## FULL PAPER

# Synthesis, characterization and application of graphene palladium porphyrin as a nanocatalyst for the coupling reactions such as: Suzuki-Miyaura and Mizoroki-heck

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Kiumars Bahrami, Nanoscience and Nanotechnology Research Center (NNRC), Razi University, Kermanshah, 67149-67346, Iran. Email: kbahrami2@hotmail.com The palladium(II)-coordinated 5,10,15,20-tetrakis-(4-hexyloxyphenyl)-porphyrin as a macrocyclic palladium complex was covalently grafted to the surface of graphene oxide (denoted as GO-CPTMS@Pd-TKHPP). GO-CPTMS@Pd-TKHPP was characterized using microscopic and spectroscopic techniques for confirmation of functionalization. The synthesized catalyst was checked in the Suzuki-Miyaura and the Mizoroki-Heck coupling reactions. The catalyst is very easy to handle, environmentally safe and economical. Also, this catalytic system shows high catalytic activity and the yields of the products are excellent. Moreover, the suggested catalyst was reusable for five runs with no significant decrease in catalytic activity.

#### **KEYWORDS**

cross-coupling reactions, graphene oxide, heterogeneous catalysis, metalloporphyrin, nanocatalysts

# **1** | INTRODUCTION

Cross-coupling reactions have appeared as powerful in chemistry, because they provide key steps in building complex, bio-active molecules developed as medicines and agrochemicals.<sup>[1]</sup> Among various cross-coupling reactions, Suzuki-Miyaura and the Mizoroki-Heck reactions have emerged as a most valuable synthetic methodologies. These reactions have been applied to many areas, including natural product, pharmaceutical, in engineering materials such as conducting polymers, molecular wires, and fine chemical syntheses.<sup>[2–4]</sup> Some applications of the Suzuki – Miyaura and the Mizoroki – Heck reactions in pharmaceutical are: Production of (+)-Dynemicin,<sup>[5]</sup> Morphine<sup>[6]</sup> and Paclitaxel (Taxol<sup>®</sup>).<sup>[7]</sup>

The Suzuki – Miyaura and the Mizoroki – Heck reactions are usually performed in organic solvents using homogeneous palladium salts and complexes, that can lead to many issues are harmful effects of human activity on the biophysical environment. To overcome these problems, it is highly desirable to develop new catalytic systems that combine the many advantages of heterogeneous catalysts with the versatility of homogeneous catalysts. Therefore, the heterogenization of palladium catalyst is a encouraging option.

Heterogeneous catalysts are present in a different phase, usually solid. The main benefits of using a heterogeneous catalyst is the relative ease of catalyst separation from the product stream which assists in the creation of continuous chemical processes.<sup>[8]</sup> Nevertheless, heterogeneous catalysts are easy to recover but the active sites in heterogeneous catalysts are not as accessible as in homogeneous catalysts, and so the catalytic activity is usually decreased. On the other hand, homogeneous catalysts are known for their higher activity and selectivity, but the separation of costly transition metal catalysts from substrates and products remains a key issue for industrial applications.<sup>[1,8]</sup> Consequently, we need a catalytic system that not only exhibits high activity and selectivity (such as a homogeneous system) but also possesses the ease of catalyst separation and recovery (such as a heterogeneous system). These objectives can be achieved by nanocatalysis.<sup>[9]</sup> 2 of 9 WILEY-Organometallic Chemistry

Nanocatalysts bridge the gap between homogeneous and heterogeneous catalysts, keeping the desirable attributes of both catalysts. With the coming of nanotechnology to manufacture catalysts, nanocatalysts were produced.<sup>[10,11]</sup> Nanocatalyst shows excellent stability and catalytic activity, relative cheap, environmentally friendly, easy available, non-expission, reusability, easy to handle and excellent yields.<sup>[12–14]</sup>

A wide variety of metalloporphyrin compounds with highly symmetrical D<sub>4</sub>h planar structure are known; almost every metal can be coordinated inside the macro cycle, different metallic oxidation states are possible and further coordination is possible at the axial positions.<sup>[15]</sup> Accordingly, a great variety of materials with very different properties have already been prepared and studied.<sup>[16,17]</sup> Some palladium porphyrins as homogeneous catalyst have been used for the Suzuki-Miyaura and the Mizoroki-Heck coupling reactions.<sup>[18,19]</sup> Although these homogeneous palladium porphyrins improve catalytic activity significantly as a result of electron-donating functionality, but they often suffered from the separation of these expensive catalysts after the reactions have completed. In addition, these homogeneous catalysts often result in heavy metal contamination of the desired isolated products.

