Synthesis of monodispersed palladium nanoparticle at room temperature and its catalytic activity for Suzuki-Miyaura cross-coupling reaction

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A new method has been developed for the synthesis of spherical palladium nanoparticles with narrow size distribution. Pd nanoparticles of average particle size of around 7 nm have been prepared from $Pd(OAc)_2$ at room temperature in THF using 2-(trimethyl silyl)-ethanol (TMSE) as a reducing as well as capping agent. The catalytic activity of the Pd-nanoparticles has been examined for ligand free Suzuki-Miyaura cross-coupling reaction.

In recent years metal nanopartices are gaining great scientific interest due to their promising properties and applications in various fields[1-6]. When, materials are fabricated in nanoscale dimension, they show spectacular size dependent properties, which are different from the bulk materials. Because of high surface area to volume ratio, nanoparticles are finding wide applications as catalyst for organic transformations[7-9]. However, effective control of particle size continues to be the most difficult challenge for researchers because nanoparticles often tend to agglomerate due to nuclear growth. High activity of palladium makes it one of the most resourceful catalysts in organic synthesis[10,11]. Efforts have therefore been devoted to device convenient and effective method for the synthesis of palladium nanoparticles (Pd NPs) with uniform shape and size. Usually, palladium nanostructures were synthesized by reducing Pd(II) salts in ethylene glycol at elevated temperature in presence of poly(vinyl pyrrolidone) as stabilizing agent[12-16]. Depending on the reaction condition and palladium source, various shapes such as dots, nanocubes, nanocages, nanorods, *etc*. of palladium nanostructures were obtained. Treatment of palladium acetate in polyethylene glycol at 80 °C also results in the formation of Pd NPs[17]. Zhu and co-workers reported a method for the synthesis of spherical shaped Pd-nanoparticles using pulse sonoelectrochemical technique in the presence of cetyl trimethylammonium bromide at RT[18]. RNA has also been used for palladium nanoparticle synthesis from Pd (0) compounds in THF-water mixture[19]. Few other synthetic methods for Pd NPs were also reported[20-32]. Although, many methods are available for fabrication of palladium nano structures[33-37], simple synthetic process for monodispersed Pd NPs is still desirable. In particular, development of methods for the synthesis of palladium nano catalyst with spherical shape is of primary concern because nano-spheres have large surface area to volume ratio. In this paper, we are reporting a novel method for the synthesis of monodispersed Pd-nanoparticles at RT in presence of 2-(trimethyl silyl)-ethanol (TMSE) as a reducing as well as capping agent. To best of our knowledge, the use of TMSE for nanoparticle synthesis is not known in the literature. The catalytic activity of the Pd NPs was examined for ligand free Suzuki-Miyaura cross-coupling reaction.

Results and Discussion

Synthesis of Pd-nanoparticles

Synthesis of Pd-nanoparticles was achieved by adding TMSE to a solution of $Pd(OAc)_2$ in THF and stirring the resulting mixture at RT under inert atmosphere. Formation of the Pd NPs was monitored with the help of a UV-visible spectrophotometer. In general formation of nanoparticle was observed after 4- 5 h at RT which was indicated by the formation of a black dispersion. Disappearance of the peak around 400 nm in the UV-visible spectra (Figure 1) confirmed the complete conversion of Pd(II) species to Pd(0) nanoparticles. The FT-IR spectrum
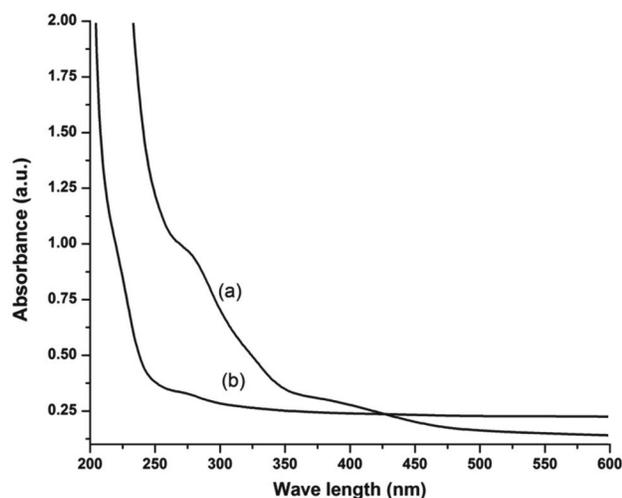
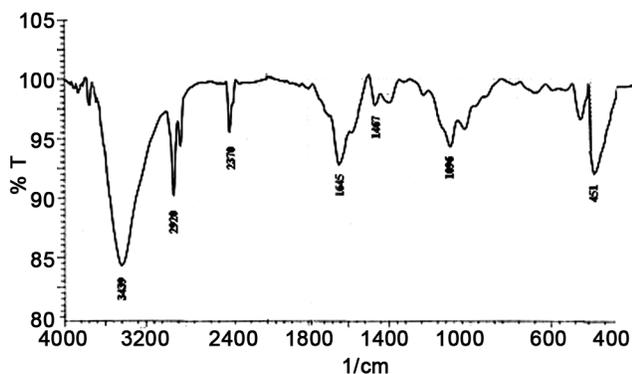Figure 1 — UV-visible spectra of (a) Palladium acetate and (b) Pd nano particles in ethanol

