

Coupling Reactions by Highly Efficient Octacalix[4] Pyrrole Wrapped Scrupulous Nano-Palladium Catalyst

Keyur D. Bhatt ¹, Ajay Desai ^{1,*}, Krunal Modi ¹, Anita Kongor ²

¹ Department of Chemistry, Mehsana Urban Institute of Sciences, Ganpat University, Kherva, Mehsana 380412, Gujarat, India

² Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad-38009, Gujarat, India

* Correspondence author email address: drkdbhatt@outlook.com;

Scopus Author ID 55258010600

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Abstract: Work is focused on OHCP-PdNPs synthesis with the help of meso-modified OHCP derivatives. OHCP-PdNPs utilized for the C-C coupling reactions as an efficient nanocatalyst. This study includes the stability as well as pH studies of fine PdNps. OHCP is an electron-rich ligand that is capable of reducing as well as encapsulate the metal ions because of the availability of electron-rich hydrazide functional group and H-bonding promoter four pyrrole units. In comparison with normal hydrazine, CP-hydrazide has a higher withdrawal ability, so Pd-NPs periphery is surrounded by them and undergoes stronger web-like capping on palladium. Similarly, OHCP-PdNPs are aqueous and air-stable, besides affordable alternatives for the synthesis of stable PdNPs. Moreover, encapsulating the periphery of PdNPs using OHCP enhances its activity and selectivity. Which indicates the perfect association of metal-cage recognition? This recognition may lead to numerous promising applications towards an efficient catalytic activity.

Keywords: Calix(4)pyrrole; Palladium Nanoparticle; Catalyst; Coupling reaction and Metal.

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1. Introduction

Nanoscience is the field as an ingenious and interdisciplinary science with vast applications in catalysis, electroanalysis, sensor, dyes, sciences, and medicine, among different fields [1-3]. The metal nanoparticles have increased extensive enthusiasm for academic and industrial fields [4] as they have remarkable properties in electronics, biological activity, optics, and organic synthesis [5]. The definition of nanocatalysis means the new way to the interesting and enlarging field of catalysts, which is designed, and the mechanism takes place at the nanoscale level [6]. A metal derived nanoparticles have attracted the interest of research as catalysts in chemical reactions and are currently an imperative field in nanoscience and nanotechnology [7, 8].

The significance of size, shape, well-controlled monodispersity, and different chemical composition; metal nanoparticles synthesis is becoming a key tool in nanoparticle research [9, 10]. Catalysis is taken place on a metal surface, so surface to volume ratio possesses enormous impact, and as a part of it, the reactivity of metal nanoparticle is higher and unique than their metal counterparts [11, 12]. Catalysis by palladium nanoparticles (PdNps) has evoked great interest because of its boundless applications in organic synthesis, including C-C bond-forming reactions [13]. The nature of the active catalytic species in reactions such as the Suzuki-Miyaura reaction [14], Heck reaction [15, 16], Hiyama reaction [17], Stille reaction

[18], Hydrogenation reaction [19], etc. reactions are of great interest since few decades. There are a large number of complex organic compounds synthesized by using catalytically active palladium complexes [20]. Many carbon-carbon and carbon-heteroatom coupling reactions take place with the help of palladium complexes such as $(PPh_3)_4Pd$ [21]. However, those active palladium complexes are air sensitive, toxic, and due to their leaching properties difficult to separate from the reaction products. The preparation of metal nanoparticles often requires the use of chemical reduction methods in which a reducing agent and a number of stabilizers are used to prevent the accumulation of metal nanoparticles [8, 22] and the leaching of the which may include an activity of the catalyst [8]. A large number of nanoparticles have been synthesized using the chemical reduction method [23] with needful modification in the actual method. In some synthesis, there is wide use of reducing agents like borohydride [24], hydrazide [25] to form ultrafine nanoparticles. During the nanoparticle formation, aggregation is the biggest drawback to overcome such type of aggregation PdNps are stabilized by different types of stabilizing agents like polymers or organic surfactants, inorganic complexes, and bioinorganic molecules. However, sometimes the consequence of the employment of such stabilizers may subside the catalytic activity due to the adsorption over the surface of nanoparticles [26] and furthermore possibility of leaching, so it is when concerned with PdNps as a catalyst, herewith a perfect stabilizer is needed to revive this problem and generate nanoparticles of acceptable size to prove as a highly active catalyst [27]. To overcome all above issues researcher have developed a wide range of stabilizing agents but recently supramolecular class for e.g., calix[4]pyrroles [28, 29], calixarenes [30], porphyrins [31], and cyclodextrins [32], have been explored for their stabilizing properties towards PdNps.

