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Ultrasonic-assisted green synthesis of palladium nanoparticles and their nanocatalytic application in multicomponent reaction†

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This paper describes a novel one pot synthesis of palladium nanoparticles (PdNPs) using a green method. An aqueous extract of *Perilla frutescens* leaf was used as a bioreductant to reduce Pd^{2+} ions to Pd^{0} without any extra surfactants or capping agents. Polyphenols and flavonoids are believed to be actively involved in the reduction process. The formation of PdNPs was confirmed by UV-Vis spectra. Transmission electron microscopy revealed spherical nanoparticles, ranging in size between 10 and 17 nm (average ~13 nm). X-ray diffraction revealed reflections from the (111), (200), (220), (311) and (222) planes confirming the crystallinity of the nanoparticles with a face centred cubic (fcc) structure. Energy dispersive X-ray spectroscopy confirmed the presence of palladium. Fourier transform infrared spectroscopy suggested the role of polyols present in the *P. frutescens* leaf extract. The synthesized nanoparticles were used as catalysts for the synthesis of pyrazolylphosphonate derivatives in high yield. The excellent catalytic performance of the synthesized PdNPs can be associated with their extremely small size and high dispersity, so the synthesized PdNPs will be applicable for future industrial processes.

Introduction

Noble metal nanoparticles are gaining increasing importance because of their applications in diverse fields as well as their prominent stability. PdNPs have a range of applications in the field of both homogeneous (high activity) and heterogeneous (separation and reusability) catalysis.[1] The much larger surface-to-volume ratio of nanoparticles, providing many highly active metal uncoordinated sites compared to their bulk counterparts, has attracted considerable interest for potential catalytic applications.[2] PdNPs are particularly interesting because of their applicability to all arrays of palladium-catalysed reactions, such as hydrogenation,[3] Suzuki reaction,[4] Heck reaction,[5] C–N coupling,[6] Stille coupling[7] and in the oxidation of hydrocarbon.[8] The size effects and shape of nanoparticles play crucial roles in the catalytic performance, which are strongly dependent on the crystallographic planes that abort the nanoparticle surface.[9] Such catalysts have been used because of their excellent activity and high selectivity owing to their small size (1–100 nm) and exposed active metallic or organometallic compounds. In addition to their catalytic applications, they can be used in hydrogen storage[10] and sensing applications[11] owing to their tendency to adsorb hydrogen. Several synthetic methods have been developed for the preparation of metal nanoparticles including chemical, physical, and biological techniques.[12] However, biological techniques have several advantages over physical and chemical methods due to being simple, cost effective, and environmentally friendly by using bacteria, fungi, yeast as well as plants.[13] The rate of reduction of metal ions in the process using a plant extract is more stable, and the rate of synthesis is faster than that of microorganisms.[14] The organic biomolecules like polysaccharides, amino acids, lipids, proteins, and peptides are responsible for capping agents for the synthesis of nanoparticles.[15]

Moreover, the steady fabrication of the PdNPs is necessary for their exploitation, which remains an area of active research. The synthesis of PdNPs has been revealed in several papers using the plant leaf extracts of *Pulicaria glutinosa(d), Glycine max* (soya bean),[16] *Cinnamomum camphora*,[17] and *Gardenia jasminoides*.[18] In the green synthesis of metal nanoparticles, the reduction rate of metal ions by plants is much faster with the aid of ultrasonication.[19]

Perilla frutescens L. (Lamiaceae) is cultivated in East Asia, and both the seed and leaves are used as ingredients in Korean cuisine. This plant is commonly known for its antiallergic, antitumor, and antioxidant properties.[20] Recently, our group synthesized gold and silver nanoparticles in an aqueous solution using the *P. frutescens* leaf extract.[21] Organophosphorus compounds continue to attract considerable attention

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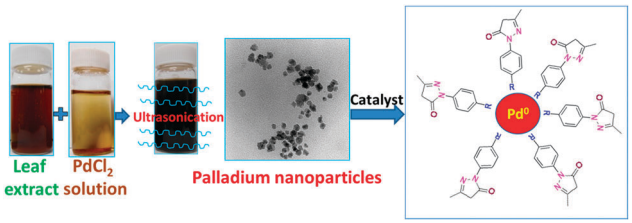


Scheme 1 Schematic diagram of the green synthesis of PdNPs using an aqueous extract of *P. frutescens* leaf and their catalytic activity for multi-component reaction.

because of their range of biological activities.[22] Phosphonyl compounds have received wide attention in modern medicinal chemistry. They are ideal for use in drug design owing to their good bioactivity,[23] low toxicity, and the ease of substitution with conventional heterocyclic ring groups.[24] We report the eco-friendly synthesis of PdNPs using *P. frutescens* and their catalytic applications in multi component reaction, as illustrated in Scheme 1.

Experimental section

Chemicals

Palladium chloride ($PdCl_2$), pyrazolone derivatives, benzaldehyde derivatives, and triethyl phosphite were purchased from Sigma-Aldrich and used as received. The leaves of *P. frutescens* are widely available in Asian countries. Air dried leaves of *P. frutescens* were obtained at a local market in Yeongchon, South Korea.

