Supporting information for manuscript

Highly Efficient Aqueous Phase Chemoselective Hydrogenation of Unsaturated Aldehydes, Ketones, Esters and Nitriles Catalysed by Palladium Nanoparticles Stabilised with Phosphine-Decorated Polymer Immobilised Ionic Liquids†

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References
Experimental

General Comments. All reagents were purchased from commercial suppliers and used without further purification. Na$_2$[PdCl$_4$] was generated *in situ* immediately prior to use as previously described. $^1$H and $^{13}$C($^1$H) NMR spectra were recorded on JEOL LAMBDA-500 or ECS-400 instruments. Solid-state $^{31}$P spectra were recorded at 161.87 MHz using a Varian VNMRS 400 spectrometer and a 4 mm (rotor o.d.) magic-angle spinning probe. They were obtained using cross-polarization with a 2 s recycle delay, 3 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 10 kHz. Between 1000 and 3600 repetitions were accumulated. Spectral referencing was with respect to an external sample of 85% phosphoric acid. Solid-state $^{13}$C spectra were recorded at 100.562 MHz using a Varian VNMRS 400 spectrometer. They were obtained using cross-polarization with a 10 s recycle delay, 1 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 6 kHz. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Thermogravimetric analysis (TGA) was performed using a TA TGA Q600 instrument, at a heating rate of 10 °C min$^{-1}$ in air. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature. SEM images were acquired on a Tescan Vega 3LMU scanning electron microscope with digital image collection. XPS measurements were carried out using a Theta Probe system (Thermo Scientific, UK) equipped with a microfocused monochromatic AlK$\alpha$ source. The X-ray source was operated at 100 W and 15 kV. Samples for transmission electron microscopy (TEM) were dispersed in ethanol using an ultrasonic bath and deposited on lacey carbon film coated copper grids. TEM images were acquired on a FEI Tecnai TF20 field emission gun microscope operating at 200 kV. NP size distribution histograms were obtained from measurements of at least 100 different NPs assuming a spherical shape and with random distribution. Powder X-ray diffraction patterns (XRD) were recorded using a PANalytical X'Pert Pro Multipurpose Diffractometer (MPD) using Cu Kα/β radiation of wavelength of 1.5418 Å. The palladium loading was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES). FT-IR spectroscopy was performed on a Varian 800 FT-IR instrument (Varian Inc.). CHN analysis was performed on a Carlo Erba 1108 Elemental Analyser and controlled with Carlo Erba Eager 200 software.
Synthesis of diphenyl(4-vinylphenyl)phosphine. A round bottom flask was charged with Mg turnings (1.77 g, 72.8 mmol) suspended in anhydrous THF (25 mL). A crystal of iodine was added to the mixture, which was subsequently cooled to 0°C. 4-chlorostyrene (4.7 mL, 39.3 mmol) was dissolved in anhydrous THF (35 mL) in a separate round bottom flask, and 20% of this solution was added dropwise to the Mg turnings to initiate Grignard formation. The remaining solution was added so to maintain a gentle reflux at 65°C for 4 hours.

Another round bottom flask was charged with chlorodiphenylphosphine (4 mL, 30 mmol) dissolved in anhydrous THF (30 mL). The solution was cooled to 0°C. The Grignard solution was added to this dropwise and left to stir overnight at room temperature. The solution was then quenched with degassed water (100 mL) and extracted into a large excess of ether (3 x 170 mL) whilst bubbling nitrogen through the solution. After drying over MgSO₄, filtering and removing the solvent via the use of an external trap, the product was obtained as a white solid and stored under nitrogen (5.26 g, 58% yield).

Synthesis of 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride. An oven dried Schlenk flask was allowed to cool under vacuum, purged with nitrogen and charged with 1,2-dimethyl imidazole (4.9 mL, 55.3 mmol) and dry chloroform (50 mL). 4-Vinylbenzyl chloride (10 mL, 71.0 mmol) was added to the flask and the mixture was stirred overnight at 50°C under nitrogen. The next day the solvent was removed under reduced pressure, the product was washed with ethyl acetate (4 x 40 mL), the remaining solvent was then removed under reduce pressure to afford a white crystalline solid (12.38 g, 50 mmol, 91%). ¹H NMR (300 MHz, CDCl₃, δ): 7.25-7.29 (m, 14H, ArH), 6.63 (dd, J_HH = 17.5, J_HH = 10.9 Hz, 1H, ArCHC₂H), 5.70 (d, J_HH = 17.5, 1H, ArCHCH₂) 5.20 (d, J_HH = 10.9, 1H, ArCHCH₂); ¹³C NMR (75 MHz, CDCl₃, δ): 137.95, 137.23, 137.09, 136.4 (Ar), 134.09, 133.86, 133.83, 133.60 (ArH), 128.75 (CH₂), 126.35 (CH₂); ³¹P NMR (121 MHz, CDCl₃, δ): -5.78.