Calixarenes [33] are well-known cone-shaped molecules with an inherent hollow cavity to encapsulate nano-sized metals in its reorganized structure [34]. We developed nano-silver [35-37], nano-gold [38, 39], and nano-palladium [25, 40, 41] compounds having compatible in both reducing and stabilizing nature. Many other Calix platforms have been explored to get desirable size PdNps [42]. Calix[4]pyrroles are from hetero-calixarene class. To our knowledge, there are several attempts found in the literature for calix[4]pyrroles based tiny-stable nanoparticles. Some groups in India have developed silver, and gold nanoparticles using calix[4]pyrroles hydrazide but differ in parent moiety. Earlier groups also concluded calix[4]pyrroles tetra hydrazide(CPTH) as reducing as well as a stabilizing agent for PdNps [43]. Here, we synthesized PdNps with the help of $Pd(OAc)_2$ and calix[4]pyrroles octahydrazide(CPOH) in aqueous media without using any guest reducing agent.

Herein this work, we have octahydrazide derivative of calix[4]pyrroles, CPOH to synthesize PdNps, and have shown them as potent and recyclable nanocatalyst for various cross-coupling reactions. The present study also addresses the stability as well as pH studies of fine PdNps. CPOH is an electron-rich ligand, which is capable of reducing as well as encapsulate the metal ions because of the availability of four pyrrole groups, which can form non-covalent hydrogen bonding and another one is the presence of electrons on amino groups of hydrazide functional group of ligand [40]. Calix hydrazide possesses electron-withdrawing amino groups over the periphery of PdNps, so it undergoes stronger web-like capping on palladium compare to simple hydrazine or other reducing agents [40]. Similarly, CPOH-PdNps are aqueous and air-stable; besides, prove to be a usual, facile, and low-cost alternative for the synthesis of stable PdNps. Moreover, encapsulating the periphery of PdNPs using CPOH enhances its activity and selectivity. Which indicates the association of physical properties of

ultrafine PdNps and the potent capping of CPOH can explore new edges of numerous promising applications towards the efficient catalytic activity.

2. Materials and Methods

2.1. Chemicals and Reagents.

All chemicals (AR) were purchased from local commercial suppliers, and they are further used without any other purification method. Palladium acetate, 4-formyl boronic acid, phenylboronic acid, bromobenzene, and all other aryl halides were bought from Sigma-Aldrich. Fluorescence active TLC plates (F-2009) were taken from Merck- Germany. Water for the experiment was prepared by using the Millipore water system with a resistance of 18 MΩ cm@25°C.

2.2. Instrumentation.

Melting points were measured by VEEGO (Model: VMP-DS- Mumbai, India) (uncorrected) in a single capillary tube. REMI (Model: C-24BL) laboratory centrifuge was used for centrifugation of the colloidal solutions. UV- absorption spectra were recorded by JASCO (Model: V-570, Tokyo, Japan) UV- Visible spectrophotometer in the range of 200-800 nm. ESI-MS was taken by a mass spectrometer (Model: micro mass Quarter2-Utah, USA) at 3000V capillary voltage & source temperature 120°C. Proton NMR and 13C NMR spectra were obtained on a Bruker (Model: AV-(III) - Frequency-400 MHz) spectrometer using a BBFO probe. TEM&SAED pattern was recorded on a JEOL (Model: JEM 2100) microscope using 200 kV of an accelerated voltage. The particle size and zeta potential were obtained by the Malvern Zeta sizer (Model: ZEN3600) as such without dilution, and at the end of the centrifugation presence of Pd were checked by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrophotometer) (Model: JY 2000-2) in the supernatant liquid collector.

