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Silica supported palladium-phosphine as a reusable catalyst for alkoxycarbonylation and aminocarbonylation of aryl and heteroaryl iodides

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Silica-supported palladium phosphine complexes were prepared for alkoxycarbonylation and aminocarbonylation of aryl iodides. These catalysts were highly efficient for the carbonylation of unprotected hydroxy-aryl, amino-aryl, iodoindole and iodopyrazole. The carbonylation of unprotected iodopyrazole is challenging and their carbonylation was achieved for the first and obtained corresponding carbonylative products are biologically active. The applicability of developed protocols tolerates wide range of functional groups with excellent yields. The catalyst was easily recovered and shows significant recyclability up to five consecutive cycles without loss in its catalytic activity and selectivity. The prepared catalysts were characterized by different techniques such as FEG-SEM, EDS, FT-IR, XPS and ICP-AES spectroscopy.

Introduction

Transition metal-catalyzed carbonylation reactions have been a versatile and most convenient methodology for the synthesis of aromatic carbonyl compounds such as ketones, aldehydes, acids, acid chlorides, esters, amides and anhydrides.[1] Moreover, they are used as essential building blocks for the fine and bulk chemical industry. Hence, these structural motifs are found in various natural products, agrochemicals, fragrances, photosensitizers, pharmaceuticals as well as biologically active compounds.[2] Typically, the most common approach for the synthesis of esters and amides by reaction of acyl halides or carboxylic acids and its derivatives with alcohols as well as amines.[3] Subsequently, different synthetic methodologies such as transamidation, hydroamination of alkynes or by oxidation of benzyl alcohols, benzyl amines and benzaldehydes with amines as well as alcohols have been widely studied.[4] Alternatively, aromatic esters and amides can be synthesized by palladium catalyzed carbonylation of aryl halides using alcohols and amines.[5] These methods demonstrated their broad applicability and tolerated the wide variety of functional groups into good yields. In 2004, Beller *et al.* explored the carbonylation of haloindoles using $Pd(PhCN)_2Cl_2$/dppf as a catalyst.[6] Carbonylation of heteroaryl halides have been also reported by employing (BINAP)$PdCl_2$ as homogeneous catalyst.[7]

Nowadays, efforts have been made by researchers to develop cost effective, simple, green and sustainable protocols. In this contexts, several groups have been disclosed the carbonylation of aryl halides by using immobilized palladium complexes on various supports such as activated carbon,[8] silica,[9] MCM-41,[10] organic polymer,[11] SBA-15,[12] ZIF-8,[13] Fe_3O_4,[14] and MOF-5.[15] Alper *et al.* demonstrated PAMAM dendrimer-palladium supported on silica for the carbonylation of aryl halides.[16] Recently, Lei *et al.* reported the palladium supported on triphenylphosphine functionalized porous organic polymer for the alkoxycarbonylation of aryl iodides.[17] However, these reported methods have limits in their substrate availability and intricate to carbonylation of unprotected nitrogen containing heterocycles. In addition, some reported methods required

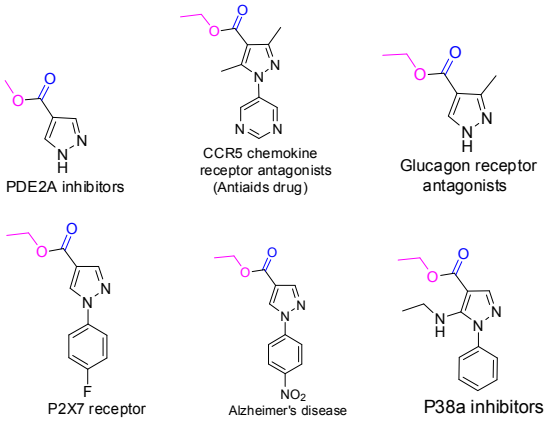

Fig. 1 Some highly biological active compounds containing 1*H*-pyrazole-4-carboxylate unit.

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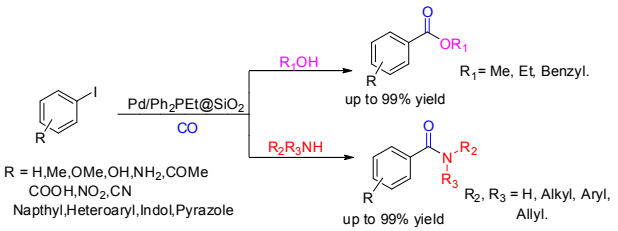
phosphine ligands, longer reaction time and non-recyclable Pd-precursors with quite severe reaction conditions. The use of homogeneous palladium precursors along with moisture sensitive phosphine ligands is a major problem associated with recovery and recycling of the catalyst. In addition, the use of heterogeneous catalyst would be valuable with respect to catalyst recycling, economically as well as environmentally benign.

In continuation of our previous work on heterogeneous catalyzed carbonylation reactions,[18] herein we demonstrate an efficient, heterogeneous and recyclable silica supported palladium phosphine complexes **I** & **II** for alkoxycarbonylation as well as aminocarbonylation of aryl and heteroaryl iodides. The carbonylation of unprotected iodopyrazole is challenging and for the first time carbonylation achieved, which important subunit is in biologically as well as pharmaceuticals active molecules shown in Fig. 1. The 1*H*-pyrazole-4-carboxylate unit plays important role in the synthesis of highly biological active molecules.[19] We can synthesize these important molecules as shown in Fig. 1 by *N*-arylartion of 1*H*-pyrazole-4-carboxylate.[20] The present protocol tolerated a wide general applicability, such as aryl, heteroaryl and unprotected indole as well as pyrazole providing good to excellent yields (Scheme 1).



Scheme 1 Alkoxycarbonylation and aminocarbonylation of aryl iodides.