Figure 2 — FT-IR spectrum of Pd-NPs

Figure 3 — Powdered XRD pattern of the TMSE stabilized Pd NPs

Figure 4 — FESEM image of Pd NPs

(Figure 2) reveals the presence of extensive silanolic hydroxyl group around 3439 cm^{-1} which is responsible for the stability of the Pd nanoparticles.

A powder X-ray diffraction pattern of the as-synthesized Pd nanoparticles is shown in Figure 3. The diffraction pattern appeared to be broad which indicates the formation of Pd (0) nanoparticles of very narrow size distribution. Presence of diffraction lines at 2θ = 40.26, 46 and 68 in the powder XRD pattern indicates the formation of Pd (0) particles. The average diameter of the palladium nano particles calculated by using Scherrer's equation[38,39] was found to be around 7 nm. Morphology of the as synthesized Pd nanoparticles was studied by FESEM analysis (Figure 4). From the FESEM image it is clear that the Pd NPs are spherical in shape and the nanoparticles are monodispersed in terms of their size.

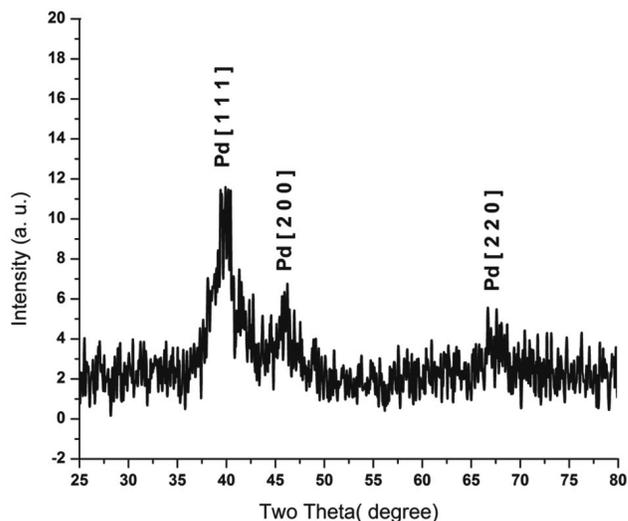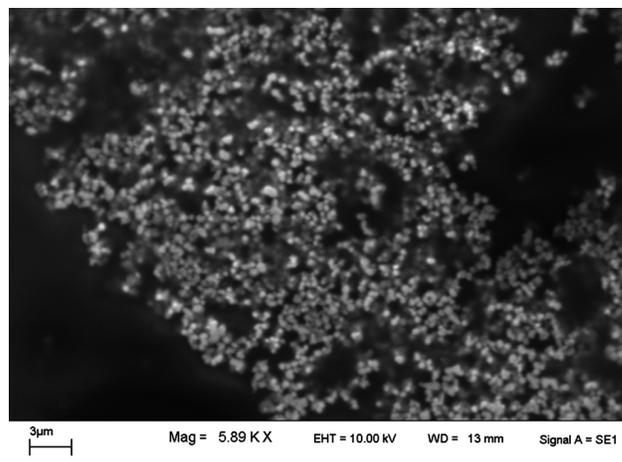Formation of palladium (0) particles in nanometer dimension was further confirmed by carrying our TEM analysis of the sample (Figure 5). From the TEM analysis it is clear that there is no agglomeration of the nanoparticles which indicates its mono-dispersed nature. From the HRTEM analysis the average size of the nanoparticles was found to be around 7 nm which was in consistent with that calculated from XRD using Scherrer's equation. The SAED pattern (Figure 5) of the Pd NPs further confirms its crystalline nature. From the particle size histogram (Figure 6) it is clear that most of the particle sizes between 5-10 nm. Formation of Pd NPs may occur through the oxidation of the hydroxyl group in 2-trimethyl silyl ethanol. In our case TMSE may acts as a reducing agents and stabilizers during the synthesis of Pd NPs, however its exact role is yet under investigation.