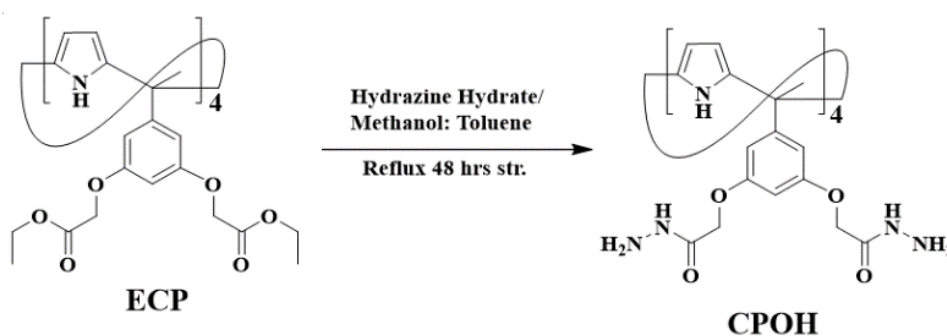


Figure 1. Synthesis of CPOH.

2.3. Synthesis.

2.3.1. Synthesis of CPOH.

Octaacetates-meso-tetra(methyl) meso-tetra(3,5-diphenoxy acetate) calix[4] pyrroles (ECP) (2 g (w/v)), 1.3 mmol) was dissolved in 120 mL of fresh distilled methanol: toluene (50:50) and refluxed for 2 hrs then hydrazine hydrate (1.3 g (w/v), 20.8 mmol) were added and reaction mass further stirred reflux for 72 hrs. The solvent was removed in vacuum, and the white solid was transferred in dichloromethane (50 mL). The suspension was filtered and washed with DCM (3X 20 mL). The crude compound was recrystallized in hot water to give pure white solid compound CPOH (46% yield) [36, 44, 45] Fig.01.

2.3.2. Synthesis of CPOH capped palladium nanoparticles.

The present experiment was carried out by rapidly adding 10 mL (1.0 mmol) aqueous CPOH solution into the 10 mL (1.0 mmol) aqueous palladium acetate solution at 70 °C for 60 minutes with vigorous stirring and heating. The confirmation of the formation of palladium nanoparticles is done by the visual color change of the solution from brownish to colloidal black and also after surface plasmon resonance band. The final yield of the recyclable nanocatalyst, CPOH-PdNps, obtained after centrifugation is 5.46 mg and water-soluble CPOH amount in CPOH-PdNps is 3.90 mg with the 0.96 mg loading of Pd. So, attempted strategy found to be the most facile and one-pot synthesis of CPOH-PdNps by using only two reagent and eco-friendly reaction conditions [28, 43, 46].

2.3.3. General procedure for coupling reactions.

2.3.3.1. Suzuki- Miyaura reaction.

Suzuki coupling reaction was performed by charging CPOH-PdNps (0.01mmol) with aryl halide (1 equiv.), aryl boronic acid (1.2 equiv.) and sodium carbonate (1.7 equiv.) in a RBF furnished with a stirrer with oil-bath in 10 mL mixture of 1,4-dioxane-water (1:1) as a solvent at 40°C for 10 min after that product was extracted from reaction mass with the help of ethyl acetate (3 ×10 mL) followed by water wash (3 ×10 mL), dried out over MgSO₄ and concentrated on getting solid product [46, 47].

2.3.3.2. Heck reaction.

10 ml of NMP + water (1:1) as a solvent, aryl halide (1 mmol), olefinic compound (2 mmol), Na₂CO₃ (2 mmol), and CPOH-PdNps (0.01mmol) were added mixture in RBF. Then the reaction mixture was refluxed and stirred at 80°C. After cooling the reaction mass, it was treated with ethyl acetate (3 X 15 mL) + water (50 mL). Then the organic phase was dried out over Na₂SO₄, filtered, and concentrated on getting crude products, and then it was purified by column chromatography using hexane or ethyl acetate (2–4%)/hexane solvent system [48, 49].

