the catalyst. Aldehyde functionalized polystyrene, PS-CHO shows its characteristic peak of CO at 1702 cm^{-1} (Supporting information, Fig. S1) which was strongly reduced in the ligand and catalyst (fig.1). IR spectra show a stretching vibration for -CH$_2$ at 2919 cm^{-1} for the polymer bound ligand and its complex. The stretching vibration of C=N bond appeared at 1698 cm^{-1} for the polymer-bound Schiff base ligand which is shifted to 1690 cm^{-1} in the metal complex.[40,41] Characteristic peak of free OH appeared at 3377 cm^{-1} for the ligand and its intensity is reduced in the complex.[42] A peak is observed at 1246 cm^{-1} (v C-O, phenolic) in the ligand and at 1243 cm^{-1} in the complex.[43] The polystyrene anchored Pd(II) complex exhibited important IR peaks at 1575 cm^{-1} (v_{assym} COO bridged), 1358 cm^{-1} (v_{sym} COO bridged) and 1733 cm^{-1} (v C=O)[44], which suggest the most probable structure of our catalyst is depicted in Scheme 1. Peaks for Pd-N[45] and Pd-O[46] appeared in the far-IR region.

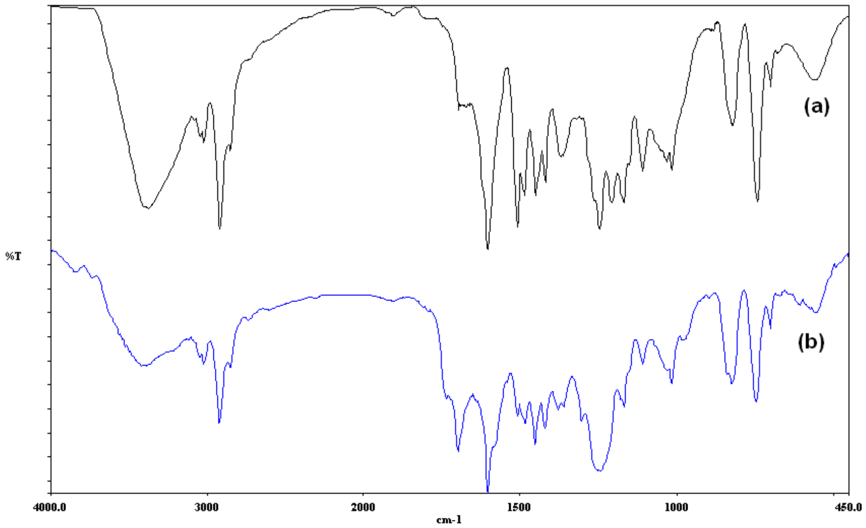


Fig. 1. FT-IR spectra of polymer anchored ligand (a) and polymer anchored Pd(II) catalyst (b).

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 Pd(II) complex shows a broad spectrum with few shoulders at a region of 260-530 nm. It may exhibit three spin-allowed d-d transitions. The bands are observed at 265-285 nm, 340-380 nm and 450-500 nm, which may be designated as $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively.[47, 48]

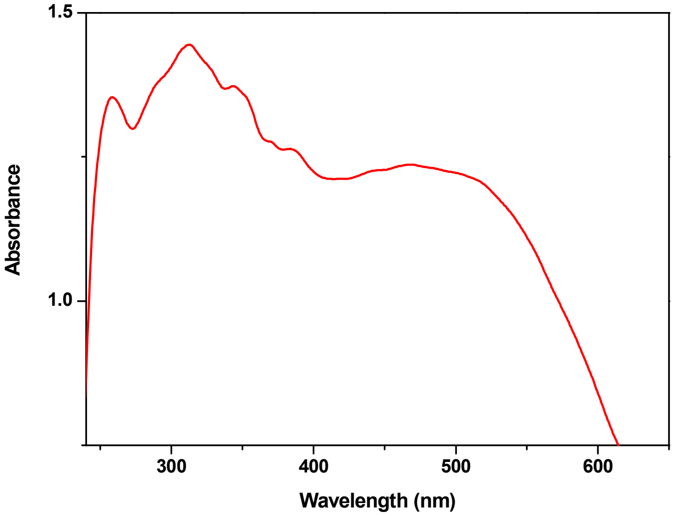


Fig. 2. DRS-UV vis spectra of polymer anchored Pd(II) complex

Field emission-scanning electron micrographs of single bead of polymer anchored ligand (PS-L) and its complex (PS-AMP-Pd) were recorded and it was observed that the morphological changes occurred on the polystyrene beads at various stages of the synthesis. The SEM images of polymer anchored ligand (A) and the immobilized palladium(II) complex (B) on functionalized polymer are shown in Fig. 3. The pure chloromethylated polystyrene bead has a smooth surface while polymer anchored ligand and complex show slight roughening of the top layer of polymer beads. This roughening is relatively more in complex. Also the presence of palladium metal can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX) (Fig. 4) which suggests the formation of metal complex with the polymer anchored ligand.