Catalytic activity of the Pd nano particles

After the success in synthesizing monodispersed Pd NPs, we intended to evaluate the catalytic efficiency. Catalytic property of the Pd NPs was tested for Suzuki-Miyaura cross-coupling reaction (Scheme I)[40,41]. Due to wide application potential in organic synthesis[42-47], several new catalysts have been developed in recent years[48-52] for Suzuki-Miyaura
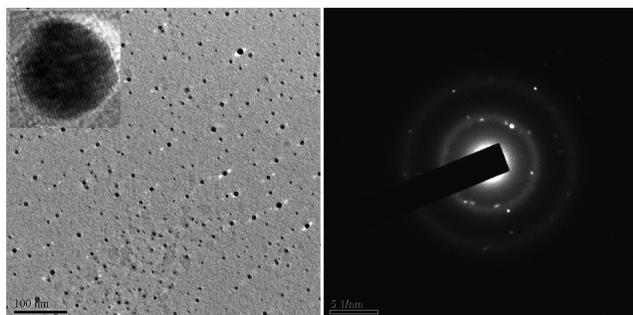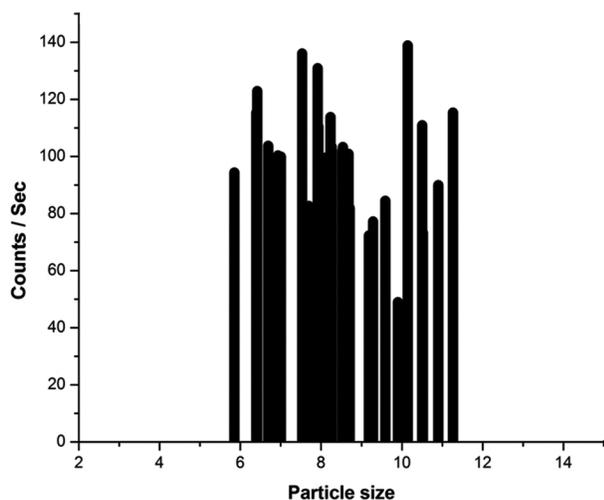

Figure 5 — TEM image (Inset-HRTEM of a single nanoparticle) and SAED pattern of Pd NPs

Figure 6 — Particle size histogram of Pd NPs

reaction. The use of Pd NPs for Suzuki coupling reaction has been outlined in various reviews[53-57].

To evaluate the optimum reaction condition a series of reactions were performed with different bases, solvents at different temperatures to get the best possible result (Table I). Experiments were performed in ethanol (5 mL) taking iodobenzene (1 mmol) and phenyl boronic acid (1.2 mmol), base (2 mmol), in presence of catalytic amount of Pd-NPs for the Suzuki coupling reaction. Initial experiments using Na_2CO_3 as base in presence of 2 mol% of Pd-NPs produced the coupled product in 59% yield after 12 h of reaction at 60°C. However, the increase of catalyst loading to 4% could produce better result under the same reaction condition. Thereafter, K_2CO_3 was used instead of Na_2CO_3 which could yield a promising result with 86% yield in 5h. Further change in the reaction condition by varying solvents such as dimethoxy ethane, dioxane and increasing the reaction temperature up to 100°C could not produce better result. Similarly, change of base such as K_3PO_4, NaOH, Cs_2CO_3 could not change the result to a better extent. The reaction also proceeds at RT. However, yield was found to be low even after 24h or reaction. After performing the Suzuki reaction using different combinations (Table I) we found that a combination of ethanol as solvent and K_2CO_3 as base in presence of 4 mol% Pd-NPs at 60 °C could produce the best result.
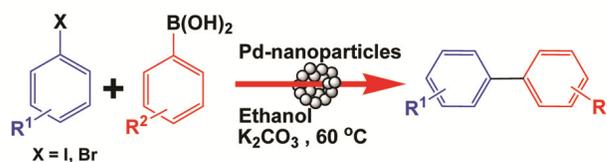
Scheme I — Suzuki-Miyaura cross-coupling reaction using Pd nano particles