Synthesis of 2-methyl-1-(4-vinylbenzyl)-1H-imidazole. An oven-dried Schlenk flask was allowed to cool to room temperature and charged with a sodium hydride (0.73 g, 30.4 mmol) which was dissolved
in dry DMF (20 mL). The reaction was stirred and cooled to 0°C. 2-methyl imidazole (3.0 g, 36.5 mmol) was added resulting in the liberation of gas and an exothermic reaction, once the exothermic subsided. The reaction mixture was cooled in an ice bath, then 4-chloromethyl styrene (4.29 mL, 30.4 mmol) was added dropwise. The reaction was heated to 75°C for 30 min. The reaction mixture was poured onto H₂O (250 mL) and the product extracted with ethyl acetate (2 × 100 mL). The combined extracts were washed with H₂O (180 mL) and then brine (50 mL) before being extracted with 6N HCl (2 × 25 mL). The aqueous layer was washed with diethyl ether (20 mL) then treated with NaOH solution (1.0 M) to pH 12.0 and the product extracted with diethyl ether (3 × 100 mL), dried over MgSO₄ and the solvent removed under reduced pressure to afford the product as a pale yellow oil in 92% yield (5.55 g). ¹H NMR (300 MHz CDCl₃, δ): 2.15 (3H, s), 4.83 (2H, s), 5.09-5.12 (1H, d, J = 9 Hz), 5.55-5.61 (1H, d, J = 18 Hz), 6.48-6.57 (1H, dd, J = 9 Hz, 18 Hz), 6.84-6.86 (2H, d, J = 6 Hz), 13C NMR (75 MHz, CDCl₃, δ): 128.51, 128.87, 133.65, 134.14, 136.09, 153.07; Anal. Calc. for C₁₃H₁₄N₂ (198.1): C, 78.75; H, 7.12; N, 14.13%. Found: C, 79.17; H, 7.77; N, 14.57%.

**Synthesis of 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride.** An oven-dried Schlenk flask was allowed to cool to room temperature and charged with 2-methyl-1-(4-vinylbenzyl)-1H-imidazole (5.16 g, 26.0 mmol) which was dissolved in dry chloroform (50 mL). 4-chloromethyl styrene was added and the reaction mixture heated at 50°C under nitrogen and stirring for 19 h. After removal of the solvent at reduced pressure the solid residue was washed with diethyl ether. The product was dried under reduced pressure, the resultant dissolved in dichloromethane then added dropwise to diethyl ether (ca. 250 mL) with vigorous stirring. After stirring for a minimum of 60 min the product was allowed to settle, isolated by filtration through a frit, washed with diethyl ether (2 × 50 mL) and dried under high vacuum to afford 12 as a white powder in 98% yield (8.961 g). ¹H NMR (300 MHz, CDCl₃, δ): 1.97 (3H, s), 2.69 (4H, s), 5.19-5.23 (2H, d, J = 12 Hz), 5.64-5.70 (2H, d, J = 18 Hz), 6.54-6.63 (2H, dd, J = 12 Hz, 18 Hz), 7.20-7.22 (4H, d, J = 6 Hz), 7.29-7.31 (2H, d, J = 6 Hz); ¹³C NMR (75 MHz, CDCl₃, δ): 11.42, 52.65, 113.28, 122.83, 128.51, 128.87, 133.65, 134.14, 136.09, 153.07; Anal. Calc. for C₂₂H₂₃ClN₂ (350.1): C, 75.31; H, 6.61; N, 7.98%. Found: C, 75.67; H, 9.93; N, 8.19%.

**Synthesis of methyl octaethylene glycol chloride.** Polyethylene glycol monomethyl ether (7.0 g, 20 mmol), pyridine (3.16 g, 40 mmol) and dry toluene (40 mL) were added to a Schlenk flask under a nitrogen atmosphere. The solution was stirred and
heated slowly to 80 °C and then thionyl chloride (4.74 g, 40 mmol) was added over 20 minutes. The mixture was stirred for an additional 2 days under reflux. After cooling to room temperature, water was added to quench the reaction (5 mL), and the lower red salts were extracted with toluene (3 x 20 mL), whichmerged into the upper organic phase. The organic phases were combined, concentrated and the pale yellow residue was dissolved in dichloromethane (40 mL), washed with water (3 x 30 mL), and then dried over anhydrous MgSO₄. The solvent was then evaporated and the product dried in vacuo to give a pale-yellow liquid. `H NMR (300 MHz, CDCl₃, δ): 3.69 (t, J = 5.6, 1.2 Hz, 2H), 3.67 – 3.52 (m, 24H), 3.50 (t, 3H), 3.31 (s, 3H); `C NMR (75 MHz, CDCl₃, δ): 71.79, 71.20, 70.50, 58.83, 42.64.

Synthesis of 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-1H-imidazole. An oven dried Schlenk was charged was NaH (0.19 g, 8 mmol) which was dissolved in anhydrous dimethylformamide (20 mL). The solution was cooled to 0 °C at which point 2-methylimidazole (0.66 g, 8 mmol) was added slowly, resulting in the liberation of gas. Once the exotherm had subsided, methyl octaethylene glycol chloride (2.5 g, 6.7 mmol) was added dropwise over 20 minutes. The resultant dark brown solution was heated to 75 °C and stirred for 45 minutes. After this time, the solution was cooled to room temperature and the water was added (5 mL) and the product was extracted with ethyl acetate (4 x 50 mL) and the organic fractions combined, dried over MgSO₄, filtered and the solvent removed in vacuo to yield a yellow/brown oil (2.43 g, 18.9 mmol) in 87% yield. `H NMR (300 MHz, CDCl₃, δ): 7.11 (d, J = 1.3, 2H), 3.94 (t, 2H), 3.90 – 3.76 (m, 22H), 3.73 (t, 2H), 3.56 (s, 3H), 2.59 (s, 3H); `C NMR (75 MHz, CDCl₃, δ): 144.46, 121.24, 71.82, 71.80, 71.26, 71.23, 70.53, 70.46, 58.90, 58.87, 58.85, 42.68, 13.79; Anal. Calc. for C₂₁H₄₀N₂O₈ (448.3): C, 56.23; H, 8.99; N, 6.25%. Found: C, 58.02; H, 9.89; N, 7.01%.