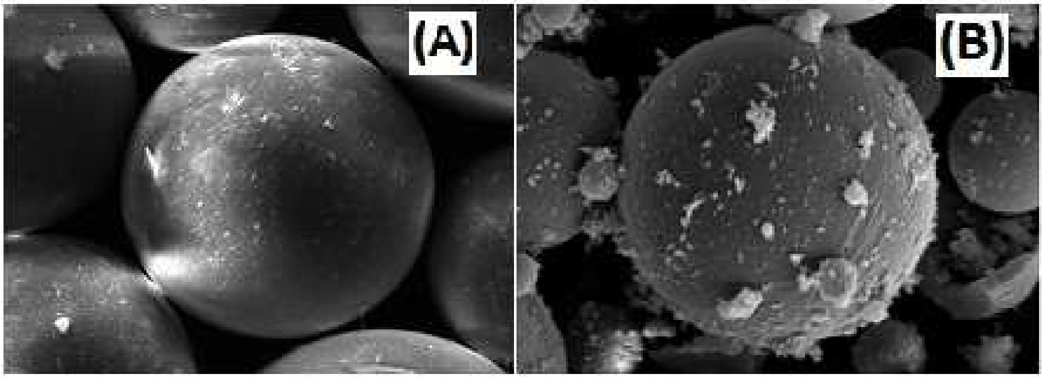


Fig. 3. FE SEM images of polymer anchored ligand (A) and polymer anchored Pd(II) complex (B)

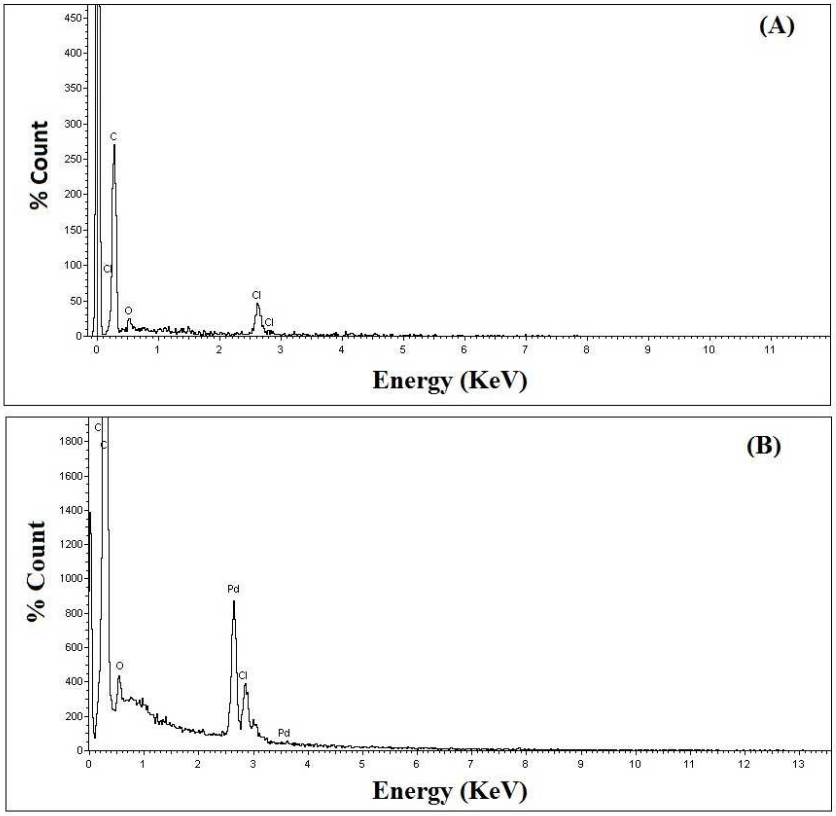


Fig. 4. EDX images of polymer anchored ligand (A) and polymer anchored Pd(II) complex (B)

Thermal stability of complex was investigated using TGA at a heating rate of 10 ^{0}C/ min in air over a temperature range of 30-600 ^{0}C. TGA curve of polymer anchored Pd(II) complex is shown in Fig. 5. Polymer anchored palladium(II) complex decomposed at 360-400 ^{0}C. So from the thermal stability, it concludes that polymer anchored metal complex degraded at considerably higher temperature.

