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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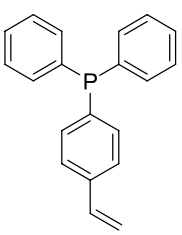
Contents

Experimental

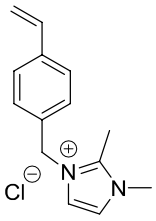
General Comments. All reagents were purchased from commercial suppliers and used without further purification. $Na_2[PdCl_4]$ was generated *in situ* immediately prior to use as previously described. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on JEOL LAMBDA-500 or ECS-400 instruments. Solid-state ^{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 AlKα 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,



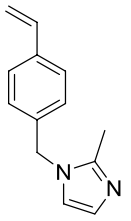
which was subsequently cooled to 0°C. 4-chlorostyrene (4.7 mL, 39.3 mmol) was dissolved in anhydrous THF (35 mL) in a separate round bottom flask, and 20% of this solution was added dropwise to the Mg turnings to initiate Grignard formation. The remaining solution was added so to maintain a gentle reflux 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 $MgSO_4$, 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). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25-7.29 (m, 14H, ArH), 6.63 (dd, J_{HH} = 17.5, J_{HH} = 10.9 Hz, 1H, ArC*H*CHH), 5.70 (d, J_{HH} = 17.5, 1H, ArCHC*H*H) 5.20 (d, J_{HH} = 10.9, 1H, ArCHCH*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 137.95, 137.23, 137.09, 136.4 (Ar) 134.09, 133.86, 133.83, 133.60 (ArH) 128.75 (CH*C*H-$_2$), 126.35 (*C*H*C*H_2); ^{31}P NMR (121 MHz, $CDCl_3$, δ): -5.78.

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%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.76 (3H, s), 3.95 (3H, s), 5.25 (1H, d, J = 9 Hz), 5.56 (2H, s), 5.76 (1H, d, J = 12 Hz), 6.60-6.70 (1H, dd, J = 9 Hz, 12 Hz), 7.28-7.44 (4H, m), 7.44-7.77 (2H, q); ^{13}C NMR (75 MHz $CDCl_3$, δ): 10.79, 35.76, 51.93, 115.93, 121.94, 122.91, 126.94, 128.47, 132.45, 135.71, 138.19, 144.02. Anal. Calc. for $C_{14}H_{17}ClN_2$ (248.1): C, 67.60; H, 6.89; N, 11.27%. Found: C, 67.94; H, 7.22; N, 11.51%.



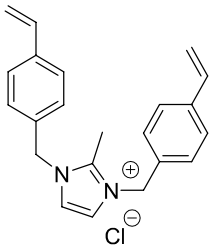
Synthesis of 2-methyl-1-(4-vinylbenzyl)-1H-imidazole. An oven-dried Schlenk flask was allowed to cool to room temperature and charged with a sodium hydride (0.73 g, 30.4 mmol) which was dissolved

in dry DMF (20 mL). The reaction was stirred and cooled to 0°C. 2-methyl imidazole (3.0 g, 36.5 mmol



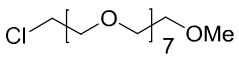
was added resulting in the liberation of gas and on exothermic reaction, once the exothermic subsided. The reaction mixture was cooled in an ice bath, then 4-chloromethyl styrene (4.29 mL, 30.4 mmol) was added dropwise. The reaction was heated to 75°C for 30 min. The reaction mixture was poured onto H_2O (250 mL) and the product extracted with ethyl acetate (2 × 100mL). The combined extracts wear washed with H_2O (180 mL) and then brine (50 mL) before being extracted with 6N HCl (2 × 25mL). The aqueous layer was washed 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 $MgSO_4$ and the solvent removed under reduced pressure to afford the product as a pale yellow oil in 92% yield (5.55 g). ^{1}H NMR (300 MHz $CDCl_3$, *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), 7.20-7.22 (2H, d, *J* = 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, *δ*): 12.85, 49.30, 114.32, 119.83, 126.60, 126.81, 126.96, 137.14, 135.77, 135.98, 144.77; Anal. Calc. for $C_{13}H_{14}N_2$ (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 ethyl acetate. 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). ^{1}H NMR (300 MHz, $CDCl_3$, *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); ^{13}C NMR (75 MHz, $CDCl_3$, *δ*): 11.42, 52.65, 113.28, 122.83, 128.51, 128.87, 133.65, 134.14, 136.09, 153.07; Anal. Calc. for $C_{22}H_{23}ClN_2$ (350.1): C, 75.31; H, 6.61; N, 7.98%. Found: C, 75.67; H, 9.93; N, 8.19%.

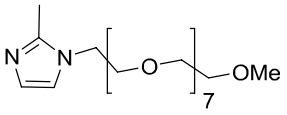
Synthesis of methyl octaethylene glycol chloride. Polyethylene glycol monomethyl ether (7.0 g,



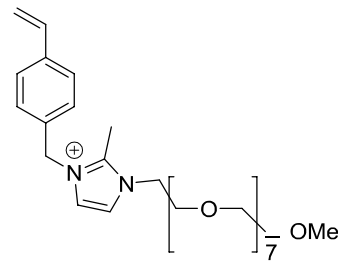
20 mmol), pyridine (3.16 g, 40 mmol) and dry toluene (40 mL) were added to a Schlenk flask under a nitrogen atmosphere. The solution was stirred and

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), which merged 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 × 30 mL), and then dried over anhydrous $MgSO_4$. The solvent was then evaporated and the product dried *in vacuo* to give a pale-yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, *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); ^{13}C NMR (75 MHz, $CDCl_3$, *δ*): 71.79, 71.20, 70.50, 70.44, 70.35, 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-methyl-imidazole (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 $MgSO_4$, filtered and the solvent removed *in vacuo* to yield a yellow/brown oil (2.43 g, 18.9 mmol) in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$, *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); ^{13}C NMR (75 MHz, $CDCl_3$, *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 $C_{21}H_{40}N_2O_8$ (448.3): C, 56.23; H, 8.99; N, 6.25%. Found: C, 58.02; H, 9.89; N, 7.01%.

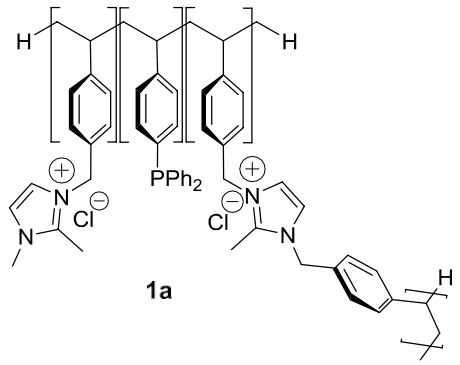


Synthesis of 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride. 1-bromomethyl-4-vinyl-benzene (0.31 g, 1.57 mmol) was added to a solution of 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-1H-imidazole (0.55 g, 1.31 mmol) dissolved in anhydrous 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. ^{1}H NMR (300 MHz, $CDCl_3$, *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,



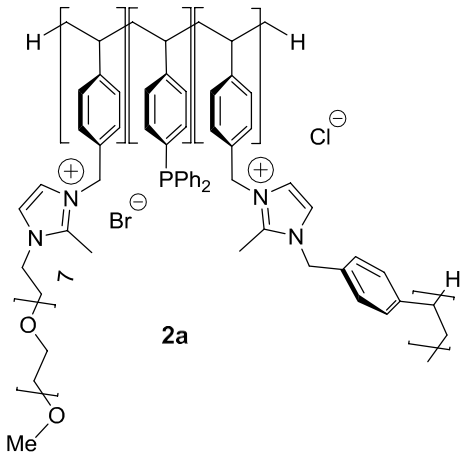
19H), 3.34 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 144.56, 144.53, 137.81, 135.57, 132.52, 132.49, 128.32, 128.17, 128.14, 126.67, 121.93, 121.87, 121.74, 114.89, 71.55, 71.47, 70.19, 70.14, 70.07, 69.95, 69.13, 58.65, 58.62, 51.52, 48.61, 10.99, 10.97, 10.95; Anal. Calc. for $C_{30}H_{49}ClN_2O_8$ (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%).



1a

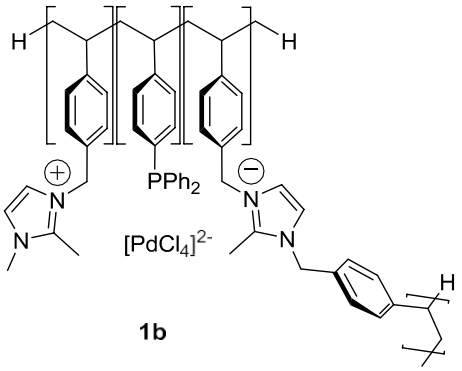
Synthesis of PPh_2-PEGPIILP (2a). An oven dried Schlenk was charged with 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride (3.61 g, 6.38 mmol), diphenyl(4-vinylphenyl)phosphine (1.0 g, 3.47 mmol), 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium 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



2a

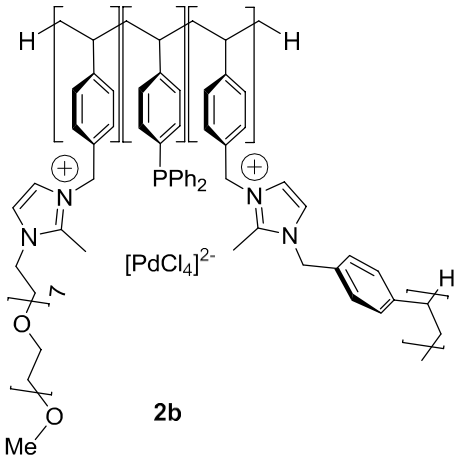
to settle. The mixture was filtered and the solid washed with ether to yield a yellow/brown solid (4.2 g, 89%).

Synthesis of $[PdCl_4]$@PPh_2-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}.



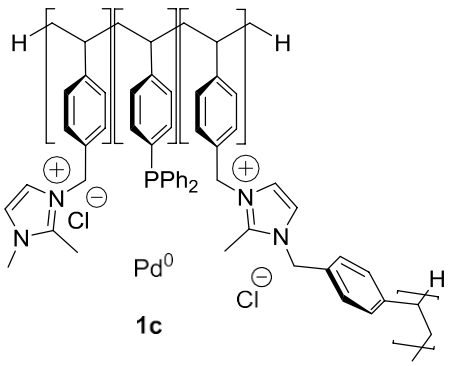
1b

Synthesis of $[PdCl_4]$@PPh_2-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}.



2b

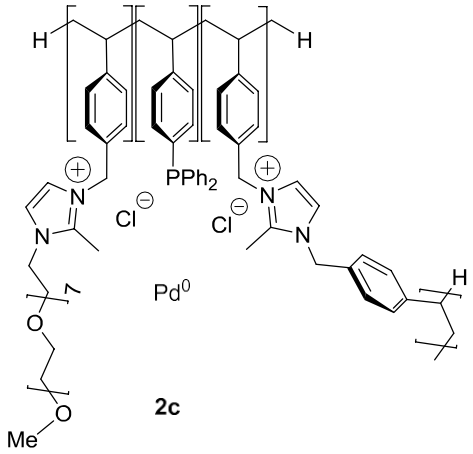
Synthesis of PdNP@PPh_2-PIILP (1c). An oven-dried Schlenk was charged with **1b** (1.0 g, 0.96 mmol) and ethanol (20 mL) and cooled in an ice bath. A solution of $NaBH_4$ (0.25 g, 6.7 mmol) in water (4 mL) was added dropwise to the cooled mixture during which the suspension turned black. The resulting 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 Et_2O (20 mL) to yield a black solid (0.51 g, 58%). ICP-OES



1c

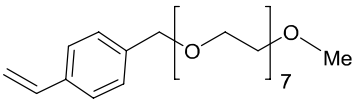
data: 10.9 wt% palladium and a palladium loading of 1.1 mmol g^{-1}.

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 (20mL), 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}.



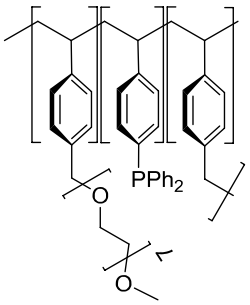
2c

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 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, $CDCl_3$, *δ*): δ 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, $CDCl_3$, δ): 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%.



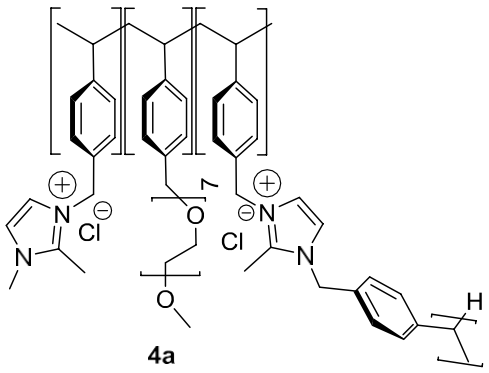
Synthesis of PPh_2PEGstyrene (3a). An oven dried Schlenk was charged with 1-(4-vinylphenyl)-2,5,8,11,14,17,20,23,26-nonaoxaheptacosane (8.67 g, 18.6 mmol), diphenyl(4-vinylphenyl)phosphine (2.8 g, 10 mmol), divinyl benzene (0.19 mL, 1.4 mmol), AIBN (0.22 g, 1.4 mmol), ethanol (35 mL) and THF (50 mL). 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 heated at the same temperature for a further 24 h. The solvent was removed *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%).



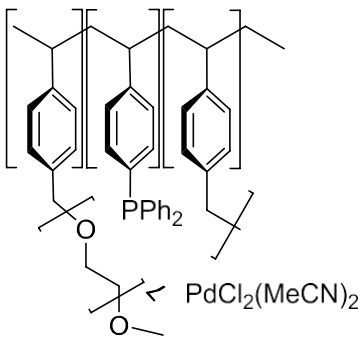
3a

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 *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%).



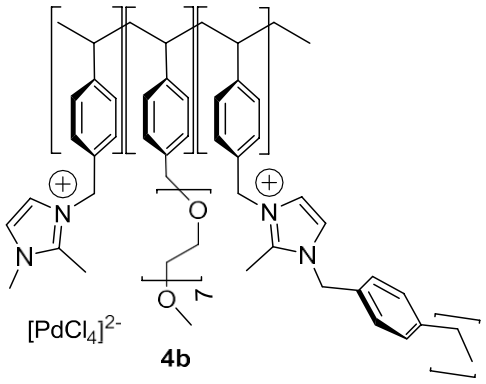
4a

Synthesis of $PdCl_2(MeCN)_2$@PPh_2PEGstyrene (3b). A round bottomed flask was charged with PPh_2PEGstyrene 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}.



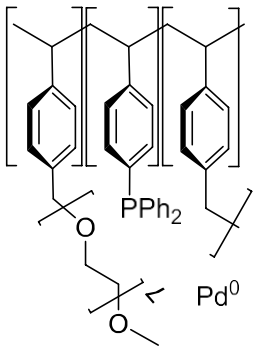
3b

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_2PdCl_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}.



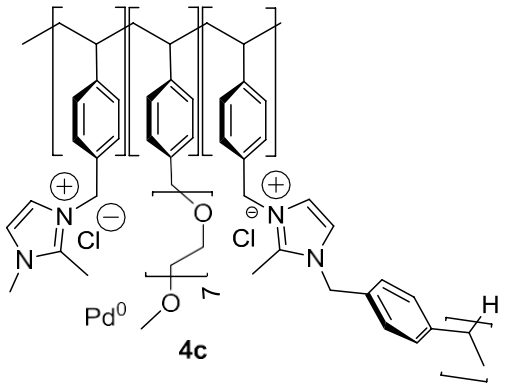
4b

Synthesis of PdNP@PPh_2PEGstyrene (3c). A round bottom flask was charged with $PdCl_2(MeCN)_2$@PPh_2PEGstyrene (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}.



3c

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}.



4c

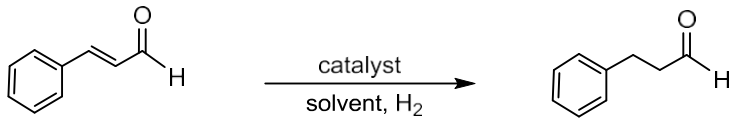
General procedures for catalytic hydrogenation studies

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 ^{1}H NMR spectroscopy. For reactions conducted in water, the product was extracted into ethyl acetate (3 x 25 mL) the organic fractions combined, dried over $MgSO_4$, filtered and the solvent removed. The resulting residue was analysed by ^{1}H 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 ^{1}H 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 ^{1}H 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 t_r = 17.26 min, cinnamaldehyde t_r = 29.08 min, 3-phenyl-propanol t_r = 42.54 min, cinnamyl alcohol t_r = 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 $MgSO_4$, 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[a]



Catalyst	Solvent	Temp (°C)	Conv (%)[b]	TOF (h^{-1})	Selectivity (%)[b]
1c	toluene	25	0	0	0
2c	toluene	25	23	46	78
1c	ethanol	25	57	57	69
2c	ethanol	25	54	108	76
1c	hexane	25	35	35	58
2c	hexane	25	52	104	82
1c	ethyl acetate	25	10	10	58
2c	ethyl acetate	25	29	58	85
1c	2-MeTHF	25	22	22	48
2c	2-MeTHF	25	35	70	62
1c	water	25	75	75	74
2c	water	25	81	162	85
1c	water/ethanol	25	82	82	72
2c	water/ethanol	25	75	150	74
Pd/C	Water[c]	25	60	60	67
1c	Water[d]	20	25	50	85
2c	Water[d]	20	38	152	85
1c	Water[d]	30	35	70	84
2c	Water[d]	30	43	172	88
1c	Water[d]	40	41	82	84
2c	Water[d]	40	65	260	92
1c	Water[d]	50	53	106	91
2c	Water[d]	50	77	308	92
1c	Water[d]	60	57	114	91
2c	Water[d]	60	82	328	92

[a] Reaction conditions: 1 mmol cinnamaldehyde, **1c** (1.0 mol %), **2c** (0.5 mol%), 10 mL solvent, 70 psi H_2, time = 1 h, temperature. [b] Yields and selectivities determined by ^1H 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_2PIILP (1a)**

