

# Pd salen complex@CPGO as a convenient, effective heterogeneous catalyst for Suzuki–Miyaura and Heck– Mizoroki cross-coupling reactions

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**Abstract** A Pd(II) Schiff base complex supported on graphene oxide nanosheets (Pd(II) salen@CPGO) has been synthesized and characterized by FT-IR, ICP-AES, XRD, SEM/EDX and TEM. The synthesized nanocatalyst has been found to be an efficient heterogeneous catalyst for Suzuki–Miyaura and Heck–Mizoroki coupling reactions. Pd(II) salen@CPGO could be separated and recovered easily from the reaction mixture and recycled several times without a discernible decrease in its catalytic activity. The construction of a solid sheet-supported Pd catalyst would be expected to be a promising system to perform heterogeneous catalytic reactions.

Keywords Suzuki–Miyaura reaction  $\cdot$  Heck–Mizoroki reaction  $\cdot$  Pd(II) salen@CPGO nano catalyst  $\cdot$  Heterogeneous catalyst  $\cdot$  Recyclable catalyst

# Introduction

Suzuki–Miyaura and Heck–Mizoroki coupling reactions are two of most widely used methods for carbon–carbon bond-forming reactions [1–6]. They have been shown to be an effective method for the construction of C–C bonds and play a basic role in the synthesis of plenty of natural products, biologically active compounds, herbicides, pharmaceuticals, many organic building blocks and therapeutic drugs and their intermediates. Regarding the significance of these coupling reactions, a

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great number of homogeneous palladium catalysts such as  $[Pd(PPh_3)_4]$ ,  $[Pd(OAc)_2]$ and  $[PdCl_2(PPh_3)_2]$  [7–9] have been reported. Although these catalysts exhibit excellent activity, there remain some noticeable problems, such as tedious separation, poor recyclability, high-cost ligands and sensitivity to air oxidation. These drawbacks can be overcome by the use of heterogeneous catalysts. As a suitable solution, covalent binding of Pd complexes onto the solid support through a ligand spacer is the most efficient and widely used strategy. Therefore, a wide range of matrixes have been developed for metal complexes covalent attachment, like polymers [10], zeolites [11], silica spheres [12], magnetic particles [13] and carbon nanotubes [14]. However, these immobilized catalysts' potential and utility are largely related to the support's structural nature. For example, Pd nanomaterials which were supported on functionalized silica were gradually deactivated after three runs in Suzuki coupling reactions [15]. Recently, graphene and graphene oxide (GO) with fascinating two-dimensional structures and exclusive characteristics have emerged as ideal supports for various catalytic species. In addition to the availability of surface functionalization, their two-dimensional structures allow excellent dispersion of the catalytic species. They also facilitate mass transfers in the reaction processes [16]. Reactive species can readily have access to the active sites with restricted mass transfer resistance. Graphene oxide (GO) is a lamellar flexible material having a great number of functional groups such as epoxy (C-O-C), hydroxyl (OH) on basal planes and carboxyl (COOH) on the edges. Extra hydroxyl groups on its surface provide the capability of reaction with different linkers and ligands which could be available for immobilization of metal ions. The nontoxicity, availability, thermal and mechanical stability of a graphene oxide nanosheet makes it an excellent support, especially in heterogeneous catalysis. With these considerations in mind, and to solve the problem of regeneration and reuse of the expensive catalyst, the use of a Pd(II) salen@CPGO nanocatalyst is thus both elegant and efficient. Additionally, GO is inexpensive in comparison with zeolites such as MCM-41 and SBA-15 allowing GO to be the ideal option for catalyst supports [17]. We here describe the synthesis of a Pd(II) salen@CPGO nanocatalyst and demonstrate its application in Suzuki-Miyaura and Heck-Mizoroki coupling reactions. The results show that the new catalyst, Pd(II) salen@CPGO, retains the reactivity characteristic of a homogeneous catalyst but at the same time is easy to separate off and reuse.