2.3.3.3. Negishi Couplings reaction.

A 50 mL RBF was charged with CPOH-PdNps catalyst (0.30mmol) and dioxane (7 mL). The aryl halide (0.5 mmol, 1 equiv) was added. Alkyl zinc halide (0.5 M in THF, 0.75 mmol, 1.5 equiv) was then added dropwise at 0°C. The resulting mixture was stirred at room temperature for 4-5hrs, and the reaction was monitored by TLC. The reaction mass was quenched with saturated NH₄Cl solution, and extracted with EA (3 × 15 mL). The organic layer was dried out over Na₂SO₄, and concentrated on getting crude followed by column chromatography in Ethyl acetate (2-4%)–hexane system [50, 51].

2.3.3.4. Stille reaction.

In 50 mL RBF, 100 mg (0.5 mmol) of 4-iodobenzoic acid and 685 mg (2.5mmol) of phenyltintrichloride (PhSnCl₃) were dissolved in 6mL of 3M aqueous KOH and 2mL of H₂O. CPOH-PdNps (0.1mol) catalyst was added to the reaction mixtures. The reaction mass was stirred for 24hrs at room temperature. After successful completion of the reaction confirmed by TLC, the reaction mass was quenched with 50.0 mL of 5% aqueous HCl. The product of the reaction was extracted from the aqueous mixture using diethyl ether (3 X 30.0 mL). The

organic layer was treated with a saturated NaCl solution (2 X 20.0 mL), dried with anhydrous Na₂SO₄, and filtered. The organic layer was dried out over Na₂SO₄, and concentrated on getting crude followed by column chromatography in Ethyl acetate (2-4%) – hexane system [52, 53].

2.3.3.5. *Sonogashira reaction*

In 50 mL RBF, iodobenzene(5.4 mmol), phenylacetylene (0.5 gm., 4.9 mmol), CPOH-PdNps catalyst (0.01mmol), Na₂CO₃ (6mmol),(NMP):Water, were loaded and stirred for 20hrs at 60°C. The reaction was monitored by TLC. The reaction mixture was treated with water and extracted with EA (3 × 15 mL). The combined organic phase was washed with saturated NaCl aqueous solution two times and dried out over anhydrous MgSO₄ to get crude product followed by column chromatography in Ethyl acetate (2-4%) - hexane solvent system to obtain pure compound [54-56].

2.3.3.6. *Fukuyama reaction.*

Here in this reaction, solvent acetone 1 mL thioester (1 mmol) and 1.2 eq. aryl zinc halide was added to 0.02mmol of CPOH-PdNps at room temperature, After stirring for 1 h at room temperature, the catalyst was filtered off, and the reaction mass was concentrated and separation on column chromatography (2-4% EA/hexane) gave the desired aldehyde or ketone in 94% yield [57].

2.3.3.7. *Hiyama reaction.*

For the successful completion of the Hiyama coupling reaction mixture of aryl bromide and aryl siloxane in water was stirred at 100°C in oil bath in the presence of a small amount of CPOH-PdNps, and NaOH (3 M) for less than 20 minutes [58-61].

2.3.3.8. *Kumada reaction.*

CPOH-PdNps catalyst (0.01 mmol), THF: water (5 mL), and aryl chloride (1.0 mmol), to the solution formed was added a solution of phenyl magnesium bromide in THF (1.2 mmol, 1 M) in it at room temperature and allowed to stir for 24 hrs. The reaction was ceased by the addition of excess water. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried out over MgSO₄. The filtrate was concentrated by rotary evaporator, and the product was further purified by column chromatography (2-4% EA/hexane) to obtain the desired product [62-64].

3. Results and Discussion

3.1. *Characterization of CPOH-PdNPs.*

Thus the one-pot PdNps formation was investigated by UV–Vis spectrophotometry, TEM, and Energy-dispersive X-ray spectroscopy (EDX). The primarily color change of the solution from brownish yellow to black while adding palladium acetate into CPOH solution suggests the successful formation of CPOH-PdNps(Fig.2). UV–Visible spectrum clearly shows the formed CPTH-PdNps. In palladium acetate solution UV–Vis spectra show a broad absorption band near 400 nm, which indicates the state of palladium is +2 [65]. The disappearance of the band at 400 nm was found due to the reduction of Pd⁺² to Pd⁰ oxidation state, confirming the formation of PdNps (Fig. 3b). The obtained black colloidal nanoparticles

were imaged to characterize their size using TEM [66]. Fig. 3a & 3b shows TEM images that visualize the presence of roughly spherical shaped CPTH-PdNps of an average size range of 5–9 nm. High-resolution TEM (HRTEM) image, as shown in Fig. 3c, reveals the atomic lattice fringe, demonstrating the crystalline nature of the nanoparticles. Energy-dispersive X-ray spectroscopy (EDX) analysis spectrum giving the elemental composition of CPTH-PdNps was collected from TEM data. Strong signals from Pd atoms while weaker signals from Si and Cu atoms were observed (Fig. 2d). The invariable presence of copper signals in the EDX spectra is due to copper in the TEM grid.