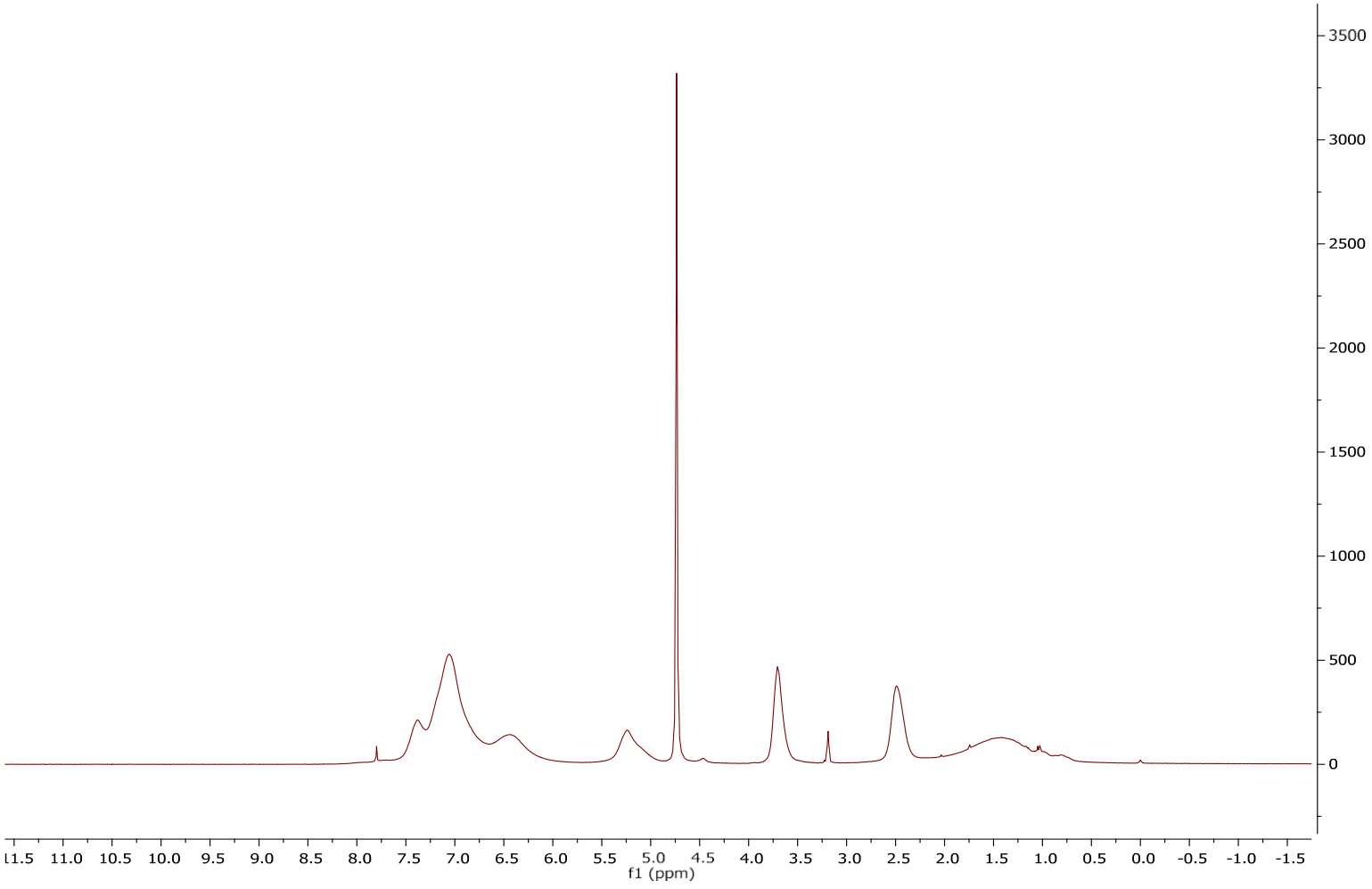


Figure S2 **Solid State ^{13}C NMR spectrum of PPh_2PIILP (1a)**

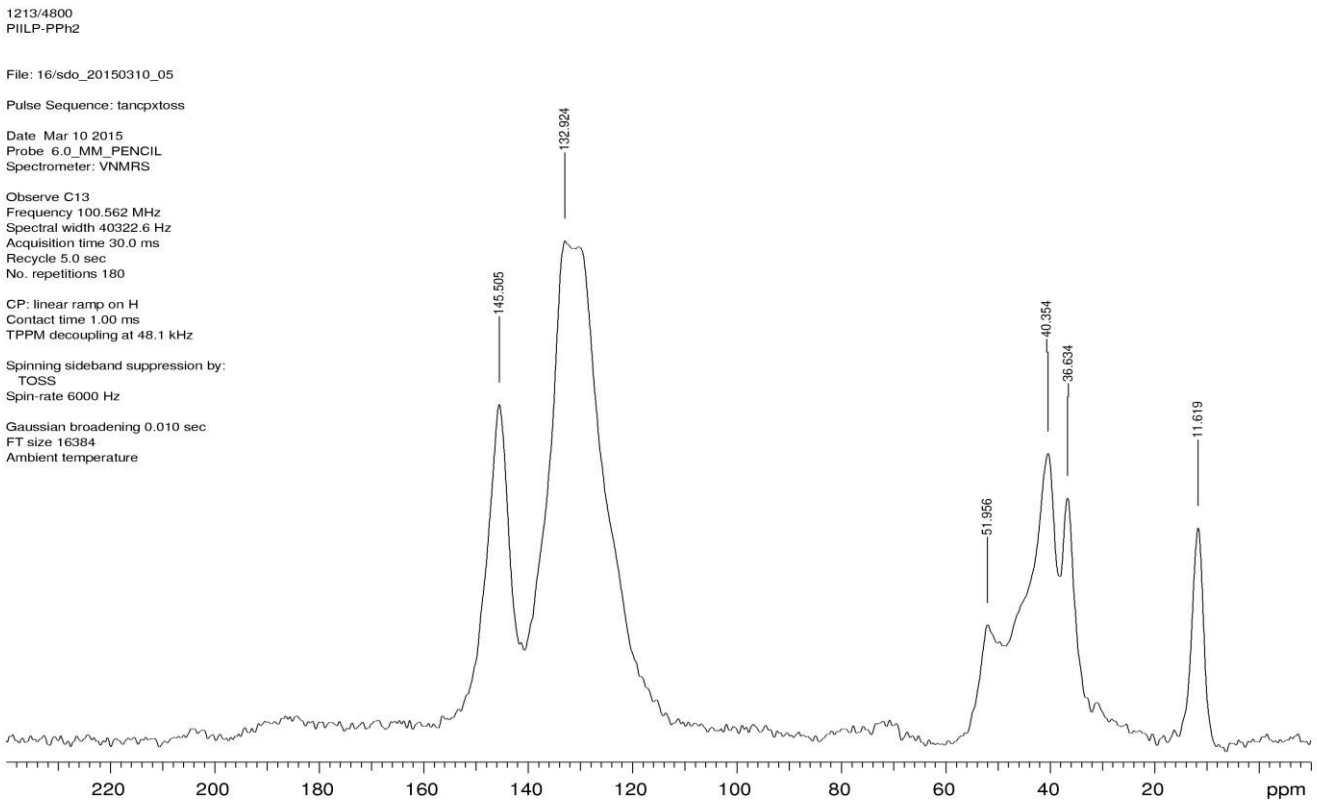


Figure S3 **Solid State ^{31}P NMR spectrum of PPh_2PIILP (1a)**

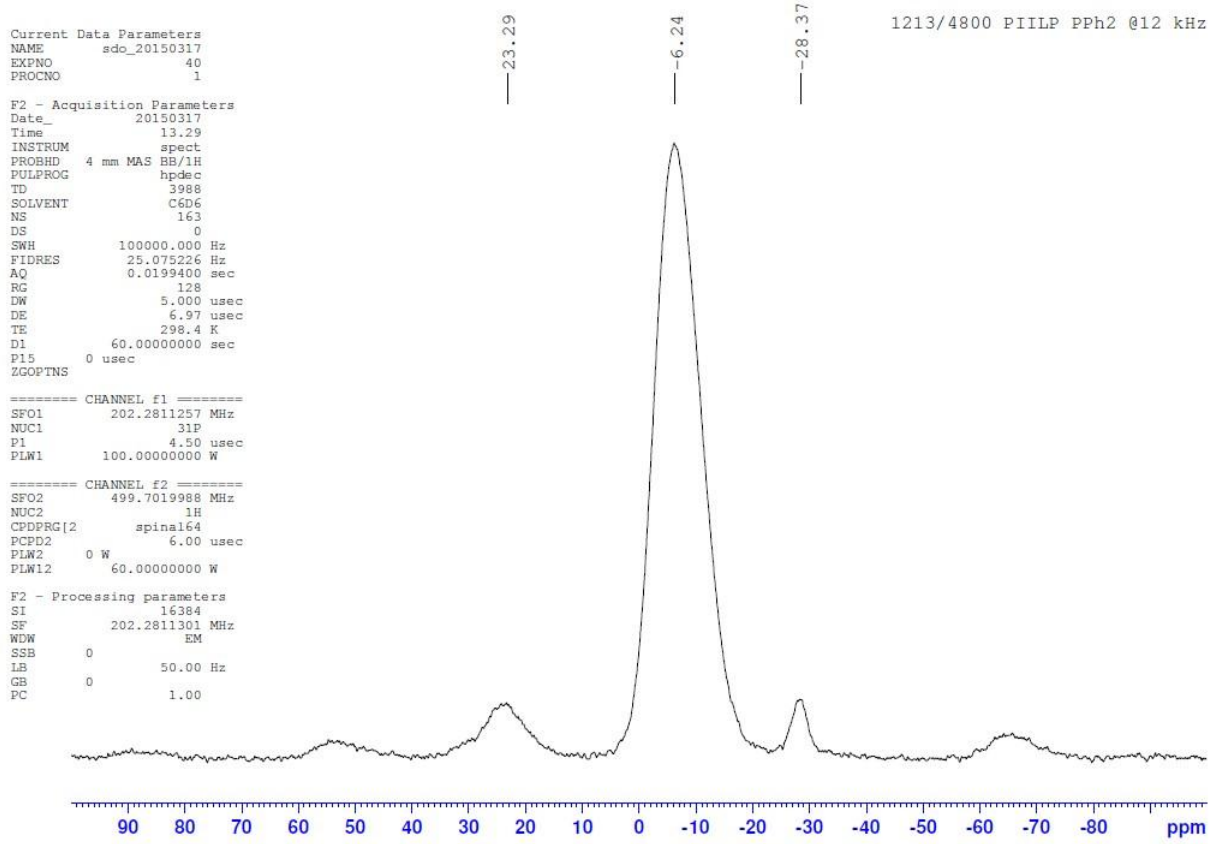
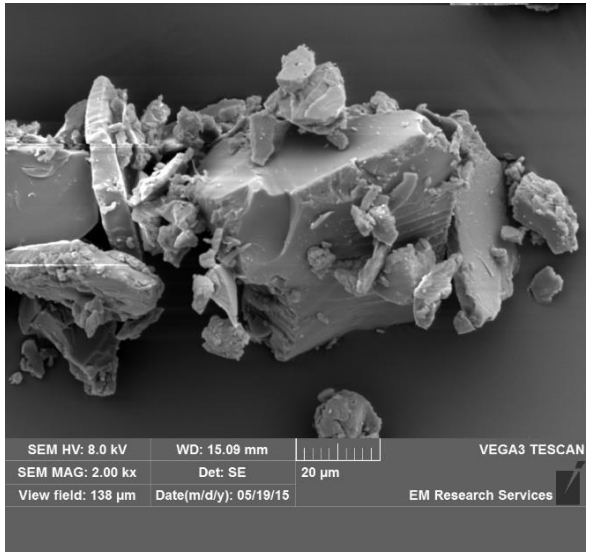


Figure S4 **SEM image of freshly prepared PPh_2PIILP co-polymer (1a)**



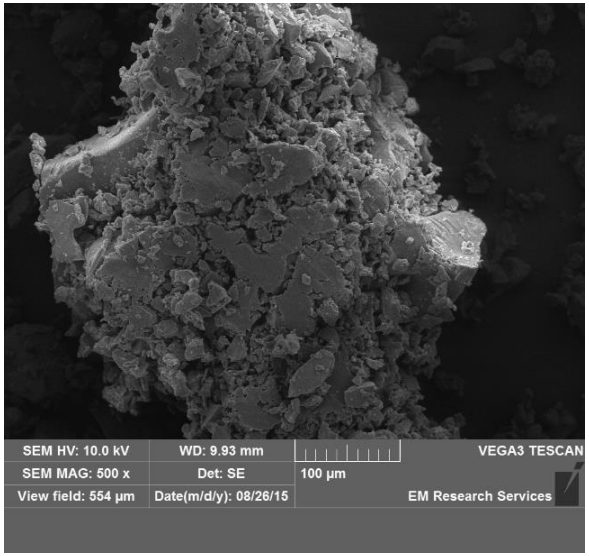


Figure S5 **TGA curve for PPh_2PIILP co-polymer (1a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air**