# Experimental

#### Materials and methods

Highly pure chemical materials were purchased from Merck. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus. The infrared (IR) spectra (cm<sup>-1</sup>) were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. The size and morphology of the magnetic nanoparticles were observed by using a Philips CM10 transmission electron microscope operating at 100 kV. NMR spectra were

recorded in CDCl<sub>3</sub> on a Bruker Advance DRX-400 MHz instrument spectrometer using TMS as internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. The Pd content of the catalysts was determined using ICP-AES of the model Thermo Electron IRIS INTREPID II XSP DUO. The yields were determined by a Shimadzu GC-17A gas chromatograph (GC) equipped with a flame ionization detector with a capillary column (CBP-1, 30 m × 0.32 mm × 0.25 mm), using helium as carrier gas.

# Synthesis of 3-chloropropyltrimethoxysilane functionalized GO (CPGO, 1)

GO was prepared as described in the literature [18]. Brown powder of GO (1 g) was dispersed in 70 mL of dry toluene for 20 min followed by dropwise addition of 3-chloropropyltrimethoxysilane (3 mL) diluted in 20 mL dry toluene [19]. The resulting mixture was heated to reflux with continual stirring for 24 h under a nitrogen atmosphere. After cooling the mixture, the black powdery sample was filtered, washed with toluene four times and then washed with EtOH. The solid was dried at 70 °C under vacuum for 6 h.

# **Preparation of salen**

To a stirred solution of 2-hydroxybenzaldehyde (2.0 mmol) in 5 mL of ethanol, diethylentriamine (1.0 mmol) was added dropwise and the reaction mixture was stirred under reflux condition for 4 h. N,N-Bis(salicylidene)-ethylenetriamine was obtained by being washed three times with water and methanol, as well as ethanol, and dried at 80 °C in an oven under vacuum. In order to achieve the pure product, the crude product was recrystallized from ethanol.

# Synthesis of Pd(II) salen complex (2)

Salen ligand (1.0 mmol) was dissolved in MeOH (20 mL) and then a solution of  $PdCl_2$  (1 mmol) in absolute MeOH (3 mL) was added dropwise. The resulting mixture was stirred for 3–5 h at room temperature. After evaporating the solvent from the filtrate, a solid mass was obtained which was washed with cold methanol and dried under vacuum to obtain the Pd(II) salen complex **2**.

# General procedure for the preparation of Pd(II) salen@CPGO

For the preparation of the nanocatalyst, 1 g of CPGO(1) was dispersed in 75 mL of dry toluene for 20 min. Later, 0.5 g of homogeneous Pd(II) salen complex (2) and 1.5 mmol triethylamine were added to the suspension. The mixture was refluxed for 20 h and the obtained immobilized catalyst was then washed successively with dry toluene, EtOH and dichloromethane. The solid was dried at 70 °C under vacuum condition for 6 h. The immobilized Pd(II) salen complex on CPGO was characterized by XRD, TEM, FT-IR, SEM–EDX and ICP-AES (Scheme 1).



Scheme 1 Schematic for the preparation of the catalyst

#### General procedure for catalytic Suzuki-Miyaura coupling

In a typical experiment, known quantities of aryl halides (1.0 mmol) and arylboronic acid (1.2 mmol), were dissolved in DMF (3.0 mL) in a 50-mL roundbottomed flask and stirred for 10–15 min.  $K_2CO_3$  (2.0 mmol) and Pd salen@CPGO nanocatalyst (0.7 mol%) were added to the reaction flask. The reaction mixture was heated at 80 °C and stirred. The progress of the reaction was monitored by TLC at regular intervals. After completion, the reaction mixture was cooled to room temperature and the mixture was filtered and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were treated with saturated brine solution and dried over anhydrous sodium sulfate. The removal of the solvent yields the crude product, which after purification by column chromatography afforded the desired products.

#### General procedure for Heck-Mizoroki coupling reaction

A 50-mL round-bottomed flask was charged with aryl haides (1.0 mmol), methyl acrylate/styrene (1.2 mmol),  $Et_3N$  (2.0 mmol), and Pd(II) salen@CPGO nanocatalyst (1 mol%) in DMSO (3.0 mL). The reaction mixture was heated to 110 °C for an appropriate time. At the end of the reaction, the mixture was cooled to room temperature. The reaction mixture was diluted with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the removal of solvent yielded the crude product, which after purification by column chromatography afforded the desired products.