Synthesis of 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-31,4-imidazolium chloride. 1-bromomethyl-4-vinyl-benzene (0.31 g, 1.57 mmol) was added to a solution of 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-1H-imidazole (0.55 g, 1.31 mmol) dissolved in anhydrous dichloromethane (8 mL) and the mixture was stirred at 35 °C for 24 hours. The solvent was removed under reduced pressure to afford a viscous oil which was washed with diethyl ether (30 mL) and dried under high vacuum. `H NMR (300 MHz, CDCl₃, δ): 7.90 (s, 1H) 7.58 (s, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 5.76 (d, J = 17.6 Hz, 1H), 5.52 (s, 2H), 5.30 (d, J = 12.1 Hz, 2H), 4.53 (t, J = 4.8 Hz, 2H), 3.89 (t, J = 4.8 Hz, 2H), 3.73 – 3.41 (m,
19H), 3.34 (s, 3H), 2.79 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 144.56, 144.53, 137.81, 135.57, 132.52, 132.49, 128.32, 128.17, 128.14, 126.67, 121.93, 121.87, 121.74, 114.89, 71.55, 71.47, 70.19, 70.14, 70.07, 69.95, 69.13, 58.65, 58.62, 51.52, 48.61, 10.99, 10.97, 10.95; Anal. Calc. for C$_{30}$H$_{49}$ClN$_2$O$_8$ (600.3): C, 59.94; H, 8.22; N, 4.66%. Found: C, 61.07; H, 8.98; N, 5.25%.

**Synthesis of PPh$_2$-PIILP (1a).** An oven dried Schlenk was charged with 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (3.17 g, 12.76 mmol), diphenyl(4-vinylphenyl)phosphine (2.0 g, 6.93 mmol), 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (0.34 g, 0.97 mmol), AIBN (0.16 g, 0.97 mmol), ethanol (35 mL) and THF (50 mL). The resulting mixture was degassed using the freeze thaw method repeatedly six times before being heated at 80 °C for 4 days. After this time, a further equivalent of AIBN (0.16 g, 0.97 mmol) was added and the degassing procedure repeated before being heated for a further 24 h at 80 °C. The solvent was removed in vacuo and the resulting residue was dissolved in dichloromethane (30 mL) and added dropwise to a beaker of diethyl ether (350 mL) with vigorous stirring. The solution was left to stir for 45 minutes and then left to settle. The mixture was filtered and the solid washed with ether to yield a white solid (4.3 g, 87%).

**Synthesis of PPh$_2$-PEGPIILP (2a).** An oven dried Schlenk was charged with 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride (3.61 g, 6.38 mmol), diphenyl(4-vinylphenyl)phosphine (1.0 g, 3.47 mmol), 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (0.17 g, 0.49 mmol), AIBN (0.09 g, 0.49 mmol), ethanol (30 mL) and THF (45 mL). The resulting mixture was degassed using the freeze thaw method repeatedly six times before being heated at 80 °C for 4 days. After this time, a further equivalent of AIBN (0.09 g, 0.49 mmol) was added and the degassing procedure repeated before being heated for a further 24 h at 80 °C. The solvent was removed in vacuo and the resultant residue was dissolved in dichloromethane (35 mL) and added dropwise to a beaker of diethyl ether (350 mL) with vigorous stirring. The solution was left to stir for 45 minutes and then left
to settle. The mixture was filtered and the solid washed with ether to yield a yellow/brown solid (4.2 g, 89%).

**Synthesis of [PdCl₄]@PPh₂-PiILP (1b).** A 200mL round bottom flask charged with palladium dichloride (0.39 g, 2.2 mmol), NaCl (2.2 g, 37.6 mmol) and water (45 mL) was heated to 80 °C for ca. 40 min to afford a clear deep red solution. The solution was cooled and a suspension of 1a (1.5 g, 1.8 mmol) in water (10 mL) was added with the resulting mixture stirred vigorously for 5 hours. The precipitate was collected by filtration through a frit and the resulting solid washed with ethanol (12 mL) and diethyl ether (20 mL) to yield 1b as a free flowing pale brown solid (1.3 g, 77%). ICP-OES data: 6.2 wt% palladium and a palladium loading of 0.58 mmol g⁻¹.

**Synthesis of [PdCl₄]@PPh₂-PEGPiILP (2b).** A 200mL round bottom flask charged with palladium dichloride (0.39 g, 2.2 mmol), NaCl (2.2 g, 37.6 mmol) and water (45 mL) was heated to 80 °C for ca. 40 min to afford a clear deep red solution. The solution was cooled and a suspension of 2a (2.2 g, 1.8 mmol) in water (10 mL) was added with the resulting mixture stirred vigorously for 5 hours. The precipitate was collected by filtration through a frit and the resulting solid washed with ethanol (12 mL) and diethyl ether (20 mL) to yield 1b as a free flowing pale brown solid (1.80 g, 67%). ICP-OES data: 9.1 wt% palladium and a palladium loading of 0.86 mmol g⁻¹.