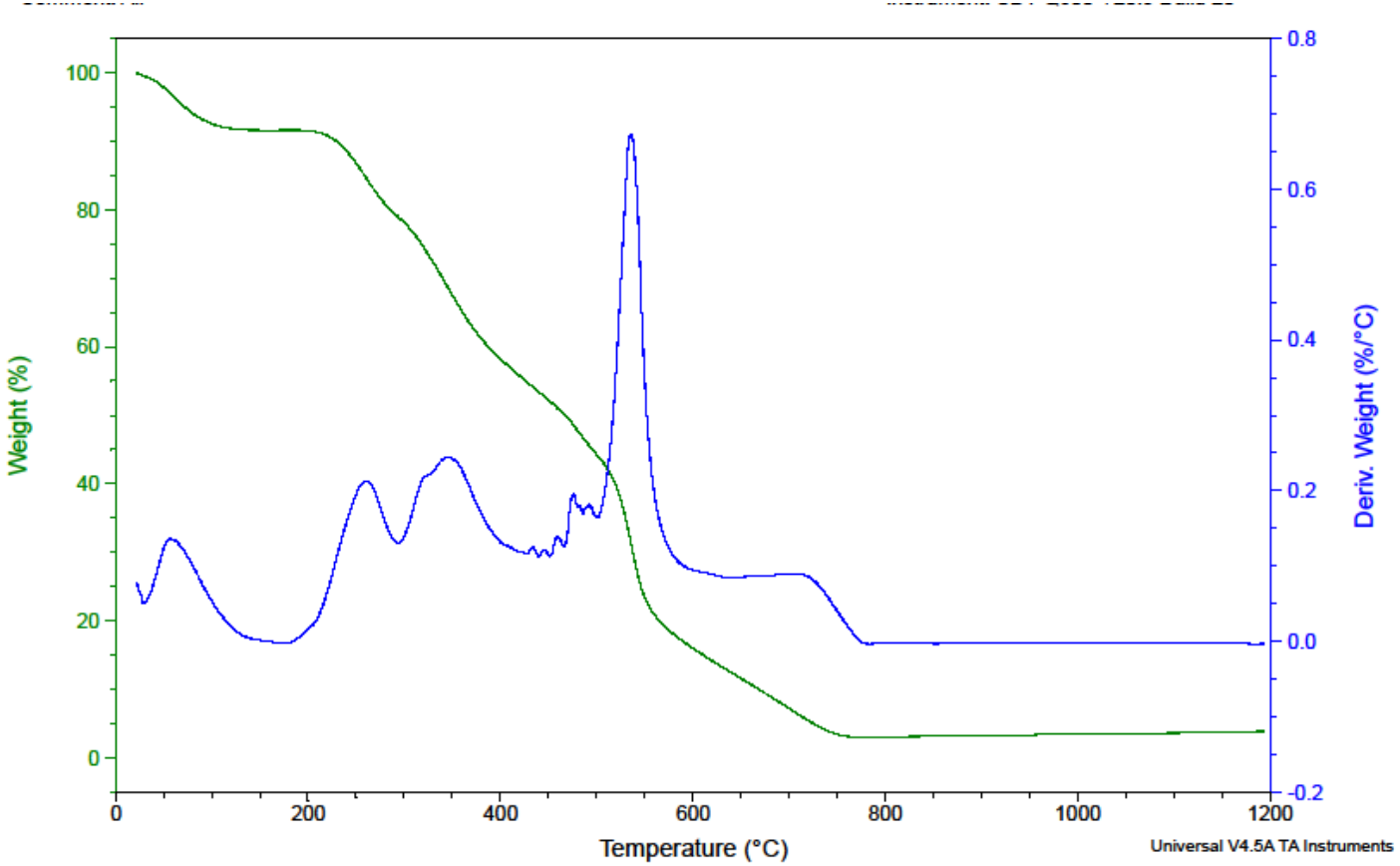


Figure S6 **FT-IR spectrum of freshly prepared PPh_2PIILP co-polymer (1a)**

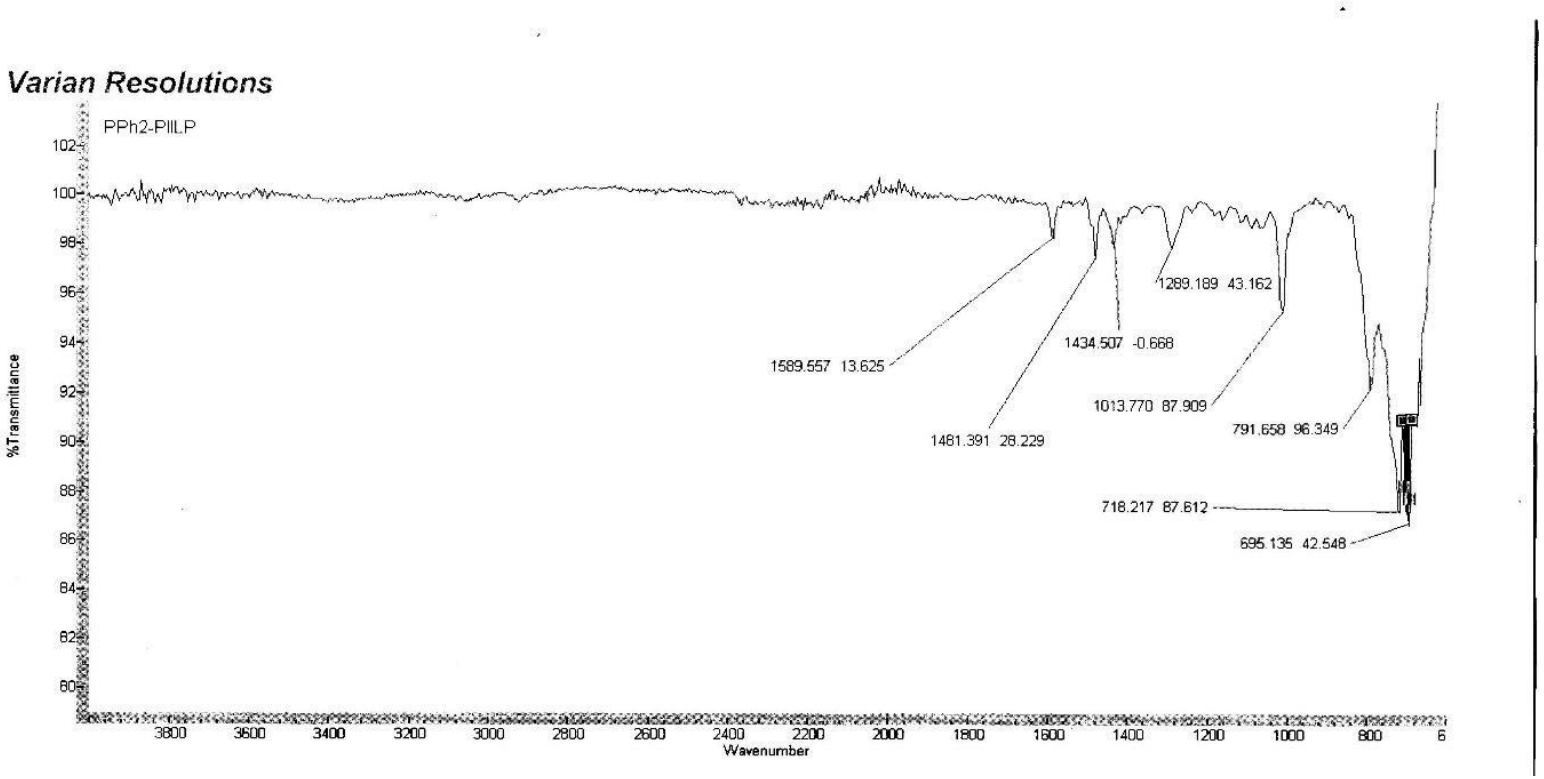


Figure S7 **^{1}H NMR spectrum of $PPh_2PEGIILP$ (2a)**

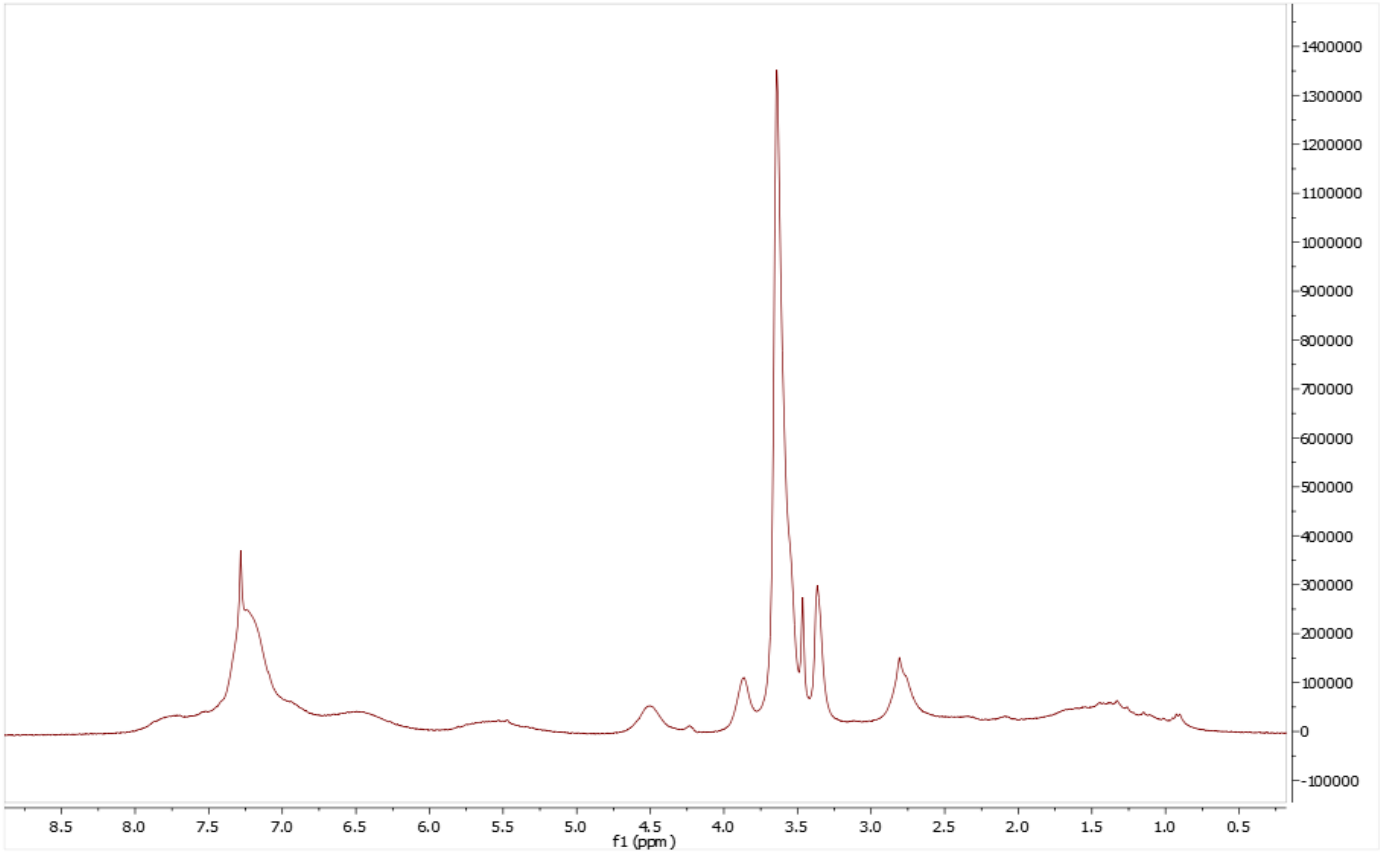


Figure S8 **Solid state ^{13}C NMR spectrum of $PPh_2PEGPIILP$ (2a)**

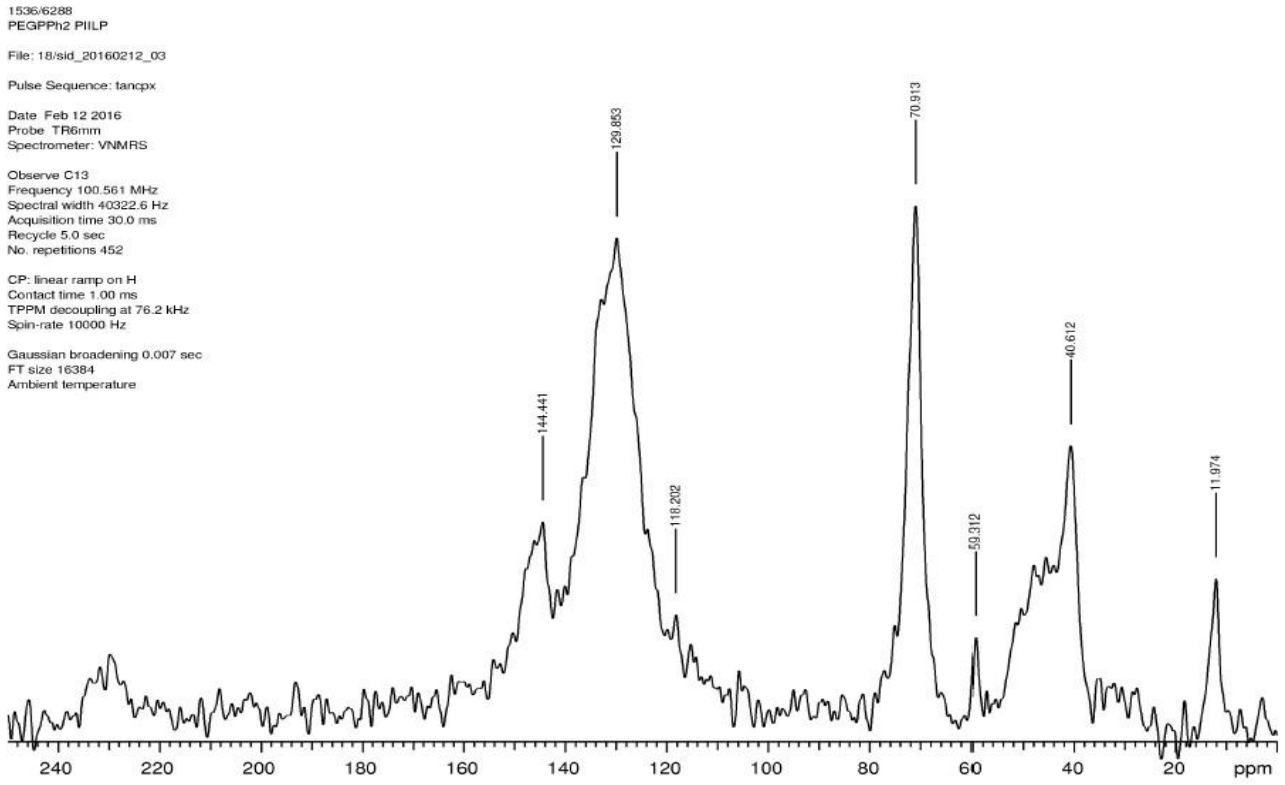


Figure S9 **Solid state ^{31}P NMR spectrum of $PPh_2PEGPIILP$ (2a)**

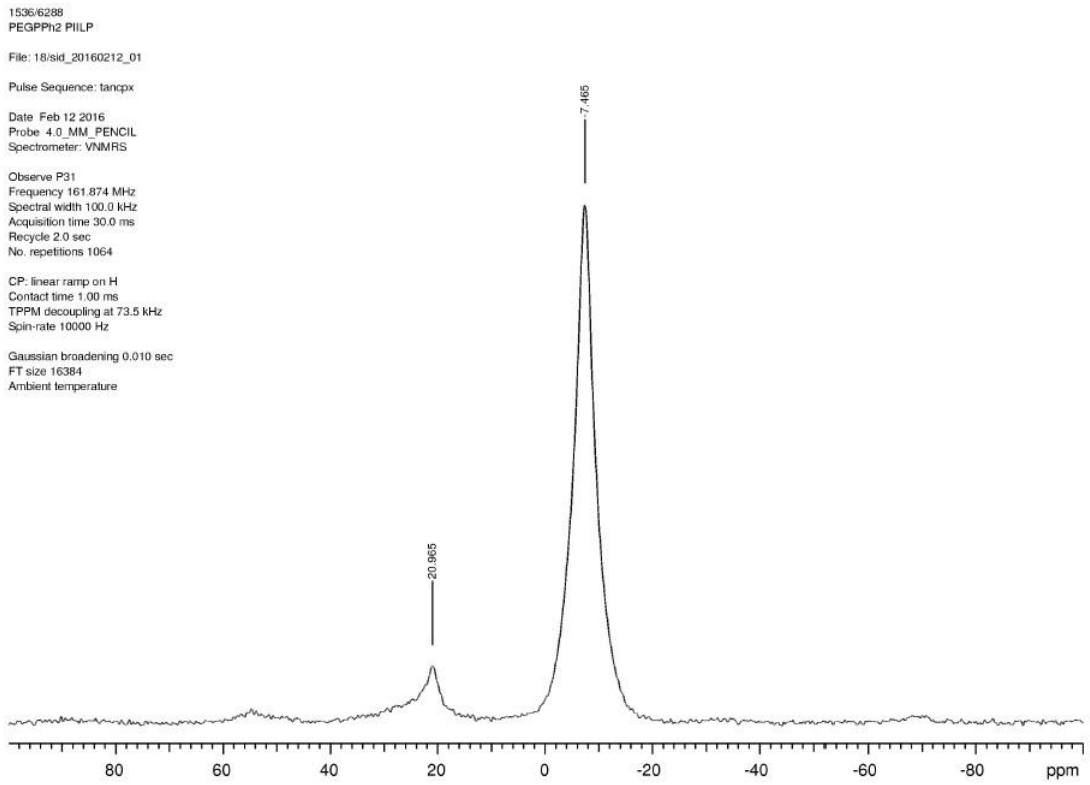


Figure S10 **SEM image of freshly prepared PPh_2PEGPIILP co-polymer (2a)**

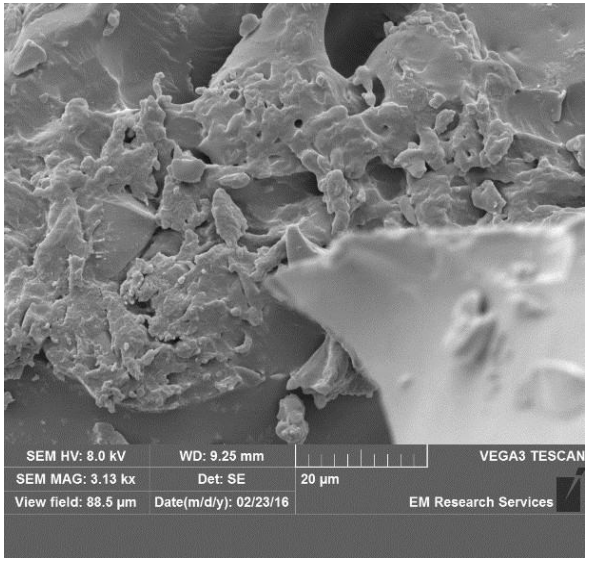


Figure S11 **TGA curve for $PPh_2PEGPIILP$ co-polymer (2a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air**

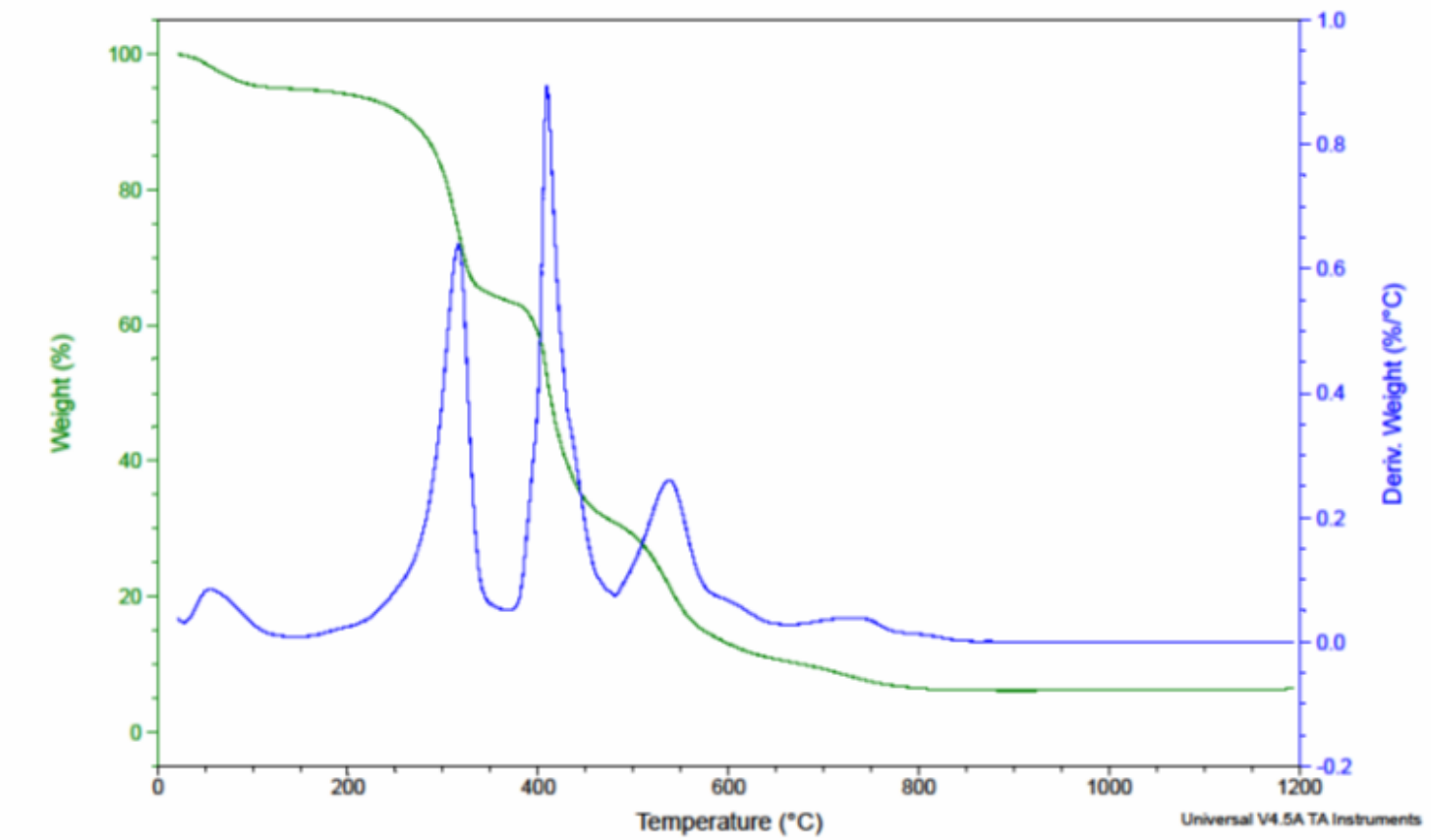


Figure S12 **FT-IR spectrum of freshly prepared $PPh_2PEGPIILP$ co-polymer (2a)**

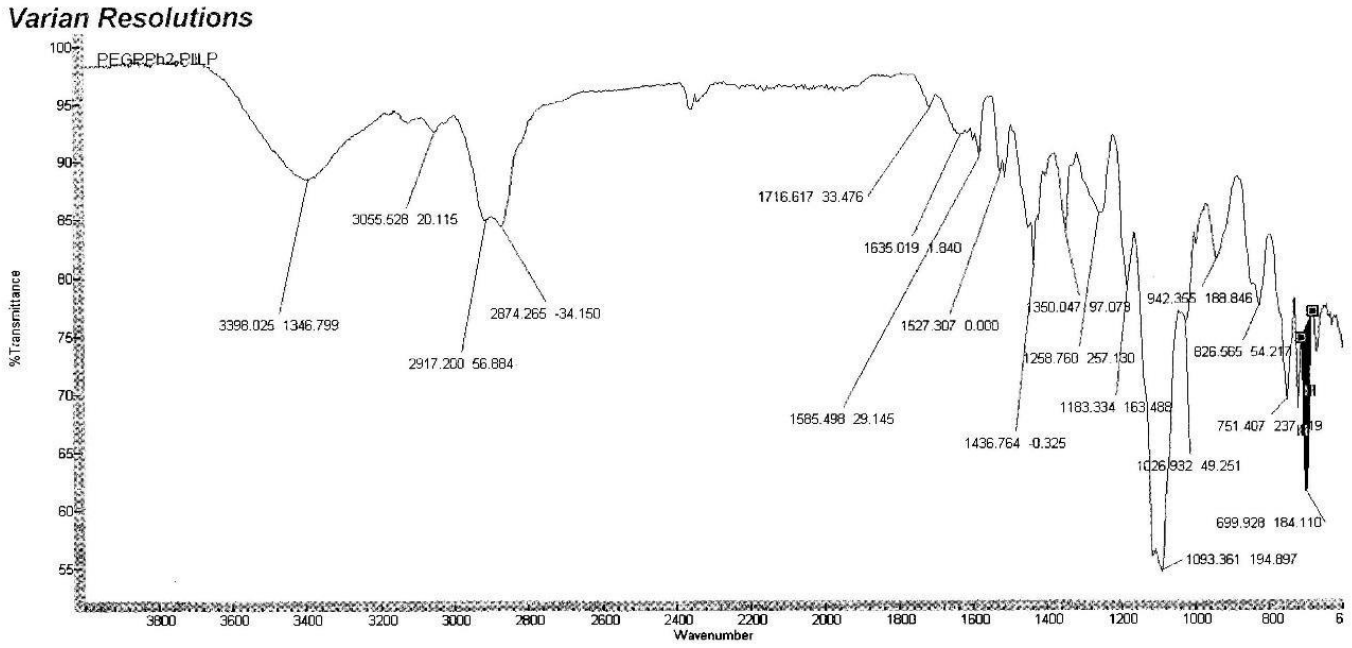


Figure S13 ^{1}H NMR spectrum of $PPh_2PEGstyrene$ (3a)