#### General procedure for recycle reaction

After the reaction, the catalyst was obtained by centrifugation separation. The catalyst could be directly reused for several runs after being washed three times with ethanol and was dried under vacuum (Fig. 1).

#### **Results and discussion**

#### Characterization of the heterogeneous catalyst

As shown in Scheme 1, the Pd (II) salen complex was immobilized on a CPGO support through an in situ strategy. Briefly, in order to produce a Schiff base, salicyl aldehyde was condensated with the diethylentriamine, then PdCl<sub>2</sub> was added to prepare the Pd salen complex. Eventually, the synthesized Pd salen complex anchored onto the CPGO. The Pd(II) Salen@CPGO catalyst was characterized by FT-IR, TEM, SEM/EDX, XRD and ICP-AES. 3-Chloropropylterimethoxysilane, which plays the role of coupling agent, provided a large surface to anchor the active complex and increased the efficiency of the heterogeneous catalyst which was used for anchoring the homogeneous Cu(II) catalyst onto the GO.

The FT-IR spectrum of GO (Fig. 2e) shows a broad peak appearing at  $3399 \text{ cm}^{-1}$ , assigned to the stretching mode of an O–H bond, revealing the



Fig. 1 Reuse performance of the catalyst



Fig. 2 The FT-IR spectra of (a) Schiff base, (b) Pd salen complex 2, (c) Pd salen@CPGO heterogeneous catalyst, (d) CPGO, (e) GO

abundance of hydroxyl groups in GO. The strong bands at 1735, 1619, 1220 and 1059 cm<sup>-1</sup> revealed the presence of C=O, C=C, C-OH and epoxy functional groups, respectively, in the GO. Figure 2d which is assigned to CPGO shows an obvious decrease in the intensities of peaks such as 3399 and 1728 cm<sup>-1</sup> which correspond to the OH and C=O stretching vibrations, respectively, and we can see a clear increase in the intensities of the peaks at 1049 and 1080 which provide direct evidence for the strong stretching vibrations of Si-O in CPGO. The FTIR spectrum of the Schiff base shows an enhanced sharp band near 1636 cm<sup>-1</sup> which is assigned to stretching vibration of the C=N group (Fig. 2a). In the spectrum of Pd(II) salen 2 (Fig. 2b), the band related to the C=N functional group shifts to a lower position  $(\sim 20 \text{ cm}^{-1})$  compared to the Schiff base. This red shift to a relatively lower frequency might be attributed to the coordination of Pd through C=N. In the spectrum of Pd(II) salen@CPGO (Fig. 2c), the new stretching vibration bands at 1620 and 1080  $\text{cm}^{-1}$  and a significant decrease in the intensities of peaks such as 3399 and 1737  $\text{cm}^{-1}$  which correspond to the OH and C=O stretching vibrations, respectively, suggesting the grafting of the homogeneous Pd(II) salen ligand complex on the CPGO surface. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** are consistent with the structure of the complex. In the <sup>1</sup>H NMR spectrum, a proton due to -CH=N was observed at 8.3 ppm, which upon coordination to the Pd(II) ion showed a downfield shift and occurred at 8.5 ppm for 2. Also, the <sup>13</sup>C NMR signals for iminecarbon of salen ligand appeared at 166.84 and this value undergoes a downfield shift (169.44 ppm) upon coordination to the Pd(II) ion.



Fig. 3 The XRD patterns of (a) GO, (b) CPGO, and (c) heterogeneous catalyst

Figure 3 shows the XRD patterns of GO and CPGO and the heterogeneous catalyst. Upon oxidation of the graphite, the basal reflection (002) peak appearing at  $2\theta = 26.6^{\circ}$  (*d* spacing = 0.335 nm) shifts to a lower angle ( $2\theta = 11.79^{\circ}$ , *d* spacing = 0.79 nm) (Fig. 3a). The increase in *d* spacing is due to the intercalation of water molecules and the formation of oxygen-containing functional groups between the layers of the graphite. By immobilization of 3-chloropropyltrimethoxysilane on the GO, a broad peak appears at  $2\theta = 15-27^{\circ}$ , depending on amorphous silica (Fig. 3b). The decrease in the intensity of the 002 reflection peak of GO and the appearance of a broad peak at  $2\theta = 15-27^{\circ}$  in the CPGO indicated the immobilization of 3-chloropropyltrimethoxysilane on the GO. By immobilization of the homogeneous Pd(II) salen complex on CPGO, the 002 reflections peak of GO completely disappeared (Fig. 3c).