Experimental section

General

All the reactions were performed in inert conditions under the nitrogen atmosphere by using 100 mL stainless steel reactor. All the chemicals and reagents were purchased form sigma Aldrich, S. D. Fine and WAKO commercial suppliers. The solvents were purchased with high purity from commercial suppliers and used without purification. Prepared catalyst was characterized by using FEG-SEM, EDS, FT-IR, XPS and ICP-AES (See the ESI). The loading of catalyst was calculated by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). The XPS of $PdCl_2$_$PPh_2Et@SiO_2$ and $Pd(OAc)_2$_$PPh_2Et@SiO_2$ was measured using a PHI5000 Versa Probe with a monochromatic focused (100 µm × 100 µm) Al Kα X-ray radiation (15 kV, 30 mA) and dual beam neutralization using a combination of argon ion gun and electron irradiation. Reaction monitor by using Perkin Elmer Clarus-400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 µm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 µm, was used for the mass analysis of the products. Products were purified by column chromatography on silica (100-200 mesh). The ^{1}H NMR spectrum was recorded on Bruker (400 MHz spectrometer) in $CDCl_3$ and DMSO-d6 using tetramethylsilane (TMS) as an internal standard. The ^{13}C NMR spectrum was recorded on Bruker (100 MHz spectrometer) in $CDCl_3$ and DMSO-d6. The chemical shifts values are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. The *J* (coupling constant) values were described in Hz. Splitting patterns of proton are depicted as s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC, GC-MS, ^{1}H and ^{13}C NMR spectra with those of authentic data.

Preparation of $PdCl_2$_$PPh_2Et@SiO_2$ (I) catalyst

The silica supported $PdCl_2$_PPh_2Et was prepared in a 100 mL round bottom flask 0.372 g of $PdCl_2$ and 3.0 g of $PPh_2Et@SiO_2$ (Aldrich 538019-5G, 2-diphenylphosphinoethyl functionalized silica, 0.7 mmol/g) were mixed, stirred and refluxed with acetonitrile under nitrogen atmosphere for 48 hours. The material showing yellow was filtered with 0.45 µm PTFE filter, washed with acetonitrile several time and dried at room temperature. The metal loading of $PdCl_2$_$PPh_2Et@SiO_2$ was 6.6 wt% as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). The as prepared $PdCl_2/PPh_2Et$ catalyst was characterized with FEG-SEM, EDS, FT-IR and XPS techniques. The FEG-SEM images of fresh and spent $PdCl_2$_$PPh_2Et@SiO_2$ catalyst were shown in Fig. 2a-c which shows rough surface morphology of catalyst. Fig. 2d shows the elemental analysis of catalyst by EDS measurement, displays the presence of Si, P, Cl and Pd for fresh catalyst.

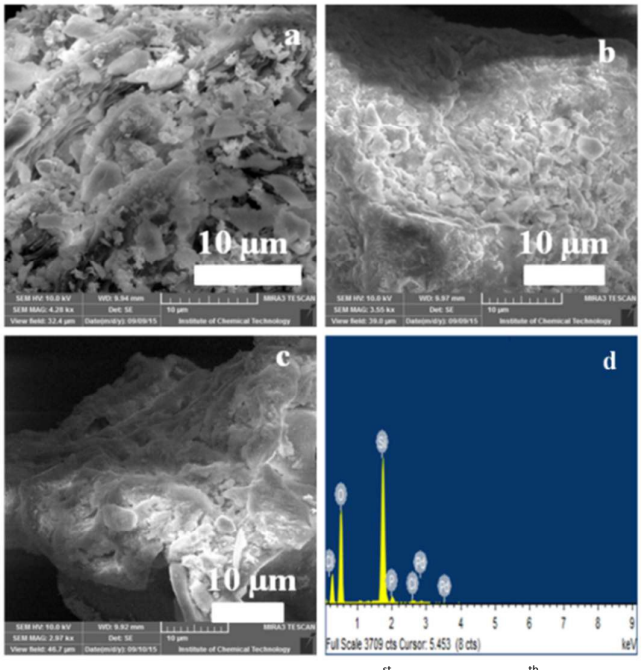


Fig. 2 FEG-SEM images of (a) Fresh, (b) 1st recycled (c) 4th recycled $PdCl_2/PPh_2Et@SiO_2$ catalyst and (d) EDS spectrum of Fresh catalyst.

Preparation of $Pd(OAc)_2$_$PPh_2Et@SiO_2$ (II) catalyst

The silica supported $Pd(OAc)_2$_PPh_2Et was prepared as, in 100 mL round bottom flask 0.472 g of $Pd(OAC)_2$ and 3.0 g of $PPh_2Et@SiO_2$ (Aldrich 538019-5G, 2-diphenylphosphinoethyl functionalized silica, 0.7 mmol/g) were mixed, stirred and refluxed with acetonitrile under nitrogen atmosphere for 48 hours. The material showing yellow was filtered with 0.45 µm PTFE filter, washed with acetonitrile several time and dried at room temperature. The metal loading of $Pd(OAc)_2$_$PPh_2Et@SiO_2$ was 6.4 wt% as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). The FEG-SEM and EDS analysis of fresh $Pd(OAc)_2$_$PPh_2Et@SiO_2$ catalyst are shown in supporting information (See ESI Fig. S4).

General experimental procedure for alkoxycarbonylation reaction

To a 100 mL reactor, **1a** (1 mmol), alcohol (5 mL), Pd catalyst (**I**) (0.6 mol%), and Et_3N (3 mmol) were added. The reactor was closed, purged three times with nitrogen, pressurized with 0.5 MPa of CO, and heated at 100 °C for 1-2 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was vented carefully, and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 × 10 mL) to remove any traces of product and catalyst. 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) to afford the desired purified product.

General experimental procedure for recycling of $PdCl_2$_$PPh_2Et@SiO_2$ catalyst

At the end of the reaction, the reactor was cooled to room temperature, and the catalyst was recovered by simple filtration. The filtered catalyst was washed methanol (3 × 5 mL) to remove all traces of product or reactant present. The filtered catalyst was then dried under reduced pressure for 5 h. The dried catalyst was then used for the next run for the alkoxycarbonylation reaction.