Preparation of the *P. frutescens* leaf extract

The dried leaves were first ground to a fine powder. 6 g of crushed powder was added to 300 mL of deionized Milli-Q water followed by boiling for 10 min. The broth solution obtained was filtered through a 0.2 μm filter paper and stored at 4 °C for further use.

Biosynthesis of PdNPs using the aqueous *P. frutescens* leaf extract

A volume of 5 mL of the *P. frutescens* extract (about 20 mg after drying) was mixed with 50 mL of an aqueous solution of 2 mM palladium chloride ($PdCl_2$). The synthesis of PdNPs with the *P. frutescens* leaf extract was carried out by sonicating the solution for 2 h at 60 °C in an ultrasonic bath (Fischer Scientific, FS-60), operated at 50 Hz with a maximum power of 260 W.

Characterization of PdNPs

The reduction of palladium ions by the *P. frutescens* leaf extract was monitored by the changes in colour. The absorption spectrum of this solution was recorded using a UV-visible spectrometer (Optizen 3220, Double beam) at wavelengths between 300 and 600 nm. The spectra were recorded using deionized Milli-Q water as a blank, and the data were plotted. The crystallinity of the nanoparticles was determined by powder XRD (PANalytical X'Pert MRD at 30 kV, 40 mA, with Cu Kα (1.5418 Å) radiation). The presence of bioactive molecules necessary to cap the nanoparticles was analysed by FT-IR analysis (JASCO FT-IR spectrophotometer at the range of 400–4000 cm^{-1}). The morphology and size of the synthesized particles were analysed by FE-TEM (FEI Tecnai G2 F20 ST operated at 200 kV, a point resolution of 0.24 nm and a Cs of 1.2 mm) and coupled with EDAX. The TGA experiments were performed to monitor the % weight loss of the nanoparticles, using TG-DTA, SDT-Q600 V20.5 Build 15, heated under a N_2 atmosphere from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}.

Catalytic activity of PdNPs

The synthesized PdNPs were used as catalysts for the synthesis of variety of pyrazolylphosphonates with multi substituents on the pyrazolone ring.

General procedure for the synthesis of compounds 4a–4j.

To a mixture of 3-methyl-1-phenyl-5-pyrazolone (1.0 mmol, 174.2 mg), arylaldehyde (1.2 mmol), and triethylphosphite (2.0 mmol, 0.347 mL) in ethanol (10 mL) were added the PdNPs (5 mol%, 5.321 mg) at room temperature. The reaction mixture was stirred at room temperature for 6–8 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed using a reduced pressure evaporator. The residue was purified by column chromatography on silica gel to give the product.

Characterization data

Diethyl[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)-methyl]phosphonate (4a). Yield: 93%, yellow solid: m.p. 71–73 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.45 (1H, s), 7.67 (2H, d, J = 7.8 Hz), 7.27–7.22 (4H, m), 7.18–7.06 (4H, m), 4.06 (1H, d, J = 27.9 Hz), 3.98–3.90 (2H, m), 3.76–3.68 (1H, m), 3.43–3.35 (1H, m), 1.98 (3H, s), 1.10 (3H, t, J = 7.1 Hz), 0.89 (3H, t, J = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.2 (d, $J_{c\text{-}p}$ = 5.0 Hz), 148.0 (d, $J_{c\text{-}p}$ = 12.0 Hz), 139.2, 136.4 (d, $J_{c\text{-}p}$ = 3.8 Hz), 133.1, 130.1, 129.1 (d, $J_{c\text{-}p}$ = 6.0 Hz), 128.9, 128.4, 127.7 (d, $J_{c\text{-}p}$ = 3.0 Hz), 125.9, 122.0, 93.9, 64.5 (d, $J_{c\text{-}p}$ = 5.0 Hz), 63.7 (d, $J_{c\text{-}p}$ = 7.5 Hz), 41.2 (d, $J_{c\text{-}p}$ = 135.8 Hz), 16.5 (d, $J_{c\text{-}p}$ = 6.0 Hz), 16.2 (d, $J_{c\text{-}p}$ = 5.3 Hz), 12.8; IR (KBr) 2989, 2911, 2733, 2602, 1720, 1593,1517,1503, 1449, 1418,1360, 1193, 1174, 1027, 978, 762, 698, 562 cm^{-1}; HRMS: m/z [M^+] calcd for $C_{21}H_{25}N_2O_4P$: 400.1552; found: 400.1553.