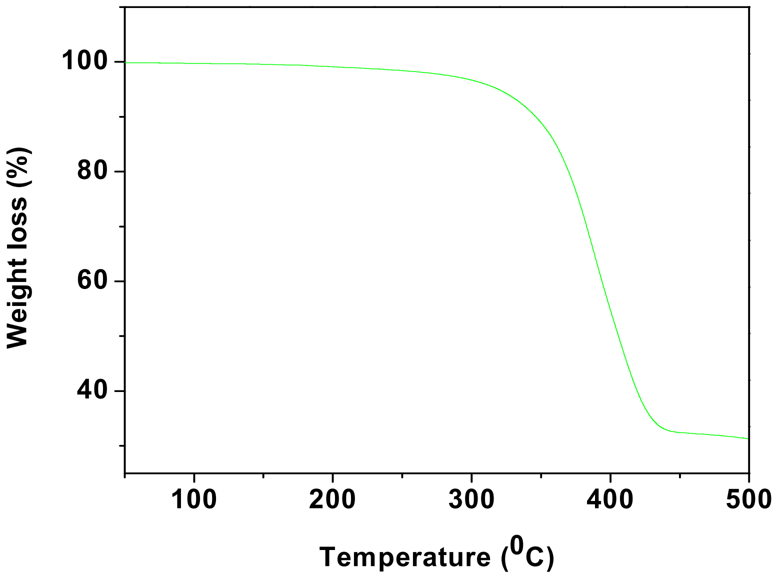
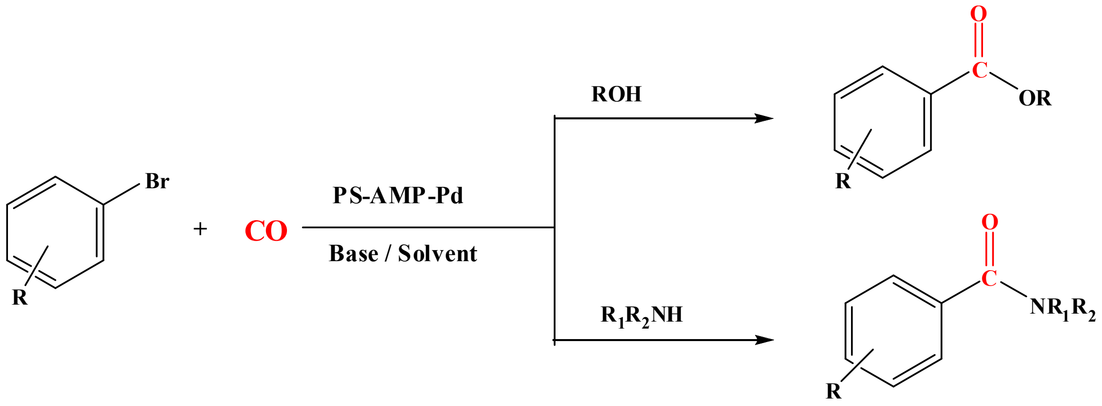


Fig. 5. TGA curve of polymer anchored Pd(II) complex

Catalytic activities

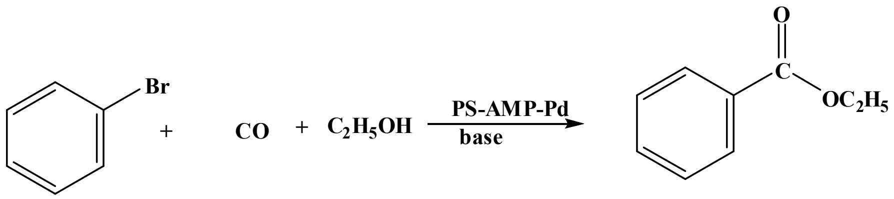
Since supported palladium catalyst exhibit high catalytic activity in a wide range of industrially important processes and have been extensively studied for C-C coupling,[49] thus we decided to investigate the catalytic activity of the PS-AMP-Pd in the field of carbonylation reactions.



Scheme 2 Palladium catalyzed alkoxy and amino carbonylation of aryl bromides

Alkoxycrbonylation reaction of aryl bromide and alcohol catalyzed by PS-AMP-Pd

Alkoxycarbonylation was carried out with bromobenzene and ethyl alcohol under CO pressure and maintaining basic medium using the polymer anchored Pd(II) catalyst. Ethyl benzoate was obtained as a product with 96% yield (Scheme 3).



Scheme 3 Alkoxycarbonylation of bromobenzene with ethanol

Initially, the reaction was carried out with various inorganic bases, such as K_2CO_3 (80%) and Cs_2CO_3 (79%), and organic bases, such as DBU (85%), NaOEt (91%) and Et_3N (96%). Because Et_3N provides the maximum yield of the corresponding product, it was used for further study. The temperature effect for the reaction was also studied (Table 2). No profound increase in the yield of the desired product was observed when the reaction temperature was increased from 70 to 100 ^{0}C; therefore, 70 ^{0}C was considered as an optimum reaction temperature for further studies.

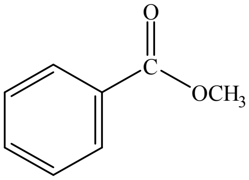
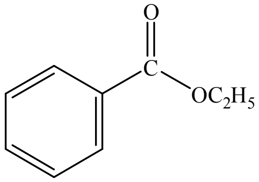
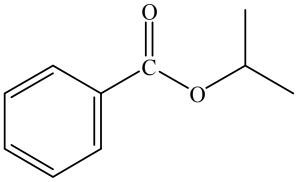
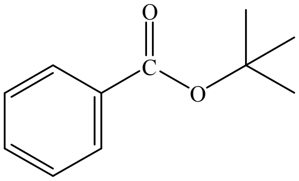
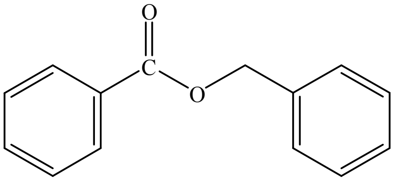
Table 2 Effect of bases and temperature on the alkoxy carbonylation of bromobenzene

Entry	Base	Temperature (^{0}C)	Conversion (%)
1	K_2CO_3	70	80
2	Cs_2CO_3	70	79
3	DBU	70	85
4	NaOAc	70	91
5	Et_3N	70	96
6	Et_3N	90	96
7	Et_3N	100	96

Reaction conditions: bromobenzene (1 mmol), alcohol (5 mL), PS-AMP-Pd (4 x 10^{-4} mmol), base (3 mmol), 1 atm CO pressure, temp. (70 ^{0}C), time (3 h).