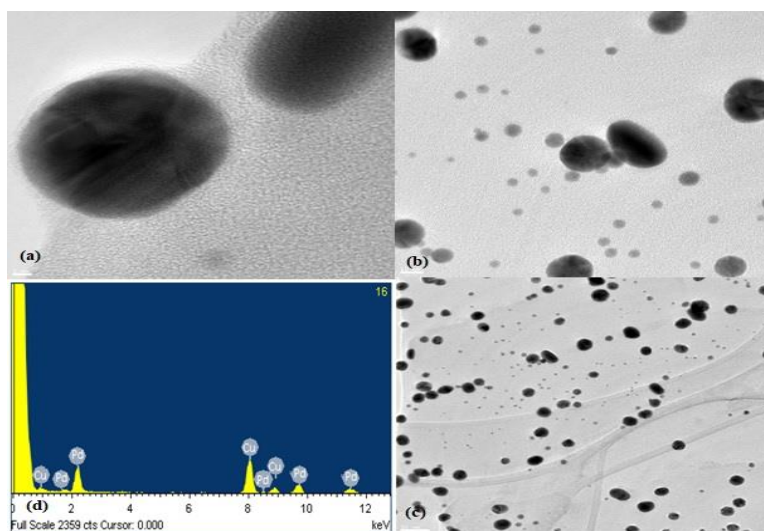


Figure 2. TEM and EDX images of CPOH-PdNps.

The particle size analysis shows the successful formation of CPTH-PdNps of 16 ± 2 nm. The extended size of the palladium nanoparticles core is observed due to the organic layer of stabilizing ligand (CPOH) on the surface of PdNps depending on the density of surface coverage [67].

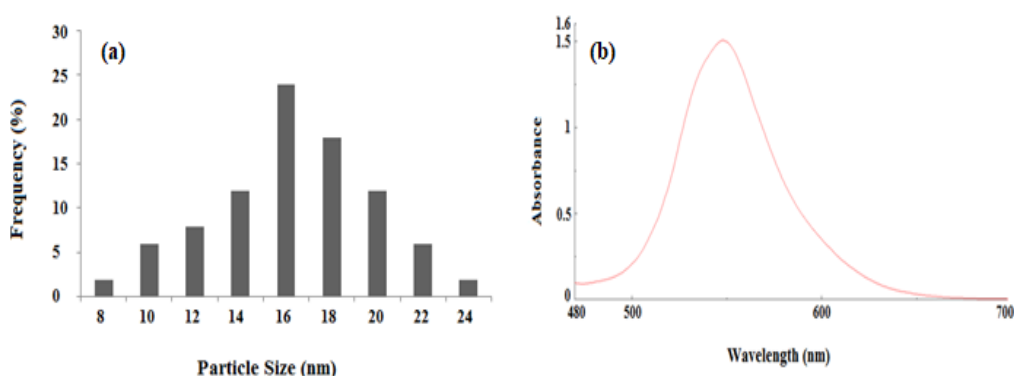


Figure 3. PSA and SPR spectra of CPOH-PdNps.

According to Debye–Scherrer equation [68], the average size of CPTH-PdNps calculated from the Pd(111) peak was 7.9 nm, which falls in line with the TEM observations. FT-IR study was carried out to investigate the existence of stabilizing ligand (CPOH) on the surface of the PdNps. The bands for (a) CPOH and (b) CPOH-PdNps at 3325 cm^{-1} and 1680 cm^{-1} which clearly indicate the free $-\text{NH}$ and $-\text{CONH}$ groups, respectively. It means there was no direct bonding between CPOH and PdNps. However, the broadening of the band around 1680 cm^{-1} [69] may consist of some other chemical interactions.