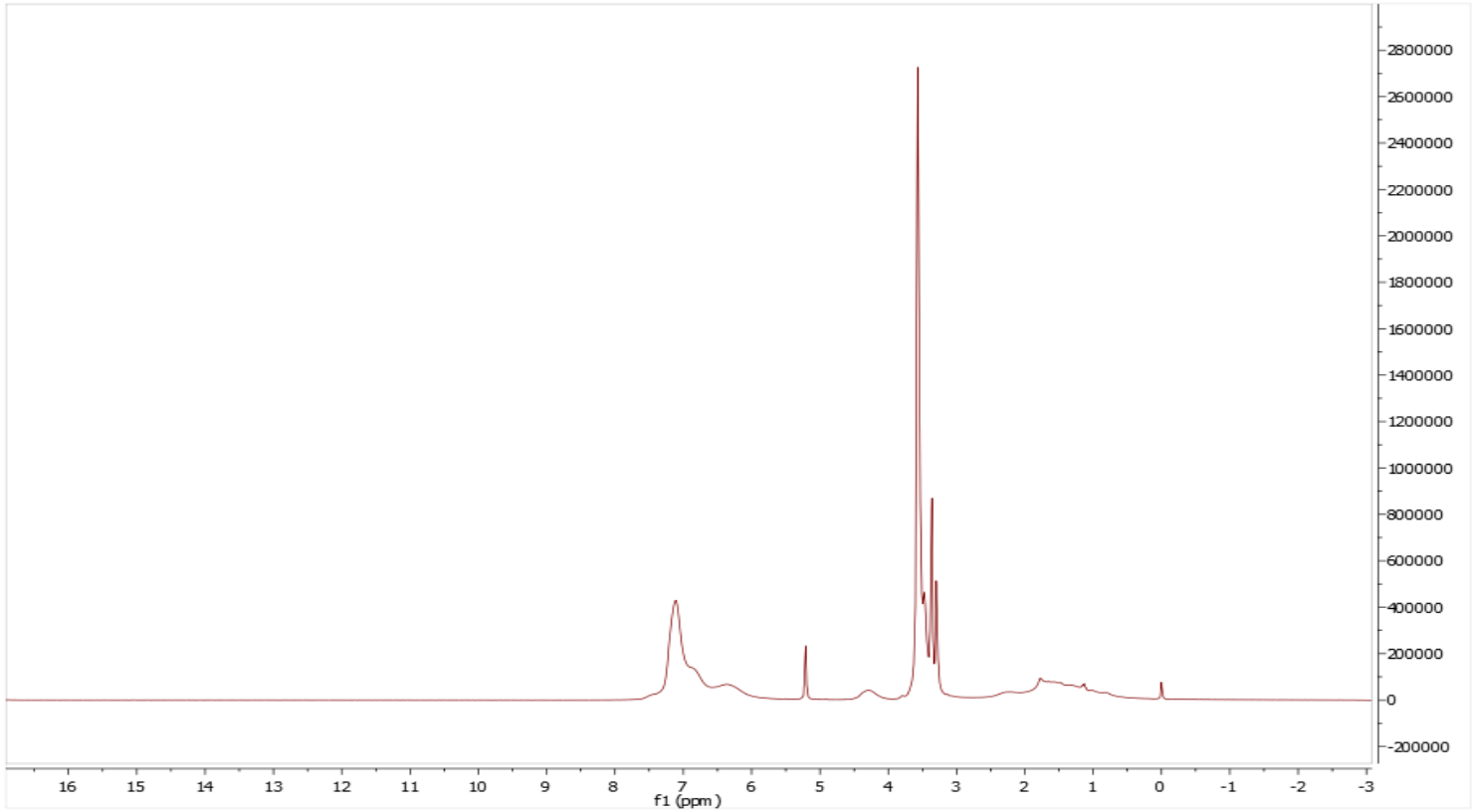


Figure S14 **Solid state ^{13}C NMR spectrum of $PPh_2PEGstyrene$ (3a)**

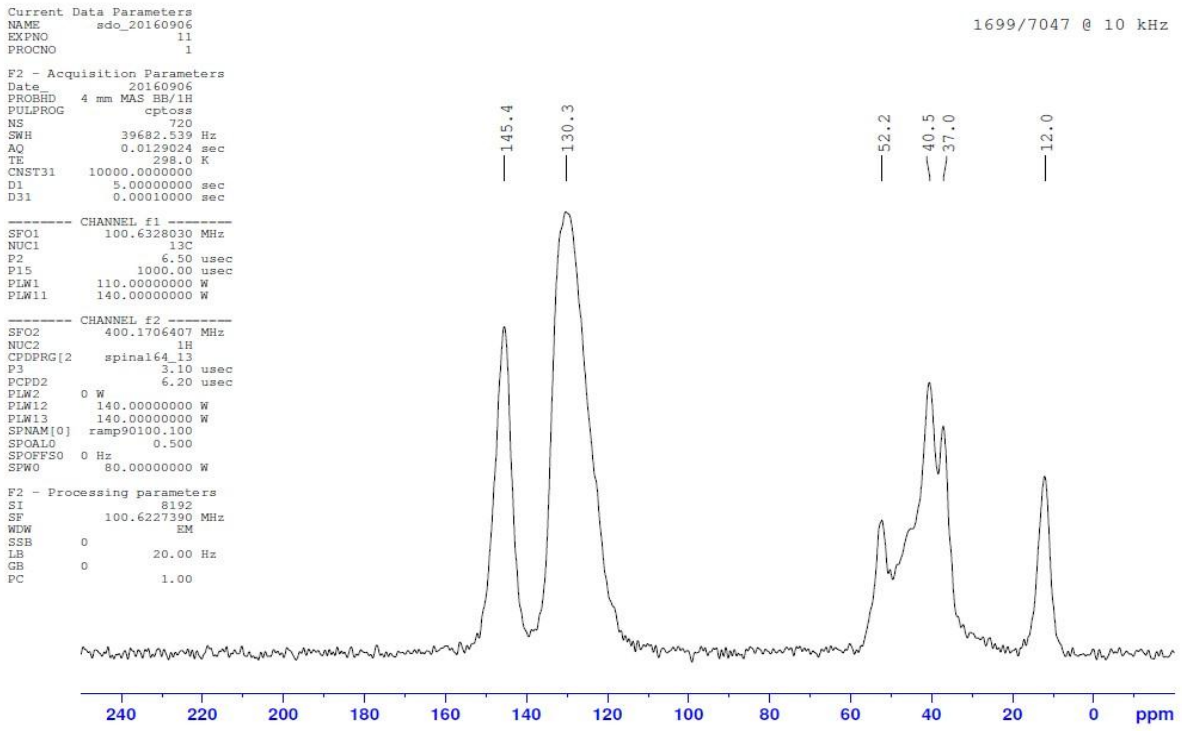


Figure S15 **Solid state ^{31}P NMR spectrum of PPh_2PEGstyrene (3a)**

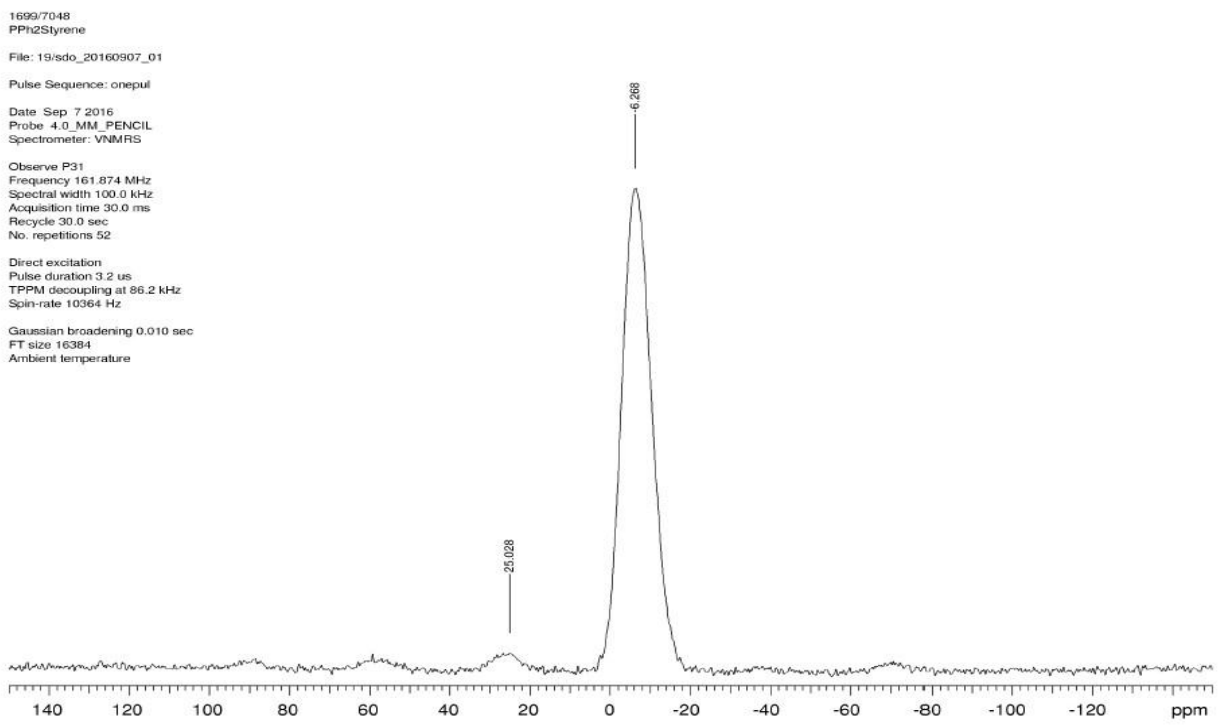
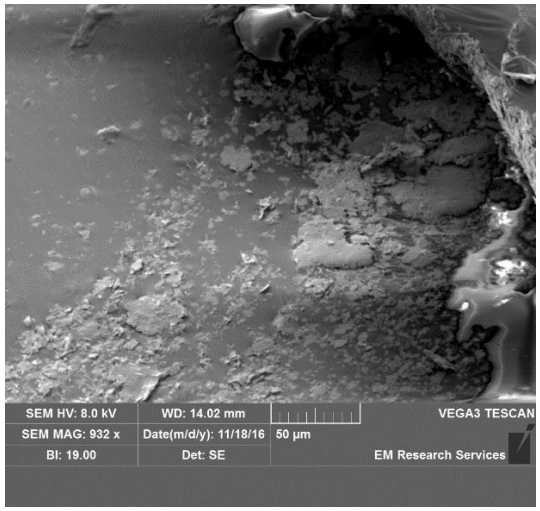


Figure S16 **SEM images of freshly prepared PPh_2PEGstyrene (3a)**



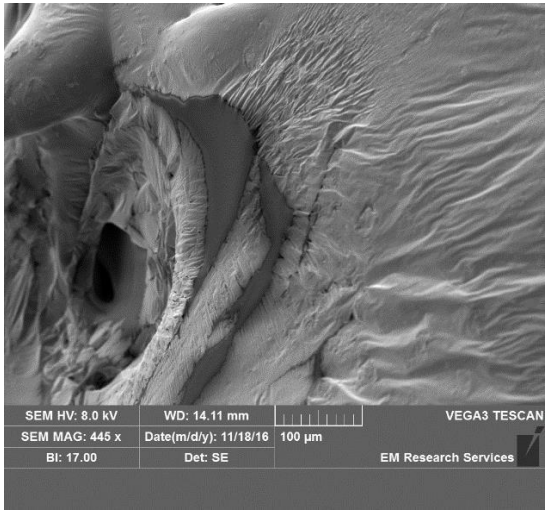


Figure S17 **TGA curve for $PPh_2PEGstyrene$ (3a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air**