The reaction was carried out at 1 atm of CO pressure, providing an excellent yield of the desired product within 3h. Various alcohols were reacted with bromobenzene and the results are summarized in Table 3. Changing the alcohol substrate from a primary (MeOH, EtOH) (Table 3, entry 1 and 2) to a secondary alcohol (^{i}PrOH) (Table 3, entry 3) did not have a significant effect on product yield. However, moving to a tertiary alcohol (^{t}BuOH) was not successful, a low product yield being obtained presumably due to steric bulk (Table 3, entry 4). Excellent yield was also obtained with benzyl alcohol (Table 3, entry 5). It was observed that among all the alcohols used, EtOH gave the maximum yield with bromobenzene. Hence, the finalized reaction conditions were the following: base, Et_3N; temperature, 70 ^{0}C; solvent, alcohol (also as a nucleophile, here EtOH); time, 3 h; and 1 atm of CO pressure. These reaction parameters were then successfully applied for carbonylation of a variety of aryl bromides with EtOH (Table 4, entries 1-17).

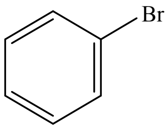
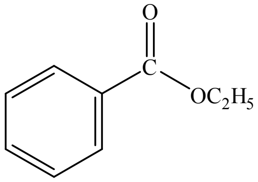
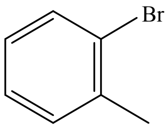
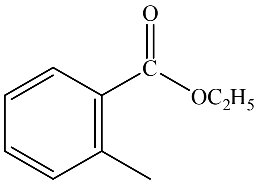
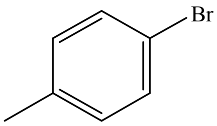
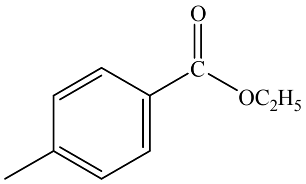
Table 3 Effect of various alcohols on alkoxycarbonylation reaction.

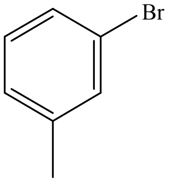
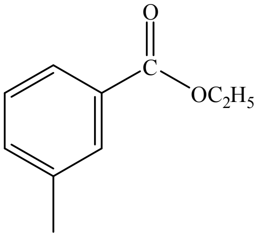
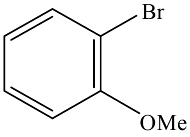
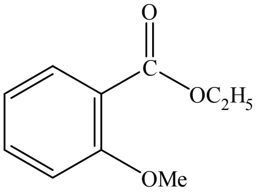
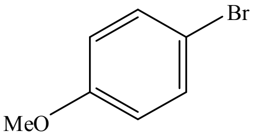
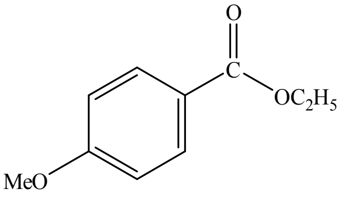
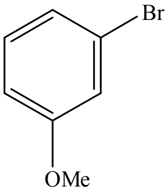
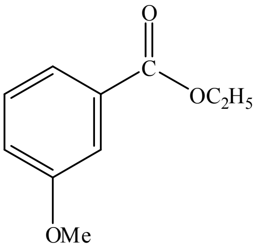
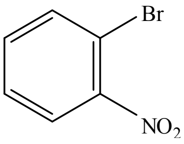
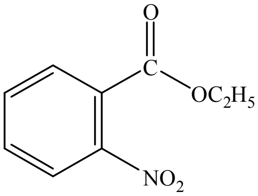
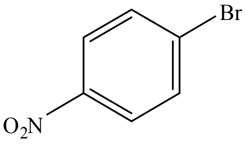
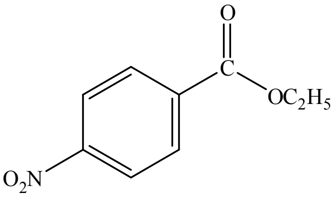
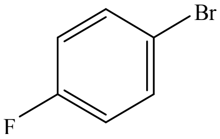
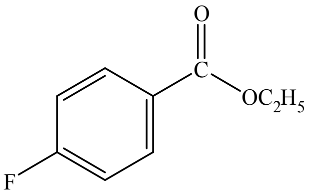
Entry	Alcohol	Product	Yield (%)
1	MeOH		95
2	EtOH		96
3	^{i}PrOH		93
4	^{t}BuOH		20
5	Benzyl alcohol		94