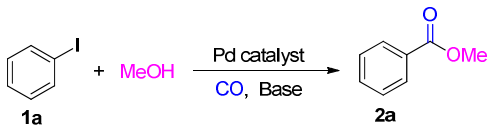
General experimental procedure for aminocarbonylation reaction

To a 100 mL reactor, aryl iodide **1a** (1 mmol), amine (2 mmol), Pd catalyst (**I**) (0.5-1.0 mol%), in toluene (8 mL), and Et_3N (3 mmol) were added. The reactor was closed, purged three times with nitrogen, and then pressurized with 0.5 MPa of CO, and heated at 100 °C for 8 h (the subsequent procedure is the same as that discussed above for the alkoxycarbonylation reaction).

Results and discussion

In order to evaluate the catalytic activity of prepared catalyst **I** and **II** were studied for the alkoxycarbonylation and aminocarbonylation of aryl iodides. The optimization study, iodobenzene **1a** (1 mmol), Et_3N (3 mmol) in a methanol (5 mL) under 0.5 MPa of CO pressure was chosen as model reaction. For the progress of reaction yield, we examined various reaction parameters such as, effect of catalyst, catalyst loading, effect of solvents, effect of bases, effect of CO pressure and time. The results are summarised in Table 1. At first, the prepared silica supported palladium phosphine complexes **I** and **II** were used for the alkoxycarbonylation reaction (Table 1, entry 1 and 2). The catalyst loading was successfully reduced to 0.6 mol% of palladium under the optimized reaction conditions, and the 99% yield of **2a** was obtained, while decreasing the catalyst loading results in decreased the yield of desired product **2a** (Table 1, entry 3 and 4). Next, the effect of various catalysts were studied such as Pd/C, $Pd(OAc)_2/PPh_3$ and $PdCl_2/PPh_3$; among them complex **I** gave an excellent yield of **2a** (99%) (Table 1, entries 1, 2 and 5-7). Then, we examined the effect of solvents using 3 mmol of MeOH with **1a** under optimized condition, the obtained yield of corresponding esters were poor (Table 1, entries 8-10). However, methanol as a solvent as well as nucleophile was considered for the further optimization study. Next, we studied base effect and it was observed that the base played a crucial role in this transformation (Table 1). Various bases

Table 1 Optimization reaction parameters for the alkoxycarbonylation of iodobenzene[a]

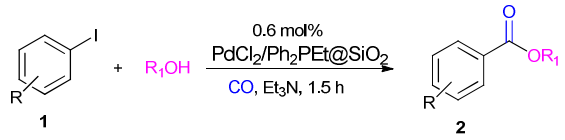


1a 2a

Entry	Pd catalyst	Base	Solvent	T (°C)	Time h	Conversion 1a/ Yield[b] 2a (%)
Effect of catalyst and catalyst loading						
1	**I**	Et_3N	MeOH	100	3	100/99
2	**II**	Et_3N	MeOH	100	3	100/92
3[c]	**I**	Et_3N	MeOH	100	3	100/99
4[d]	**I**	Et_3N	MeOH	100	3	93/85
5	Pd/C	Et_3N	MeOH	100	3	83/73
6	$Pd(OAc)_2/PPh_3$	Et_3N	MeOH	100	3	94/81
7	$PdCl_2/PPh_3$	Et_3N	MeOH	100	3	89/85
Effect of solvent						
8[e]	**I**	Et_3N	DMF	100	3	74/40
9[e]	**I**	Et_3N	THF	100	3	59/55
10[e]	**I**	Et_3N	Toluene	100	3	65/48
Effect of base						
11	**I**	DBU	MeOH	100	3	58/0
12	**I**	DABCO	MeOH	100	3	63/56
13	**I**	K_2CO_3	MeOH	100	3	42/40
14	**I**	Na_2CO_3	MeOH	100	3	50/46
Effect of time, temperature and CO pressure						
15	**I**	Et_3N	MeOH	100	2	100/99
16	**I**	**Et_3N**	**MeOH**	**100**	**1.5**	**100/99**
17	**I**	Et_3N	MeOH	100	1	93/87
18	**I**	Et_3N	MeOH	80	1.5	86/82
19	**I**	Et_3N	MeOH	70	1.5	75/73
20	**I**	Et_3N	MeOH	110	1.5	100/95
21[f]	**I**	Et_3N	MeOH	100	1.5	100/99
22[g]	**I**	Et_3N	MeOH	100	1.5	91/85

[a] Reaction conditions: **1a** (1 mmol), base (3 mmol), solvent (5 mL), catalyst (1 mol%), CO (0.5 MPa). [b] Conversion and Yield were determined by GC. [c] 0.6 mol% and [d] 0.4 mol% Catalyst Loading. [e] MeOH (3 mmol). [f] 1 MPa and [g] 0.2 MPa CO pressure.

Table 2 Scope of aryl iodides for the alkoxycarbonylation reaction[a]



1 2

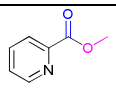
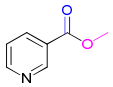
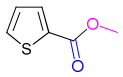
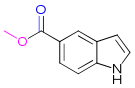
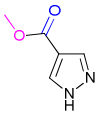
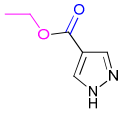
Entry	R	R_1OH	Yield[b] (%)
1	**1a** (H)	MeOH	**2a**, 99
2	**1a** (H)	EtOH	**2b**, 99
3	**1a** (H)	*tert*-BuOH	**2c**, 43, <10[c]
4	**1a** (H)	Cyclohexanol	**2d**, 69, <10[c]
5	**1a** (H)	PhOH	**2e**, 83[c]
6	**1a** (H)	BnOH	**2f**, 97, 28[c]
7	**1b** (4-Me)	MeOH	**2g**, 99
8	**1c** (2-Me)	MeOH	**2h**, 98
9	**1d** (4-OMe)	MeOH	**2i**, 98
10	**1e** (2-OMe)	MeOH	**2j**, 96
11	**1f** (4-OH)	MeOH	**2k**,99
12	**1g** (4-NH_2)	MeOH	**2l**, 99
13	**1h** (3-NO_2)	MeOH	**2m**, 99
14	**1i** (4-NO_2)	MeOH	**2n**, 95
15	**1j** (4-$COCH_3$)	EtOH	**2o**, 96
16	**1k** (4-COOH)	MeOH	**2p**, 92
17	**1l** (4-CN)	MeOH	**2q**, 99
18	**1m** (1-naphthyl)	MeOH	**2r**, 98