**Synthesis of PdNP@PPh₂-PiILP (1c).** An oven-dried Schlenk was charged with 1b (1.0 g, 0.96 mmol) and ethanol (20 mL) and cooled in an ice bath. A solution of NaBH₄ (0.25 g, 6.7 mmol) in water (4 mL) was added dropwise to the cooled mixture during which the suspension turned black. The resulting reaction mixture was warmed to room temperature and left to stir for 5 hours after which the solid was filtered and washed with water (20 mL), ethanol (20 mL) and Et₂O (20 mL) to yield a black solid (0.51 g, 58%). ICP-OES
data: 10.9 wt% palladium and a palladium loading of 1.1 mmol g\(^{-1}\).

**Synthesis of PdNP@PPh\(_2\)PEGPIILP (2c).** An oven-dried Schlenk was charged with 2b (1.0 g, 0.63 mmol) and ethanol (20 mL). The resulting mixture was cooled in an ice bath and a solution of NaBH\(_4\) (0.16 g, 4.4 mmol) in water (4 mL) added dropwise with stirring. The suspension rapidly turned black and after the addition was complete the flask was allowed to warm to room temperature and the stirred for 5 hours. After this time, the solid was filtered and washed with water (20 mL), ethanol (20 mL) diethyl ether (20 mL) to yield a fine powdery black solid (0.53 g, 58%). ICP-OES data: 3.8 wt% palladium and a palladium loading of 0.36 mmol g\(^{-1}\).

**Synthesis of 1-(4-vinylphenyl)-2,5,8,11,14,17,20,23,26-nonaoxaheptacosane.** A Schlenk flask was charged with NaH (0.20 g, 8.6 mmol) suspended in dry THF (5 mL). Another Schlenk was charged with polyethyleneglycol monomethyl ether (2 g, 5.7 mmol) dissolved dry THF (10 mL) which was added dropwise via cannula transfer over 15 min. After the mixture was stirred at room temperature under \(\text{N}_2\) atmosphere for 1 h, a solution of 4-vinylbenzyl chloride (0.56 mL, 4 mmol) was added dropwise. The reaction mixture was heated at reflux for 16 hours. The mixture was then poured into a 250 mL beaker and neutralized by slow addition of a dilute aqueous HCl. The mixture was then placed in dropping funnel and the organic phase was separated, and the aqueous layer was extracted with diethyl ether four times. The organic phase and extracts were combined and dried over MgSO\(_4\). The solvents were removed under reduced pressure to yield the desired product as a yellow oil (1.84 g, 3.95 mmol, 98% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): \(\delta\) 7.36 (d, 2H), 7.28 (d, 2H), 6.69 (dd, 1H), 5.72 (dd, 1H), 5.21 (dd, 1H), 4.53 (s, 2H), 3.51-3.67 (m, 12H), 3.35 (s, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\), \(\delta\)): 137.85, 136.90, 136.51, 127.90, 126.16, 113.70, 72.90, 71.90, 70.60, 70.51, 69.34, 59.01; Anal. Calc. for C\(_{24}\)H\(_{40}\)O\(_8\) (456.2): C, 63.14; H, 8.83%. Found: C, 63.97; H, 9.44%.

**Synthesis of PPh\(_2\)PEGstyrene (3a).** An oven dried Schlenk was charged with 1-(4-vinylphenyl)-2,5,8,11,14,17,20,23,26-nonaoxaheptacosane (8.67 g, 18.6 mmol), diphenyl(4-vinylphenyl)phosphine (2.8 g, 10 mmol), divinyl benzene (0.19 mL, 1.4 mmol), AlBN (0.22 g, 1.4 mmol), ethanol (35 mL) and THF (50 mL). The resulting mixture was degassed using the freeze thaw method repeatedly six times
before being heated at 80°C for 4 days. After this time, a further equivalent of AIBN (0.22 g, 1.4 mmol) was added and the degassing process repeated before being heated at the same temperature for a further 24 h. The solvent was removed \textit{in vacuo} and the resulting residue was dissolved in dichloromethane (30 mL) and added dropwise to vigorous stirring diethyl ether (350 mL). The solution was left to stir for 45 minutes, allowed to settle then filtered and the resulting solid washed with ether to yield 10.21 g of yellow solid (87%).

**Synthesis of PEGPIILP (4a).** An oven dried Schlenk was charged with 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (2.48 g, 10 mmol), 1-(4-vinylphenyl)-2,5,8,11,14,17,20,23,26-nonaoxaheptacosane (2.5 g, 5.4 mmol), 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (0.25 g, 0.7 mmol) and AIBN (0.11 g, 0.7 mmol) and dissolved in ethanol (60 mL). The resulting mixture was degassed using the freeze thaw method repeatedly six times before being heated at 90°C for 4 days. After this time, a further equivalent of AIBN (0.11 g, 0.7 mmol) was added, the degassing process repeated and the solution heated at the same temperature for a further 24 h. The solvent was removed \textit{in vacuo} and the resulting residue dissolved in dichloromethane (30 mL) and added dropwise to vigorous stirring diethyl ether (350 mL). The solution was stirred for 45 minutes, then left to settle, filtered and the solid washed with ether to afford 4a as a pale yellow solid (4.22 g, 82%).