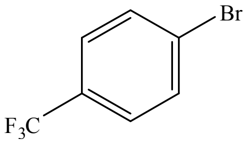
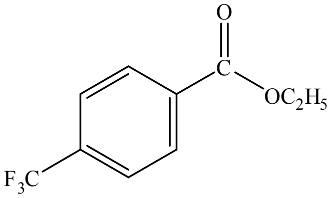
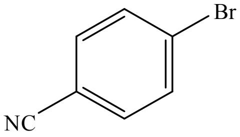
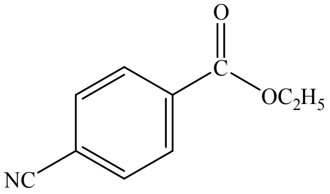
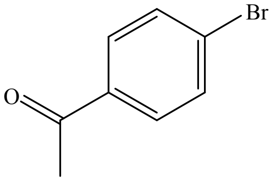
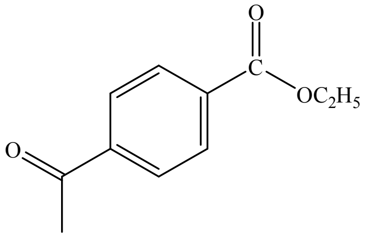
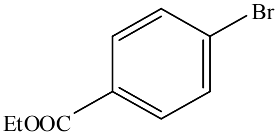
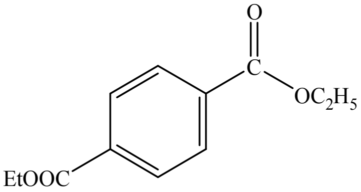
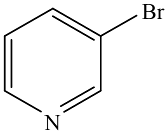
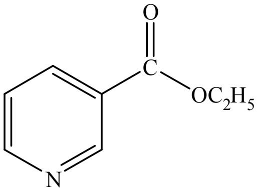
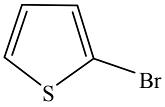
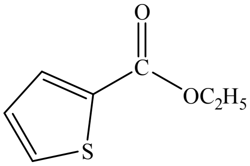
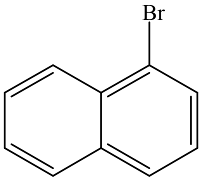
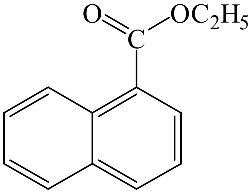
[a]Reaction conditions: aryl bromide (1 mmol), alcohol (5 mL), PS-AMP-Pd (4 x 10^{-4} mmol), Et_3N (3 mmol), 1 atm CO pressure, temp (70 ^{0}C), time (3 h). [b]Isolated yield

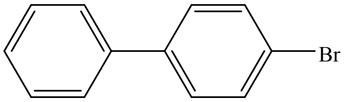
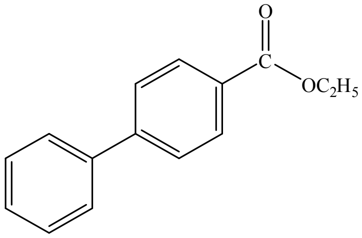
A range of aryl bromides can be converted to the ethyl esters including *ortho*-substituted examples (Table 4, entries 2, 5 and 8). The yields of different electrophiles varied from 70 to 99%. Functional groups such as methoxy, cyano, ketone, ester, and nitryl groups were well tolerated (Table 4, entries 5–9, 12-14). Fluoro and trifluoromethyl group at *para* –positions were also effectively converted into their corresponding carbonylative products in excellently high yields (Table 4, entries 10-11). As representatives of hetero-aromatic substrates, 3-bromopyridine, gave a high yield of the desired ester (Table 4, entry 15) while 2-bromothiophene only resulted in moderate yield, probably because of the volatility of the product (Table 4, entry 16). 2-bromonaphthalene and biaryl compound 4-bromobiphenyl was effectively converted (Table 4, entries 17 and 18).

Table 4 Alkoxycarbonylation Reaction of Aryl bromides with EtOH.[a]

Entry	Bromides	Product	Yield (%)	TON
1			96	2400
2			98	2450
3			99	2475

4			98	2450
5			96	2400
6			98	2450
7			98	2450
8			98	2450
9			95	2375
10			96	2400

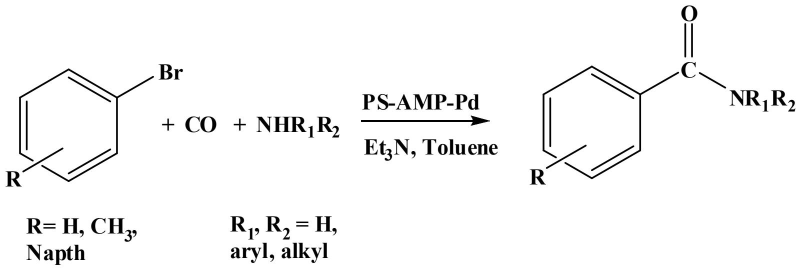
11			95	2375
12			96	2400
13			96	2400
14			95	2375
15			98	2450
16			70	1750
17			98	2450

18			98	2450

[a]Reaction conditions: aryl bromide (1 mmol), Ethanol (5 mL), PS-AMP-Pd (4 x 10^{-4} mmol), Et_3N (3 mmol), CO (1 atm), temp (70 ^0C), time (3 h). [b]Isolated yield.

Aminocarbonylation reaction of aryl bromide and amine catalyzed by PS-AMP-Pd

The scope of PS-AMP-Pd was further extended for aminocarbonylation of aryl bromides with a range of aliphatic, aromatic, primary, and secondary amines (Scheme 4).



Scheme 4 Aminocarbonylation of aryl bromides with various amines

The reaction of bromobenzene with aniline was selected as a model reaction for optimization. The influence of solvent and reaction temperature on the catalytic performance of this system was investigated by employing various solvents temperature (Table 5). Various solvents, such as DMF (90%), water (85%), anisole (64%), and toluene (96%), were screened for the reaction, but toluene was found to be the best solvent. Similarly, various temperatures were screened to get the best result (Table 5).