Diethyl[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(4-methoxy-phenyl)methyl]phosphonate (4b). Yield: 95%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.74 (2H, d, J = 8.7 Hz), 7.35–7.23 (4H, m), 7.16–7.11 (1H, m), 6.76 (2H, d, J = 8.7 Hz), 4.09 (1H, d, J = 27.6 Hz), 4.02–3.96 (2H, m), 3.84–3.76 (1H, m), 3.67 (3H, s), 3.51–3.45 (1H, m), 2.05 (3H, s), 1.16 (3H, t, J = 7.1 Hz), 1.00 (3H, t, J = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.4, 159.1 (d, $J_{c\text{-}p}$ = 3.1 Hz), 151.0 (d, $J_{c\text{-}p}$ = 4.9 Hz),147.9, 147.7, 139.0, 130.1 (d, $J_{c\text{-}p}$ = 5.9 Hz), 128.9, 128.1 (d, $J_{c\text{-}p}$ = 4.7 Hz), 125.8, 121.8, 114.2 (d, $J_{c\text{-}p}$ = 2.5 Hz), 94.2 (d, $J_{c\text{-}p}$ = 4.1 Hz), 64.5 (d, $J_{c\text{-}p}$ = 7.4 Hz), 63.5 (d, $J_{c\text{-}p}$ = 7.5 Hz), 55.3, 40.0 (d, $J_{c\text{-}p}$ = 136.5 Hz), 16.4 (d, $J_{c\text{-}p}$ = 5.6 Hz), 16.2 (d, $J_{c\text{-}p}$ = 5.8 Hz), 12.7; IR (KBr) 2986, 2911, 2838, 2745, 2623, 1722, 1595, 1511, 1252, 1178, 1029, 972, 757, 695, 573 cm^{-1}; HRMS: m/z [M^+] calcd for $C_{22}H_{27}N_2O_5P$: 430.1658; found: 430.1659.

Diethyl[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(3-methoxyphenyl)methyl]phosphonate (4c). Yield: 93%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 7.8 Hz), 7.38 (2H, t, J = 7.8 Hz), 7.21–7.18 (2H, m), 6.99–6.97 (2H, m), 6.77 (1H, d, J = 7.8 Hz), 4.18 (1H, d, J = 27.6 Hz), 4.11–4.01 (2H, m), 3.91–3.85 (1H, m), 3.74 (3H, s), 3.59–3.53 (1H, m), 2.12 (3H, s), 1.22 (3H, t, J = 7.1 Hz), 1.05 (3H, t, J = 7.1 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 159.9 (d, $J_{c\text{-}p}$ = 3.8 Hz), 151.1, 147.8 (d, $J_{c\text{-}p}$ = 20.2 Hz), 139.0, 137.7 (d, $J_{c\text{-}p}$ = 5.6 Hz), 129.8, 128.7 (d, $J_{c\text{-}p}$ = 31.2 Hz), 125.8, 121.9, 121.3 (d, $J_{c\text{-}p}$ = 11.0 Hz), 114.8 (d, $J_{c\text{-}p}$ = 11.0 Hz), 112.9 (d, $J_{c\text{-}p}$ = 5.6 Hz), 93.9, 64.5 (d, $J_{c\text{-}p}$ = 12.8 Hz), 63.6 (d, $J_{c\text{-}p}$ = 11.0 Hz), 55.3, 41.0 (d, $J_{c\text{-}p}$ = 217.2 Hz), 16.3 (d, $J_{c\text{-}p}$ = 5.6 Hz), 16.1 (d, $J_{c\text{-}p}$ = 5.8 Hz), 12.7; IR (KBr) 2983, 2921, 2839, 2747, 2623, 1722, 1595, 1495, 1450, 1261, 1175, 1030, 971, 757, 694, 545 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{22}H_{27}N_2O_5P$: 430.1658; found: 430.1655.

Diethyl[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(4-nitrophenyl)methyl]phosphonate (4d). Yield: 88%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.42 (1H, s), 7.66 (2H, d, J = 7.8 Hz), 7.24 (2H, t, J = 7.8 Hz), 7.17–7.03 (5H, m), 4.05 (1H, d, J = 27.9 Hz), 3.98–8.3.85 (2H, m), 3.75–3.67 (1H, m), 3.42–3.33 (1H, m), 1.97 (3H, s), 1.09 (3H, t, J = 7.1Hz), 0.88 (3H, t, J = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.5, 151.2,147.9 (d, $J_{c\text{-}p}$ = 12.5 Hz), 139.1, 136.4 (d, $J_{c\text{-}p}$ = 4.3 Hz), 129.1 (d, $J_{c\text{-}p}$ = 6.1 Hz), 128.9, 128.9, 127.6 (d, $J_{c\text{-}p}$ = 3.1 Hz), 125.9, 121.9, 93.9, 64.5 (d, $J_{c\text{-}p}$ = 7.4 Hz), 63.7 (d, $J_{c\text{-}p}$ = 7.4 Hz), 41.1 (d, $J_{c\text{-}p}$ = 135.8 Hz), 16.4 (d, $J_{c\text{-}p}$ = 5.6 Hz), 16.1 (d, $J_{c\text{-}p}$ = 5.8 Hz), 12.8; IR (KBr) 2807, 2747, 2625, 1722, 1593, 1499, 1175, 1027, 970, 757, 697, 562 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{21}H_{24}N_3O_6P$: 445.1403 found: 445.1403.