**Synthesis of PdCl$_2$(MeCN)$_2$@PPh$_2$PEGstyrene (3b).** A round bottomed flask was charged with PPh$_2$PEGstyrene co-polymer 3a (2.0 g, 1.7 mmol) and dissolved in dichloromethane (8 mL). To this solution was added a solution of PdCl$_2$(MeCN)$_2$ (0.48 g, 1.9 mmol) in dichloromethane (15 mL) dropwise. The resulting clear yellow solution was stirred at room temperature for 24 hours during which time a deep orange solid formed. The solid was isolated by filtration and the mother liquor concentrated and added dropwise to an excess of rapidly stirred ethanol to induce precipitation of a second crop of orange solid (2.1 g, 1.46 mmol, 86% yield). ICP-OES data: 1.1 wt% palladium and a palladium loading of 0.10 mmol g$^{-1}$. 
Synthesis of [PdCl$_4$]@PEGPIILP (4b). A round bottomed flask was charged with PEGPIILP 4a (2.0 g, 2 mmol) and water (10 mL) and stirred vigorously while adding a solution of Na$_2$PdCl$_4$ (0.62 g, 2.1 mmol) in water (4 mL). The solution instantly turned yellow and was left to stir at room temperature for a further 24 hrs during which time a red/brown precipitate formed. The reaction mixture was added dropwise to a large volume of acetone (ca. 250 mL) to induce complete precipitation of the product, which was isolated by filtration, washed with diethyl ether (2 x 30 mL) and dried under vacuum for 3 hours to afford 1.84 g of product (76% yield). ICP-OES data: 6.3 wt% palladium and a palladium loading of 0.59 mmol g$^{-1}$.

Synthesis of PdNP@PPh$_2$PEGstyrene (3c). A round bottom flask was charged with PdCl$_2$(MeCN)$_2$@PPh$_2$PEGstyrene (1.0 g, 0.7 mmol) and ethanol (30 mL) and the resulting suspension treated dropwise with a solution of NaBH$_4$ (0.18 g, 4.9 mmol) in water (1 mL). The solution instantly turned from orange to black. After stirring at room temperature for 5 hr the solvent was removal under vacuum and the resulting solid was dissolved in the minimum volume of dichloromethane and filtered through a pad of celite. After removal of the solvent under vacuum the product was obtained as a black solid (0.77 g, 86%). ICP-OES data: 4.4 wt% palladium and a palladium loading of 0.42 mmol g$^{-1}$.

Synthesis of PdNP@PEGPIILP (4c). A solution of [PdCl$_4$]@PEGPIILP (0.33 g, 0.33 mmol) in ethanol (10 mL) was treated dropwise with solution of NaBH$_4$ (0.09 g, 2.3 mmol) in water (0.5 mL). The solution instantly turned from red/orange to black and stirring was continued for a further 5h. After this time the solvent was removed under vacuum and the solid residue dissolved in the minimum volume of dichloromethane and filtered through a pad of celite. The desired product was isolated as a black solid in 78% yield (0.22 g) by removing the solvent under vacuum and drying (0.22 g, 79%). ICP-OES data: 6.7 wt% palladium and a palladium loading of 0.64 mmol g$^{-1}$.
General procedures for catalytic hydrogenation studies

Solvent, pressure, temperature and substrates screening- All hydrogenation reactions were conducted in a 50 mL temperature controlled Parr reactor equipped with a magnetically coupled stirrer and gas ballast. Reactions were conducted in a glass insert for 1 hour with 1 mmol substrate, 0.5-1 mol% catalyst loading, 13 mL solvent, 20 °C and 70 psi unless otherwise stated. After assembling the apparatus, the reactor was pressurized to 70 psi of hydrogen and left to stand for 10 s before releasing the gas through an outlet valve. After this sequence had been repeated ten times the reactor was pressurized to 70 psi and the solution stirred vigorously at the desired temperature. For reactions conducted in organic solvent, the pressure was released, the reaction mixture diluted with ethyl acetate (5 ml) and passed through a short silica plug and the solvent removed. Conversion and selectivity were determined using 1H NMR spectroscopy. For reactions conducted in water, the product was extracted into ethyl acetate (3 x 25 mL) the organic fractions combined, dried over MgSO₄, filtered and the solvent removed. The resulting residue was analysed by 1H NMR spectroscopy to quantify the composition of starting material and products and to determine the selectivity; for each substrate tested an internal standard of 1,3-dinitrobenzene was initially employed to ensure mass balance. For each substrate tested 1H NMR spectra were recorded with relaxation delays of 10, 20 and 30 sec to establish the optimum time to ensure accurate integration of the signals chosen to determine the selectivity and conversion. Well-resolved resonances were used to calculate the yield and conversion by normalising the integration according to the number of protons. For cinnamaldehyde, conversions and selectivities were also determined using gas chromatography with decane as the internal standard (response factors were determined for cinnamaldehyde and each of the possible products) and the results obtained were in good agreement with those determined by 1H NMR spectroscopy. Gas chromatography was performed on a Shimadzu 2010 series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detection using a Supelco Beta DEX column. (injection temp 200°C; column conditions 90 °C for 4 min ramp to 120 at 4 °C/min hold for 20 min ramp to 180 at 7 °C/min hold for 15 min total run time = 56 min): 3-phenyl-propionaldehyde tᵣ = 17.26 min, cinnamaldehyde tᵣ = 29.08 min, 3-phenyl-propanol tᵣ = 42.54 min, cinnamyl alcohol tᵣ = 44.70 min.