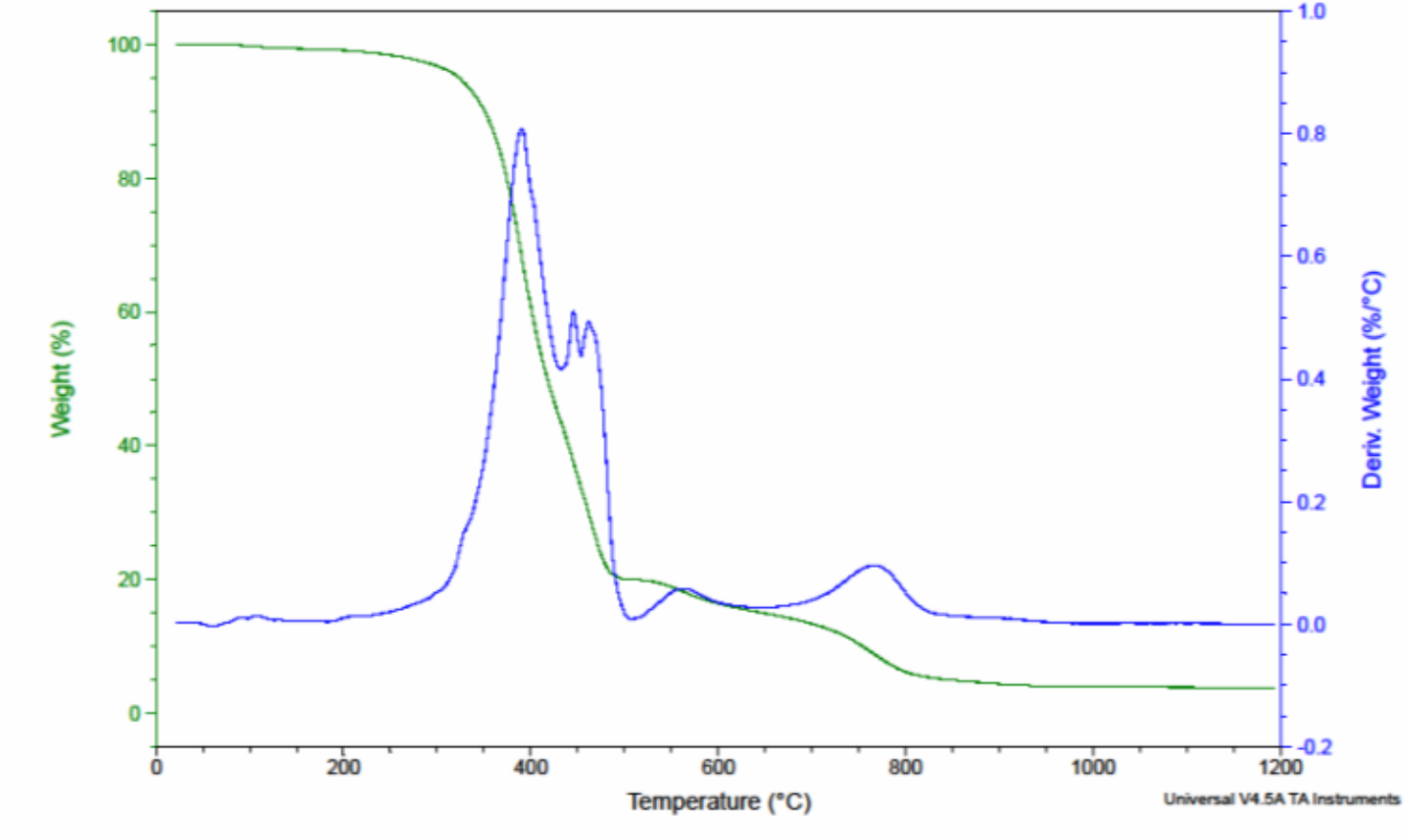


Figure S18 **FT-IR spectrum of freshly prepared PPh_2PEGstyrene (3a)**

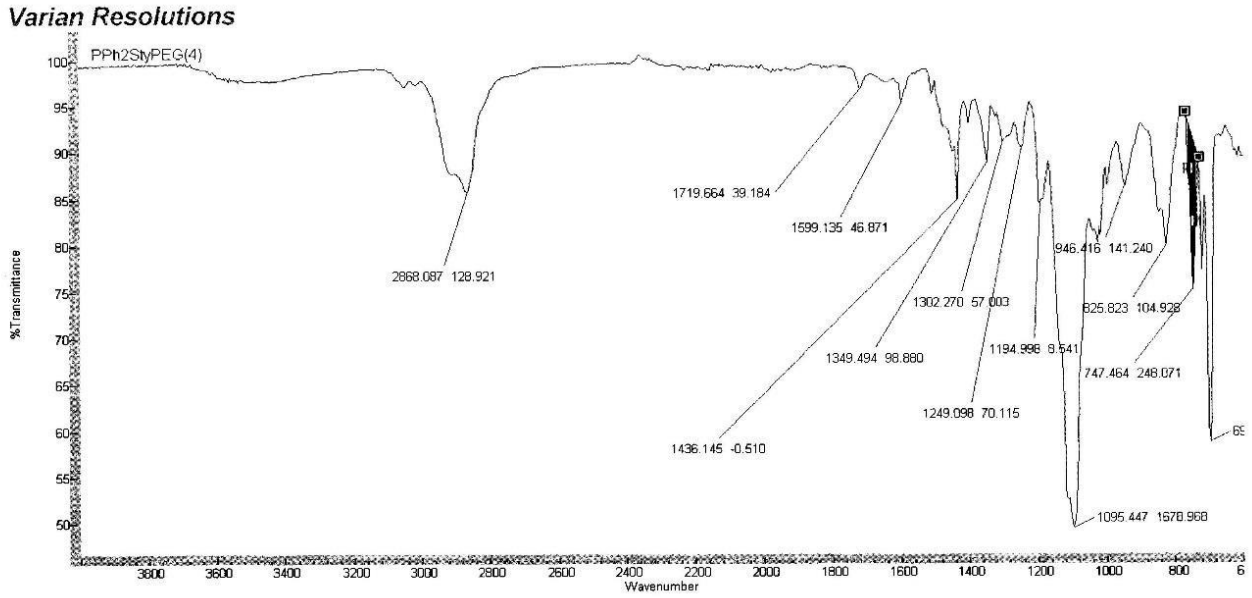


Figure S19 ^{1}H NMR spectrum of PEGPIILP co-polymer 4a

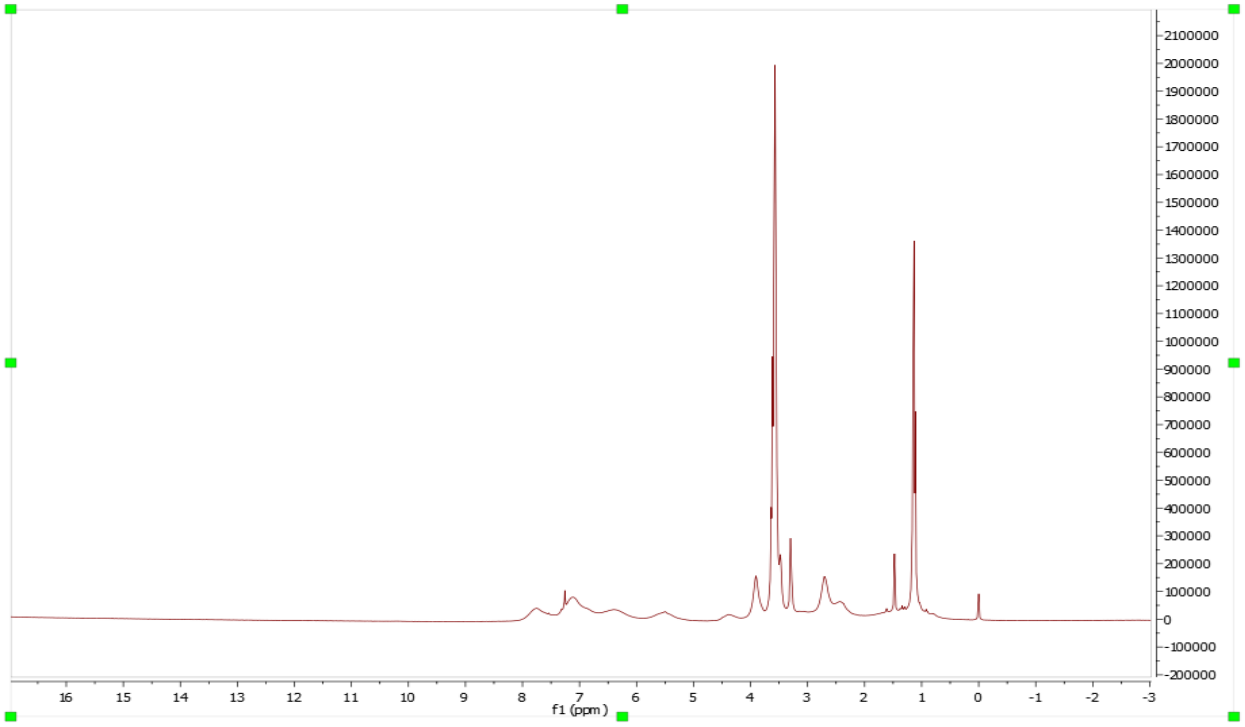


Figure S20 **Solid state ^{13}C NMR spectrum of PEGPIILP co-polymer 4a**

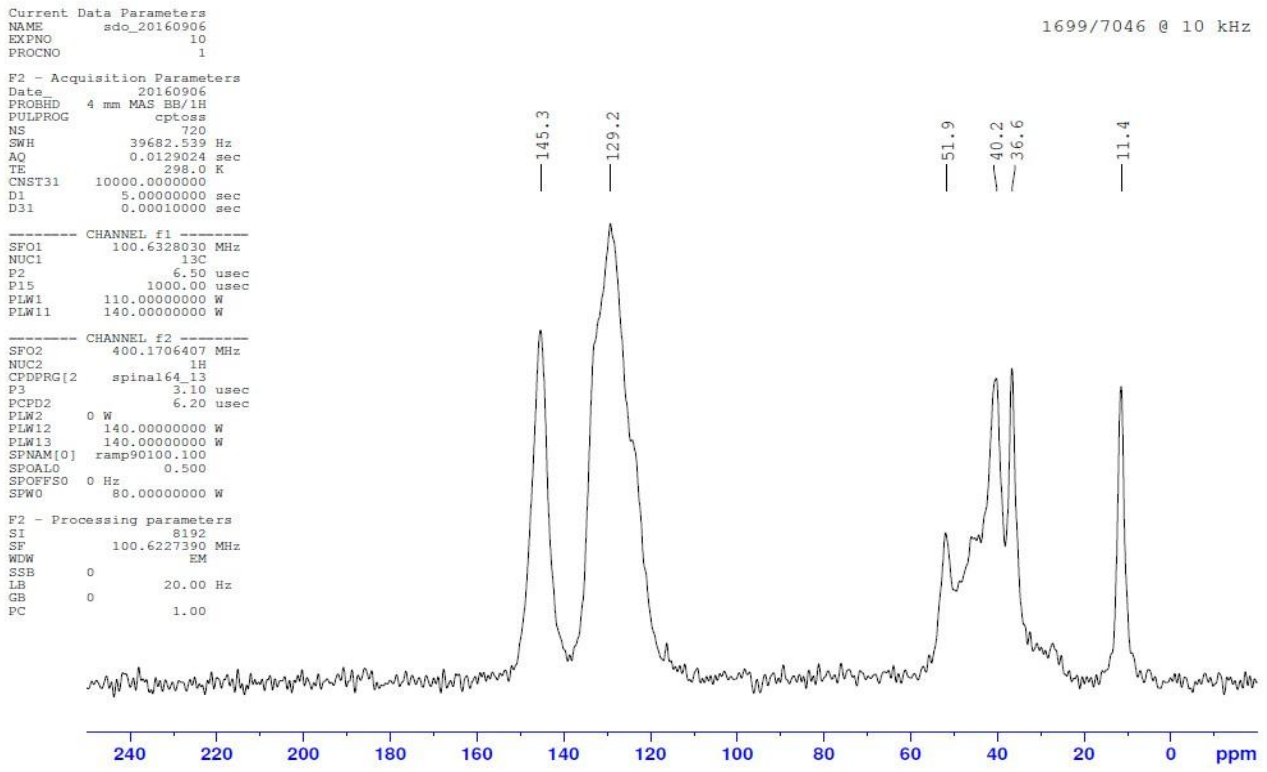
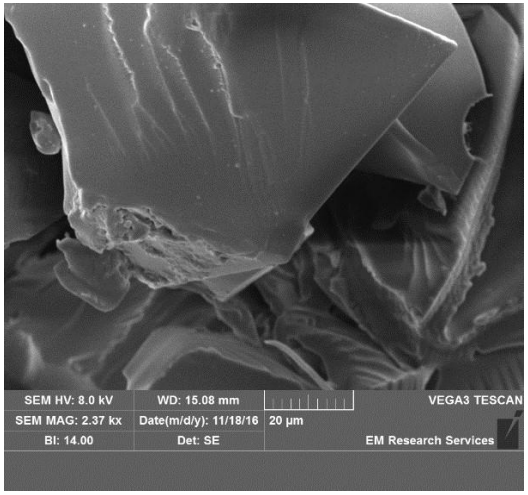


Figure S21 SEM images of freshly prepared PEGPIILP co-polymer 4a



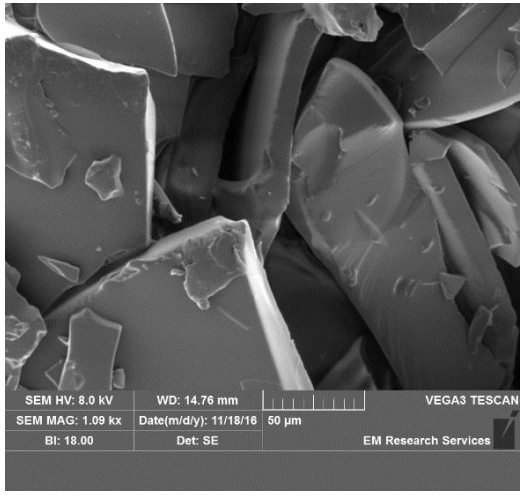


Figure S22 **TGA curve for PEGPIILP copolymer (4a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air**

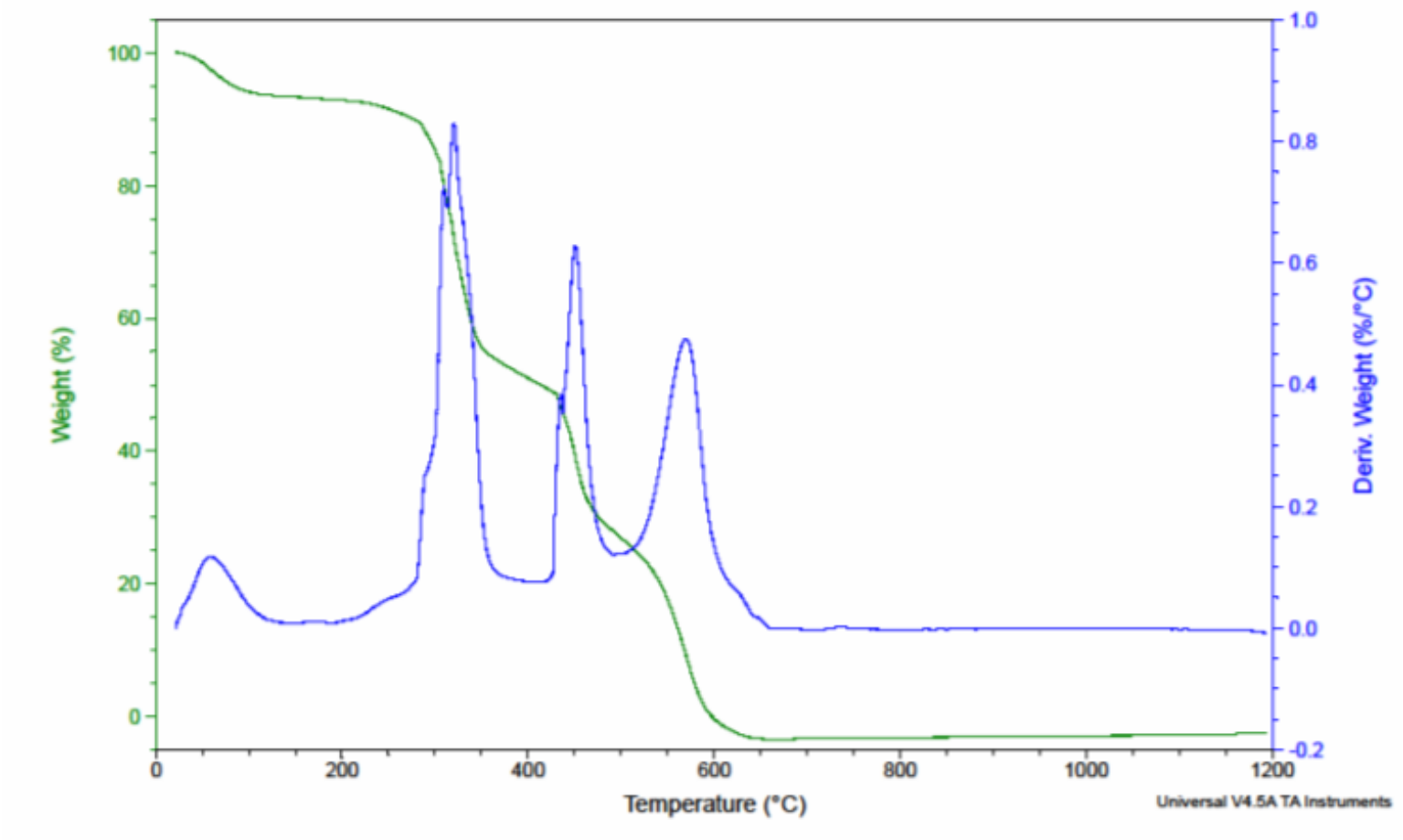


Figure S23 FT-IR spectrum of freshly prepared PEGPIILP (4a)