3.1.1. PdNPs for C-C coupling reaction.

Palladium-catalyzed Homogeneous reactions widely explored C-C coupling reactions like *Suzuki*, *Buchwald-Hartwig*, *Stille*, *Heck*, and *Sonogashira* reaction. Pd properties depend upon ligand organization. The major drawback of homogeneous is the recyclability of catalyst result in the erosion of expensive metal also generates many impurities. To overcome the above complexity created by homogeneous catalysis, researchers are diverted to the heterogeneous alternate. Here, in the present case, OHCP cage is found ideal recognition partner for Pd, which can be easily separated after the successful completion of catalysis. But the fact is that the contribution of OHCP-PdNPs in catalysis controversial that the catalysis is homogeneous or heterogeneous [25, 70].

3.1.2. General synthesis method for catalytic activity.

3.1.2.1. Suzuki coupling reaction.

Suzuki-Miyaura coupling reaction was performed by charging OHCP-PdNPs (0.01 mmol) with iodobenzene (1 equiv.), 4- formyl boronic acid (1.2 equiv.) and sodium carbonate (1.7 equiv.) in a RBF furnished with a stirrer with oil-bath in 1,4-dioxane-water (1:1)(15 mL) mixture at 45°C for 10 min. After that product was extracted from reaction mass with the help of ethyl acetate (3 ×10 mL) followed by 2-3 water wash and dried by MgSO₄ and evaporate to dryness to get solid compound [25, 47].Fig.04.

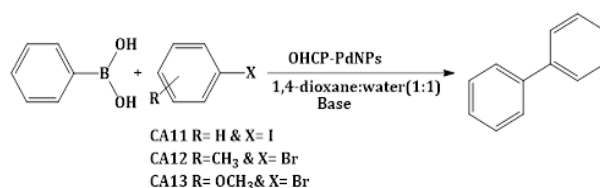


Figure 4. Suzuki coupling reaction.

3.1.2.2. Heck reaction.

In 10 ml of methanol + water (1:1) solvent, styrene (2 mmol), iodobenzene (2.5 mmol), Na₂CO₃ (2.5 mmol) as a base, and OHCP-PdNPs (0.01 mmol) nanocatalyst was taken in RBF. Then the reaction mass was refluxed with continuous stirring at 50°C. Then after the mixture was cooled down and treated with 3 wash of ethyl acetate + water and then the organic medium dried, filtered, and evaporate to dryness to get the crude product. The crude was passed through the column using ethyl acetate/hexane in a slightly polar medium [40, 48].Fig.05.

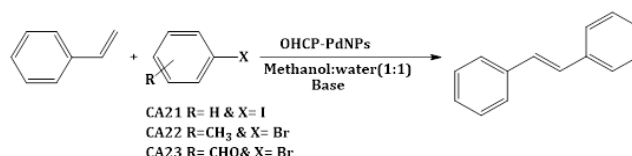


Figure 5. Heck coupling reaction.

3.1.2.3. Stille coupling.

In 50 mL RBF, 685 mg (1.7 mmol) of phenyltintrichloride (PhSnCl₃) and 100 mg (1.8 mmol) of iodobenzene was taken by adding aqueous (KOH 6 mL, 3M) and 2 mL water. OHCP-PdNPs (0.1 mol) catalyst was introduced to the reaction mixtures followed 24 hrs RT

stirring. The entire process was observed by TLC. In the end, the mixture was poured into 50 mL aqueous HCl (5 percent). The product extraction was carried out by diethyl ether (3 wash) followed by saturated sodium chloride treatment and dried over Na₂SO₄. Crude passed through a moderate polar EA-hexane gravity column [53, 71].Fig.06.

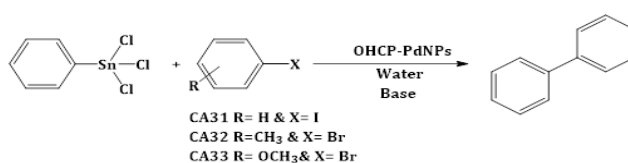


Figure 6. Stille coupling reaction.