Graphene oxide (GO) is fundamentally a wrinkled two-dimensional carbon sheet with various oxygenated functional groups on its basal plane and peripheries, with the thickness around 1 nm and lateral dimensions varying between a few nanometers and several microns.<sup>[20]</sup> Because of its mechanical and electrical properties, thermal stability and high surface area it has been used as a significant supporting material and has been found as a promising material for fuel cells,<sup>[21]</sup> sensors,<sup>[22]</sup> solar cells,<sup>[23]</sup> lithium batteries<sup>[24]</sup> and as support materials for synthesis of heterogeneous catalysts.<sup>[25]</sup>

Liu and co-workers have reported Pd-porphyrin supported on SBA-15 as a catalyst for solvent-free Heck reaction.<sup>[26]</sup> Moghadam and coworkers have described Pdporphyrin supported on Dowex 50WX8 and Amberlite IR-120 as a reusable catalysts in C–C coupling reactions.<sup>[27,28]</sup> In addition, Hagiwara and coworkers have offered a protocol for Heck arylation reactions by using Pd/C as a stable catalyst in ionic liquid.<sup>[29]</sup> But, these protocols were performed in high temperature, very long reaction times, and low active sites on catalyst support.

In this work, we report the design, synthesis, and application of 5,10,15,20-tetrakis-(4-hexyloxyphenyl)-porphyrin (TKHPP) linked to graphene oxide (GO) as a catalyst support. TKHPP is semi-rigid molecule, with planar molecular conformation that has an inner hole with diameter of 4. This arrangement makes THPP possible to coordinate with metal ions efficiently.<sup>[15,30]</sup> Accordingly, we synthesized the TKHPP linked GO support

(denoted as GO-CPTMS@TKHPP) with a two-dimensional (2D) layered-sheet structure. The synthesized GO-CPTMS@TKHPP complex is an ideal complex for incorporating a variety of metal ions. Because, it has catalytic active sites and shows high stability to thermal treatments, water, and most of the organic solvents.

As an example, the palladium(II)-coordinated TKHPP complex (denoted as GO-CPTMS@Pd-TKHPP) was facilely synthesized via a simple treatment of GO-CPTMS@TKHPP with PdCl<sub>2</sub> at 80 °C. We then applied the GO-CPTMS@Pd-TKHPP nanocatalyst in the Suzuki-Miyaura and the Mizoroki-Heck coupling reactions (Scheme 1).

The excellent catalytic activity of GO-CPTMS@Pd-TKHPP was clarified using the broad scope of the reactants and the excellent yields of the reaction products, together with the high stability and easy recyclability of the catalyst.

## 2 | RESULTS AND DISCUSSION

#### 2.1 | Catalyst characterization

The GO-CPTMS@Pd-TKHPP was prepared by the route outlined in Scheme 2. As shown, the GO-CPTMS@TKHPP complex could be reproducibly synthesized by heating the GO-CPTMS@THPP and 1-bromohexane in a mixture of DMF  $K_2CO_3$  within a round bottom flask (see Scheme 2 for details). The synthesized GO-CPTMS@TKHPP complex is insoluble in water or common organic solvents (such as DMF, THF, DMSO, CHCl<sub>3</sub>, etc.).