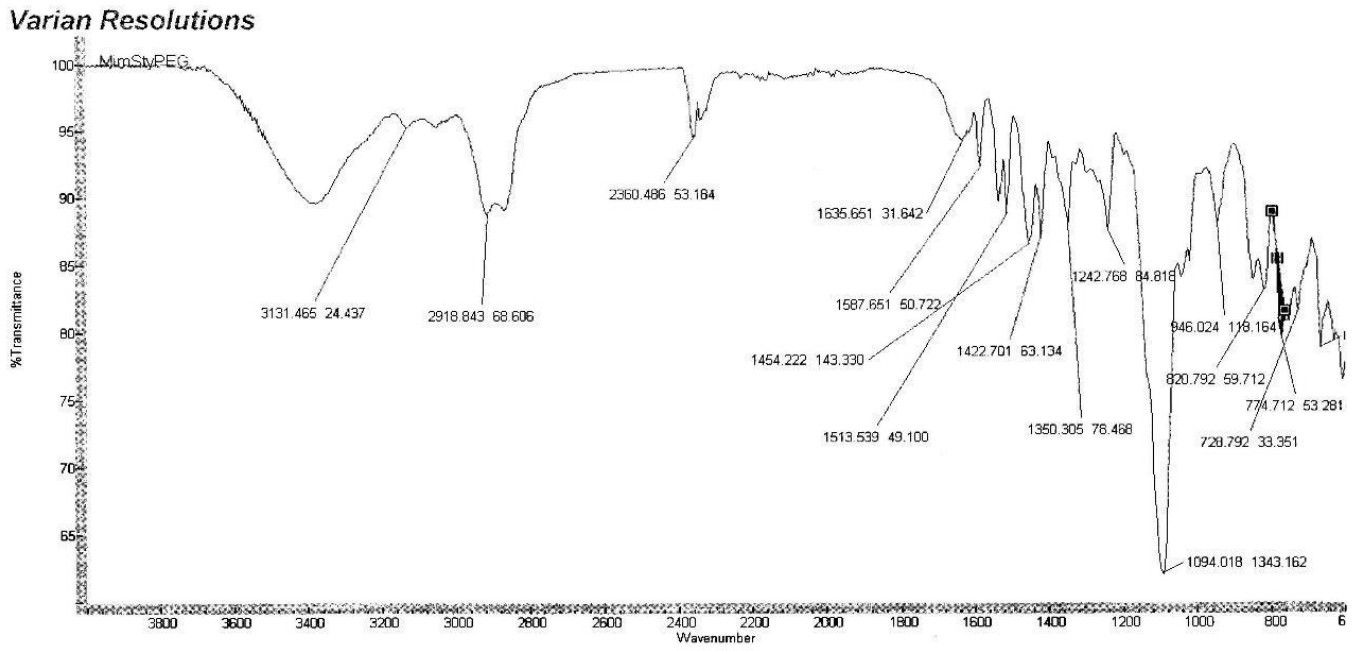


Figure S24 **Solid state ^{13}C NMR spectrum of $[PdCl_4]$@PPh_2PIILP (1b)**

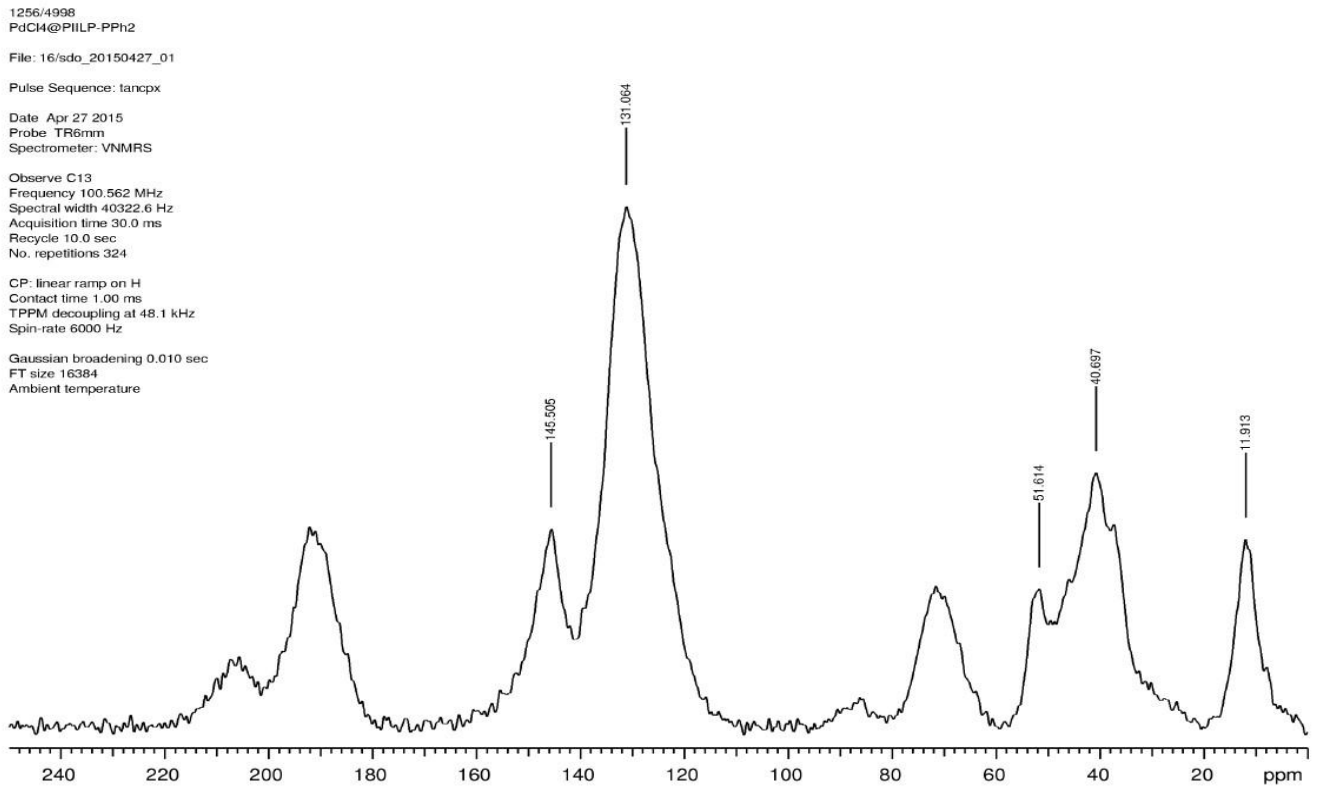


Figure S25 **Solid state ^{31}P NMR spectrum of $[PdCl_4]@PPh_2PIILP$ (1b)**

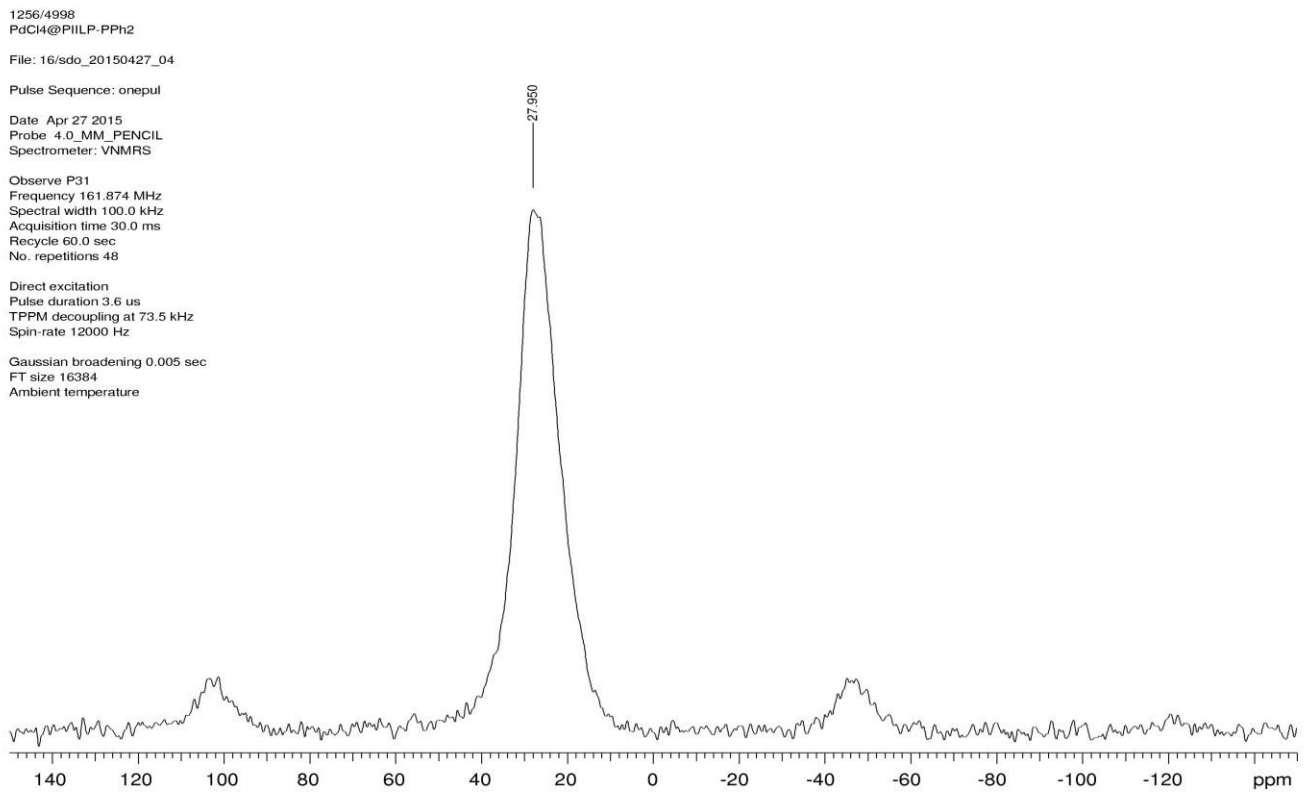


Figure S26 **SEM images of freshly prepared $[PdCl_4]$@PPh_2PIILP (1b)**

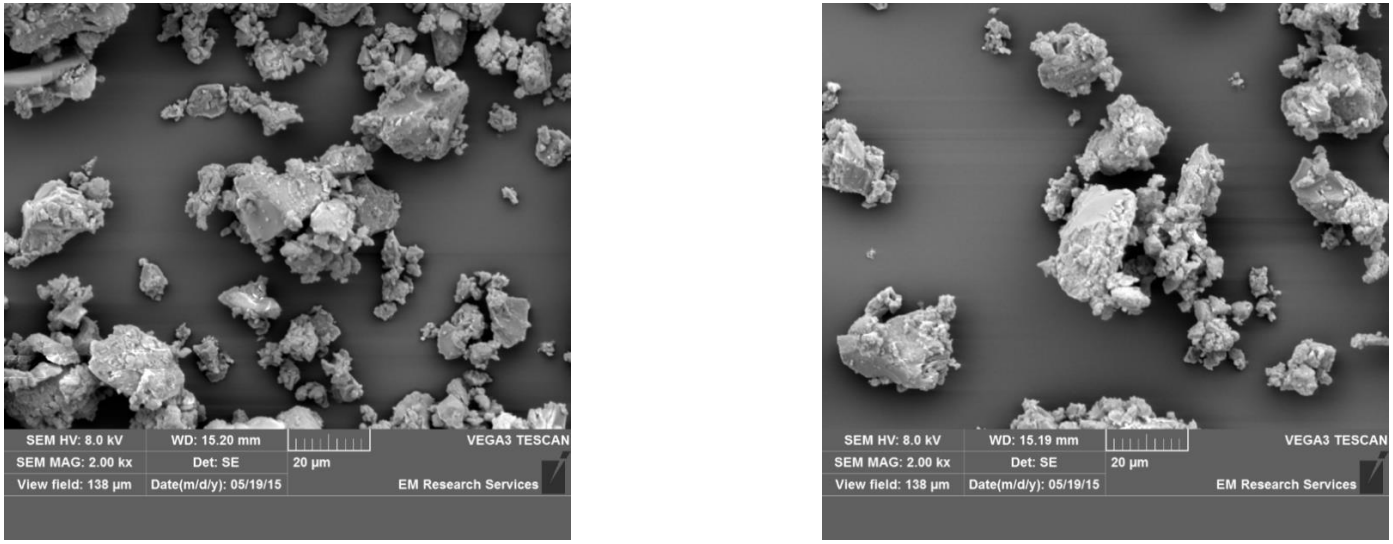


Figure S27 **FT-IR spectrum of freshly prepared [$PdCl_4$]@PPh_2PIILP (1b)**

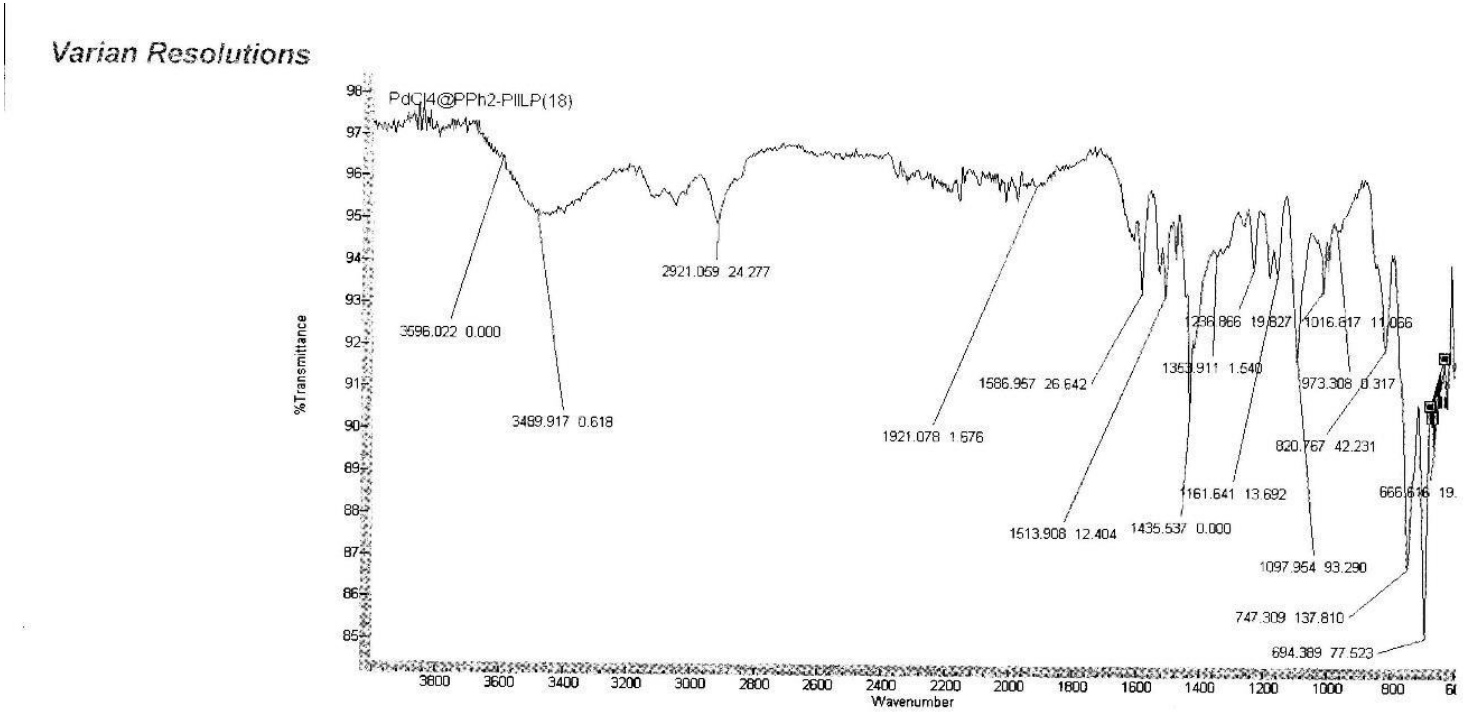


Figure S28 **Pd 3d core level XPS spectrum of $[PdCl_4]$@PPh_2PIILP (1b) referenced to the hydrocarbon C 1s**

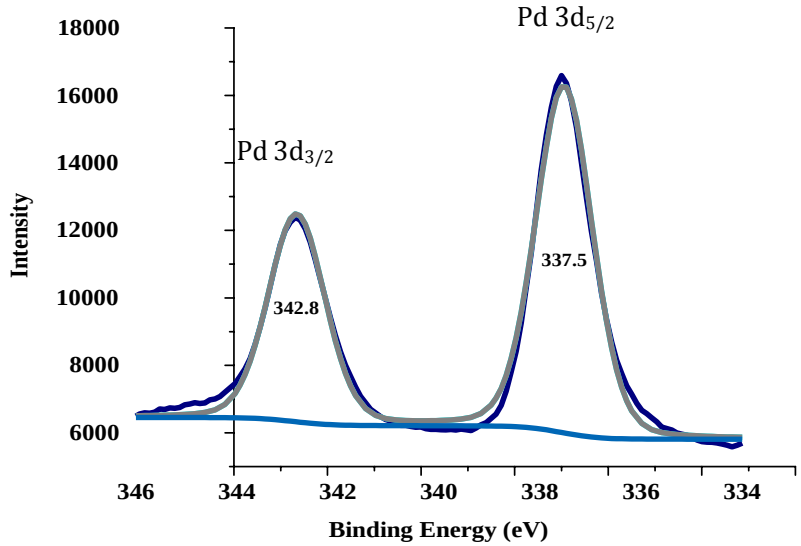


Figure S29 **Solid state ^{13}C NMR spectrum of $[PdCl_4]$@PPh_2PEGPIILP (2b)**

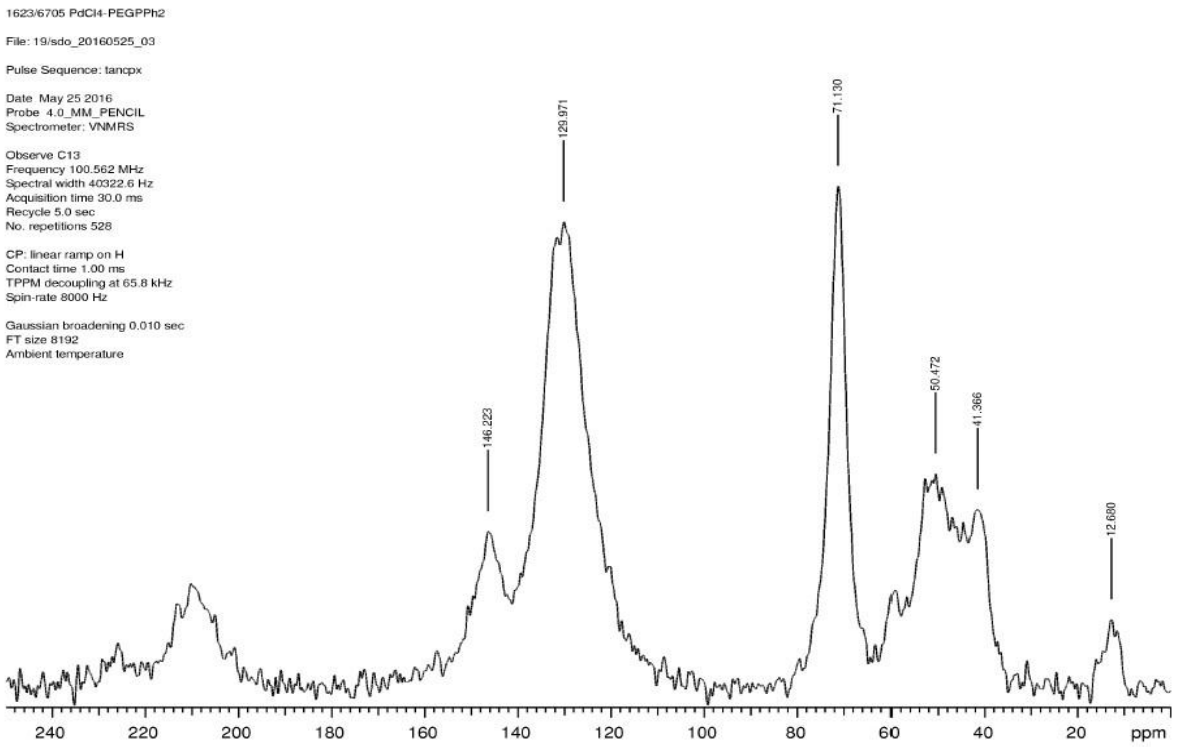


Figure S30 **Solid state ^{31}P NMR spectrum of $[PdCl_4]$@PPh_2PEGPIILP (2b)**

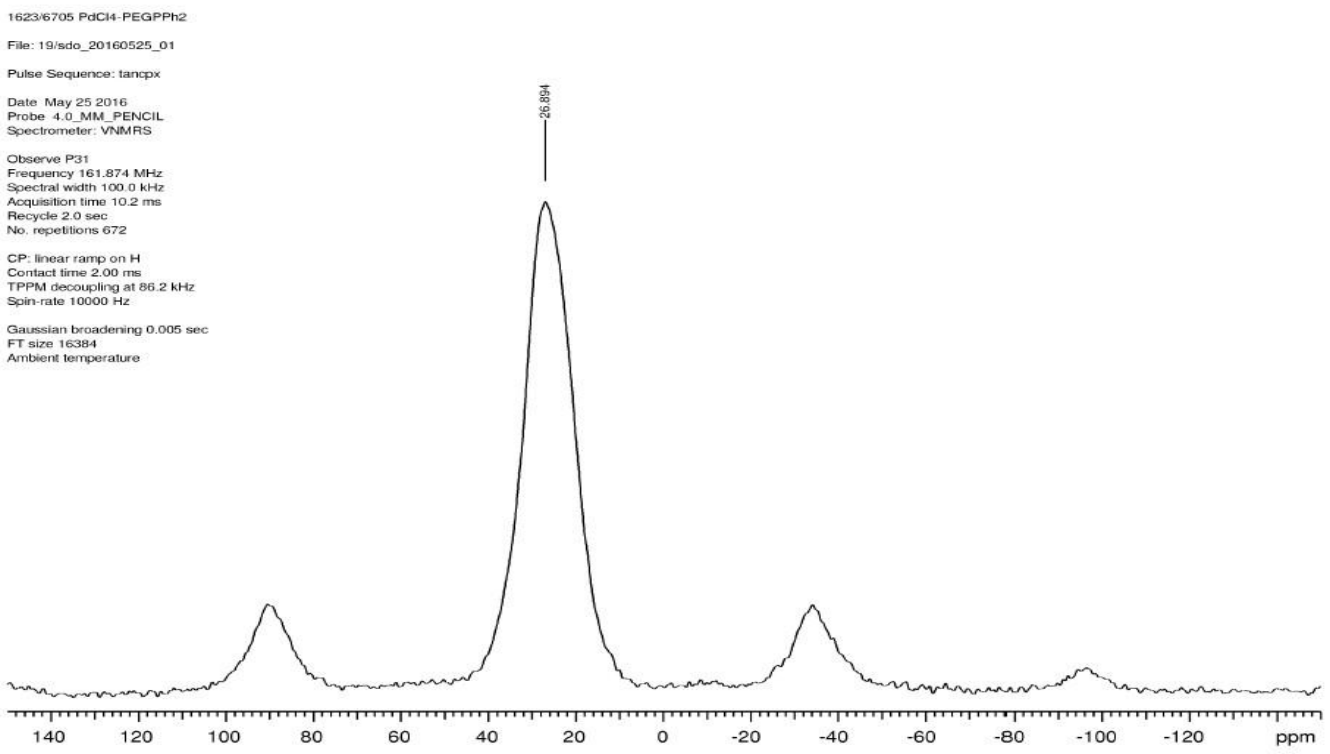
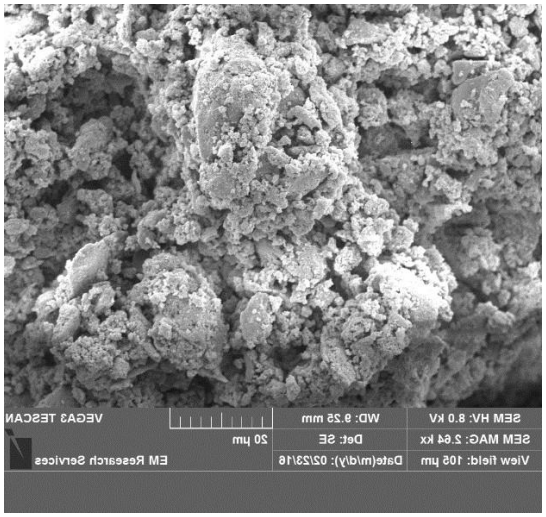


Figure S31 **SEM images of freshly prepared $[PdCl_4]$@PPh_2PEGPIILP (2b)**



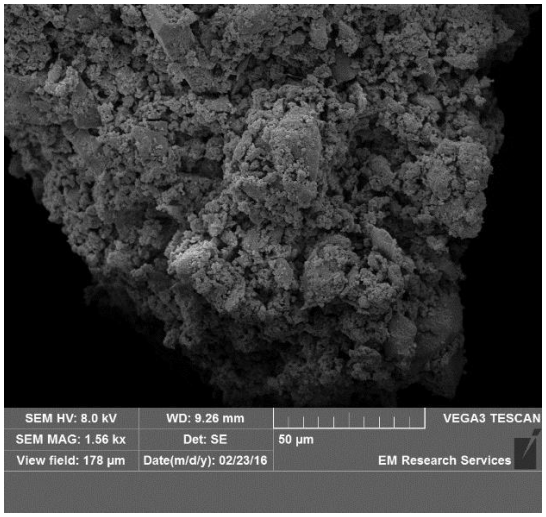


Figure S32 **FT-IR spectrum of freshly prepared [$PdCl_4$]@PPh_2PEGPIILP (2b)**

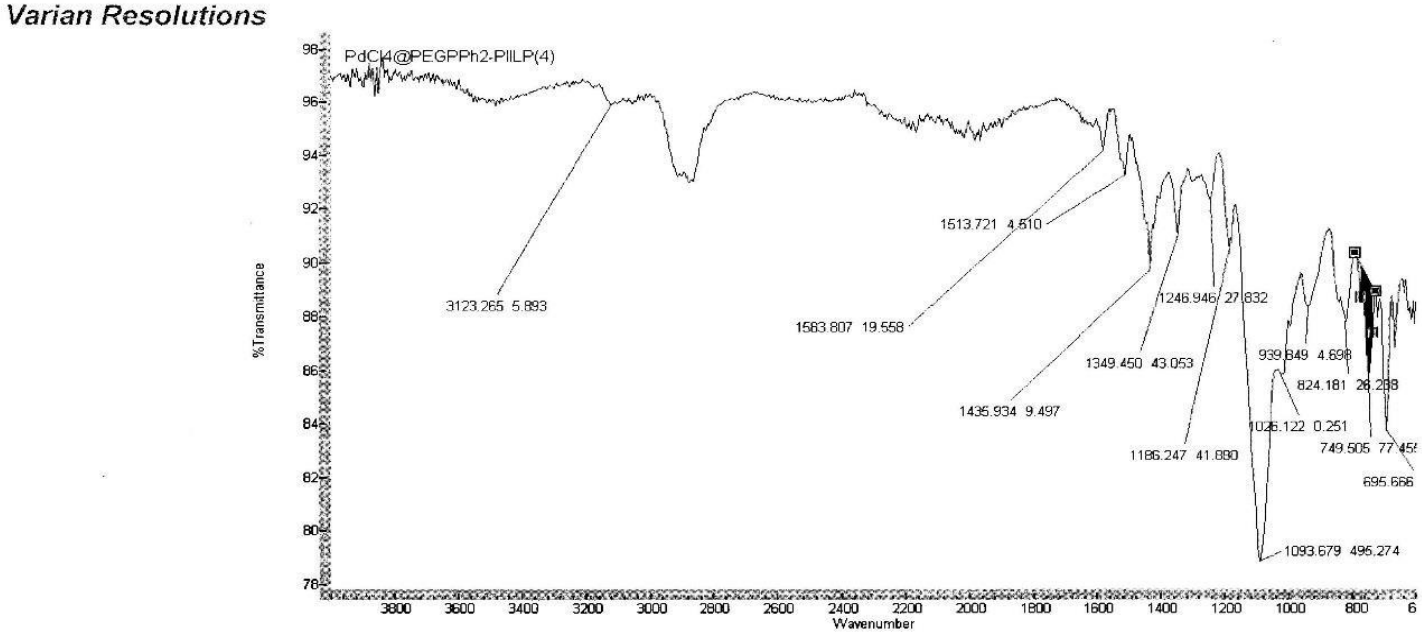


Figure S33 **Pd 3d core level XPS spectrum of $[PdCl_4]$@PPh_2PEGPIILP (2b) referenced to the hydrocarbon C 1s**

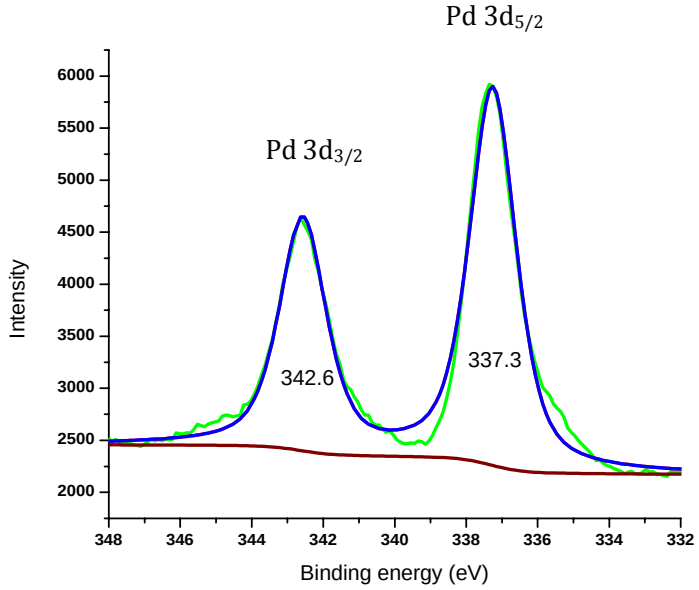


Figure S34 **Solid state ^{13}C NMR spectrum of $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (3b)**

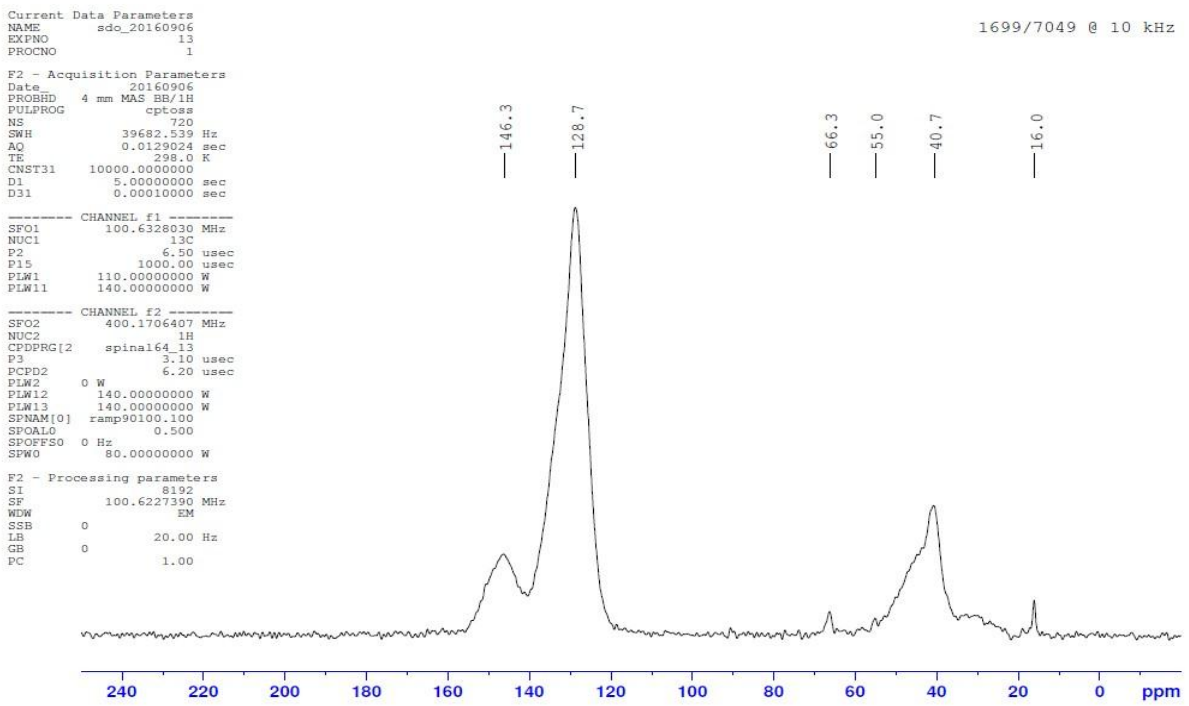


Figure S35 **Solid state ^{31}P NMR spectrum of $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (3b)**