Base additive screening studies- Reactions were conducted in a 50 mL temperature controlled Parr reactor equipped with a magnetically coupled stirrer and gas ballast. A glass insert was charged with 1 mmol cinnamaldehyde, 0.5 mol% catalyst, 13 mL water and varying quantities of base ranging from 0.1 mmol – 1 mmol. The reactor was assembled, pressurised with 70 psi of hydrogen, left to stand for 10 sec and then the gas released through an outlet valve. This sequence was repeated ten times after which the reactor was pressurized to 70 psi and the solution stirred vigorously at 20 °C for 75 min. The
product was extracted into ethyl acetate (3 x 25 mL) the organic fractions combined, dried over MgSO₄, filtered and the solvent removed. The resulting residue was analysed by ¹H NMR spectroscopy to quantify the composition of starting material and products and to determine the selectivity; for each substrate tested an internal standard of 1,3-dinitrobenzene was initially employed to ensure mass balance.

Table S1 Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde as a function of catalyst, solvent and temperature

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<th>Conv (%)</th>
<th>TOF (h⁻¹)</th>
<th>Selectivity (%)</th>
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*a Reaction conditions: 1 mmol cinnamaldehyde. 1c (1.0 mol %), 2c (0.5 mol%). 10 mL solvent, 70 psi H₂, tᵢₘₑ = 1 h, temperature. \(^{b}\)Yields and selectivities determined by \(^{1}\)H NMR spectroscopy using nitrobenzene as internal standard. \(^{c}\)1 mol% Pd/C, reaction run at 60 C. \(^{d}\)Reaction time = 30 min. Average of three runs.
Characterization Data for Polymers and Palladium Loaded Polymers
Figure S1  $^1$H NMR spectrum of PPh$_2$PILP (1a)
Figure S2  Solid State $^{13}$C NMR spectrum of PPh$_2$PIILP (1a)
Figure S3  Solid State $^{31}$P NMR spectrum of PPh$_2$PIILP (1a)
Figure S4  SEM image of freshly prepared PPh$_2$PiILP co-polymer (1a)
Figure S5  
TGA curve for PPh$_2$PIILP co-polymer (1a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min$^{-1}$ in air.
Figure S6 FT-IR spectrum of freshly prepared PPh₂PIILP co-polymer (1a)

Varian Resolutions

PPh₂PIILP

Wavenumber cm⁻¹

Transmission
Figure S7  
$^1$H NMR spectrum of PPh$_2$PEGIILP (2a)
Figure S8  Solid state $^{13}$C NMR spectrum of PPh$_2$PEGPIILP (2a)
Figure S9  Solid state $^{31}$P NMR spectrum of PPh$_2$PEGPILP (2a)
Figure S10  SEM image of freshly prepared PPh$_2$PEGPIILP co-polymer (2a)
Figure S11  TGA curve for PPh$_2$PEGPIILP co-polymer (2a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min$^{-1}$ in air.
Figure S12  FT-IR spectrum of freshly prepared PPh$_2$PEGPIILP co-polymer (2a)
Figure S13  $^1$H NMR spectrum of PPh$_2$PEGstyrene (3a)
Figure S14  Solid state $^{13}$C NMR spectrum of PPh$_2$PEGstyrene (3a)
Figure S15  Solid state $^{31}$P NMR spectrum of PPh$_2$PEGstyrene (3a)
Figure S16  SEM images of freshly prepared PPh$_2$PEGstyrene (3a)
Figure S17  TGA curve for PPh$_2$PEGstyrene (3a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min$^{-1}$ in air.
Figure S18  FT-IR spectrum of freshly prepared PPh$_2$PEGstyrene (3a)
Figure S19  $^1$H NMR spectrum of PEGPIILP co-polymer 4a
Figure S20  Solid state $^{13}$C NMR spectrum of PEGPILP co-polymer 4a
Figure S21  SEM images of freshly prepared PEGPIILP co-polymer 4a
Figure S22  TGA curve for PEGPIILP copolymer (4a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min⁻¹ in air.
Figure S23 FT-IR spectrum of freshly prepared PEGPIILP (4a)
Figure S24  Solid state $^{13}$C NMR spectrum of [PdCl$_4$]@PPh$_2$PIILP (1b)
Figure S25  Solid state $^{31}$P NMR spectrum of [PdCl$_4$]@PPh$_2$PIILP (1b)
Figure S26 SEM images of freshly prepared [PdCl$_4$]@PPh$_2$PIILP (1b)
Figure S27: FT-IR spectrum of freshly prepared [PdCl₄]@PPh₂PIILP (1b)
Figure S28  Pd 3d core level XPS spectrum of [PdCl₄]@PPh₂PILP (1b) referenced to the hydrocarbon C 1s
Figure S29  Solid state $^{13}$C NMR spectrum of [PdCl$_4$]@PPh$_2$PEGPIILP (2b)
Figure S30  Solid state $^{31}$P NMR spectrum of [PdCl$_4$]@PPh$_2$PEGIIILP (2b)
Figure S31  SEM images of freshly prepared [PdCl₄]@PPh₃PEGPIILP (2b)
Figure S32 FT-IR spectrum of freshly prepared [PdCl₂@PPh₂PEGIIILP (2b)]