Diethyl[(2-chlorophenyl)(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methyl]phosphonate (4e). Yield: 95%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.64 (1H, s), 7.66 (2H, d, J = 7.5 Hz), 7.52–7.50 (1H, m), 7.26 (3H, m), 7.06 (3H, m), 4.84 (1H, d, J = 27.9 Hz), 4.00–3.94 (2H, m), 3.75–3.67 (1H, m), 3.47–3.42 (1H, m), 1.99 (3H, s), 1.11 (3H, t, J = 6.9 Hz), 0.87 (3H, t, J = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.4, 148.2 (d, $J_{c\text{-}p}$ = 12.5 Hz), 139.1, 134.8 (d, $J_{c\text{-}p}$ = 3.7 Hz), 133.4 (d, $J_{c\text{-}p}$ = 8.1 Hz), 131.1 (d, $J_{c\text{-}p}$ = 4.5 Hz), 129.5 (d, $J_{c\text{-}p}$ = 2.3 Hz), 128.9, 128.8, 127.8 (d, $J_{c\text{-}p}$ = 3.1 Hz), 125.9, 121.9, 93.8, 64.5 (d, $J_{c\text{-}p}$ = 7.6 Hz), 63.9 (d, $J_{c\text{-}p}$ = 7.4 Hz), 36.6 (d, $J_{c\text{-}p}$ = 137.6 Hz), 16.4 (d, $J_{c\text{-}p}$ = 5.6 Hz), 16.1 (d, $J_{c\text{-}p}$ = 5.6 Hz), 12.9; IR (KBr) 3065, 2985, 2926, 1725, 1593,1501, 1447, 1412, 1179, 1028, 971, 751, 692, 566 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{21}H_{24}ClN_2O_4P$: 434.1162; found: 434.1163.

Diethyl[(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(naphthalen-1-yl)methyl]phosphonate (4f). Yield: 90%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.90 (1H, s), 8.25 (1H, d, J = 8.4 Hz), 7.90 (3H, d, J = 7.8 Hz), 7.82 (2H, m), 7.64 (1H, t, J = 7.4 Hz), 7.57–7.43 (4H, m), 7.29–7.24 (1H, m), 5.25 (1H, d, J = 27.9 Hz), 4.26–4.11 (2H, m), 3.71–3.58 (1H, m), 3.10–2.97 (1H, m), 2.09 (3H, s), 1.35 (3H, t, J = 6.9 Hz), 0.62 (3H, t, J = 6.9 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.7 (d, $J_{c\text{-}p}$ = 5.5 Hz), 148.1 (d, $J_{c\text{-}p}$ = 12.5 Hz), 139.3, 134.4, 132.4 (d, $J_{c\text{-}p}$ = 5.3 Hz), 131.5 (d, $J_{c\text{-}p}$ = 5.8 Hz), 129.1 (d, $J_{c\text{-}p}$ = 26.0 Hz), 128.4 (d, $J_{c\text{-}p}$ = 3.8 Hz), 126.6, 126.0 (d, $J_{c\text{-}p}$ = 3.9 Hz), 125.9 (d, $J_{c\text{-}p}$ = 3.2 Hz), 123.0, 122.0, 94.6 (d, $J_{c\text{-}p}$ = 4.4 Hz), 64.5 (d, $J_{c\text{-}p}$ = 5.3 Hz), 63.6 (d, $J_{c\text{-}p}$ = 7.5 Hz), 35.6 (d, $J_{c\text{-}p}$ = 137.0 Hz), 16.5 (d, $J_{c\text{-}p}$ = 5.5 Hz), 15.7 (d, $J_{c\text{-}p}$ = 5.6 Hz), 13.0; IR (KBr) 3058, 2983, 2911, 1593, 1500, 1404, 1202, 1027, 966, 776, 696, 535 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{25}H_{27}N_2O_4P$: 450.1708; found: 450.1709.

Diethyl[(5-hydroxy-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-4-yl)(phenyl)-methyl]phosphonate (4g). Yield: 94%, light yellow solid: m.p. 73–75 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59 (2H, d, J = 8.1 Hz), 7.33 (2H, d, J = 6.6 Hz), 7.25–7.12 (5H, m), 4.14 (1H, d, J = 27.9 Hz), 4.05–3.94 (2H, m), 3.85–3.72 (1H, m), 3.52–3.84 (1H, m), 2.27 (3H, s), 2.06 (3H, s), 1.17 (3H, t, J = 7.1 Hz), 0.96 (3H, t, J = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.0 (d, $J_{c\text{-}p}$ = 5.3 Hz), 147.5 (d, $J_{c\text{-}p}$ = 12.4 Hz), 136.4, 136.4, 136.3, 135.7, 130.0, 129.4, 129.0 (d, $J_{c\text{-}p}$ = 6.1 Hz), 128.9 (d, $J_{c\text{-}p}$ = 2.5 Hz), 127.6 (d, $J_{c\text{-}p}$ = 3.2 Hz), 122.1, 93.8 (d, $J_{c\text{-}p}$ = 4.5 Hz), 64.4 (d, $J_{c\text{-}p}$ = 7.4 Hz), 63.6 (d, $J_{c\text{-}p}$ = 7.4 Hz), 41.0 (d, $J_{c\text{-}p}$ = 135.9 Hz), 21.1, 16.4 (d, $J_{c\text{-}p}$ = 5.6 Hz), 16.1 (d, $J_{c\text{-}p}$ = 5.7 Hz), 12.6; IR (KBr) 2985, 2925, 2754, 2633, 1715, 1583, 1518, 1449, 1416, 1365, 1217, 1182, 1028, 973, 819, 562 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{22}H_{27}N_2O_4P$: 414.1708; found: 414.1709.