Table 5 Effect of solvents and Temperature on the amino carbonylation of bromobenzene

Entry	Solvent	Temperature (^{0}C)	Conversion (%)
1	DMF	90	90
2	water	90	85
3	anisole	90	64
4	toluene	70	68
5	toluene	80	75
6	Toluene	90	96
7	toluene	100	96

Reaction conditions: bromobenzene (1 mmol), aniline (2 mmol), PS-AMP-Pd (4 x 10 $^{-4}$ mmol), Et_3N (3 mmol), solvent (10 mL).

Further reaction was optimized with respect to other reaction parameters, including time and CO pressure and the best optimized reaction conditions were then applied for the aminocarbonylation of a variety of bromoaryls and amines (Table 7, entries 1−13). The conversion of amino carbonylation is dependent on the CO pressure applied. The effect of the amount of CO on the amino carbonylation of bromobenzene into corresponding amide was studied and the results are shown in Table 6. The influence of reaction time was also investigated by performing the reaction at a time range from 5h to 10h with all other parameters fixed. The results are given in Table 6 which reveals that the conversion is dependent on reaction time and maximum conversion was recorded at 9h. Therefore, 9h was selected as the optimum reaction time.

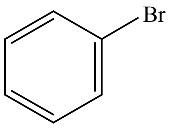
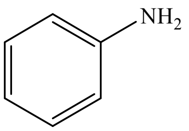
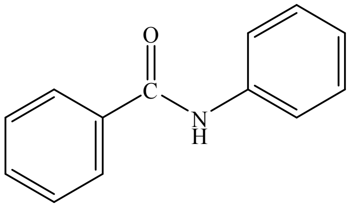
Table 6 Effect of CO pressure and reaction time on the amino carbonylation of bromobenzene

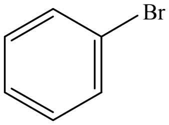
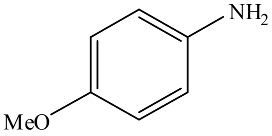
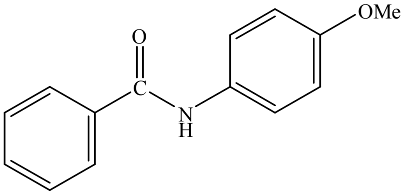
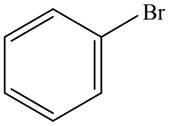
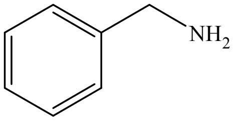
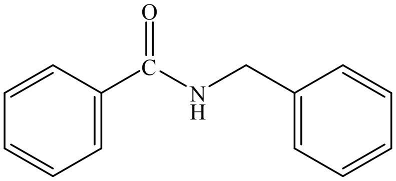
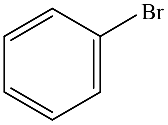
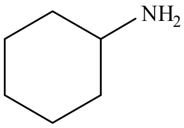
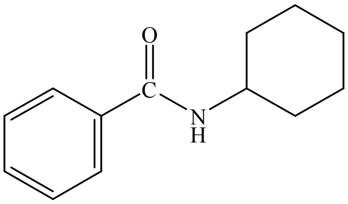
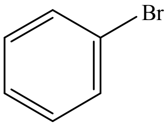
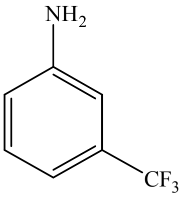
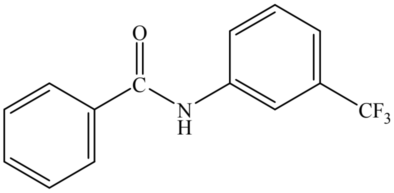
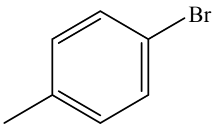
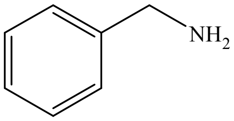
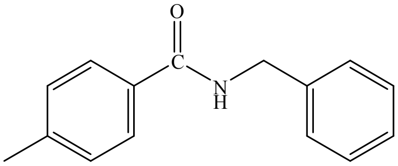
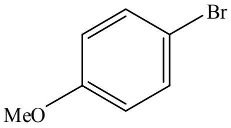
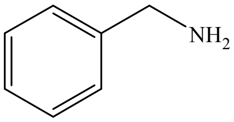
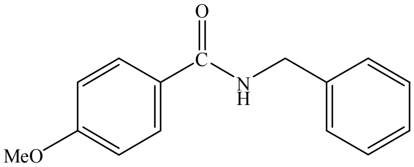
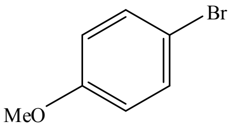
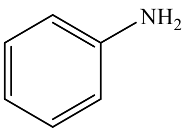
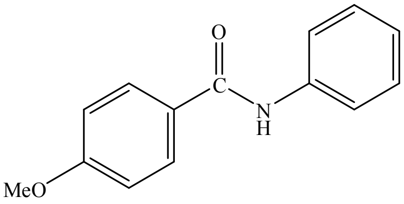
Entry	CO Pressure (atm)	Reaction time (h)	Conversion (%)
1	1	9	55
2	2	9	72
3	3	9	96
4	4	9	96
5	3	5	49
6	3	7	74
7	3	10	96