The successful synthesis of the GO-CPTMS is confirmed from the FT-IR spectra (Figure 1c). The band at 1107 cm<sup>-1</sup> corresponds to Si–O–Si antisymmetric stretching. The peak appearing at 810 cm<sup>-1</sup> is due to the symmetric vibration of Si–O–Si. In the case of GO-CPTMS@TKHPP (Figure 1e), it was found that the N-H bond stretching and bending frequencies of free base porphyrins located at ~3,300 cm<sup>-1</sup> and ~960 cm<sup>-1</sup>. When the palladium ion was inserted into the porphyrin ring, the N-H bond vibration frequency of free base porphyrins disappeared and the characteristic functional groups of Pd-N bond formed at ~1,009 cm<sup>-1</sup> (Figure 1f), that disclosed the formation of a metal–ligand bond.



**SCHEME 1** GO-CPTMS@Pd-TKHPP catalyzed Suzuki and Heck coupling reactions



**SCHEME 2** Schematic representation for the synthesis of GO-CPTMS, GO-CPTMS@THPP and GO-CPTMS@Pd-TKHPP materials (1,2 and 3)

The layer structure of GO-CPTMS@Pd-TKHPP was also observed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image of GO-CPTMS@Pd-TKHPP (Figure 2) shows morphology, particle size and surface uniformity. TEM image of the GO-CPTMS@Pd-TKHPP catalyst exhibits which complex Pd(II)-TKHPP was supported on the surface of graphene oxide (Figure 3).

Additionaly, EDX analysis of the nanocatalyst showed the presence of the expected elements in the structure of the nanocatalyst such as palladium, oxygen, silicon, nitrogen, and carbon (Figure 4).

XRD pattern of GO-CPTMS@Pd-TKHPP exhibits peaks at  $2\theta = 28.5$ , 40.4, 46.8 and 68°, which correspond to (111), (200), (220) and (331) crystalline planes of Pd, respectively, indicating that Pd element exists in the form of Pd(0), not Pd(II)<sup>[31, 25a]</sup> (Figure 5).

## 2.2 | Catalytic studies

For the optimization of the Suzuki C-C coupling reaction, parameters such as kind of base and solvent, temperature and catalyst amount was examined (Table 1). The coupling of iodobenzene (1 mmol) and phenylboronic acid (1.5 mmol) under air was selected as model reaction. The progress of the reaction was monitored by TLC. In the optimization of the catalyst amount, the best results were obtained using 0.1 g of catalyst. We also checked the effect of amount of catalyst, the yield of the product does not change much (Table 1, entry 5). As shown in



**FIGURE 1** FT-IR spectrum of (a) FT-IR spectra of GO; (b) GO-OH (c) GO-CPTMS; (d) GO-CPTMS@THPP; (e) GO-CPTMS@TKHPP; (f) Recycled GO-CPTMS@Pd-TKHPP



FIGURE 2 SEM images of GO-CPTMS@Pd-TKHPP

4 of 9 WILEY-Organometallic Chemistry





FIGURE 5 XRD pattern of GO-CPTMS@Pd-TKHPP

FIGURE 3 TEM images of GO-CPTMS@Pd-TKHPP

Table 1, this coupling reaction was found to be highly sensitive to the reaction temperature. When the model reaction was run at 25, 50 and 70 °C 20%, 62% and 77% of the desired product was obtained respectively (Table 1, entries 6–8). A reaction temperature of 80 °C was found to be optimal for the model reaction. Then, the same reaction was performed in different solvents. The results showed when the reaction was carried out in solvents such as EtOH/H<sub>2</sub>O and DMF, the higher yields were obtained. The use of EtOH, MeCN, N-methylpyrrolidin-2-one (NMP) and tetrahydrofuran (THF) as solvent led to lower yield of the prodct. It was also observed low tendency to do cross coupling reaction in a non-polar solvent such as toluene (Table 1, entry 14).

Among organic and inorganic bases such as  $K_2CO_3$ ,  $Na_3PO_4$  and  $NEt_3$  used for the model reaction  $K_2CO_3$  was found to be the most efficient base (Table 1). Base

on the obtained results, the optimum reaction conditions involved iodobenzene (1 mmol), phenylboronic acid (1.5 mmol),  $K_2CO_3$  (1.5 mmol) and 0.1 g of GO-CPTMS@Pd-TKHPP nanocatalyst, containing 0.1 mmol of Pd in EtOH/H<sub>2</sub>O (2:1, 3 ml) at 80 °C under air atmosphere (Table 1, entry 4).