The morphological properties of Pd(II) salen@CPGO were determined by means of TEM and SEM. The TEM of Pd salen@CPGO (Fig. 4a, b) revealed the nanoscopic features of CPGO. The quantitative energy dispersive spectroscopy (EDX) mapping of Pd salen @CPGO demonstrates that the elements N, O, Pd and Si are homogeneously distributed on the whole surface of this compound, which indicates that the functional groups are anchored uniformly on the GO, whereas the EDX of CPGO only recognizes the elements C, O, Cl and Si (Fig. 4c, d). These results proved that the Pd salen complex (2) was successfully immobilized on the CPGO (1) surface. The crumpling characteristic of Pd(II) salen @CPGO along with the homogeneous distribution of the active sties should be of benefit for its catalytic performance. Analysis by ICP-AES demonstrated that 0.66 mmol g<sup>-1</sup> based on the Pd element was the loading of the homogeneous Pd (II) complex (2) in the heterogeneous catalyst.



Fig. 4 a, b The TEM of heterogeneous catalyst Pd(II) salen@CPGO, c the SEM images and corresponding EDX analysis of CPGO, d the Pd(II) salen@CPGO heterogeneous catalyst

# Catalytic performance of the Pd(II) salen@CPGO for the Suzuki–Miyaura cross-coupling reaction

The catalytic feature of Pd(II) salen@CPGO was studied in C–C bond formation by means of Suzuki–Miyaura cross-coupling of iodoobenzene with phenylboronic acid as a model reaction. The critical factors for the reaction outcomes, like the catalyst amount, solvent, base and temperature, were compared for the purpose of attaining the optimal conditions. The conclusion of the optimization of the conditions is shown in Table 1. The reaction was carried out when various amounts of the heterogeneous Pd(II) salen@CPGO (0.5–1 mol% based on the Pd element) were present at 80 °C. By using 0.7 mol% of the nanocatalyst, the highest yield of the catalyst, a significant decrease in the reaction yield was observed, while additional amounts of catalyst (1 mol%) did not importantly increase the efficiency of the yield nor the rate of the reaction (Table 1, entries 1–3). In order to compare the homogeneous Pd (II) complex (2) was also investigated under the same reaction conditions (Table 1, entry 4).

To clarify the specific catalytic activity of Pd(II) salen@CPGO in the Suzuki– Miyaura cross-coupling reaction, the model reaction was performed in the presence of GO and when no catalyst was present. The application of just GO afforded a low yield of the corresponding cross-coupling product and, when the heterogeneous catalyst was absent, we did not observe any product (Table 1, entries 5, 6).

In addition, the different solvent effects on the model reaction were investigated in depth to achieve the best optimal catalyst conditions (Table 1, entries 2, 7–12). When DMF was applied, the best performance of the catalytic system was obtained (Table 1, entry 2). The results of Table 1 proved that a basic environment was also