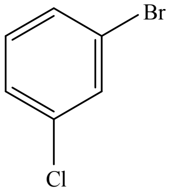
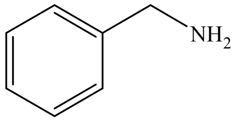
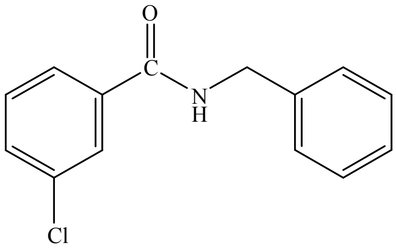
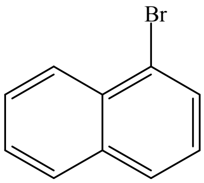
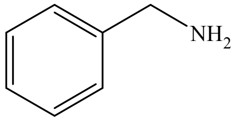
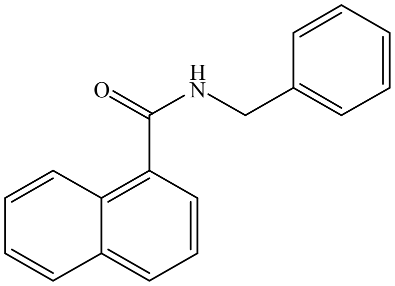
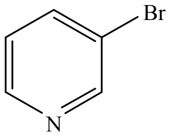
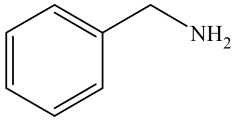
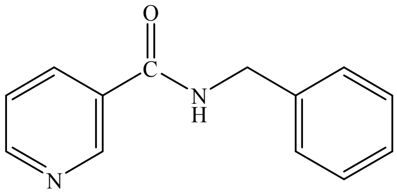
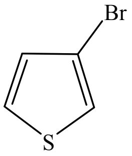
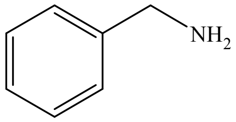
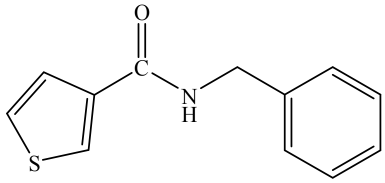
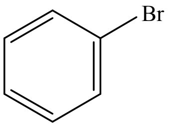
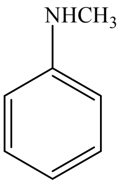
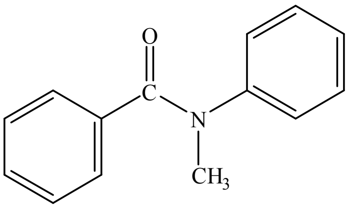
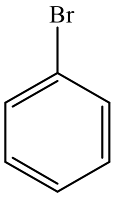
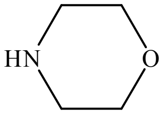
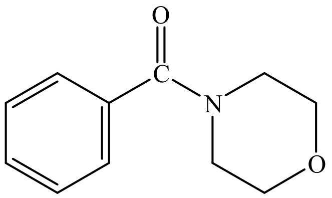
Reaction conditions: bromobenzene (1 mmol), aniline (2 mmol), PS-AMP-Pd (4 x 10 $^{-4}$ mmol), Et_3N (3 mmol), toluene (10 mL), temp (90 ^{0}C).

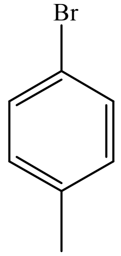
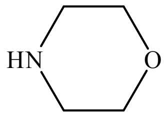
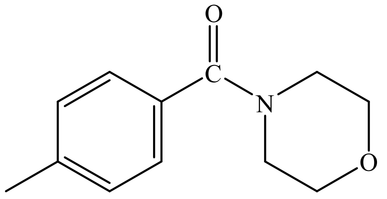
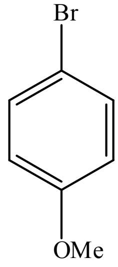
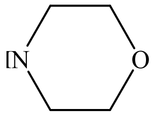
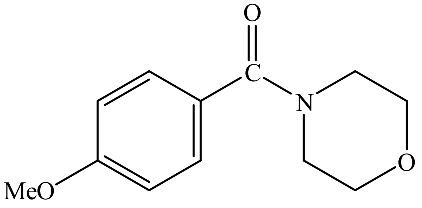
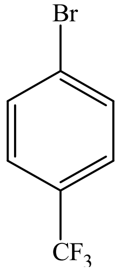
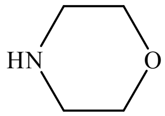
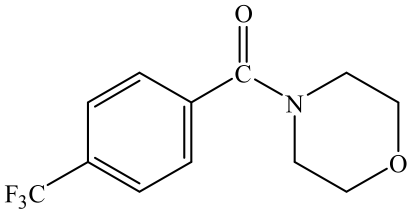
Various substituted aryl and heteroaryl bromides reacted with aromatic and aliphatic amines to give the desired amides in good to excellent yields. The substitution of electron withdrawing and electron donating groups on the aromatic ring of aryl bromides did not have any appreciable influence on the outcome of the reaction. Aryl bromides bearing either electron-donating or electron-withdrawing substituents, afforded the corresponding carbonylative products in excellent yields. Strong electron donating groups on arylhalides are generally known to slow down the oxidative addition step of the catalytic cycle[50] and therefore give lower yields (Table 7, entries 7, 16). The model reaction of bromobenzene with aniline provides a 96% yield of the desired product under optimized reaction conditions (Table 7, entry 1). 4-methoxyaniline reacts with bromobenzene, providing 93% yield of the desired product (Table 7, entry 2). Furthermore, aliphatic amines, such as benzyl amine and cyclohexyl amine, provide excellent yields of the corresponding product (Table 7, entries 3−4). 3-(Trifluoromethyl) aniline provides a moderate yield of the desired product (Table 7, entry 5). A variety of *meta-* and *para*-electron deficient and –electron-rich aryl bromides gave excellent yields ranging from 90-99% (Table 7, entries 6-9). 1-bromonaphthalene furnishes 86% yield of the corresponding amide product (Table 7, entry 10). Heteroaryl bromides 3-bromopyridine and 3-bromothiophene also performed well in this reaction (Table 7, entries 11-12). Secondary amines, such as N-methyl aniline and morpholine were also tested with aryl bromides for the synthesis of the corresponding carbonylative products (Table 7, entries 13-17).