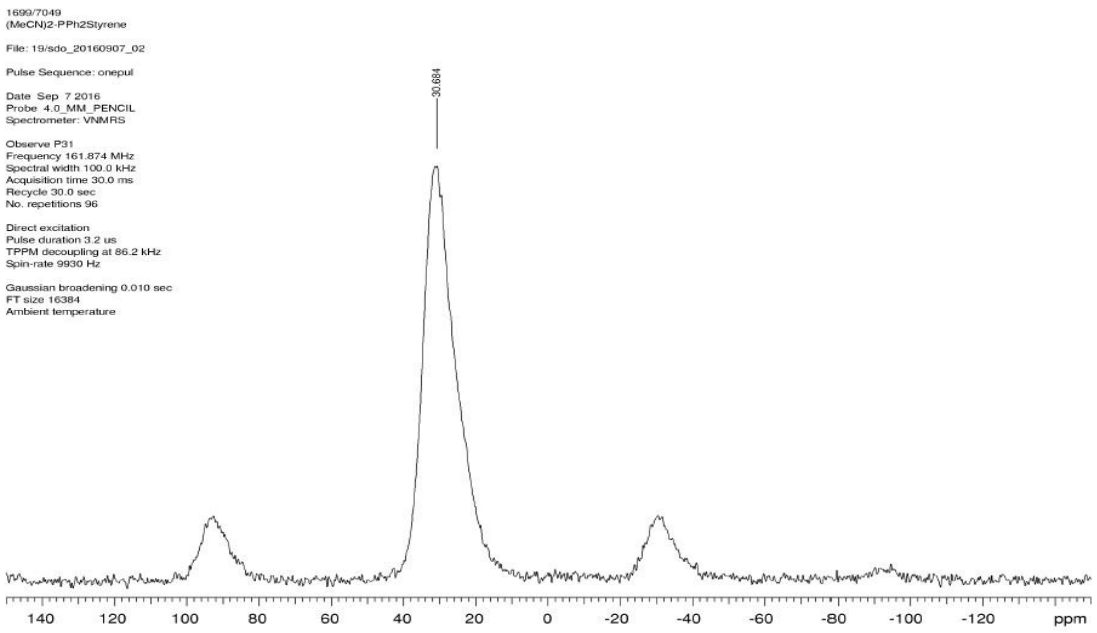
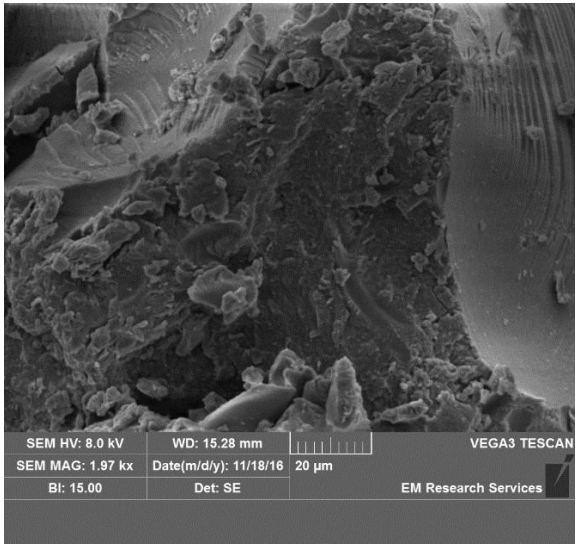


Figure S36 **SEM images of freshly prepared $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (3b)**



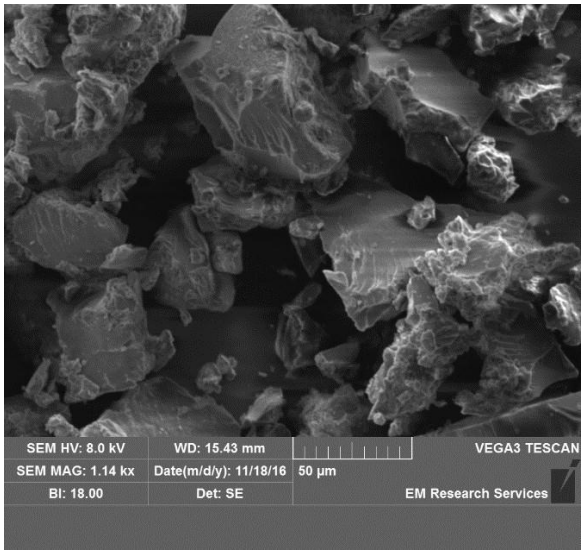


Figure S37 **FT-IR spectrum of freshly prepared $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (3b)**

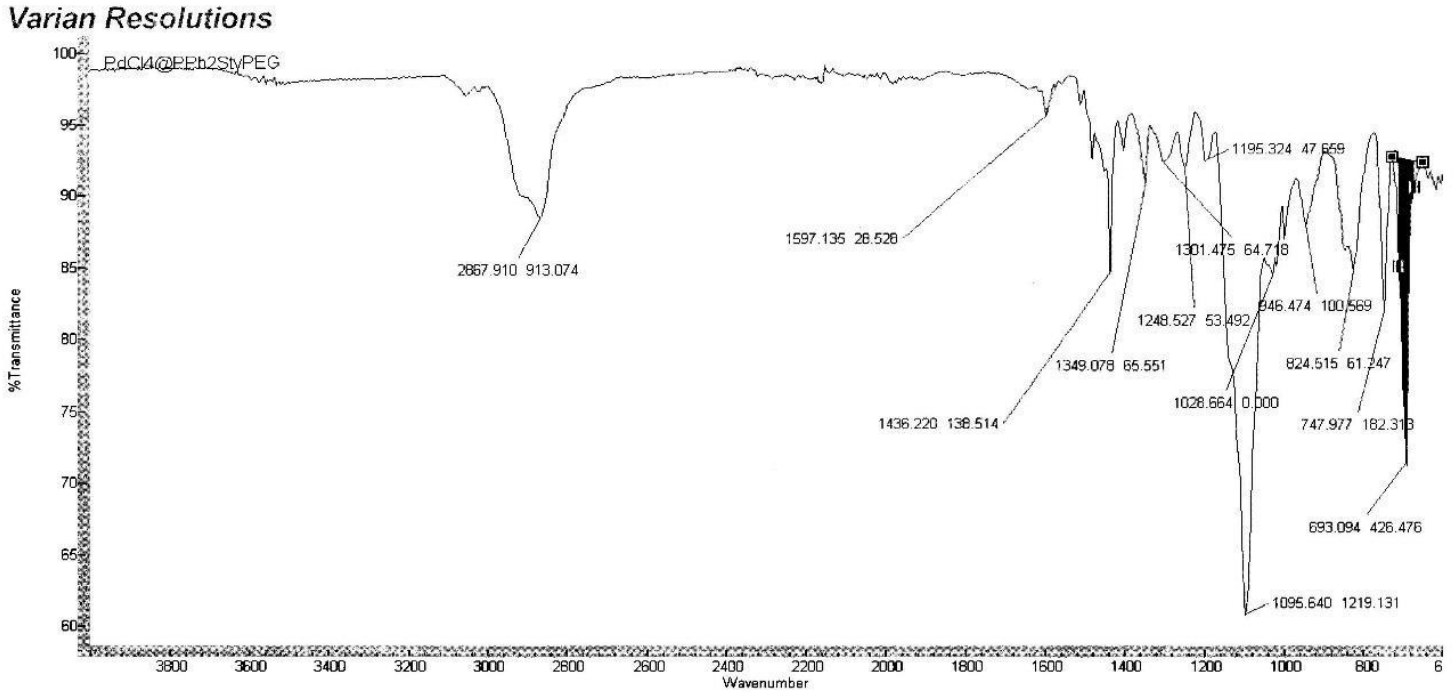


Figure S38 **Pd 3d core level XPS spectrum of $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (3b) referenced to the hydrocarbon C 1s**

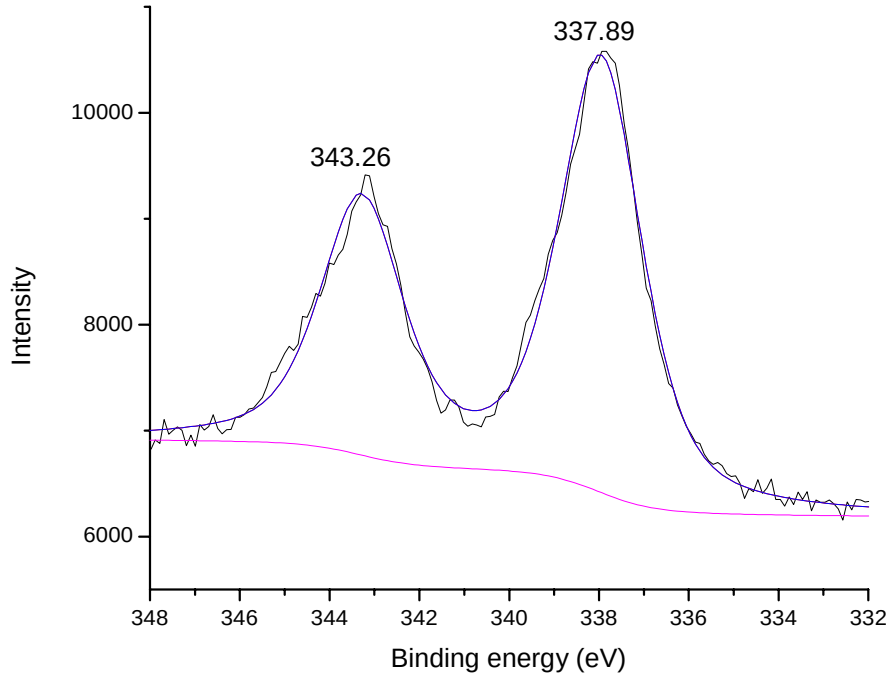


Figure S39 **Solid state ^{13}C NMR spectrum of $[PdCl_4]$@PEGPIILP (4b)**

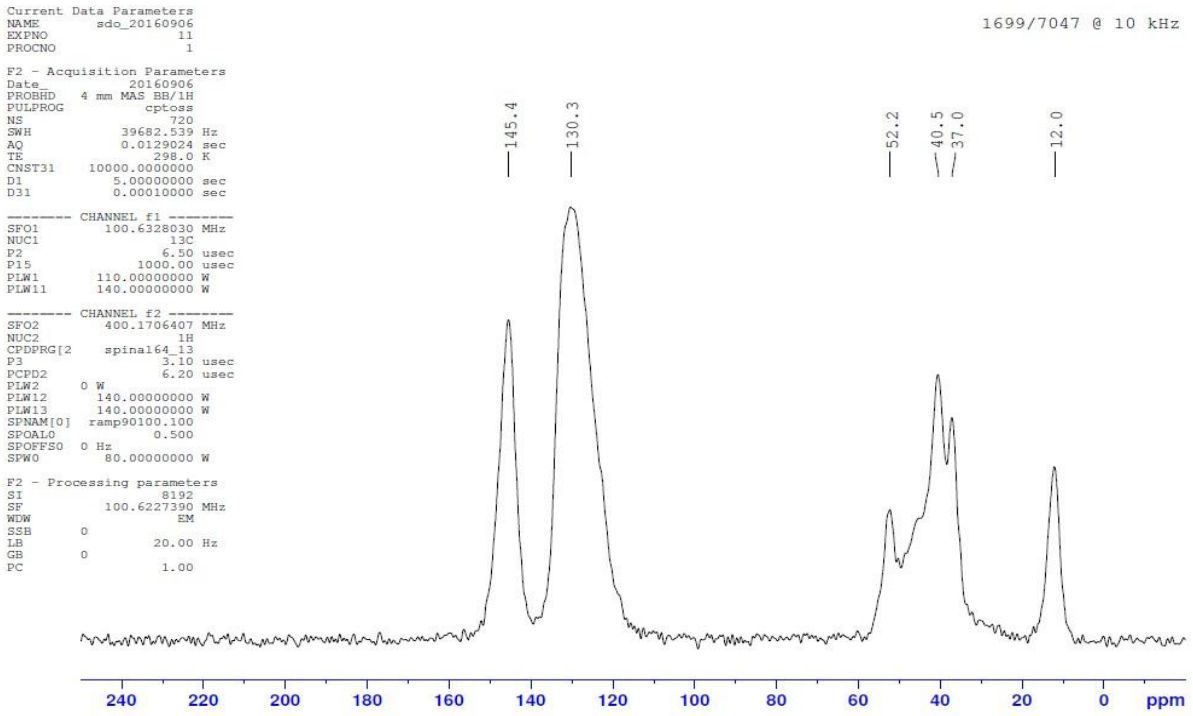
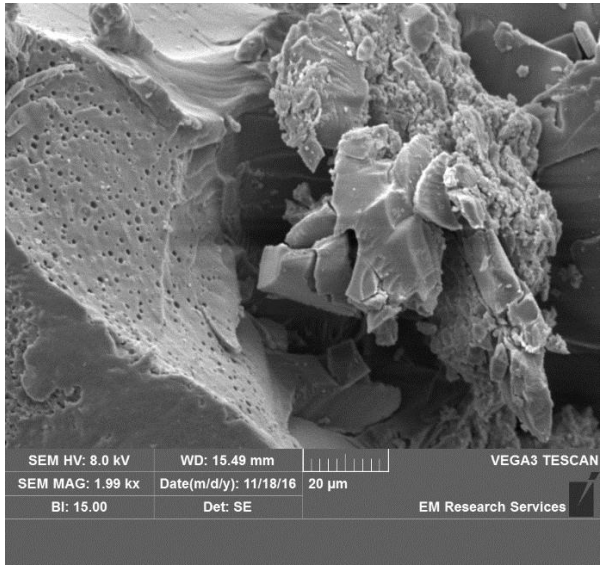


Figure S40 **SEM images of freshly prepared [$PdCl_4$]@PEGPIILP (4b)**



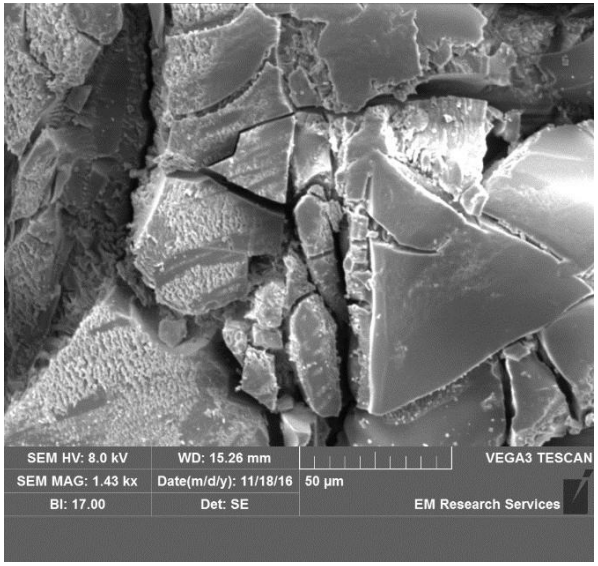


Figure S41 **FT-IR spectrum of freshly prepared [$PdCl_4$]@PEGPIILP (4b)**

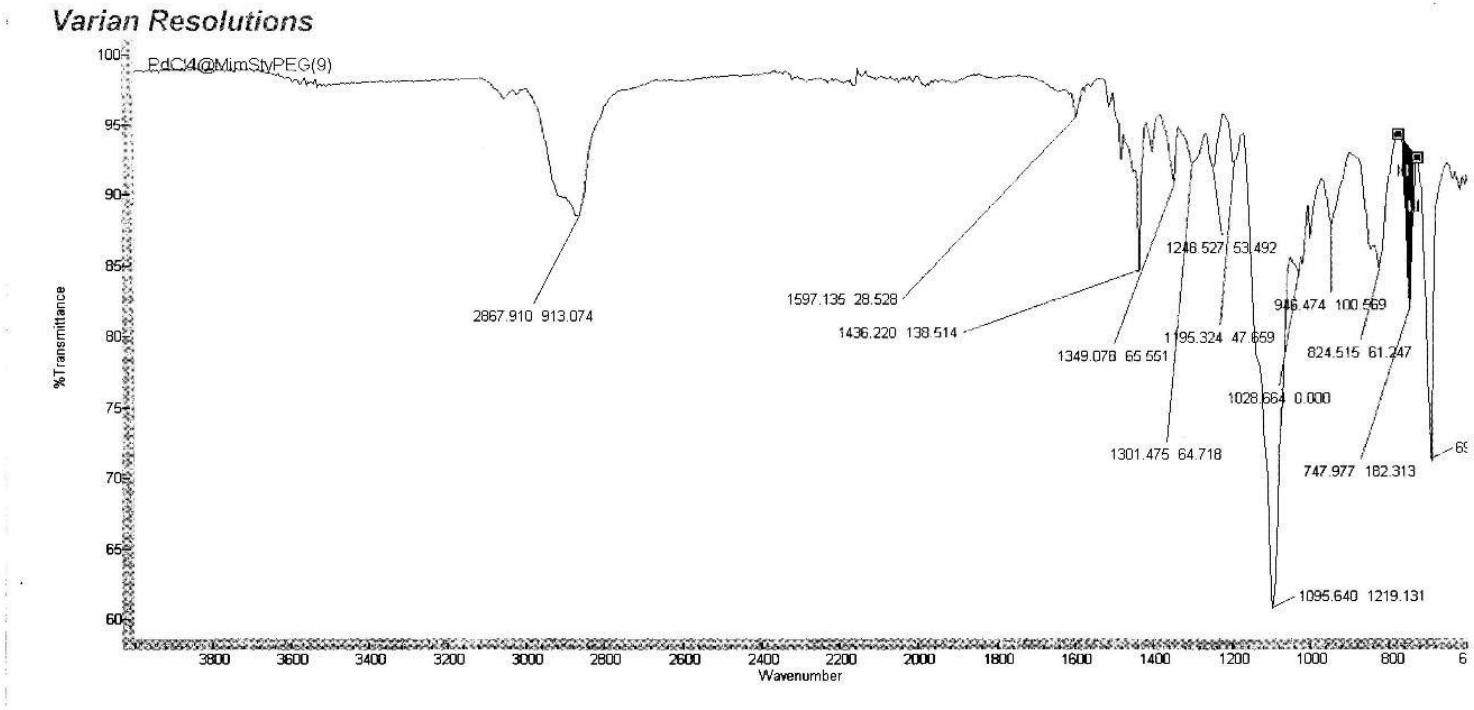


Figure S42 **Pd 3d core level XPS spectrum of [$PdCl_4$]@PEGPIILP (4b) referenced to the hydrocarbon C 1s**