Diethyl[(5-hydroxy-3-methyl-1-(4-nitrophenyl)-1*H*-pyrazol-4-yl)-(phenyl)methyl]phosphonate (4h). Yield: 89%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.19 (2H, d, J = 9.0 Hz), 8.07 (2H, d, J = 9.0 Hz), 7.34–7.19 (5H, m), 4.17–3.99 (3H, m), 3.84–3.76 (1H, m), 3.50–3.41 (1H, m), 2.05 (3H, s), 1.21 (3H, t, J = 7.1 Hz), 0.97 (3H, t, J = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 152.3 (d, $J_{c\text{-}p}$ = 8.5 Hz), 150.2, 150.1, 144.5 (d, $J_{c\text{-}p}$ = 10.9 Hz), 135.9 (d, $J_{c\text{-}p}$ = 7.1 Hz), 131.9, 129.1, 129.1, 129.0, 128.0 (d, $J_{c\text{-}p}$ = 5.0 Hz), 124.8, 120.5, 95.2 (d, $J_{c\text{-}p}$ = 7.0 Hz), 64.9 (d, $J_{c\text{-}p}$ = 12.0 Hz), 63.7 (d, $J_{c\text{-}p}$ = 12.1 Hz), 41.1 (d, $J_{c\text{-}p}$ = 218.0 Hz), 16.4 (d, $J_{c\text{-}p}$ = 9.1 Hz), 16.2 (d, $J_{c\text{-}p}$ = 9.0 Hz), 12.9; IR (KBr) 2983, 2923, 2720, 2542, 1718, 1592, 1514, 1334, 1172, 1025, 979, 852, 748, 565 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{21}H_{24}N_3O_6P$: 445.1403; found: 445.1405.

Diethyl[(1-(4-chlorophenyl)-5-hydroxy-3-methyl-1*H*-pyrazol-4-yl)(phenyl)methyl]phosphonate (4i). Yield: 96%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 11.69 (1H, s), 7.73 (2H, d, J = 8.4 Hz), 7.34–7.15 (7H, m), 4.13 (1H, d, J = 27.9 Hz), 4.07–3.96 (2H, m), 3.83–3.75 (1H, m), 3.39–3.41 (1H, m), 2.05 (3H, s), 1.19 (3H, t, J = 7.1 Hz), 0.98 (3H, t, J = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 151.0, 148.1 (d, $J_{c\text{-}p}$ = 19.3 Hz), 137.5, 135.9 (d, $J_{c\text{-}p}$ = 7.0 Hz), 130.8, 129.8 128.8, 128.7, 128.7, 128.2, 127.5 (d, $J_{c\text{-}p}$ = 4.4 Hz), 122.6, 93.9, 64.4 (d, $J_{c\text{-}p}$ = 12.2 Hz), 63.4 (d, $J_{c\text{-}p}$ = 11.5 Hz), 40.8 (d, $J_{c\text{-}p}$ = 217.0 Hz), 16.2 (d, $J_{c\text{-}p}$ = 8.8 Hz), 15.9 (d, $J_{c\text{-}p}$ = 9.7 Hz), 12.5; IR (KBr) 2991, 2912, 2723, 2609, 1592, 1497, 1447, 1412, 1171, 1023, 979, 833, 795, 562 cm^{-1}; HRMS: m/z [M$^+$] calcd for $C_{21}H_{24}ClN_2O_4P$: 434.1162; found: 434.1164.

Diethyl[(5-hydroxy-3-methyl-1-(4-nitrophenyl)-1*H*-pyrazol-4-yl) (3-methoxyphenyl) methyl]phosphonate (4j). Yield: 93%, light yellow solid: m.p. >300 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 12.19 (1H, s), 8.25 (2H, d, J = 8.8 Hz), 8.11 (2H, d, J = 8.8 Hz), 7.24–7.21 (1H, m), 6.97–6.94 (2H, m), 6.79 (1H, d, J = 8.4 Hz), 4.17–4.07 (3H, m), 3.90–3.86 (1H, m), 3.76 (3H, s), 3.56–3.52 (1H, m), 2.12 (3H, s), 1.25 (3H, t, J = 7.0 Hz), 1.06 (3H, t, J = 7.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 160.1, 152.2,150.1, 150.0, 144.5 (d, $J_{c\text{-}p}$ = 5.6 Hz), 137.3 (d, $J_{c\text{-}p}$ = 7.4 Hz), 130.0 (d, $J_{c\text{-}p}$ = 3.6 Hz), 124.8, 121.4 (d, $J_{c\text{-}p}$ = 9.4 Hz), 120.4, 115.0 (d, $J_{c\text{-}p}$ = 9.4 Hz), 113.0, 95.1 (d, $J_{c\text{-}p}$ = 7.2 Hz), 65.0 (d, $J_{c\text{-}p}$ = 11.0 Hz), 63.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 55.4, 41.0