The scope and generality of this procedure were investigated in the reaction of substituted aryl halides with phenylboronic acid. As can be seen in Table 2, different aryl iodides, bromides and chlorides containing electronreleasing and electron-withdrawing groups reacted efficiently with phenylboronic acid under the optimized conditions to produce the corresponding cross-coupling products in high yields. The experimental results demonstrated that the nature of the substituents on the aromatic rings of starting materials does not significant influence on the reaction. Substituents such as methyl, methoxy and nitro groups were well tolerated (Table 2). As expected; aryl iodides and bromides are generally much more reactive than chlorides. All products are known



FIGURE 4 EDX pattern of GO-CPTMS@Pd-TKHPP

**TABLE 1** Optimization of conditions in the Suzuki-Miyaura coupling reaction<sup>a</sup>

$(\text{GO-CPTMS}@Pd-TKHPP) \longrightarrow (\text{GO-CPTMS}@Pd-TKHPP)$						
Run	Catalyst (g)	Base	Solvent	T (°C)	Yield (%) <sup>b</sup>	
1	0	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	0	
2	0.05	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	30	
3	0.08	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	81	
4	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	99	
5	0.15	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	99	
6	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	r.t.	20	
7	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	50	62	
8	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	70	77	
9	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	80	98	
10	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH	80	55	
11	0.1	K <sub>2</sub> CO <sub>3</sub>	MeCN	80	62	
12	0.1	K <sub>2</sub> CO <sub>3</sub>	NMP	80	82	
13	0.1	K <sub>2</sub> CO <sub>3</sub>	THF	80	44	
14	0.1	K <sub>2</sub> CO <sub>3</sub>	Toluene	80	50	
15	0.1	No base	EtOH/H <sub>2</sub> O (2:1)	80	4	
16	0.1	Na <sub>3</sub> PO <sub>4</sub>	EtOH/H <sub>2</sub> O (2:1)	80	70	
17	0.1	NEt <sub>3</sub>	EtOH/H <sub>2</sub> O (2:1)	80	35	

<sup>a</sup>Reaction conditions: Iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), base (1.5 mmol), solvent (3 ml), GO-CPTMS@Pd-TKHPP (0.1 g, containing 0.1 mmol of Pd), under air atmosphere, 5 min.

<sup>b</sup>Isolated yield.

$Y X + (HO)_2 B X + (HO)_2 B Y $							
Entry	Y	Х	Time (min)	Yield (%) <sup>b</sup> /(TON)	M.p.	Ref.	
1	Н	Br	15	99 (99)	67–68	[32]	
2	4-Me	Br	30	97 (97)	44–47	[33]	
3	4-MeO	Br	40	97 (97)	85-88	[33]	
4	4-NO <sub>2</sub>	Br	14	99 (99)	107-110	[34]	
5	4-NO <sub>2</sub>	Ι	5	98 (98)	107–110	[34]	
6	Н	Ι	5	99 (99)	67–68	[32]	
7	4-Me	Ι	10	97 (97)	44–47	[33]	
8	4-MeO	Ι	15	97 (97)	85-88	[33]	
9	4-MeO	Cl	85	92 (92)	85-88	[33]	
10	Н	Cl	90	92 (92)	67–69	[32]	

TABLE 2 Suzuki – Miyaura coupling reactions of aryl halides with phenylboronic acid<sup>a</sup>

<sup>a</sup>Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), EtOH/H<sub>2</sub>O (3 ml), GO-CPTMS@Pd-TKHPP (10 mol%), under air atmosphere, 80 °C.

<sup>b</sup>Isolated yield.

compounds and were identified by comparison of their physical and spectra data with those reported in the literature (see supporting information).

For practical application of heterogeneous nanocatalyst, the reusability of catalyst is a very important factor. In order to prove this issue, catalytic recycling 6 of 9 WILEY-Organometallic Chemistry

experiments were performed using a Suzuki – Miyaura reaction of bromobenzene and phenylboronic acid as a model reaction. After completion of the reaction, the catalyst was filtered and washed with DMF,  $H_2O$ , and acetone. Then, catalyst dried under reduced pressure at 60 °C and used in the next run. As shown in Table 3, GO-CPTMS@Pd-TKHPP as a heterogeneous nanocatalyst, showed slight loss in its activity up to five reaction cycles. The slight decrease of catalytic activity should be due to thenormal loss of the catalyst during the work-up stage.