Entry	Catalyst (mol%)	Solvent	Base	Temp (°C)	Time (min)	Yield (%) <sup>a</sup>
1	Pd salen@CPGO (0. 5)	DMF	K <sub>2</sub> CO <sub>3</sub>	80	60	75
2	Pd salen@CPGO (0.7)	DMF	$K_2CO_3$	80	35	97
3	Pd salen@CPGO (1)	DMF	K <sub>2</sub> CO <sub>3</sub>	80	35	98
4	Pd salen complex (0.7)	DMF	K <sub>2</sub> CO <sub>3</sub>	80	35	97
5	GO (0.7)	DMF	K <sub>2</sub> CO <sub>3</sub>	80	160	Trace
6	No catalyst	DMF	K <sub>2</sub> CO <sub>3</sub>	80	160	n.r
7	Pd salen@CPGO (0.7)	EtOH/H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	120	68
8	Pd salen@CPGO (0.7)	DMF/H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	60	75
9	Pd salen@CPGO (0.7)	DMSO	K <sub>2</sub> CO <sub>3</sub>	80	35	85
10	Pd salen@CPGO (0.7)	$H_2O$	$K_2CO_3$	80	120	45
11	Pd salen@CPGO (0.7)	EtOH	K <sub>2</sub> CO <sub>3</sub>	60	120	60
12	Pd salen@CPGO (0.7)	THF	K <sub>2</sub> CO <sub>3</sub>	60	120	52
13	Pd salen@CPGO (0.7)	DMF	NaHCO <sub>3</sub>	80	120	78
14	Pd salen@CPGO (0.7)	DMF	Et <sub>3</sub> N	80	120	74
15	Pd salen@CPGO (0.7)	DMF	Na <sub>2</sub> CO <sub>3</sub>	80	50	85
16	Pd salen@CPGO (0.7)	DMF	Cs <sub>2</sub> CO <sub>3</sub>	80	60	80
17	Pd salen@CPGO (0.7)	DMF	KOH	80	120	63
18	Pd salen@CPGO (0.7)	DMF	No base	80	160	n.r
19	Pd salen@CPGO (0.7)	DMF	K <sub>2</sub> CO <sub>3</sub>	r.t	160	Trace
20	Pd salen@CPGO (0.7)	DMF	K <sub>2</sub> CO <sub>3</sub>	60	160	75
21	Pd salen@CPGO (0.7)	DMF	K <sub>2</sub> CO <sub>3</sub>	110	35	98

Table 1 Optimization of reaction conditions for Suzuki-Miyaura coupling reaction

Reaction conditions: Iodobenzene (1 mmol), phenylbronic acid (1.2 mmol), Pd(II) salen@CPGO, base (2 mmol), solvent (3 mL), at different temperature

<sup>a</sup>Determined by GC with a CBP1 column (Shimadzu 30 m  $\times$  0.32 mm  $\times$  0.25 mm)

essential for the Suzuki–Miyaura cross-coupling reaction (Table 1, entry 18). Therefore, in order to investigate its impact, several inorganic and organic bases were tested in the Suzuki–Miyaura reaction of iodobenzene (1 mmol) and phenylboronic acid (1.2 mmol) with the Pd(II) salen@CPGO catalyst (0.7 mol%) in dimethylformamide (3 mL). The common organic bases such as Et<sub>3</sub>N generally used in the Suzuki–Miyaura reaction were found to be less reactive in our catalytic system (Table 1, entry 14). The same behavior was also observed with hydroxide ion (Table 1, entry 17) and sodium bicarbonate base (Table 1, entry 13), as in both cases the reaction did not complete even after 120 min. In contrast, carbonate bases, i.e., Na<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, provided excellent yields of the cross-coupling product (Table 1, entries 2, 15, 16). Thus, we have considered K<sub>2</sub>CO<sub>3</sub> for further optimization.

Moreover, temperature plays a significant role in the reaction yield. We performed the model reaction at various temperatures (25, 60, 80 and 110 °C) in DMF in the presence of the heterogeneous catalyst and  $K_2CO_3$ . There was a remarkable fall in the yield at 25 °C (Table 1, entry 19). The reaction proceeded

faster at 60 °C in comparison with 25 °C. However, when the temperature was higher than 60 °C (80 and 110 °C), a clear rise in intensity was observed in the yield of the coupling reaction (Table 1, entries 2, 21). Thus, we concluded that the optimum temperature is 80 °C.