(d, $J_{c\text{-}p}$ = 217.2 Hz), 16.4 (d, $J_{c\text{-}p}$ = 9.4 Hz), 16.2 (d, $J_{c\text{-}p}$ = 9.2 Hz), 12.9; IR (KBr) 2987, 2928, 2834, 2615, 1593, 1518, 1338, 1256, 1189, 1014, 856, 761, 690, 546 cm^{-1}; HRMS: *m*/*z* [M^+] calcd for $C_{22}H_{26}N_3O_7P$: 475.1508; found: 475.1508.

Results and discussion

Characterization of PdNPs

The synthesis of PdNPs using the *P. frutescens* leaf extract was initially monitored visually and then by UV-visible spectroscopy (Fig. 1). During visual monitoring, the colour of the reaction mixture changed gradually from yellowish into dark brown within 2 h after sonication at 60 °C indicating the formation of PdNPs. In UV-visible spectroscopy, the $PdCl_2$ solution showed a distinct peak approximately at 425 nm indicating the existence of Pd^{2+} ions. During the formation of PdNPs, the peak of the Pd^{2+} ions present at 425 nm began to disappear and vanished within 2 h. Generally PdNPs do not show any distinct peak due to the surface plasmon.[25] This is because of the reduction of Pd^{2+} ions to Pd^0. Similarly, Kesarla *et al.*[26] and Khan *et al.*[27] reported that the disappearance of an absorption band at approximately 425 nm confirmed the complete reduction of Pd(II) to PdNPs. In order to find active components of the reduction process, some control experiments were carried out. In the presence of naringenin of flavonoid or gallic acid of polyphenol as a reducing reagent, PdNPs were synthesized. These results indicated that flavonoid and polyphenol were responsible to reduce Pd^{2+} ions to Pd^0 (Fig. S1 and S2, the ESI†).

The morphology and size of the PdNPs produced were analysed by transmission electron microscopy. Aliquots of the Pd nanoparticle solutions were placed on a carbon coated copper grid and allowed to dry under ambient conditions. The TEM images were recorded at different magnifications. Fig. 2a shows that PdNPs were almost spherical with a few irregularly shaped particles due to the agglomeration of small PdNPs dispersed over a thin layer of bioorganic compounds. Fig. 2b shows a particle size distribution histogram. Fig. 2c presents a magnified overview image of a single particle and the inset shows the selected area electron diffraction (SAED) patterns corresponding to the (111), (200), (220), (311), and (222) face centred cubic planes, which confirmed the crystalline nature of PdNPs. The size of the PdNPs ranged from 10 to 17 nm with a mean of ~13 nm. Energy dispersive X-ray analysis (EDAX) revealed a strong signal in the palladium region and confirmed the formation of PdNPs (Fig. 2d), which showed a typical optical absorption peak at ~2.8 keV because of surface plasmon resonance.[28] The C and Cu peaks were probably due to the carbon coated copper grid used for sample preparation.

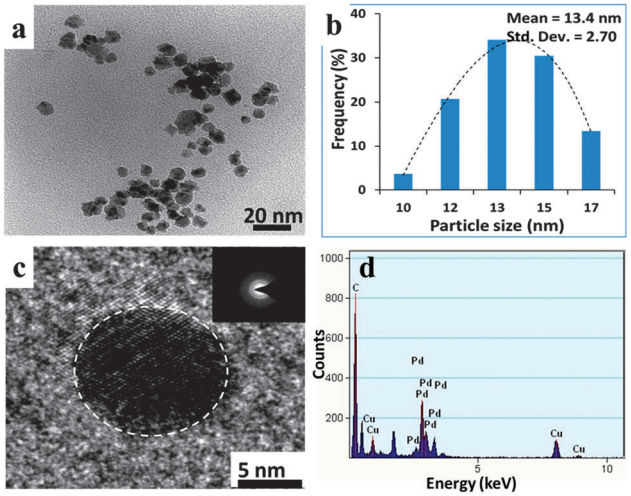


Fig. 2 TEM images of the PdNPs (a) scale bar at 20 nm, (b) size distribution histogram, (c) 5 nm (inset: SAED pattern), and (d) EDAX results showing the formation of PdNPs.