To test for leaching, we filtered the catalyst after 7.5 min reaction Table 3 (50% conversion was achieved at this stage) and the reaction continued uninterrupted in the absence of the catalyst. We found that the reaction was not completed, even at long reaction times. This indicated that the leakage of Pd NPs during catalytic experiments was negligible and the nature of reaction was heterogeneous.

Having found that the GO-CPTMS@Pd-TKHPP was a highly efficient nanocatalyst for the Suzuki - Miyaura reactions, its activity was also investigated in the Mizoroki - Heck reaction of aryl halides and styrene. In order to obtain the optimal reaction conditions, a series of experiments were performed using iodobenzene and styrene as a model reaction. Among the various organic and inorganic bases investigated, K<sub>2</sub>CO<sub>3</sub> was found to be the best base. The effect of solvent on Heck coupling reaction was also examined in different polar and non-polar solvents such as DMF, NMP, THF, EtOH, MeCN and toluene. The highest catalytic activity was observed in DMF. Toluene as nonpolar solvent was not favorable for this reaction. Moreover, the effect of temperature on the activity of this catalyst was examined in the range 80-140 °C. By increasing the temperature to 120 °C, the yield was increased but the effect of temperature on the yield became slight when the temperature was beyond 120 °C. Therefore, the preferable temperature for this reaction is 120 °C. The effect of catalyst amount on the Heck reaction was also studied. The results showed that the highest catalytic activity was observed with 0.1 g of catalyst. Therefore, the highest yield was obtained using  $K_2CO_3$ (2 mmol) as base and DMF (2 ml) as solvent in the presence of GO-CPTMS@Pd-TKHPP (0.1 g) as catalyst at 120 °C (Table 4, entry 4).

This protocol was then applied for coupling of various aryl halides with styrene (Table 5). As shown, electrondonating groups such as methyl and methoxy and

**TABLE 3** Recycling and reuse of GO-CPTMS@Pd-TKHPP in theSuzuki-Miyaura coupling reaction<sup>a</sup>

Run	1	2	3	4	5
Yield%	99	95	95	93	91

electron-withdrawing groups such as nitro and cyano were successfully reacted with styrene under the optimized reaction conditions. Styrene was also found to couple smoothly with less reactive aryl halides such as bromo and chlorobenzene.

# 3 | EXPERIMENTAL

### 3.1 | Material and physical measurements

Yields refer to isolated products. All of the known products were characterized by comparison of their spectral data and physical properties with those reported in the literature. Progress of the reaction was followed by TLC (Thin Layer Chromatography) using silica gel polygrams SIL G/UV 254 plates. Infrared spectra were prepared on a Ray Leigh Wqf-510 FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker (300 MHz) spectrometer in CDCl<sub>3</sub> as solvent. Melting points were determined in open capillaries with a Gallen-Kamp melting point apparatus. Chemicals were purchased from the Merck chemical company. The elemental palladium content of nanocatalyst was determined by Perk in Elmer Optima 2000DV inductively coupled plasma-atomic emission spectrometry (ICP-AES). TEM measurements were performed using a Philips CM120 operated at 100 kV electron beam accelerating voltage and equipped with a CCD camera. One drop of the sample solution was deposited onto a copper grid and the excess of the droplet was blotted off the grids with filter paper; then the sample was dried under ambient conditions. X-rays diffraction (XRD) patterns were obtained with an MSALXRD2 diffractometer using Cu K $\alpha$  radiation. SEM and energy-dispersive X-ray (EDX)measurements were performed using a KYKY-EM3200 operated at 26 kV with the electron gun filament: tungsten.