Table I — Suzuki reaction of iodobenzene and phenylboronic acid using Pd-NPs [a]

Entry	Catalyst amt.	Solvent	Base	Temp (°C)	Time (h)	Yield (%) [b]
1	2 mol%	Ethanol	Na_2CO_3	60	12	59
2	4 mol%	Ethanol	Na_2CO_3	60	8	75
3	4 mol%	Ethanol	K_2CO_3	60	5	86
4	4 mol%	Dimethoxy ethane	K_2CO_3	80	9	80
6	4 mol%	Dioxane	K_2CO_3	100	8	47
7	4 mol%	Ethanol	K_3PO_4	60	10	69
8	4 mol%	Ethanol	NaOH	60	14	60
9	4 mol%	Ethanol	Cs_2CO_3	60	6	85
10	4 mol%	Ethanol	K_2CO_3	30	24	31

[a] Reaction conditions: Iodobenzene (1 mmol), phenylboronic acid (1.2 mmol). [b] Isolated yield by column chromatography

Optimization of reaction conditions for Pd NPs catalyzed Suzuki-cross coupling reaction

After establishing the optimum reaction condition, the scope of the reaction was examined with different combinations of iodobenzene and boronic acids under the same reaction condition. Results are summarized in Table II. It can be seen from Table II that various aryl iodides produced excellent yields under ligand-free condition. Among all the substrates, 4-nitro iodobenzene produced the highest yield. Thereafter, the reaction was extended to various bromobenzenes. However, yields are slightly lower than those produced by iodobenzenes.
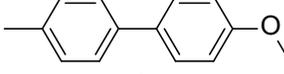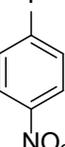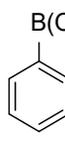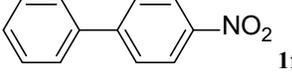
Experimental Section

Reagents and solvents are procured from commercial sources. Synthesized Pd nanoparticles were characterized by UV-Vis spectroscopy (Shimadzu UV-1800 Spectrometer), FT-IR (Perkin Elmer Spectrum RX I FT-IR Spectrometer), XRD (Philips-Xpert Pro X-ray diffractometer with Cu-Kα radiation having λ = 1.5418 A), Field emission scanning electron microscopy (Carl Zeiss, IGMA) and Transmission electron microscopy, TEM (JEOL JEM 2100- 200 Kv). All the desired cross-coupling products were characterized by NMR (Bruker Avance 300 MHz NMR spectrophotometer) and FT-IR spectroscopy (Perkin Elmer Spectrum RX I FT-IR Spectrometer).
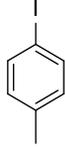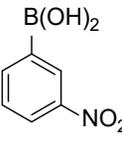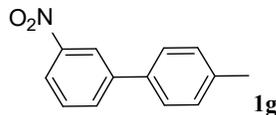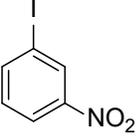
Synthesis of palladium nanoparticle

Palladium nanoparticles were synthesized by adding a solution of 2-(trimethyl silyl)-ethanol (1.1 g, 10 mmol) in THF (5 mL) drop wise to a stirred

Table II — Suzuki reaction between aryl iodide and phenyl boronic acid catalyzed by Pd nano particles [a]

Entry	Aryl halide	Boronic acid	Time (h)	Products	Yield(%) [b]
1		B(OH)$_2$	5	1a	86
2		B(OH)$_2$	7	1b	75
3		B(OH)$_2$	5	1c	80
4		B(OH)$_2$	6	1d	77
5		B(OH)$_2$	5	1e	80
6	NO$_2$	B(OH)$_2$	5	NO$_2$ 1f	91
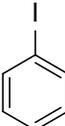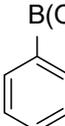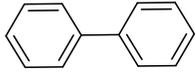
(*Contd.*)