[a] Reaction conditions: **1** (1 mmol), R_1OH (5 mL), Et_3N (3 mmol), **I** (0.6 mol%), CO (0.5 MPa), 100 °C, 1.5 h. [b] Isolated yield. [c] R_1OH (3 mmol) in THF (5 mL).

such as Et_3N, DBU, DABCO, K_2CO_3 and Na_2CO_3 were tested and among them Et_3N was found to be an excellent base to providing the desired product **2a** in 99% yield (Table 1, entries 1 and 11-14). Next, we studied the effect of time on reaction condition and we observed that time 1.5 h provides 99% yield of the product **2a** (Table 1, entry 16). Further, decreasing the reaction time to 1 h decreases the yield of the desired product to 87%. When the reaction temperatures were decreased to 70 °C, the yield of **2a** was dramatically decreased to 73%. Then, we increased the reaction temperature up to 110 °C had no significant effect on reaction yield and it was observed that the 100 °C temperature was adequate for this complete consumption of starting material. Next, we checked the effect of CO pressure on the yield, the reaction were carried out with 0.2, 0.5 and 1 MPa (Table 1, entry 21 and 22). Hence, we concluded that Iodobenzene **1a** (1 mmol), Et_3N (3 mmol), Pd catalyst (0.6 mol%) in 5 mL MeOH under 0.5 MPa CO pressure at 100 °C for 1.5 h was adequate for the excellent yield of **2a** (Table 1, entry 16).

To explore the applicability of developed catalytic system were applied to a variety of aryl iodides with diverse alcohols under the optimized reaction condition to promote the corresponding esters shown in Table 2. The results of alkoxycarbonylation of iodobenzene demonstrate that changing the alcohol substrate from methanol had no significant effect on product yield (Table 2, entries 2, 4–6). But with a *ter*-butanol, a lower yield (43%) of carbonylation product was obtained (Table 2, entry 3). Both the electron-rich and electron-deficient substituents on the aryl iodides

Table 3 Scope of heteroaryl iodides for the alkoxycarbonylation reaction[a]

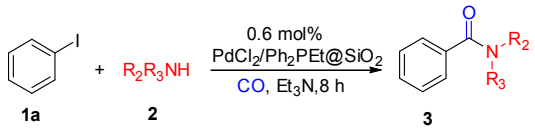
Entry	R_1OH	Products	Yield[b] (%)
1	MeOH		99
2	MeOH		98
3	MeOH		96
4	MeOH		99
5	MeOH		70, 87[c]
6	EtOH		90[c]

[a] Reaction conditions: heteroaryl iodide (1 mmol), R_1OH (5 mL), Et_3N (3 mmol), **I** (0.6 mol%), CO (0.5 MPa), 100 °C, 1.5 h. [b] Isolated yield. [c] 4 h.

afforded in good to excellent yield of the corresponding products. At different position of substituents on the phenyl ring of aryl iodides had not affected on the reaction yield. For instance, substrate with electron-donating groups, such as 2-Me, 4-Me, 2-OMe and 4-OMe groups proceeded well towards the corresponding products (Table 2, entries 7-10). It was worth to note that the 4-OH and 4-NH_2 aryl iodides also worked very well under this transformation to achieve an excellent yield (Table 2, entries 11 and 12). Aryl iodides bearing electron deficient substituents such as 3-NO_2 4-NO_2, 4-$COCH_3$, 4-COOH and 4-CN afforded an excellent yield of the corresponding esters (Table 2, entries 13-17). Unfortunately, the bromobenzene and chlorobenzene were failed to give the desired product under optimized conditions. Remarkably, the heteroaryl iodides such as 3-iodopyridine, 3-iodopyridine and 2-iodothiophene were also proven to be compatible reaction with aryl iodides and showed an excellent yield of corresponding esters (Table 3). To our delight, the carbonylation of unprotected 5-iodoindoles and 4-iodopyrazoles were also offered an excellent yield (Table 3, entries 4-6). The alkoxycarbonylation of 4-iodo-1*H*-pyrazole challenging and that was the first example afforded the corresponding product **2t** in 70% yield under the optimal reaction condition. While, increasing the reaction time up to 4 h, the 87% and 90% yield of desired products **2t, 2u** were obtained. The derivatives of 1*H*-pyrazole-carboxylate showed their potential application in pharmaceuticals and biologically active molecules.

To extend the scope of the developed catalytic system was tested for the aminocarbonylation reaction. With the standard reaction conditions in hand, the scopes of amines were further explored for the aminocarbonylation reaction. Thus, the standard reaction condition consists of **1a** (1 mmol),

Table 4 Aminocarbonylation of aryl iodides with various amines[a]



Entry	R_2	R_3	Yield[b] (%)
1	Et	Et	**3a**, 98
2	*n*-Bu	*n*-Bu	**3b**, 96
3	*n*-Pr	*n*-Pr	**3c**, 97
4	H	*ter*-Bu	**3d**, 77
5	Pyrrolidinyl		**3e**, 94
6	Piperidinyl		**3f**, 96
7	Morpholino		**3g**, 93
8	Allyl	Allyl	**3h**, 99
9	H	Allyl	**3i**, 98
10	H	Ph	**3j**, 99
11	Bn	Bn	**3k**, 95
12	H	Bn	**3l**, 98

[a] Reaction conditions: **1a** (1 mmol), **2** (2 mmol), Et_3N (3 mmol), **I** (0.6 mol%), toluene (8 mL), CO (0.5 MPa), 100 °C, 8 h. [b] Isolated yield.