A variety of structurally divergent aryl iodides, bromides, and chlorides reacted with phenylboronic acid to generate the desired coupling products under the optimized reaction conditions (Table 2). The coupling reactions of aryl iodides and aryl bromides occurred in a short time with good to high yields. Even though aryl bromides required a longer time to afford the same result in comparison with aryl iodides (compare entries 1-10 with 11-15), they gave good yields compared with their chloride counterparts. This might be due to the leaving group ability of halogens (I > Br > Cl > F). In the present catalytic system, the electronic as well as steric effects on the yields and reaction rates were also studied. A good efficiency with a range of both electron-rich and electron-poor substituted aryl halides (such as 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 4-OMeC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-CNC<sub>6</sub>H<sub>4</sub>, 4-CHOC<sub>6</sub>H<sub>4</sub> and 4-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) was shown by this catalytic system. It is noteworthy that aryl iodides containing electron-withdrawing groups, such as -COCH<sub>3</sub>, -CN and -NO<sub>2</sub>, were discovered to be more active than those including electron-donating groups, such as -CH<sub>3</sub>, -OCH<sub>3</sub> and -NH<sub>2</sub> (compare entries 2, 3 with 4, 7, 8, 9, 10). It is also true for aryl bromides and aryl chlorides (compare entries 12, 13 with 14, 15 and 17 with 18, 19).

# Catalytic performance of the Pd(II) salen@CPGO for the Heck-Mizoroki cross-coupling reaction

Encouraged by the excellent results obtained from the Suzuki–Miyaura crosscoupling reactions, we proceeded to investigate the catalytic activity of the Pd(II) salen@CPGO catalyst in Mizoroki–Heck cross-coupling reactions.

The cross-coupling reaction between iodobenzene (1 mmol) and methyl acrylate/ styrene (1.2 mmol) was taken as the model reaction. The reaction conditions were optimized by following a series of reactions as listed in Table 3. Reactions were carried out by varying different parameters such as the amounts of catalyst, solvent, base and temperature to determine the optimum conditions. Among the bases used for the reaction,  $Et_3N$  was found to be superior. Regarding the solvents, DMSO was found to be promising at a temperature of 110 °C, followed by the reaction time of 55 min with 1 mol% of palladium catalyst. For comparison, the homogeneous Pd (II) complex (2) was also investigated under the same reaction conditions (Table 3, entry 5). To demonstrate the efficiency of the catalytic activity of Pd(II) salen@CPGO in the Heck–Mizoroki cross-coupling reaction, the model reaction was performed without using a catalyst. After a long period of time, a poor yield of product was observed such as happened in the presence of GO (Table 3, entries 6, 7).

Subsequently, the optimized reaction conditions were applied for the reaction of a vast range of aryl halides involving electron-donating and electron-withdrawing groups on the aromatic ring to investigate the scope and generality of the present method in the Heck–Mizoroki cross-coupling reaction. The results are summarized in Table 4 from which if can be seen that all reactions of different substituted aryl

xx	+ B(OH) <sub>2</sub>	Pd(II) salen@CPGO K <sub>2</sub> CO <sub>3</sub> , DMF	
Entry	Ar-X	Time (mir	n) <sup>a</sup> Yield (%) <sup>b</sup>
1		35	97
2		60	84
3	MeO	65	80
4		35	92
5		45	90
6		85	80
7	онс	45	87
8	ноос-	45	91
9	H3COC	45	93
10		35	94
11	Br	50	93
12	но-К-Вг	3 h	87
13	H <sub>2</sub> NBr	3 h	90
14	O <sub>2</sub> N-	50	95
15	OHC — Br	90	89
16	CI	3 h	65
17	ноСі	4 h	63
18		4 h	85
19		4 h	90

Table 2 Suzuki-Miyaura cross-coupling reaction of different aryl halides catalyzed by Pd(II) salen@ CPGO

<sup>a</sup>Reaction conditions: Iodobenzene (1 mmol), phenylbronic acid (1.2 mmol), Pd(II) salen@CPGO (0.7 mol%), base (2 mmol), Solvent (3 mL), at 80 °C

 $^{b}$  Determined by GC with a CBP1 column (Shimadzu 30 m  $\times$  0.32 mm  $\times$  0.25 mm)