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Figure S33  Pd 3d core level XPS spectrum of [PdCl₄]@PPh₂PEGPIILP (2b) referenced to the hydrocarbon C 1s
Figure S34: Solid state $^{13}$C NMR spectrum of [PdCl$_2$(MeCN)$_2$]@PPh$_2$PEGstyrene (3b)
Figure S35  Solid state $^{31}$P NMR spectrum of [PdCl$_2$(MeCN)$_2$]@PPh$_2$PEGstyrene (3b)
Figure S36  SEM images of freshly prepared [PdCl$_2$(MeCN)$_2$]@PPh$_2$PEGstyrene (3b)
Figure S37  FT-IR spectrum of freshly prepared [PdCl₂(MeCN)₂]@PPh₃PEGstyrene (3b)
Figure S38  Pd 3d core level XPS spectrum of [PdCl$_2$(MeCN)$_2$]@PPh$_2$PEGstyrene (3b) referenced to the hydrocarbon C 1s
Figure S39  Solid state $^{13}$C NMR spectrum of [PdCl$_4$]@PEGPIILP (4b)
Figure S40  SEM images of freshly prepared [PdCl$_4$]@PEGPIILP (4b)
Figure S41  FT-IR spectrum of freshly prepared [PdCl$_4$]@PEGPIILP (4b)

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Figure S42  Pd 3d core level XPS spectrum of [PdCl₄]@PEGPIILP (4b) referenced to the hydrocarbon C 1s
Figure S43  Solid state $^{13}$C NMR spectrum of PdNP@PPh$_2$PIILP (1c)
Figure S44  Solid state $^{31}$P NMR spectrum of PdNP@PPh$_2$PIILP (1c)
Figure S45  SEM images of freshly prepared PdNP@PPh₃PIILP (1c)
Figure S46  FT-IR spectrum of freshly prepared PdNP@PPh$_2$PIILP (1c)
Figure S47  Pd 3d core level XPS spectrum of [PdNP@PPh$_2$PIILP (1c) referenced to the hydrocarbon C 1s
Figure S48 (a-d) TEM images of PdNP@PPh$_2$PIILP (1c), (e) Energy dispersive X-ray spectrum of 1c confirming the presence of Pd in the sample (the Cu peak is due to the TEM gird holder) and (f) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white).
Figure S49  X-ray powder diffraction pattern of PdNP@PPh₂PILP (1c)
Figure S50  Solid state $^{13}$C NMR spectrum of PdNP@PPh$_2$-PEGPIILP (2c)
Figure S51  Solid state $^{31}$P NMR spectrum of PdNP@PPh$_2$-PEGPIILP (2c)
Figure S52  SEM images of freshly prepared PdNP@PPh$_2$-PEGPIILP (2c)
Figure S53  
**FT-IR spectrum of freshly prepared PdNP@PPh$_2$-PEGIIILP (2c)**

*Varian Resolutions*
Figure S54  Pd 3d core level XPS spectrum of PdNP@PPh₂-PEGPIILP (2c) referenced to the hydrocarbon C 1s
Figure S55  (a-d) TEM image of PdNP@PPh$_2$-PEGPIILP (2c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)
X-ray powder diffraction pattern of PdNP@PPh₂-PEGPIILP (2c)

XRD spectrum shows no Pd peaks but some sodium chloride formed from the reduction step.
Figure S57  Solid state $^{13}$C NMR spectrum of PdNP@PPh$_2$PEGstyrene (3c)
Figure S58  Solid state $^{31}$P NMR spectrum of PdNP@PPh$_2$PEGstyrene (3c)
Figure S59  SEM images of freshly prepared PdNP@PPh$_2$PEGstyrene (3c)
Figure S60  FT-IR spectrum of freshly prepared PdNP@PPh₂PEGstyrene (3c)
Figure S61  Pd 3d core level XPS spectrum of PdNP@PPh₂PEGstyrene (3c) referenced to the hydrocarbon C 1s
Figure S62 (a-d) TEM image of PdNP@PPh$_2$PEGstyrene (3c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white).
Figure S63  
Solid state $^{13}$C NMR spectrum of PdNP@PEGPIILP (4c)

Current Data Parameters
NAME: sdc_201411101
EXPER : 13
PROCNO: 1

F2 - Acquisition Parameters
Data: 20111115
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PULPROG: spin
NS: 750
B1H: 39682.539 Hz
AQ: 0.2139352 sec
TE: 158.0 K
D1: 5.0000000000 sec

Channel F1
SFQ: 1
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DFQ: 150.00000000 W

Channel F2
SFQ: 800.000000000 MHz
NSC: 15000.00 usw
DFQ: 150.00000000 W

F2 - Processing parameters
SF: 2048
DF: 100.000000000 MHz
LM: 0
LB: 0
LB: 0
LB: 1.00