3.1.3. Recovery and recyclability of nanocatalyst.

After the successful completion of every attempt of C-C reaction, the reaction mass was centrifuged at 2500 rpm for 20 min to obtain used OHCP-PdNPs followed by 1,4-dioxane+water wash to discard organic reagents and it kept for drying overnight at 50 °C before the second attempt. OHCP-PdNPs used for further five cycles without performing any activating process, and it was showing a trivial decrement in efficiency at the end of the last cycle. So, OHCP-PdNPs found a facile and repeatable productive catalyst [72,73] for Stille coupling, Suzuki-Miyaura, and Heck reaction over five cycles with remarkable yielding of 90% in 15 min of reaction times at 40 °C.

3.1.4. Stability and pH study of nanocatalyst.

Here in the present experiment, the stability of derived fine PdNps has been done by observing changes in their SPR band data at various pH. Derived fine OHCP-PdNPs indicates tiny change at different pH (excluding pH=7) for initial 2-3 days then after coagulation occurred, but it is avoided by simple sonication for 10-15 min to obtain their original form without any notable deviation in their size and SPR band (Figure 3.3-a) but slightly decrement observed in fluorescent intensity. At pH 7 OHCP-PdNPs remain unchanged in SPR band up to 90 days. Thus, OHCP-PdNPs found to be most stable at pH 7 so, all further experiments were carried out at pH 7.

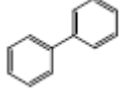
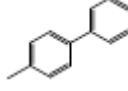
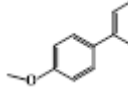
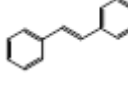
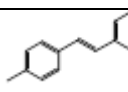
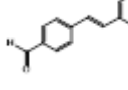
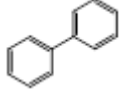
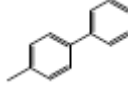
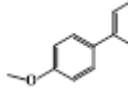
3.2. Recyclability of nanocatalyst.

After the successful completion of Suzuki reaction via the mentioned condition(table1) the reaction mass was centrifuged at 3000 rpm for 15-20 min to obtain used CPOH-PdNps followed by 1,4 dioxane and water wash to remove organic reagents and it kept for drying overnight at 50 °C before the second attempt. CPOH-PdNps used for further five cycles without performing any activating process, and it was showing trivial decrement in efficiency at the end of the last cycle. So, CPOH-PdNps found a facile and reusable productive catalyst for Suzuki-Miyaura coupling reaction over five cycles with remarkable yielding of 93% in 15 min of reaction times at 40 °C.

3.3. Stability and pH studies.

Here in the present experiment, the stability of derived fine PdNps has been done by observing changes in their SPR band and fluorescence data at various pH.

Table 1. Nano-catalyst based coupling reactions.