Entry	Catalyst (mol%)	Solvent	Base	Temp (°C)	Time (min)	Yield (%) <sup>a</sup>
1	Pd salen@CPGO (0. 25)	DMSO	Et <sub>3</sub> N	110	80	70
2	Pd salen@CPGO (0.5)	DMSO	Et <sub>3</sub> N	110	55	88
3	Pd salen@CPGO (1)	DMSO	Et <sub>3</sub> N	110	55	95
4	Pd salen@CPGO (1.5)	DMSO	Et <sub>3</sub> N	110	55	95
5	Pd salen complex (1)	DMSO	Et <sub>3</sub> N	110	55	95
6	GO (1)	DMSO	Et <sub>3</sub> N	110	160	Trace
7	No catalyst	DMSO	Et <sub>3</sub> N	110	160	n.r
8	Pd salen@CPGO (1)	EtOH/H <sub>2</sub> O	Et <sub>3</sub> N	90	140	65
9	Pd salen@CPGO (1)	DMSO/H <sub>2</sub> O	Et <sub>3</sub> N	90	80	75
10	Pd salen@CPGO (1)	DMF	Et <sub>3</sub> N	110	80	83
11	Pd salen@CPGO (1)	$H_2O$	Et <sub>3</sub> N	90	120	40
12	Pd salen@CPGO (1)	EtOH	Et <sub>3</sub> N	60	120	48
13	Pd salen@CPGO (1)	THF	Et <sub>3</sub> N	60	100	58
14	Pd salen@CPGO (1)	DMSO	NaHCO <sub>3</sub>	110	120	69
15	Pd salen@CPGO (1)	DMSO	K <sub>2</sub> CO <sub>3</sub>	110	110	65
16	Pd salen@CPGO (1)	DMSO	Na <sub>2</sub> CO <sub>3</sub>	110	110	70
17	Pd salen@CPGO (1)	DMSO	Cs <sub>2</sub> CO <sub>3</sub>	110	110	68
18	Pd salen@CPGO (1)	DMSO	KOH	110	120	52
19	Pd salen@CPGO (1)	DMSO	No base	110	160	n.r
20	Pd salen@CPGO (1)	DMSO	Et <sub>3</sub> N	r.t	160	Trace
21	Pd salen@CPGO (1)	DMSO	Et <sub>3</sub> N	80	160	62
22	Pd salen@CPGO (1)	DMSO	Et <sub>3</sub> N	160	55	95

Table 3 Optimization of reaction conditions for the Heck-Mizoroki coupling reaction

Reaction conditions: Iodobenzene (1 mmol), olefin (1.2 mmol), Pd(II) salen@CPGO, base (2 mmol), solvent (3 mL), in different temperature

<sup>a</sup>Determined by GC with a CBP1 column (Shimadzu 30 m  $\times$  0.32 mm  $\times$  0.25 mm)

iodides with methyl acrylate or styrene generated products with high yields in short reaction times (Table 4, entries 1–14). Aryl bromides also reacted efficiently with olefins under optimized conditions, resulting in good yields (Table 4, entries 15–20). However, aryl chlorides gave lower yields when compared to their iodide and bromide counterparts (Table 4, entries 21–25). Notably, aryl halides with electron-withdrawing substituents react with olefins more rapidly than the ones with electron-donating substituents. It was observed that the ortho-substituted aryl halides afforded the corresponding products with proper yields in longer reaction times than those attained with para-substituted ones showing steric effects (Table 4, compare entries 6, 17 with 7,18). From these results, it can be concluded that the Pd(II) salen@CPGO catalyst can efficiently catalyze Mizoroki–Heck cross-coupling reactions.

In order to understand the distinctiveness of the Pd(II) salen@CPGO catalyst, we compared the results of the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions of the catalyst with other supported heterogeneous catalysts [20–29], as

<b>x</b> +	or _	Pd(II) salen@CPGO	o	г о
		Et <sub>3</sub> N, DMSO		
Entry	Ar-X	Olefin	Time (min) <sup>a</sup>	Yield (%) <sup>b</sup>
1		COOMe	55	95
2			55	96
3		COOMe	65	83
4	MeO-	COOMe	75	80
5	MeO-		80	80
6	H <sub>2</sub> NI	COOMe	120	90
7		COOMe	3 h	40
8		COOMe	45	89
9	онс-	COOMe	70	82
10	ноос-	COOMe	65	87
11	H₃COC-√I	COOMe	65	92
12	H3COC		70	88
13		COOMe	60	92
14	S I	COOMe	90	70
15	Br	COOMe	100	82
16	HO-Br	COOMe	3 h	78
17	H <sub>2</sub> N-Br	COOMe	3 h	75
18	NH <sub>2</sub> Br	COOMe	5 h	45