2 (2 mmol), Pd catalyst (**I**) (0.5-1 mol%), Et_3N (3 mmol) in 5 mL of toluene under 0.5 MPa at 100 °C for 8 h. Initially, we examined the wide range of amines such as aliphatic as well as aromatic amines with iodobenzene afforded corresponding amides in good to excellent yield shown in Table 4. All the aliphatic amines were reacted smoothly under standard conditions and providing the desired products in excellent yields (Table 4, entries 1-4). The reaction with *ter*-butyl amine, gives 77% yield of **3e** was obtained, because of the sterically hindered *ter*-butyl group. In addition, the cyclic amines were also well employed in this transformation under such standard reaction condition gave an excellent yield of corresponding amides **3e**-**3g** (Table 4, entries 5-7). It was noteworthy that the allyl and diallyl amines also successfully provided 98% and 99% yields of respective amides (Table 4, entries 8-9). The benzyl amines and aniline were also examined and found to be good to excellent yield of the corresponding amides (Table 4, entries 10-12).

Recyclability study

The reusability of catalyst reduces the cost of process chemistry and makes the protocol economically as well as environmentally valuable. The recyclability study was further explored for synthesis of esters by carbonylation of **1a** with methanol under the optimal reaction condition as shown in Fig. 3. At the end of the reaction, the reactor was cooled to room temperature and remaining CO gas was carefully vented out. The catalyst was recovered from the reaction mixtures by simple filtration and resulting catalyst was found be effectively recycled up to five consecutive recycles without loss of its catalytic activity and selectivity. The 1st and 4th recycled sample was prepared for the palladium leaching study by ICP-AES analysis. The leaching of palladium was obtained below the detectable level. We also examined the leaching of palladium by hot filtration test, after 0.5 h the catalyst was filtered off from the reaction mixture and the filtrate was used as a further reaction up to 2 h and it was observed that the yield of **2a** remains constant.

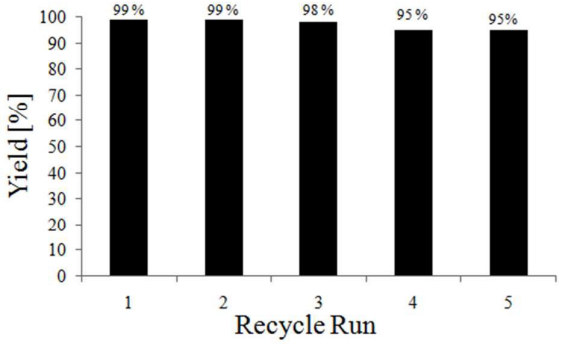


Fig. 3 Recycle study of $PdCl_2$_$PPh_2Et@SiO_2$ for alkoxycarbonylation of aryl iodide.

XPS analysis of the fresh and spent catalyst

The X-ray photoelectron spectroscopy analysis was performed for the fresh as well as spent catalyst shown in Fig. 4. The Fig. 4a indicates the wide scan of the fresh and spent $PdCl_2$_$PPh_2Et@SiO_2$ catalyst which shows the presence of Pd, P, O, C, I, Cl and Si elements on the surface of the catalyst. The high resolution XPS spectra for fresh, 1st and 4th recycled catalyst shown in Fig. 4b. This reveals that two bands of Pd 3d for the fresh catalyst appeared at 336.6 eV and 342.1 eV are assigned as Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for the Pd(II) species. Furthermore, in XPS data of 1st recycle the peaks shows at 336.4 eV to 342 eV, which assigned as Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for Pd(II) species. But in case of 4th recycle the reduction of Pd(II)

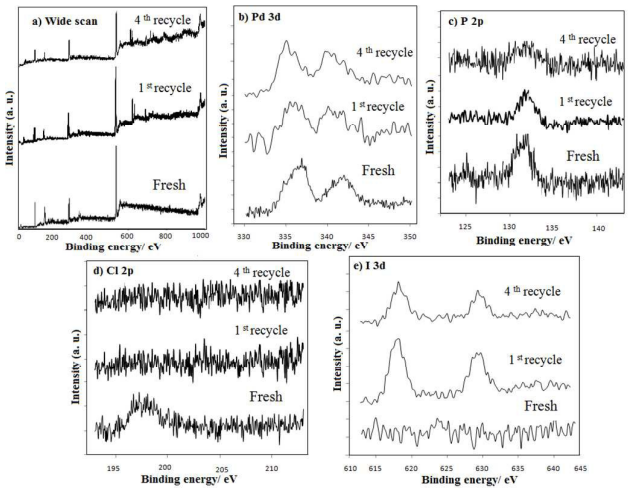


Fig. 4 (a) XPS survey spectrum; (b) Pd 3d; (c) P 2p; (d) Cl 2p and (e) I 3d for $PdCl_2$_$Ph_2PEt@SiO_2$ catalyst.

to Pd(0) species takes place during the catalytic reaction and the new peaks were appeared at 334.5 eV and 339.9 eV assigned as Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for the Pd(0) species. The peak at 132 eV corresponds to the P2p recognized to the presence of P in the catalyst shown in Fig. 4c. These results

indicate that the coordination bond between Pd and P are formed and they are still remains on silica support after 4th recycle. In 4th recycle, the region of Pd 3d shifted to lower binding energy, which indicates that Pd(0) is formed during catalytic reaction. Fig. 4d, suggests that the chlorine is replaced by iodine after first run because HI was formed during the course of reaction.

Conclusions

In summary, we prepared a novel silica supported palladium phosphine complex for the alkoxycarbonylation and aminocarbonylation of aryl iodides. The reactions were well proceeded under the optimized condition and allowing high substrate tolerance towards the corresponding products with good to excellent yields by using a well-defined heterogeneous $PdCl_2$_$PPh_2Et@SiO_2$ as a versatile catalyst. It is worth to mentioning that the alkoxycarbonylation of unprotected haloindoles and iodopyrazole was achieved in excellent yield which showed the potential application of corresponding esters in pharmaceuticals and biologically active molecules. The catalyst was found to be effectively reused up to five cycles without loss of its catalytic activity and selectivity. The catalysts were well characterized by FEG-SEM, EDS, FT-IR, XPS and ICP-AES techniques.