Fig. 3 presents XRD patterns of the synthesized PdNPs. The scanning range selected was between 20° and 90° 2θ. The XRD peaks were observed at 39.92°, 46.43°, 67.77°, 81.65°, and 86.13° 2θ, which were assigned to the (111), (200), (220), (311), and (222) Bragg's reflections of face-centred PdNPs, which are consistent with JCPDS (no. 05-0681). A few additional sharp unassigned peaks at 27.87° and 32.30° 2θ were also observed. These were attributed to the crystallization of other bioorganic compounds on the surfaces of PdNPs, which agreed with a previous report using the *Delonix regia* leaf extract.[28] Similar unassigned peaks were found for silver nanoparticles synthesized using a *Pelargonium graveolens* leaf extract.[29] Interestingly, the XRD patterns of PdNPs synthesized

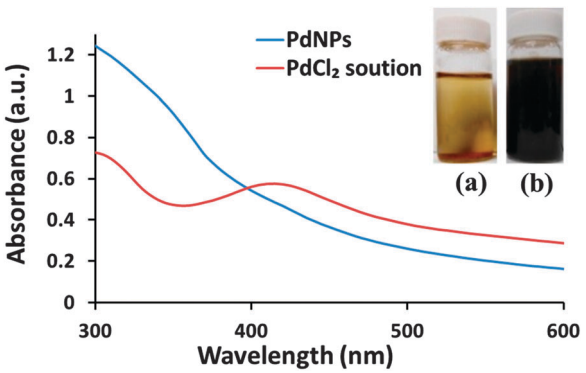


Fig. 1 UV-visible spectra and the inset of (a) $PdCl_2$ solution, and (b) biosynthesized PdNPs.

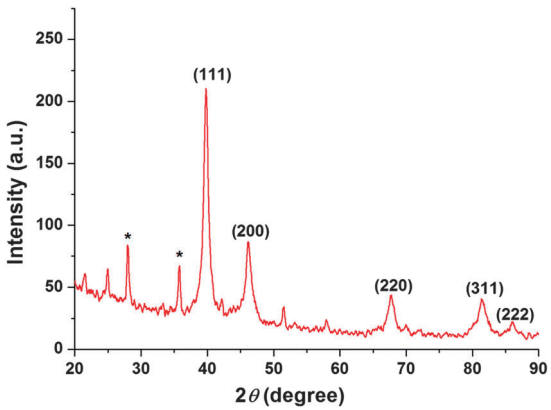


Fig. 3 XRD patterns of PdNPs.

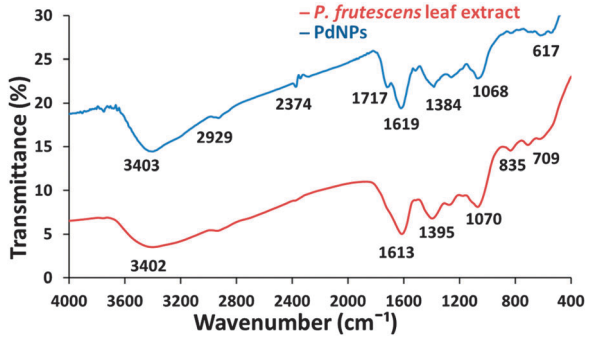


Fig. 4 FT-IR spectra of the *P. frutescens* leaf extract and PdNPs synthesized from the *P. frutescens* leaf extract.

by naringenin or gallic acid showed less crystallinity compared to the nanoparticles synthesized using the *P. frutescens* extract (Fig. S3, the ESI†).

FT-IR spectroscopy was carried out to identify possible bioactive molecules like polyphenols and flavonoids[30] in the *P. frutescens* leaf extract responsible for the reduction and stabilization of PdNPs. The spectrum of the *P. frutescens* leaf extract revealed absorption bands at 3402 and 1613 cm^{-1}, representing the O–H and C=C stretching in polyols or flavonoids, respectively (Fig. 4). The vibrations at 1070 and 1395 cm^{-1} were assigned to C–O stretching and the C–H bending of polyols or flavonoids. After the bioreduction of $PdCl_2$ by the leaf extract, some changes were noticed in positions and the magnitude of the stretching vibrations, indicating the participation of polyphenols or flavonoids. The band at 3403 cm^{-1} indicated the O–H group of polyols participating in the bioreduction process. The small peaks at 2929 and 1717 cm^{-1} were attributed to C–H and C=O stretching vibrations. The peaks at 1068 cm^{-1} were assigned to the C–O stretching vibration in polyols or flavonoids.

TGA characterization was performed at a heating rate of 10 °C min^{-1} in a N_2 atmosphere. The TGA trace of PdNPs (Fig. 5) revealed three stages of weight loss from room temperature to 1000 °C. The first stage weight loss at ~30–150 °C was 6.88%. The weight loss was found to be 33.13% at ~150–650 °C. Finally, at ~650–950 °C, the weight loss was 13.25%.

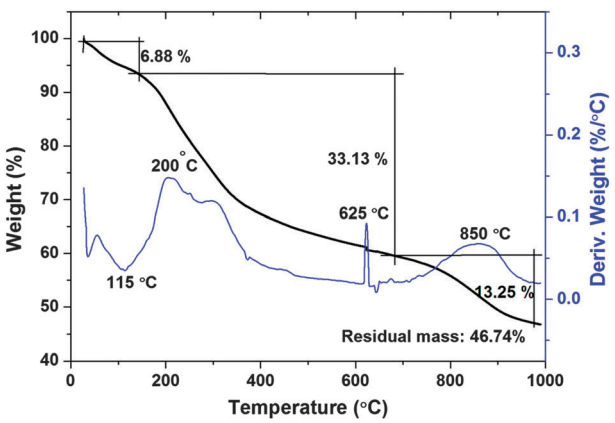


Fig. 5 TGA traces of the PdNPs.