| Reaction | Product | Code | Yield % | Time min | Mass data | 1H-NMR chemical shifts | | | |
|-------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------|----------|---------------------------------------------|-------------------------------|------------------|-----------|--|
| | | | | | | No. of H | Type of Peak | δ ppm | |
| Suzuki-Miyaura reaction |  | CA11 | 91 | 14 | 172.18 [M+H ₂ O] ⁺ | Aromatic protons | | | |
| | | | | | | 4 | dd | 7.29 | |
| | | | | | | 4 | t | 7.34 | |
| | | | | | | 2 | tt | 7.18 | |
| | |  | CA12 | 92 | 12 | 191.18 [M+Na] ⁺ | Aromatic protons | | |
| | | | | | | 2 | d | 7.78-7.79 | |
| | | | | | 2 | d | 7.61-7.69 | | |
| | | | | | 2 | t | 7.56 | | |
| | | | | | 1 | t | 7.5 | | |
| | | | | | 2 | d | 7.3-7.4 | | |
| | | | | | | Methyl protons | | | |
| | | | | | 3 | s | 2.5 | | |
| Suzuki-Miyaura reaction |  | CA13 | 94 | 15 | 186.5 [M+2] ⁺ | Aromatic protons | | | |
| | | | | | | 4 | d | 7.5 | |
| | | | | | | 2 | d | 7.37 | |
| | | | | | | 1 | t | 7.29 | |
| | | | | | | 2 | d | 6.9-6.97 | |
| | | | | | | | Methoxy protons | | |
| | | | | | 3 | s | 3.74 | | |
| Heck reaction |  | CA21 | 90 | 9 | 203.2 [M+Na] ⁺ | Aromatic protons | | | |
| | | | | | | 4 | t | 7.5 | |
| | | | | | | 4 | t | 7.48 | |
| | | | | | | 2 | d | 7.35 | |
| | | | | | | | Ethylene protons | | |
| | | | | | | 2 | s | 7.20 | |
| | |  | CA22 | 92 | 17 | 219.2 [M+Na] ⁺ | Aromatic protons | | |
| | | | | | | 4 | d | 7.31-7.40 | |
| | | | | | | 2 | t | 7.3 | |
| | | | | | 3 | d | 7.1-7.2 | | |
| | | | | | | Ethylene protons | | | |
| | | | | | 2 | s | 7.0 | | |
| | | | | | | Methyl protons | | | |
| | | | | | 3 | s | 2.3 | | |
| Heck reaction |  | CA23 | 93 | 15 | 196.5 [M+2] ⁺ | Aromatic protons | | | |
| | | | | | | 4 | d | 7.32-7.41 | |
| | | | | | | 2 | t | 7.2 | |
| | | | | | | 3 | d | 7.11-7.18 | |
| | | | | | | | Ethylene protons | | |
| | | | | | | 2 | s | 7.05 | |
| | | | | | | | aldehyde protons | | |
| | | | | | | 3 | s | 2.3 | |
| | Stille reaction |  | CA31 | 95 | 35 | 177.8 [M+Na] ⁺ | Aromatic protons | | |
| | | | | | | 4 | d | 7.48 | |
| | | | | | | 4 | t | 7.32 | |
| | | | | | | 2 | t | 7.25 | |
| | |  | CA32 | 92 | 25 | 170.4 [M+2] ⁺ | Aromatic protons | | |
| | | | | | | 2 | d | 7.70 | |
| | | | | | | 2 | d | 7.58 | |
| | | | | | | 2 | t | 7.54 | |
| | | | | | | 1 | t | 7.44 | |
| | | | | | 2 | d | 7.34 | | |
| | | | | | | Methyl protons | | | |
| | | | | | 3 | s | 2.55 | | |
| Stille reaction |  | CA33 | 90 | 26 | 207.5 [M+Na] ⁺ | Aromatic protons | | | |
| | | | | | | 4 | t | 7.45 | |
| | | | | | | 2 | t | 7.31 | |
| | | | | | | 1 | t | 7.2 | |
| | | | | | | 2 | d | 6.9 | |
| | | | | | | | Methoxy protons | | |
| | | | | | 3 | s | 3.74 | | |

Derived fine CPOH-PdNps indicates tiny change at different pH (excluding pH=7) for initial 2-3 days then after coagulation occurred, but it is avoided by simple sonication for 10-15 min to obtain their original form without any notable compromise in their SPR band and size (Fig. 3a) but slightly decrement observed in fluorescent intensity. At pH 7 CPOH-PdNps shows no changes in SPR band as well as fluorescence intensity up to 150 days. Thus, CPOH-PdNps found to be most stable at pH 7 so, all further experiments were carried out at pH 7.

4. Conclusions

A simple and facile one-pot chemical reduction method using a novel, octahydrazide derivative of calix[4]pyrrole (CPOH) for the preparation of tiny palladium nanoparticles is described in this work. The effective reduction of Pd(II) to nano-palladium Pd(0) could be possible by reducing the nature of hydrazide groups available on the Calix system, which also stabilizes the nanoparticles. This novel nanocatalyst showed high catalytic performance for *Suzuki-Miyaura*, *Heck* coupling reactions, *Negishi* reaction, *Stille* coupling, *Sonogashira* cross-coupling reaction, *Fukuyama* coupling reaction, *Hiyama* coupling reaction, and *Kumada* coupling reaction and could be reused maximum five times without considerable loss in its catalytic activity. Thus, CPOH-PdNps can become a key tool in a synthetic approach to synthesize numbers of organic compounds in the future in comparison with other Pd catalysts. Also, the antibacterial nature of the PdNps can explore its capability in biological fields. We are further looking forward to checking this nanocatalyst in a different condition to achieve the most concordant synthetic route for each reaction and its environmental applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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