Characterisation data of Products

Methyl Benzoate (2a).[14] Colourless liquid; isolated yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.46 (tt, *J* = 6.9, 1.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 3.83 (d, *J* = 1.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.92, 166.91, 132.82, 130.09, 129.48, 128.27, 51.92 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 136 [M^+] (36), 105 (100), 92 (4), 77 (61), 51 (19).

Ethyl Benzoate (2b).[3b] Colourless liquid; isolated yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 2H), 7.43 – 7.31 (m, 3H), 4.28 (qd, *J* = 7.1, 2.6 Hz, 2H), 1.29 (td, *J* = 7.1, 2.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.36, 132.67, 130.42, 129.41, 128.19, 60.76, 14.18 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 150 [M^+] (23.19), 122 (34), 105 (100), 77 (50), 51 (22).

***tert*-butyl Benzoate (2c).**[5k] White solid; isolated yield: 43%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 1.59 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.82, 133.71, 130.16, 128.79, 128.47, 28.20 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 178 [M^+] (1), 123 (100), 105 (93), 77 (42), 56 (64), 55 (33), 51 (14), 41 (27).

Cyclohexyl Benzoate (2d).[17] Colourless oil; isolated yield: 69%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.49 – 7.39 (dd, *J* = 15.1, 11.3 Hz, 3H), 5.04 (ddd, *J* = 12.7, 8.5, 3.8 Hz, 1H), 1.95 (dd, *J* = 12.2, 5.3 Hz, 1H), 1.81 – 1.79 (m, 1H), 1.62 – 1.56 (m, 2H), 1.49 – 1.27 (m, 6H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 166.05, 133.69, 132.70, 130.96, 129.52, 128.27, 73.07, 31.62, 25.47, 23.65 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 204 [M^+] (1), 177 (4), 123 (86.6), 105 (100), 82 (21), 77 (48), 67 (21), 55 (9), 41 (11).

Phenyl Benzoate (2e).[18a] White solid; isolated yield: 83%; ^{1}H NMR ((500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (td, *J* = 7.7, 0.9 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 165.22, 150.97, 133.62, 130.19, 129.53, 128.60, 125.92, 121.75 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 198 [M^+] (4), 105 (100), 77 (40.5), 65 (4), 50 (11).

Benzyl Benzoate (2f).[18a] Colourless oil; isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H, *J* = 8 Hz), 7.55-7.35 (m, *J* = 8H), 5.36 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.42, 136.01, 133.02, 130.08, 129.68, 128.58, 128.36, 128.23, 128.15, 66.68 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 212 [M^+] (16.90), 105 (100), 91 (49.35), 77 (32.70), 65 (12), 51 (11.83).

Methyl 4-methylbenzoate (2g).[8a] Colourless oil; isolated yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 7.9, 0.4 Hz, 2H), 3.89 (d, *J* = 0.7 Hz, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.16, 143.53, 129.57, 129.04, 127.38, 77.35, 77.09, 76.84, 51.91, 21.60 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 150 [M^+] (49), 119 (100), 91 (53.96), 90 (24), 65 (21.86), 51 (4).

Methyl 2-methylbenzoate (2h).[8a] Colourless oil; isolated yield: 98%; ^{1}H NMR (500 MHz, CDC_3) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 5.6, 4.9 Hz, 2H), 3.90 (d, 3H), 2.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.10, 140.16, 131.95, 131.84, 131.66, 130.54, 125.67, 51.82, 29.70, 21.72 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 150 [M^+] (46), 135 (7), 119 (100), 118 (74), 91(77.4), 90 (24), 89 (14), 65 (25), 63 (10), 51 (5).

Methyl 4-methoxybenzoate (2i).[8a] White solid; isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (d, 2H, *J* = 8 Hz), 6.89-6.87 (d, 2H, *J* = 8Hz), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.82, 163.26, 131.53, 122.50, 113.54, 55.35, 51.83 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 166 [M^+] (35.63), 135 (100), 107 (17.56), 92 (15.25), 77 (23.87), 63 (9).

Methyl 2-methoxybenzoate (2j).[8a] Colourless oil; isolated yield: 96%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.46 – 7.44 (m, 1H), 6.99 (dd, *J* = 7.4, 2.2 Hz, 2H), 3.89 (dd, *J* = 6.6, 1.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.72, 159.07, 133.54, 131.64, 120.10, 111.97, 111.61, 55.95, 52.02 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 166 [M^+] (24.3), 135 (100), 133 (44), 105 (16), 92 (20), 77 (47.5), 63 (10), 51 (7).

Methyl 4-hydroxybenzoate (2k).[18a] White solid; isolated yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (d, 2H, *J* = 8 Hz), 6.84-6.82 (d, 2H, *J* = 8Hz), 4.34 (bs, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.60, 165.57, 135.60, 135.60, 124.87, 118.87, 55.60 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 152 [M^+] (37.6), 121 (100), 93 (27.3), 65 (23.4).

Methyl 4-aminobenzoate (2l).[18a] White solid; isolated yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (d, 2H, *J* = 8 Hz), 6.60-6.58 (d, 2H, *J* = 8 Hz), 4.02 (bs, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.26, 151.02, 131.55, 138.14, 113.74, 51.62 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 151 [M^+] (45), 120 (100), 92 (37), 65 (34), 39 (13).

Methyl 3-nitrobenzoate (2m).[18a] White solid; isolated yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.38-8.33 (dd, 3H, 8.0 Hz), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.92, 148.20, 135.25, 131.79, 129.62, 127.37, 124.55, 52.79

ppm; GC-MS (EI, 70 eV): *m/z* (%) = 181 [M^+] (28), 150 (100), 135 (9), 120 (10), 104 (37.8), 76 (38), 50 (27), 39 (4).