Table II — Suzuki reaction between aryl iodide and phenyl boronic acid catalyzed by Pd nano particles [a] (*Contd.*)

Entry	Aryl halide	Boronic acid	Time (h)	Products	Yield(%) [b]
7			8	1g	85
8			8	1g	86
9			6	1h	84
10			6	1a	78
11			8	1b	70
12			6	1e	79
13			8	1j	65
14			8	1k	60
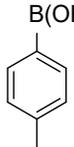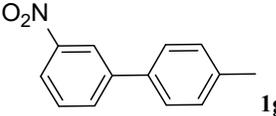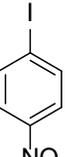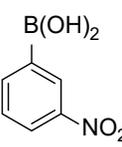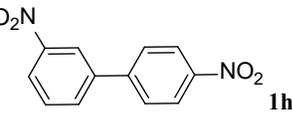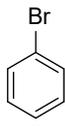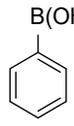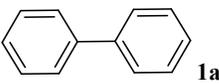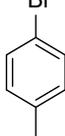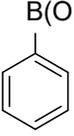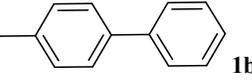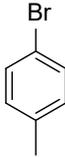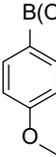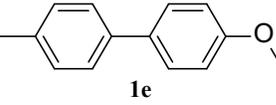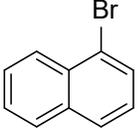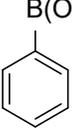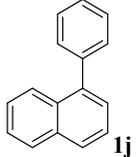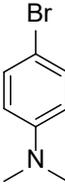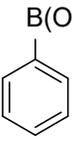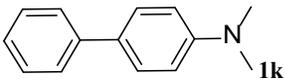
[a] Reaction condition: Iodobenzene or bromobenzene (1 mmol), phenylboronic acid (1.2 mmol) and
K_2CO_3 (2 mmol), solvent (10 mL), 60 °C. [b] Isolated yield.

solution of palladium acetate (225 mg, 1 mmol) in THF (5 mL) over a period of 15 minutes at 30 °C under nitrogen atmosphere. The reaction was further stirred at the same temperature for a period of 12 h. The solvent was removed under vacuum and acetone (10 mL) was added. Centrifugation at 14,000 rpm separated the black Pd nanoparticle which was further

dried under vacuum at RT and preserved in a desiccator for further use.

General method for Suzuki reaction catalyzed by Palladium nanoparticles

In a typical reaction, iodobenzene (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (2 mmol)

were mixed in dry ethanol (10 mL) in an oven-dried round bottom flask at 25 °C. The reaction mixture was charged with Pd NPs (4 mol% by weight) under constant stirring and the reaction mixture was heated at 60 °C for appropriate time. The reaction was monitored by thin layered chromatography (TLC). After completion of reaction, the reaction mixture was cooled to RT. The reaction mixture was passed through a thin column of celite, washed several times with ethyl acetate and the filtrate was evaporated under vacuum to get crude product. The crude product was purified by column chromatography on (230-400 mesh) using (0-2%) ethyl acetate/hexane as eluent.

1, 1'-Biphenyl, 1a: White solid, mp. 68-69 °C (Lit. 69-70 °C) (Ref. 56); IR: 3032, 1943, 1596, 1568, 1479, 1008, 984, 729 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.63 (d, J = 6 Hz, 4H), 7.5-7.45 (m, 4H), 7.4-7.36 (m, 2H).

4-Methylbiphenyl, 1b: White solid, mp. 47-48 °C (Lit. 46-47 °C) (Ref. Ref. 56); IR: 3057, 2949, 1618, 1573, 1455, 1141, 1019, 837 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.61 (d, J = 9 Hz, 2H), 7.55-7.44 (m, 4H), 7.37 (d, J = 6 Hz, 1H) 7.28 (d, J = 6 Hz, 2H), 2.43 (s, 3H).

3, 4'-Dimethylbiphenyl, 1c: (Ref. 56): Oil; IR : 3039, 2931, 1911, 1617, 1497, 1467, 1048, 833, 786 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.63 (d, J = 9 Hz, 2H), 7.53 (d, J = 9 Hz, 2H), 7.47-7.42 (m, 1H), 7.37 (d, J = 9 Hz, 2H), 7.27 (d, J = 6 Hz, 1H), 2.54 (s, 3H), 2.52 (s, 3H).