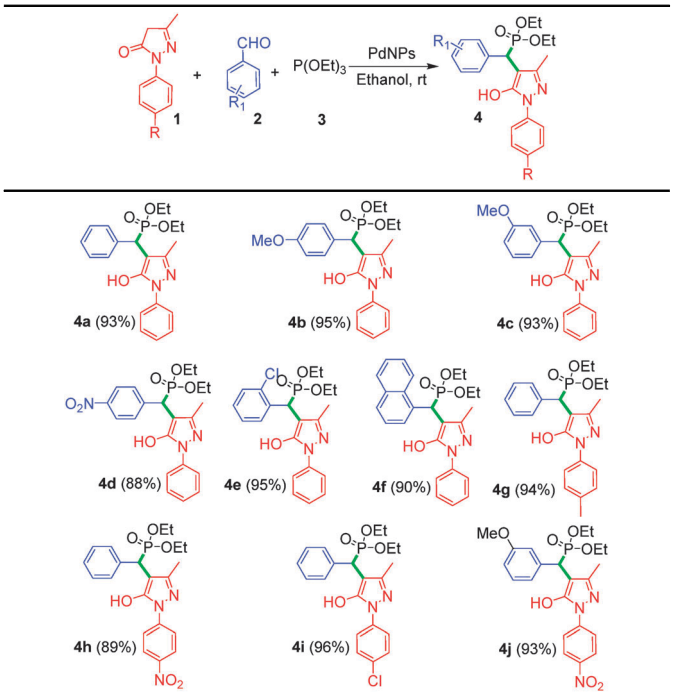
This suggests that bioactive molecules were capped on the PdNPs and were degraded completely at high temperatures, leaving a residual mass of 46.74%.

Catalytic activity

Recently, it was reported that the nanoparticles possess complex hybrid structures, so called multiple-species catalysis, which facilitate the progress of organic reactions.[31] Importantly, three-component reactions of pyrazoles with aromatic aldehydes and triethyl phosphite for pyrazolylphosphonate derivatives using nanoparticles as multiple-species catalysis have not been developed so far. To assess the possible applications of PdNPs as efficient catalysts, the synthesized PdNPs were used next for the preparation of a variety of pyrazolylphosphonate derivatives. To examine a multi-component reaction for the synthesis of pyrazolylphosphonates, reactions of pyrazolone derivatives with several arylaldehydes and triethylphosphite in the presence of PdNPs in ethanol at room temperature for 6–8 h were carried out.

The results are summarized in Table 1. Treatment of **1** (3-methyl-1-phenyl-5-pyrazolone) with benzaldehyde and triethylphosphite in the presence of 5.0 mol% of PdNPs for 6 h gave compound **4a** in 93% yield, whereas that with *p*-anisaldehyde and *m*-anisaldehyde afforded the desired product **4b** and **4c** in 95% and 93% yield, respectively. Similarly, reaction of **1** (3-methyl-1-phenyl-5-pyrazolone) with 4-nitrobenzaldehyde provided **4d** in 88% yield and that with *o*-chloro benzaldehyde gave **4e** in 95% yield. Interestingly, with 1-naphthaldehyde, the desired product **4f** was isolated in 90% yield. The pyrazolones with an electron

Table 1 Synthesis of various pyrazolylphosphonates **4a–4j** using PdNPs as catalysts[a]



[a] Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), **3** (2.0 mmol), PdNPs (5.0 mol%) in ethanol (10 mL) rt for 6–8 h.

donating group, such as methyl, nitro or chloro groups on the benzene ring gave the product **4g–4j** in 94%, 89%, 96%, and 93% yield, respectively. The PdNPs catalysed multi-component reactions provided a rapid synthetic route to a range of pyrazolylphosphonates **4a–4j** in good to excellent yield.

Conclusions

Spherical shaped palladium nanoparticles were prepared by a simple, inexpensive, and environmentally benign method using the *Perilla frutescens* leaf extract as a bioreductant. The synthetic method was highly crystalline without using any harmful reducing or capping agents and also overcame the disadvantages of temperature and pressure conditions. UV Visible spectroscopy indicated that the bioactive molecules present in the leaf extract play a vital role in the reduction of palladium chloride solution to stabilized palladium nanoparticles. Transmission electron microscopy showed that the palladium nanoparticles were spherical, 10–17 nm in size with a mean diameter of 13 nm. The synthesized palladium nanoparticles were crystalline according to X-ray diffraction. The synthesized nanoparticles have potential catalytic applications for the synthesis of pyrazolylphosphonate derivatives. This green synthetic procedure will be widely expected to use for future catalytic applications in other multicomponent reactions.

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