Methyl 4-Nitrobenzoate (2n).[4d] Colourless solid; isolated yield: 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 2H), 8.21 – 8.15 (m, 2H), 3.96 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.15, 150.48, 135.44, 130.68, 123.51, 113.73, 77.31, 77.06, 76.80, 52.83 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 181 [M^+] (3), 180 (29), 164 (23.84), 150 (100), 120 (22.56), 104 (28.55), 92 (19.6), 76 (25.75), 50 (17).

4-(methoxycarbonyl)benzoic acid (2p).[5j] Colourless solid; isolated yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.11 (d, 4H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.77, 170.62, 139.47, 137.47, 138.62, 133.30, 56.25 ppm; GC-MS (EI, 70 eV): m/z (%) = 180 [M^+] (28.60), 149 (100), 121 (26.90), 76 (8.7), 65 (27.4), 50 (10.60), 40 (10.10).

Methyl 1-naphthoate (2r).[8a] Colourless oil; isolated yield: 98%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.54 – 7.51 (m, 2H), 7.50 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.66, 132.20, 130.94, 130.06, 128.83, 128.26, 127.01, 125.16, 124.45, 123.97, 52.93 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 186 [M^+] (69), 155 (100), 127 (98.63), 101 (6), 77 (11), 63 (10), 51 (4).

Methyl picolinate (Table 3, entry 1).[7a] Colourless oil; isolated yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.7 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.51 – 7.49 (m, 1H), 4.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.69, 149.79, 147.86, 137.11, 127.01, 125.16, 52.93 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 137 [M^+] (4), 107 (30), 106 (11), 79 (100), 78 (69), 51 (22).

Methyl nicotinate (Table 3, entry 2).[7a] Yellow oil; isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.77 (s, 1H), 8.27-8.25 (d, *J* = 7.6 Hz, 1H), 7.37-8.35 (dd, *J* = 6.4, 3.1 Hz, 1H), 3.89 (s, 3H) ppm; GC-MS (EI, 70 eV): *m/z* (%) = 137 [M^+] (52.5), 136 (27.6), 106 (100), 78 (79), 51 (33), 50 (15).

Methyl thiophene-2-carboxylate (Table 3, entry 3).[4d] Yellow oil; isolated yield: 96%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 87.87 – 7.71 (m, 1H), 7.63 – 7.48 (m, 1H), 7.14 – 7.02 (m, 1H), 3.88 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.69, 133.53, 133.46, 132.35, 127.73, 77.32, 77.06, 76.81, 52.14 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 142 [M^+] (46.67), 112 (8), 111 (100), 83 (18.62), 44 (6).

Methyl 1*H*-indole-5-carboxylate (Table 3, entry 4).[6b] Colourless solid; isolated yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (bs, 1H), 8.43 (s, 1H), 7.91-7.89 (dd, 1H, 8Hz), 7.39-7.37 (dd, 1H, 8Hz), 7.24 (s, 1H), 6.83 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.50, 138.46, 127.44, 125.71, 123.71, 123.24, 121.68, 110.85, 103.85, 51.94 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 175 [M^+] (63.90), 144 (100), 116 (63.40), 89 (25.70), 63 (12.30), 58 (11.70).

Methyl 1*H*-pyrazole-4-carboxylate (Table 3, entry 5). [19b] Yellow semi-solid; isolated yield: 87%; ^{1}H NMR (400 MHz, DMSO-d6): δ 13.40 (bs, 1H, NH), 8.27 (s, 1H), 7.86 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d6): δ 163.98, 136.26, 114.13, 51.41 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 126 [M^+] (31), 96 (6.3), 95 (100), 68 (7), 39 (14.83), 31 (1).

Ethyl 1*H*-pyrazole-4-carboxylate (Table 3, entry 6).[19c] Yellow semi-solid; isolated yield: 90%; ^{1}H NMR (400 MHz, DMSO-d6): δ 13.38 (bs, 1H, NH), 8.28 (s, 1H), 7.84 (s, 1H), 4.17 (q, 2H) 1.21 (t, 3H); ^{13}C NMR (101 MHz, DMSO-d6): δ 163.11, 140.50,132.57, 113.96, 59.92, 14.73 ppm; GC-MS (EI, 70 eV): m/z (%) = 140 [M^+] (17), 112 (41), 95 (100), 68 (9), 40 (8).

***N*,*N*-diethylbenzamide (3a).**[4b] Colourless oil; isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 5H), 3.48 (s, 2H), 3.19 (s, 2H), 1.18 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.28, 137.13, 129.05, 128.33, 126.17, 77.43, 77.11, 76.79, 43.24, 39.19, 14.15, 12.84.; GC-MS (EI, 70 eV): *m/z* (%) = 177 [M^+] (11), 176 (33), 105 (100), 77 (40), 51 (9).

***N*,*N*-dibutylbenzamide (3b).**[11b] Colourless oil; isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 3.49 (s, 2H), 3.18 (s, 2H), 1.65 (s, 2H), 1.43 (dd, *J* = 20.4, 12.6 Hz, 4H), 1.13 (d, *J* = 6.7 Hz, 2H), 0.98 (s, 3H), 0.79 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.65, 137.19, 129.85, 128.95, 128.25, 128.14, 126.35, 48.71, 44.40, 30.72, 29.56, 20.23, 19.66, 13.87, 13.54, 13.54 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 233 (9) [$M]^+$, 232 (11), 190 (8), 148 (5), 134 (4), 105 (100), 77 (26), 51 (4), 40 (13).

***N*,*N*-dipropylbenzamide (3c).**[5l] Colourless oil; isolated yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 3H), 7.30 (dd, *J* = 7.3, 4.6, 2.3 Hz, 2H), 3.41 (s, 2H), 3.11 (s, 2H), 1.65 (d, *J* = 6.8 Hz, 2H), 1.48 (d, *J* = 6.8 Hz, 2H), 0.93 (t, *J* = 6.4 Hz, 3H), 0.70 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.76, 137.31, 128.96, 126.37, 50.63, 46.22, 21.85, 20.65, 11.40, 10.97 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 204 [M^+] (11.64), 176 (5.71), 134 (6.88), 105 (100), 77 (34.64), 51 (6.69), 39 (36.08).