4, 4'-Dimethylbiphenyl, 1d: White Solid, mp. 120-121 °C (Lit. 122 °C) (Ref. 57); IR: 3012, 2955, 1927, 1617, 1493, 1471, 1021, 841, 789 cm^{-1}, ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.5 (d, J = 6 Hz, 4H), 7.25 (d, J = 9 Hz, 4H), 2.41 (s, 6H).

4-Methoxy-4'-methyl-1,1'-biphenyl, 1e: White solid, mp. 109-110 °C (Lit. 111-112 °C) (Ref. 58); 3033, 2931, 2855, 1647, 1523, 1296, 1243, 1227, 1159, 1038, 877 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.53-7.45 (m, 4H), 7.24 (d, J = 6 Hz, 2H), 6.98 (d, J = 6 Hz, 2H), 3.86 (s, 3H), 2.4 (s, 3H).

4-Nitro-1, 1'-biphenyl, 1f: Yellow solid, mp. 110-111 °C (Lit. 112-114 °C) (Ref. 56); IR: 3084, 1617, 1589, 1539, 1368, 1089, 870, 755 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 8.31(d, J = 9 Hz, 2H), 7.75 (d, J = 9 Hz, 2H), 7.64 (d, J = 6 Hz, 2H), 7.54-7.46 (m, 3H).

4'-Methyl-3-nitro-1,1'-biphenyl, 1g: Yellow solid, mp. 76-77 °C (Lit. 75.5-76.5 °C) (Ref. 56); IR: 3098, 2943, 1521, 1353, 1093, 816, 749 cm^{-1};

^{1}H NMR (CDCl$_3$, 300 MHz) δ: 8.45 (s, 1H), 8.18 (d, J = 6 Hz, 1H), 7.91 (d, J = 6 Hz, 1H), 7.63-7.53 (m, 3H), 7.31(d, J = 6 Hz, 2H), 2.43 (s, 3H).

3, 4'-Dinitro-1,1'-biphenyl, 1h: Yellow solid, mp. 169-170 °C (Ref. 59); IR: 3069, 2967, 1510, 1359, 1087, 823, 759 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 8.51(d, J = 3 Hz, 1H), 8.39-8.31 (m, 3H), 7.97 (d, J = 6 Hz, 1H), 7.81 (d, J = 9 Hz, 2H), 7.74-7.68 (m, 1H).

3-Nitro-1,1'-biphenyl, 1i: Yellow solid, mp. 61-62 °C (Lit. 60-61 °C) (Ref. 56); IR: 3059, 2909, 1611, 1541, 1347, 1051, 846, 731 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 8.46 (s, 1H), 8.21 (d, J = 9 Hz, 1H), 7.93 (d, J = 9 Hz, 1H), 7.65-7.49 (m, 6H).

1-Phenylnaphthalene, 1j (Ref. 56): Oil, IR: 3078, 1605, 1509, 1410, 816, 793, 783, 639 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.93-7.86 (m, 3H), 7.52-7.45 (m, 9H).

[1,1'-Biphenyl]-4-(N,N-dimethyl)amine, 1k: White solid, mp. 120-121 °C (Lit. 121-122 °C) (Ref. 58); IR: 2937, 1601, 1493, 1272, 1249, 1196, 1133, 1049, 827, 769 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.6-7.52 (m, 4H), 7.44-7.39 (m, 2H), 7.3-7.28 (m, 1H), 6.84 (d, J = 9 Hz, 2H), 3.01 (s, 6H).

Conclusion

In conclusion, a simple novel method for the synthesis of spherical monodispered Pd nanoparticles has been developed. Synthesized palladium nanoparticles were found to be spherical in shape with average particle size of 7 nm. Use of 2-(trimethyl silyl)-ethanol as both reducing and stabilizing agent led to the synthesis of stable Pd NPs at RT. The as synthesized nanoparticles show excellent dispersibilty in ethanol. The Pd NPs were found to be very effective for ligand free Suzuki-Miyaura cross-coupling reaction in environment friendly solvent ethanol.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/58776.

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