## 3.2 | Synthesis of GO-CPTMS@TKHPP

The GO (1 g) was dispersed in 20.0 ml of toluene. Then, CPTMS (1.25 ml, 6.8 mmol) was added to the mixture. Next, the resulting mixture was refluxed and stirred for 24 h. In the last step, the solid was filtered and dried at room temperature to yield GO-CPTMS as a black-coloured powder. GO-CPTMS (0.03 g) was dissolved in 5 ml of 1,4-dioxane. Then, 5,10,15,20-tetrakis-(4-hydroxyphenyl)-porphyrin (THPP) (0.06 g, 0.08 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.138 g, 1 mmol) and KI (0.16 g, 1 mmol) were added to the reaction mixture. The mixture was stirred under reflux conditions for 24 h. After 24 h the mixture was dried at room temperature to yield GO-CPTMS@THPP as a black powder. The prepared GO-

Applied Organometallic-Chemistry TABLE 4 Optimization of conditions in the heck reaction of iodobenzene and styrene catalyzed by GO-CPTMS@Pd-TKHPP<sup>a</sup>

7 of 9

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Run	Catalyst (g)	Base	Solvent	T (°C)	Yield (%) <sup>b</sup>
1	0	K <sub>2</sub> CO <sub>3</sub>	DMF	120	0
2	0.05	K <sub>2</sub> CO <sub>3</sub>	DMF	120	40
3	0.08	K <sub>2</sub> CO <sub>3</sub>	DMF	120	75
4	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	120	95
5	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	80.	60
6	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	100	76
7	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	110	85
8	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	140	96
9	0.1	K <sub>2</sub> CO <sub>3</sub>	EtOH	Reflux	51
10	0.1	K <sub>2</sub> CO <sub>3</sub>	MeCN	Reflux	55
11	0.1	K <sub>2</sub> CO <sub>3</sub>	NMP	Reflux	60
12	0.1	K <sub>2</sub> CO <sub>3</sub>	THF	Reflux	40
13	0.1	K <sub>2</sub> CO <sub>3</sub>	Toluene	Reflux	10
14	0.1	No base	DMF	120	0
15	0.1	Na <sub>3</sub> PO <sub>4</sub>	DMF	120	80
16	0.1	NEt <sub>3</sub>	DMF	120	47

<sup>a</sup>Reaction conditions: Iodobenzene (1 mmol), styrene (1.5 mmol), base (1.5 mmol), solvent (3 ml), GO-CPTMS@Pd-TKHPP (0.1 g, containing 0.1 mmol of Pd), under air atmosphere, 2 min.

<sup>b</sup>Isolated yield.

	Y	∕-∕_X +	(GO-CPTMS@Pd-TK			
Entry	Y	Х	Time (min)	Yield (%) <sup>b</sup> /(TON)	M.p.	Ref.
1	Н	Ι	20	95 (95)	121–123	[35]
2	4-Me	Ι	30	90 (90)	114–117	[36]
3	4-MeO	Ι	35	91 (91)	130–132	[35]
4	4-NO <sub>2</sub>	Ι	10	96 (96)	150-152	[37]
5	4-Cn	Ι	15	93 (93)	113–115	[35]
6	Н	Br	40	88 (88)	120–122	[35]
7	4-Me	Br	60	85 (85)	114–117	[36]
8	4-MeO	Br	75	85 (85)	130-132	[35]
9	4-NO <sub>2</sub>	Br	35	90 (90)	150-152	[37]
10	Н	Cl	85	70 (70)	120–122	[35]

**TABLE 5** Coupling reactions of aryl halides with styrene<sup>a</sup>

<sup>a</sup>Reaction conditions: Aryl halide (1 mmol), styrene (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (3 ml), GO-CPTMS@Pd-TKHPP (10 mol%), under air atmosphere, 120 °C.

<sup>b</sup>Isolated yield.

BAHRAMI AND KAMRANI

8 of 9 WILEY-Organometallic Chemistry

CPTMS@THPP (0.1 g) and 1-bromohexane (0.03 mL, 0.21 mmol) were added to a solution of  $K_2CO_3$  in DMF (4:4) in a round-bottom flask and the mixture was stirred under reflux condition for 24 h then, dried at room temperature, to give GO-CPTMS@TKHPP as gray powder (yield 90%).