1750/7271, PdNP@MnstyFEG @ 10kHz, RT, EH

S81
Figure S64  SEM images of freshly prepared PdNP@PEG-PIILP (4c)
Figure S65  FT-IR spectrum of freshly prepared PdNP@PEGPIILP (4c)
Figure S66 (a-d) TEM image of PdNP@PEGPIILP (4c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)
Figure S67  X-ray powder diffraction pattern of PdNP@PEGPIILP (4c)

XRD scattering pattern shows some sodium chloride from reduction step as well as broadened peaks for Pd indicating formation of nanoparticles.
Figure S68  Sample $^1$H NMR spectrum for calculating the selectivity from the hydrogenation of trans-cinnamaldehyde$^1$

Sample spectrum used to determine selectivity; ▪ cinnamaldehyde, ● 3-phenyl-propionaldehyde, ◊ ethyl acetate
Figure S69  Sample $^1$H NMR spectrum for calculating selectivity from the hydrogenation of trans-2-pentenal$^2$

Sample spectrum used to determine selectivity; ● trans-2-pentenal, ◊ pentan-1-ol
Figure S70  Sample $^1$H NMR spectrum for calculating the selectivity from the hydrogenation of 3-(furan-2-yl)acrolein$^3$

Sample spectrum used to determine selectivity; ▪ 3-(furan-2-yl)acrolein, ● 3-(2-furyl)propanal, □ 3-(tetrahydrofuran-2-yl)propanal, ○ 3-furan-2-yl-propan-1-ol, ◊ ethyl acetate
Figure S71  Sample $^1$H NMR spectrum for calculating the selectivity from the hydrogenation of 2,6,6-trimethyl-2-cyclohexene-1,4-dione$^4$

Sample spectrum used to determine selectivity; ⋄ 2,6,6-trimethyl-2-cyclohexene-1,4-dione, ● 2,6,6-trimethyl-1,4-cyclohexanediode (levodione), □ 4-hydroxy-3,3,5-trimethylcyclohexanone, ◊ 4-hydroxy-3,5,5-trimethyl-cyclohex-2-enone.
Figure S72  Sample $^1$H NMR spectrum for calculating the selectivity from the hydrogenation of trans-4-phenyl-3-buten-2-one$^5$

Sample spectrum used to determine selectivity; ● 4-phenylbutan-2-one, ◊ ethyl acetate, □ ethanol
Figure S73  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of *trans*-chalcone$^6$

Sample spectrum used to determine selectivity; ● 1,3-diphenylpropan-1-one
Figure S74  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of citral$^7$

Sample spectrum used to determine selectivity; ● 3,7-dimethyl-oct-6-enal, ◊ ethyl acetate
Figure S75  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of cyclohexenone$^6$

Sample spectrum used to determine selectivity; ● cyclohexanone, ◊ ethyl acetate
Figure S76  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of trans-4-methoxycinnamaldehyde\textsuperscript{9}

Sample spectrum used to determine selectivity; • trans-4-methoxycinnamaldehyde, ● 3-(4-methoxyphenyl)propionaldehyde,
○ 3-(4-dimethylaminophenyl)-propan-1-ol, ◊ ethyl acetate
Figure S77  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of cinnamonic acid.

Sample spectrum used to determine selectivity; ▪ cinnamonic acid, ● 3-phenylpropan-1-amine, ◊ ethyl acetate
Figure S78  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of 4-dimethylaminocinnamaldehyde$^{11}$

Sample spectrum used to determine selectivity;  ● 4-dimethylaminocinnamaldehyde, ● 3-(4-dimethylaminophenyl)propionaldehyde,
○ 3-(4-dimethylaminophenyl)-propan-1-ol, ◊ ethyl acetate
Figure S79  Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of ethyl cinnamate$^{12}$

Sample spectrum used to determine selectivity; ● ethyl cinnamate, ● ethyl 3-phenylpropionate, ◊ ethyl acetate
Figure S80  
Sample $^1$H NMR spectrum for calculating the selectivity for the hydrogenation of 3-methyl-2-butenal$^{13}$

Sample spectrum used to determine selectivity; ● 3-methylbutyraldehyde, ◊ ethyl acetate; water
Figure S81  Comparison of the $^1$H NMR spectrum and GC trace of the reaction mixtures obtained from the hydrogenation of cinnamaldehyde using catalyst 2a and showing a reliable correlation at high conversion and selectivity (100 conversion, 99% selectivity). (a) $^1$H NMR spectrum, (b) GC trace

- ● 3-phenyl-propionaldehyde, ○ 3-phenyl-1-propanol

(a)

(b)
Comparison of the $^1$H NMR spectrum and GC trace of the reaction mixtures obtained from the hydrogenation of cinnamaldehydes using catalyst 2a and showing a reliable correlation at high conversion and reduced selectivity when the reaction was conducted with less than one equivalent of base (100% conversion, 96% selectivity). (a) $^1$H NMR spectrum, (b) GC trace

- 3-phenyl-propionaldehyde, ○ 3-phenyl-1-propanol

(a) [NMR spectrum image]

(b) [GC trace image]
Figure S823  (a-d) TEM images of PdNP@PPh2-PEGPIILP (2c) and (e-f) histograms of particle size (diameter, nm) after 1 (top) and 5 (bottom) reaction cycles. Scale bars 25 nm (black) and 5 nm (white)
References