***N*-(*tert*-butyl)benzamide (3d).**[4b] Colourless solid; isolated yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.68 (d, 2H, *J* = 8Hz), 7.44-7.36 (m, 3H), 5.95 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.90, 135.85, 131.05, 128.43, 126.66, 51.57, 28.83 ppm; GC-MS (EI, 70 eV): m/z (%) = 177 [M^+] (11), 162 (12), 122 (14.9), 105 (100), 77 (44), 51 (13), 41 (8).

phenyl(pyrrolidin-1-yl)methanone (3e).[5l] Colourless oil; isolated yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.36 – 7.32 (m, 3H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.37 (t, *J* = 6.6 Hz, 2H), 1.90 (dd, *J* = 13.7, 6.5 Hz, 2H), 1.82 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.70, 137.11, 129.74, 128.19, 127.00, 49.58, 46.14, 26.33, 24.41 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 175 [M^+] (3), 174 (17), 156 (9), 146 (10), 105 (100), 95 (8), 77 (68), 56 (13), 51 (27), 41 (13).

phenyl(piperidin-1-yl)methanone (3f).[5l] Colourless oil; isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 3.66 (s, 2H), 3.29 (s, 2H), 1.62 (s, 4H), 1.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.28, 136.40, 129.32, 128.36, 126.71, 48.73, 43.07, 26.50, 25.58, 24.53 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 188 [M^+] (73.80), 160 (2.19), 105 (100), 84 (10), 77 (67.40), 51 (19.09).

morpholino(phenyl)methanone (3g).[4b] Colourless oil; isolated yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 5H), 3.83 – 3.38 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.43, 135.15, 129.85, 128.51, 127.01, 66.80, 48.17, 42.50, 20.65; GC-MS (EI, 70 eV): *m/z* (%) = 191 [M^+] (8), 190 (25.58), 176 (7), 105 (100), 91 (5), 86 (12), 77 (48), 56 (14), 51 (14).

***N,N*-diallylbenzamide (3h).**[4c] Yellowish oil; isolated yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.37 – 7.33 (m, 3H), 5.85 (s, 1H), 5.70 (s, 1H), 5.26 – 5.22 (d, *J* = 20.0 Hz, 1H), 5.19 (d, *J* = 1.0 Hz, 2H), 5.14 (s, 1H), 4.10 (s, 2H), 3.80 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.76, 136.15, 133.13, 132.69, 129.31, 128.33, 126.52, 117.61, 50.71, 46.92 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 201 [M^+] (3), 160 (9), 105 (100), 96 (6), 51 (11.25), 41 (10), 39 (8).

***N*-allylbenzamide (3i).**[4b] Yellowish oil; isolated yield: 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.50 – 7.41 (m, 1H), 7.37 (td, *J* = 7.0, 1.0 Hz, 2H), 6.63 (s, 1H), 5.96 – 5.80 (m, *J* = 16 Hz, 1H), 5.24 – 5.09 (m, *J* = 16 Hz 2H), 4.02 (tt, *J* = 10 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.56, 134.36, 134.12, 131.44, 128.49, 126.95, 116.49, 42.40 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 161 [M^+] (9), 146 (7), 105 (100), 77 (51), 56 (7), 51 (16), 39 (4).

***N*-phenylbenzamide (3j).**[18a] White solid; isolated yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.47 (dd, *J* = 11.1, 4.0 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.14 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.83, 137.91, 134.97, 131.84, 129.09, 128.77, 127.03, 124.58, 120.24; GC-MS (EI, 70 eV): *m/z* (%) = 197 [M^+] (43.6), 105 (100), 91 (6), 77 (48), 65 (9), 51 (13.83).

***N,N*-dibenzylbenzamide (3k).**[4b] White solid; isolated yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.38 – 7.31 (m, 8H), 7.29 (t, *J* = 7.0 Hz, 4H), 7.13 (d, *J* = 5.7 Hz, 2H), 4.70 (s, 2H), 4.39 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.26, 136.09, 129.65, 128.84, 128.71, 128.55, 128.39, 127.65, 127.51, 127.01, 126.68, 51.50, 46.81 ppm; GC-MS (EI, 70 eV): *m/z* (%) = 301 [M^+] (8.1), 210 (31.20), 105 (100), 91(16.40), 77 (30.32), 65 (5.96), 51 (4).

***N*-benzylbenzamide (3l).**[18a] White solid; isolated yield: 98%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.23 (m, 8H), 6.67 (bs, 1H), 4.62 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.44, 138.21, 134.34, 131.54, 128.76, 128.57, 127.88, 127.57, 126.99, 44.09, 29.71; GC-MS (EI, 70 eV): *m/z* (%) = 211 [M^+] (56), 210 (21), 106 (28), 105 (100), 91 (10), 77 (59), 51 (14).

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Silica supported palladium-phosphine as a reusable catalyst for alkoxycarbonylation and aminocarbonylation of aryl and heteroaryl iodides†

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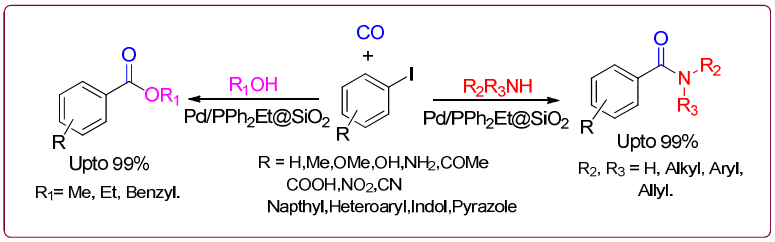
Graphical Abstract



Novel, simple, stable and reusable silica-supported palladium phosphine complexes were prepared and found to be highly efficient for the carbonylation of unprotected hydroxy, amino, iodoindole and iodopyrazole under optimized conditions.