# 3.3 | Synthesis of GO-CPTMS@Pd-TKHPP

Palladium chloride (0.01 g, 0.056 mmol) was dissolved in 3 ml ethanol, and then GO-CPTMS@TKHPP (0.1 g) was added. Then, the mixture was stirred under reflux condition for 24 h. After 24 h, the mixture was dried at room temperature to yield GO-CPTMS@Pd-TKHPP as a black-colored (79% yield). 0.1 g of GO-CPTMS@Pd-TKHPP, containing 0.1 mmol of Pd, as determined by ICP.

# 3.4 | General procedure for the Suzuki-Miyaura reaction catalyzed by GO-CPTMS@Pd-TKHPP

A round-bottomed flask was charged with aryl halides (1.0 mmol), phenylboronic acids (0.183 g, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 g, 1.5 mmol), GO-CPTMS@Pd-TKHPP (0.1 g, containing 0.1 mmol of Pd), and aqueous 80% ethanol ( $\nu/v\%$ , 5.0 ml). The reaction mixture was stirred and heated under reflux conditions for a specific time with complete consumption of the starting material (Table 1). The progress was tracked by TLC analysis. After the completion of the reaction, the nanocatalyst was removed by filtration, washed with ethanol  $(3 \times 5 \text{ ml})$  and dried under vacuum at 60 °C for the next run. The organic fractions were then concentrated under reduced pressure to give the crude product. The product was further purified by recrystallization from EtOAc. The spectral and physical properties of known products were compared to those reported in the literature. In every case excellent agreement was obtained.

# 3.5 | General procedure for the Mizoroki – Heck reaction catalyzed by GO-CPTMS@Pd-TKHPP

The mixture of aryl halides (1 mmol), styrene (1.5 mmol),  $K_2CO_3$  (2 mmol), GO-CPTMS@Pd-TKHPP (0.1 g, containing 0.1 mmol of Pd), and aqueous 90% DMF (v/v%, 5 ml) were added into a flask and the mixture was stirred in a preheated oil bath at 120 °C for a specific time (Table 2). The progress was monitored by TLC. Once completion of the reaction, the filtrate was extracted by diethyl ether (3 × 5 ml), the organic layer was washed with brine (5 mL), separated, and dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>. The product was obtained after removing the

ethereal solution under vacuum. The crude products were further purified by recrystallization with ethanol. All of the products are known compounds and their spectral and physical were identical to that reported in literature.

## 4 | CONCLUSIONS

In conclusion, we have successfully constructed GO-CPTMS@Pd-TKHPP as a heterogeneous nanocatalyst from simple starting materials. The two-dimensional layered-sheet structure of GO with highly symmetrical D4h planar structure of THPP complex as an ideal scaffold for coordinating metal ions. Accordingly, the robust incorporation of PdCl<sub>2</sub> into GO-CPTMS@TKHPP was realized with a simple post treatment and confirmed by spectroscopic analyses. The synthesized GO-CPTMS@Pd-TKHPP nanocatalyst was applied to catalyze the Suzuki-Miyaura and the Mizoroki-Heck coupling reactions, two important reactions for the formation of C-C bonds. The superior activity of GO-CPTMS@Pd-TKHPP nanocatalyst was testified by the broad scope of the reactants. The excellent yields, cleaner reaction profile, the high stability and easy recyclability of the catalyst are the salient features of this synthetic methodology. In with other nanocatalyst, the unique structure of GO-CPTMS@Pd-TKHPP provides efficient access to the catalytic sites and fast mass-transport of the reactants/products, which are responsible for its superior activity in catalyzing the Suzuki-Miyaura and Mizoroki-Heck coupling reactions.

#### ACKNOWLEDGEMENTS

The authors acknowledge the Razi University Research Council for support of this work.

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Organometallic Chemistry 9 of 9

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**How to cite this article:** Bahrami K, Kamrani SN. Synthesis, characterization and application of graphene palladium porphyrin as a nanocatalyst for the coupling reactions such as: Suzuki-Miyaura and Mizoroki-heck. *Appl Organometal Chem.* 2017; e4102. https://doi.org/10.1002/aoc.4102