 Table 4
 Heck-Mizoroki cross-coupling reactions of different aryl halides catalyzed by Pd(II) salen@

 CPGO

Table 4 continued

Entry	Ar-X	Olefin	Time (min) <sup>a</sup>	Yield (%) <sup>b</sup>	_
19	O <sub>2</sub> N-Br	COOMe	80	90	
20	OHC -Br	COOMe	2 h	80	
	O <sub>2</sub> N	COOMe	3 h	84	
21	С				
22	-ci	COOMe	3 h	54	
23	но-Сі	COOMe	5 h	48	
24		COOMe	2 h	50	
25		$\bigcirc \frown$	3 h	45	

<sup>a</sup>Reaction conditions: Iodobenzene (1 mmol), olefin (1.2 mmol), Pd(II) salen@CPGO (1 mol%), base (2 mmol), Solvent (3 mL), at 110  $^\circ C$ 

<sup>b</sup>Determined by GC with a CBP1 column (Shimadzu 30 m  $\times$  0.32 mm  $\times$  0.25 mm)

Table 5 Suzuki–M	Comparison of Aiyaura reaction	the catalytic efficiency of Pd(II)	salen@CPGO wi	th various c	atalysts for the
Entry	Catalyst	Experimental conditio	ns Yield (%)	Halide	References

1	PdNP@PPh2-SiO2	60 °C, 3 h	94	Br	[20]
2	Pd/SBA-15	85 °C, 5 h	88	Br	[21]
3	MCM-48-Py-Pd	90 °C, 5 h	92	Br	[22]
4	Pd-CS@SiO <sub>2</sub>	80 °C, 1 h	90	Br	[23]
5	Pd/CM	80 °C, 19 h	97	Br	[24]
6	GO-NHC-Pd (II)	80 °C, 1 h	96	Ι	[25]
7	Pd(II) salen@CPGO	80 °C, 35 min	97	Ι	This work

Reaction conditions: aryl halide, phenylbronic acid (1.2 mmol), base, solvent, in different temperature and time

 $\label{eq:comparison} \mbox{Table 6 Comparison of the catalytic efficiency of Pd(II) salen@CPGO with various catalysts for the Heck-Mizoroki reaction$ 

Entry	Catalyst	Experimental conditions	Yield (%)	Halide	References
1	Pd/CM	80 °C, 3 h	91	I	[24]
2	SiO <sub>2</sub> -SH·Pd	100 °C, 12 h	85	Ι	[26]
3	SBA-SH·Pd	120 °C, 15 h	96	Ι	[27]
4	HMS-OPPh2-Pd	120 °C, 3 h	80	Ι	[28]
5	AL(OH) <sub>3</sub> /Pd	130 °C, 19 h	99	Br	[29]
6	Pd(II) salen@CPGO	110 °C, 55 min	95	Ι	This work

Reaction conditions: aryl halide, olefin, base, solvent, in different temperature and time

shown in Tables 5 and 6, respectively. These tables illustrate clearly that the Pd(II) salen@CPGO shows a better activity in less time and milder reaction conditions for both Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions. Facile recovery of the Pd(II) salen@CPGO catalyst, mild reaction conditions, and better activity are the key advantages of the Pd(II) salen@CPGO catalyst over other reported catalysts.

# Conclusions

We have successfully synthesized a new heterogeneous Pd (II) salen complex tethered onto CPGO and evidenced by FT-IR, ICP-AES, XRD, SEM/EDX and TEM. The catalyst exhibited high catalytic activity towards the C–C coupling for the Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions with various electronically diverse substrates. Catalytic tests showed that the heterogeneous Pd(II) salen@CPGO is the most active in DMF and DMSO at 80 and 110 °C using a base for the Suzuki–Miyaura and Heck–Mizoroki couplings, respectively. Furthermore, the heterogeneous catalyst showed good recoverability and relatively high stability against leaching of active species and can be recycled many times without significant loss of catalytic activity.

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