Table 7 Aminocarbonylation reaction of various aryl bromides catalyzed by PS-AMP-Pd

Entry	Aryl bromides	Amines	Product	Yield (%)[b]	TON
1				96	2400

2				93	2325
3				96	2400
4				98	2450
5				82	2050
6				97	2425
7				90	2250
8				90	2250

9				99	2475
10				86	2150
11				96	2400
12				98	2450
13				97	2425
14				92	2300

15				94	2350
16				88	2200
17				95	2375

[a]Reaction conditions: aryl bromide (1 mmol), amine (2 mmol), PS-AMP-Pd (4 x 10 $^{-4}$ mmol), Et_3N (3 mmol), toluene (10 mL), CO (3 atm) pressure, temp (90 ^{0}C), time (7 h). [b]Isolated yield.

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). For AAS analysis, the sample PS-AMP-Pd (0.1 g) was digested with minimum amount of conc. H_2SO_4 and few drops of hydrogen peroxide. Then it was made up to the mark of 100 ml in volumetric flask with millipore water. In this way stock solution was prepared. Then four standard solution of paladdium complex was prepared. From the calibration curve the unknown amount was determined. The same procedure was followed for the sample preparation of the reused catalyst. 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 alkoxycarbonylation of bromobenzene with benzyl alcohol was carried out at 70 ^{0}C using PS-AMP-Pd catalyst, then after 1.5 h, the PS-AMP-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 PS-AMP-Pd complex during the progress of a reaction. In addition, to reconfirm this observation, ICP-AES analysis of the reaction mixture was carried out after 1.5 and 3 h, which revealed a below detectable level (below 0.01 ppm) of palladium in solution.

Recycling of catalyst

The catalyst remains insoluble in the present reaction conditions and hence can be easily separated. After completion of the reaction the catalyst was recovered by centrifuge and then washed thoroughly with dichloromethane to remove the substrates from its surface. The recovered catalyst was collected and dried at 100 ^{0}C. Alkoxycarbonylation and aminocarbonylation reactions were 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. The obtained results are presented in Fig. 6. As seen from Fig. 6, 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.

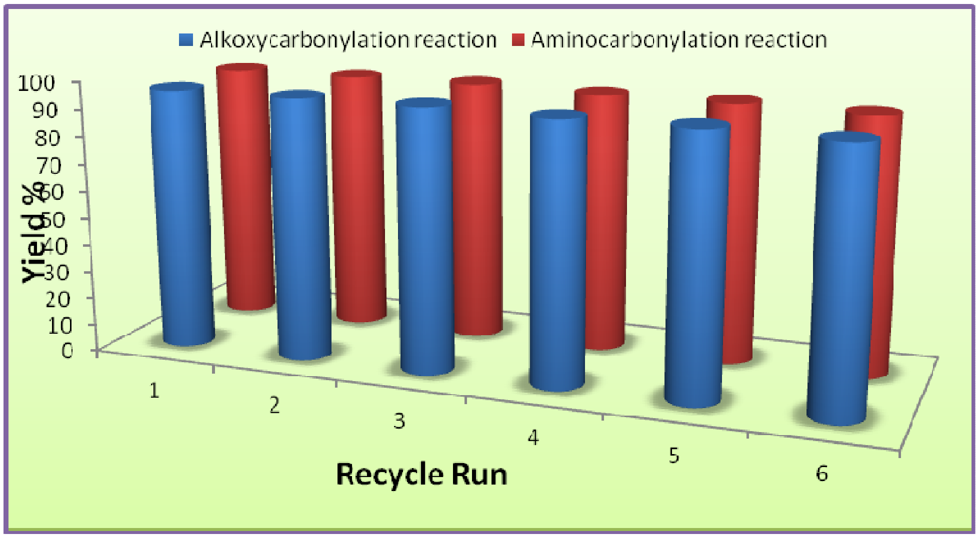


Fig. 6. Recycling efficiency of the polymer anchored Pd(II) complex for alkoxy and amino carbonylation reactions.

Conclusions

A polymer anchored palladium Schiff base complex was prepared and characterized. The complex was an active and reusable catalyst for the alkoxycarbonylation and aminocarbonylation reactions. 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 of activity, indicating effective anchoring. The reusability of this catalyst is high without significant decrease in its initial activity.

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