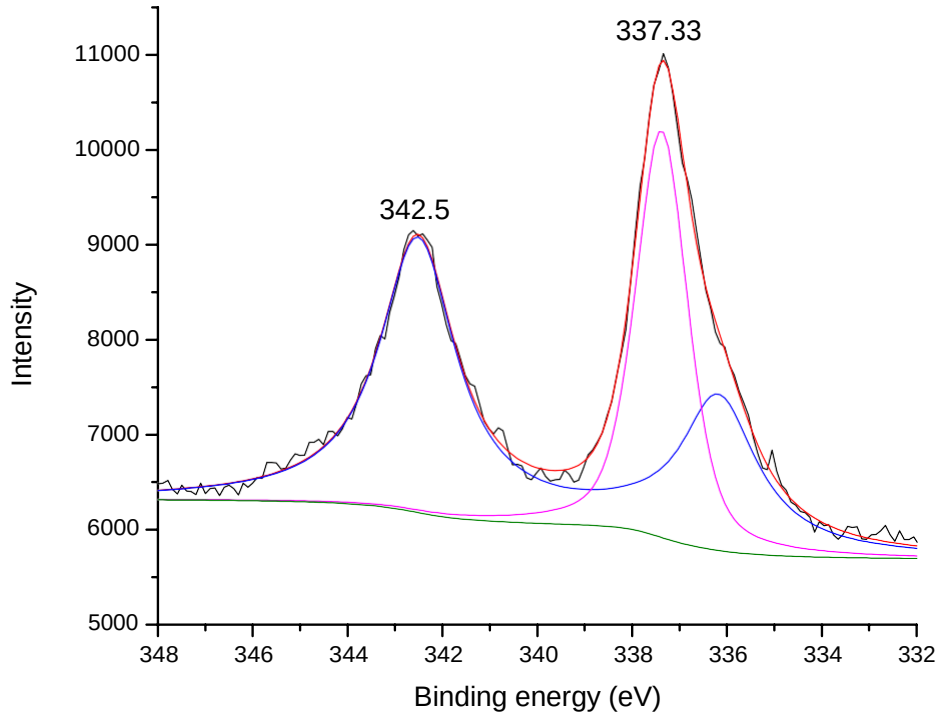


Figure S43 **Solid state ^{13}C NMR spectrum of PdNP@PPh_2PIILP (1c)**

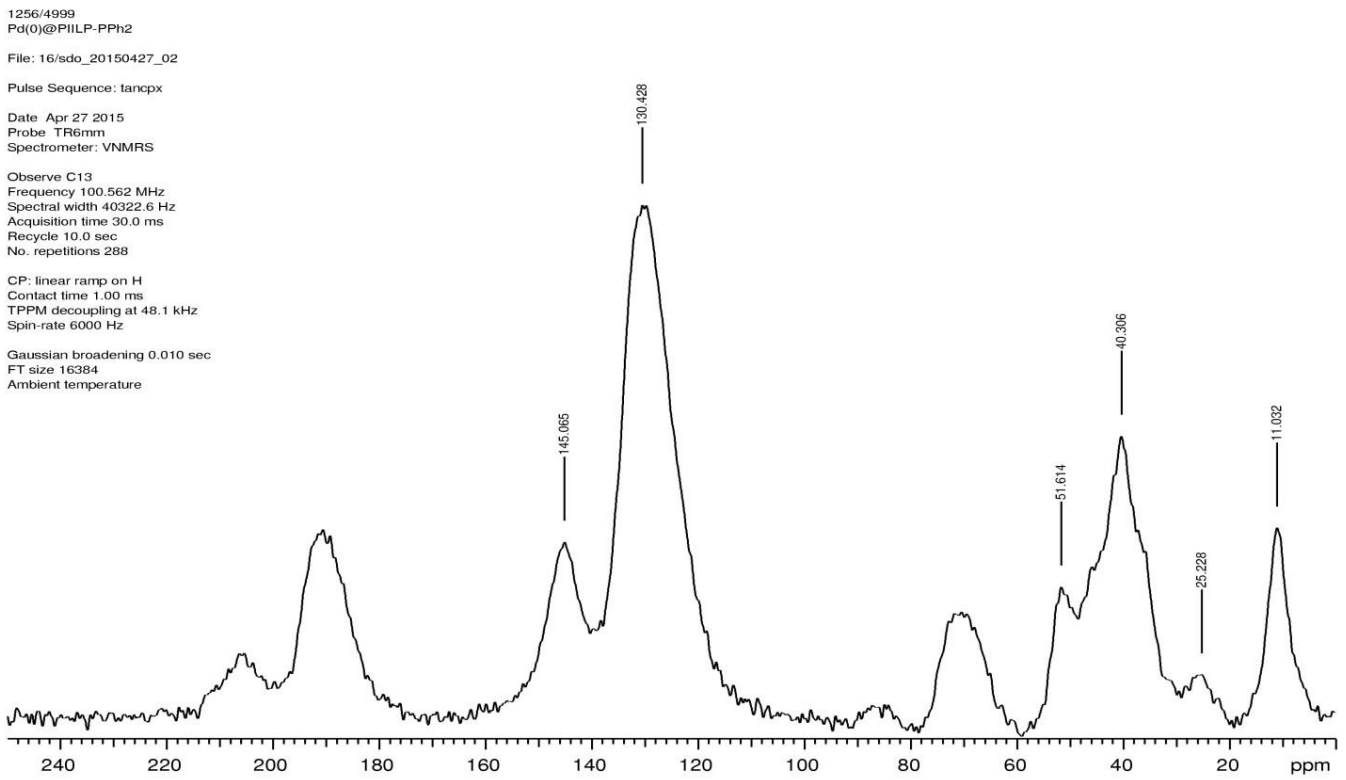


Figure S44 **Solid state ^{31}P NMR spectrum of PdNP@PPh_2PIILP (1c)**

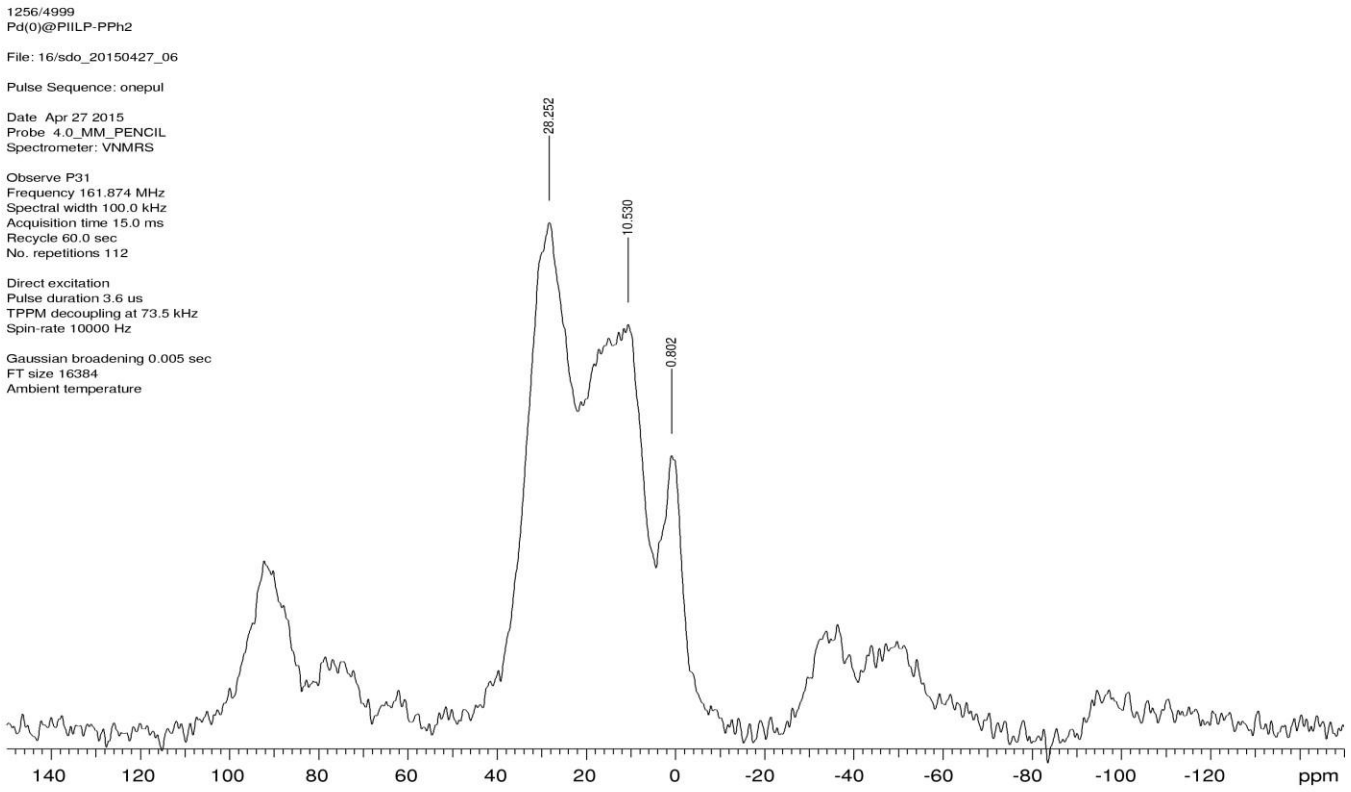
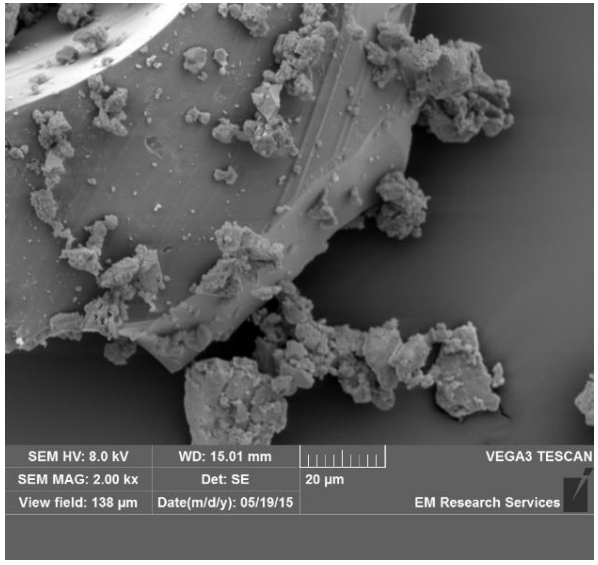


Figure S45 **SEM images of freshly prepared PdNP@PPh$_2$PIILP (1c)**



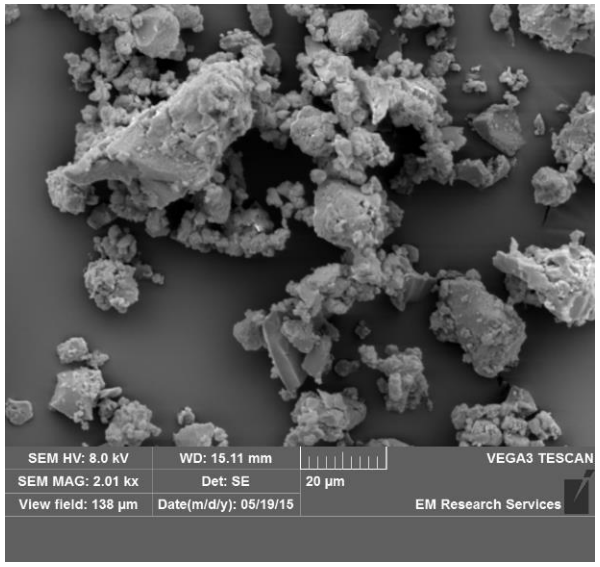


Figure S46 **FT-IR spectrum of freshly prepared PdNP@PPh$_2$PIILP (1c)**

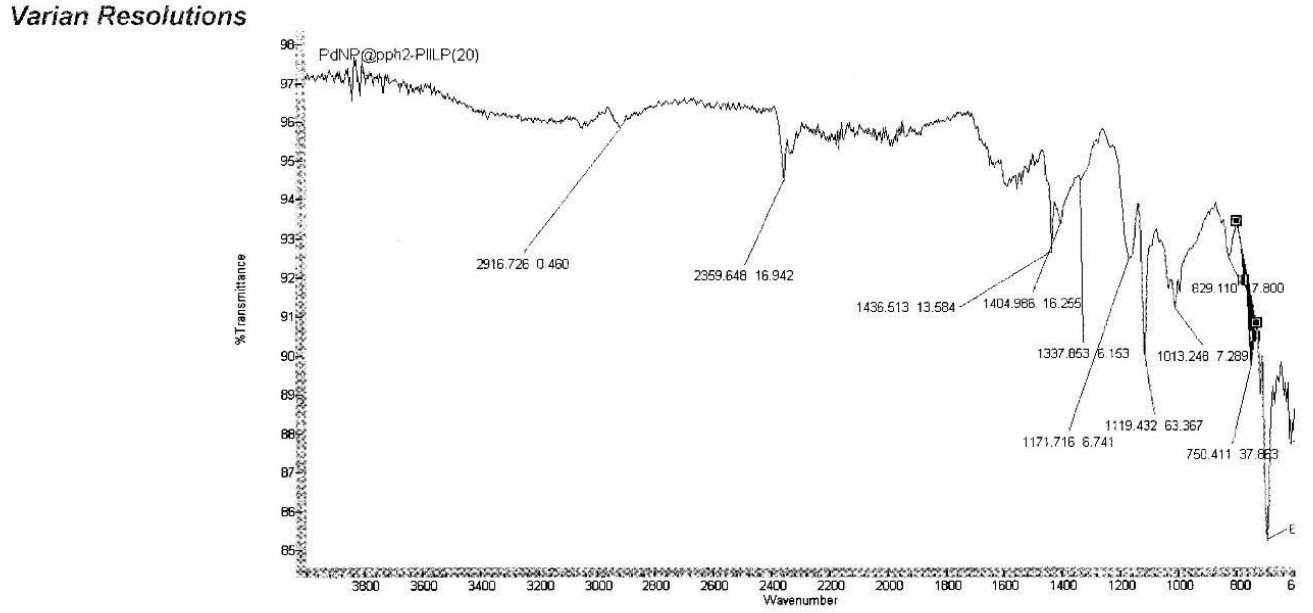


Figure S47 **Pd 3d core level XPS spectrum of [PdNP@PPh$_2$PIILP (1c) referenced to the hydrocarbon C 1s**

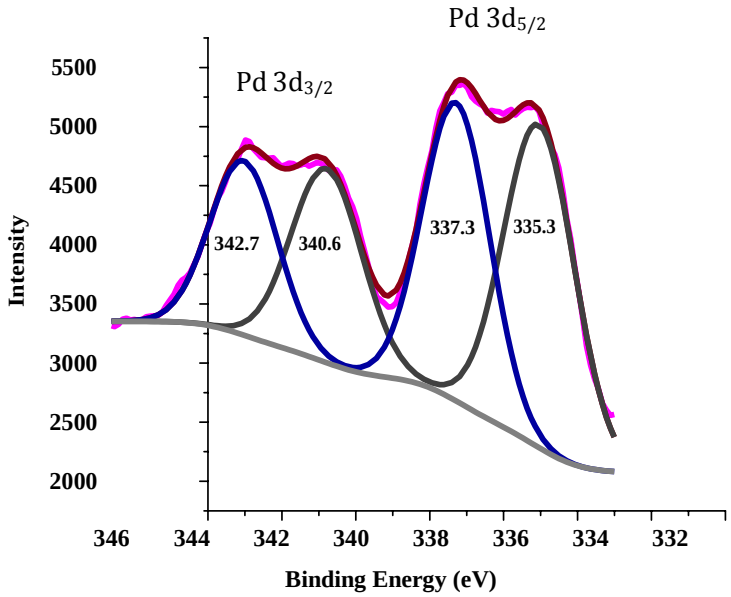


Figure S48 **(a-d) TEM images of PdNP@PPh_2PIILP (1c), (e) Energy dispersive X-ray spectrum of 1c confirming the presence of Pd in the sample (the Cu peak is due to the TEM gird holder) and (f) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)**

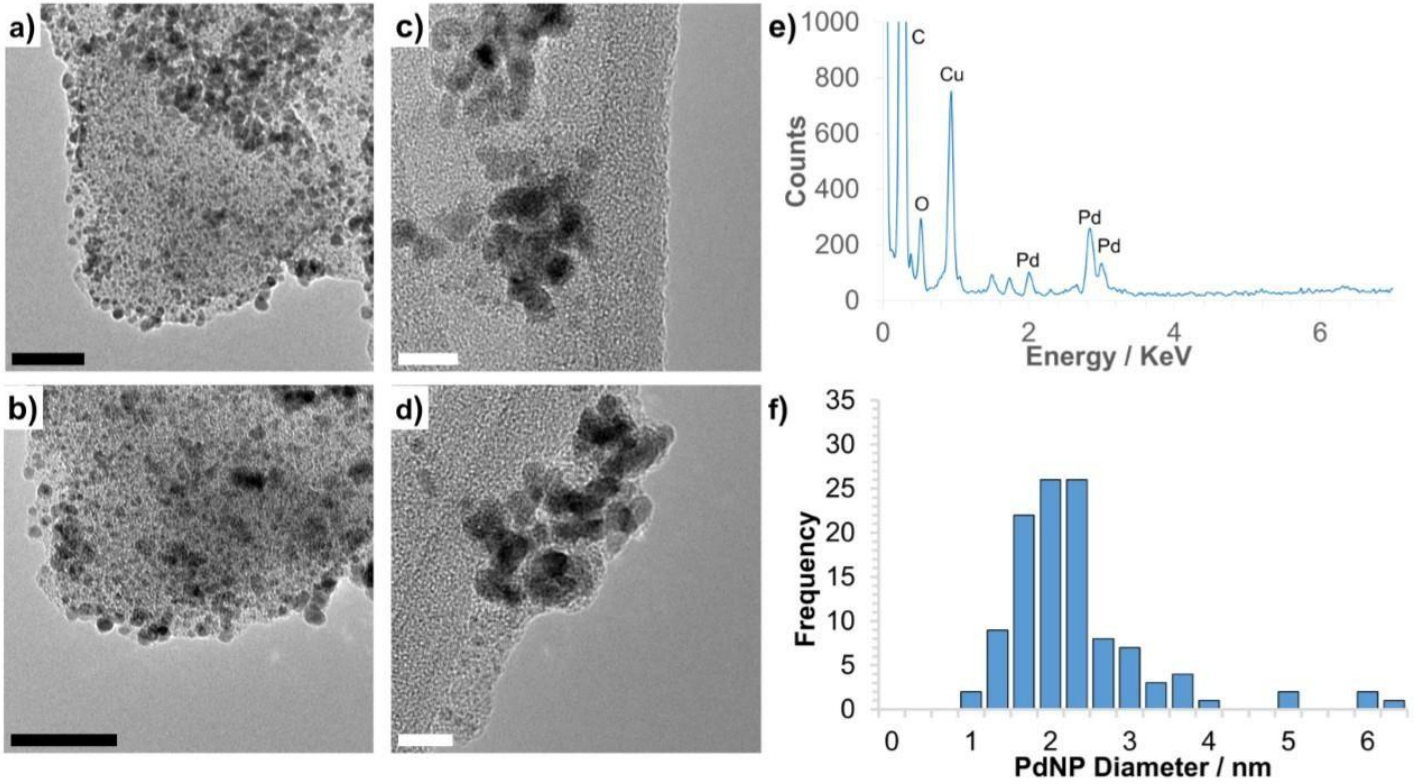


Figure S49 **X-ray powder diffraction pattern of PdNP@PPh$_2$PIILP (1c)**

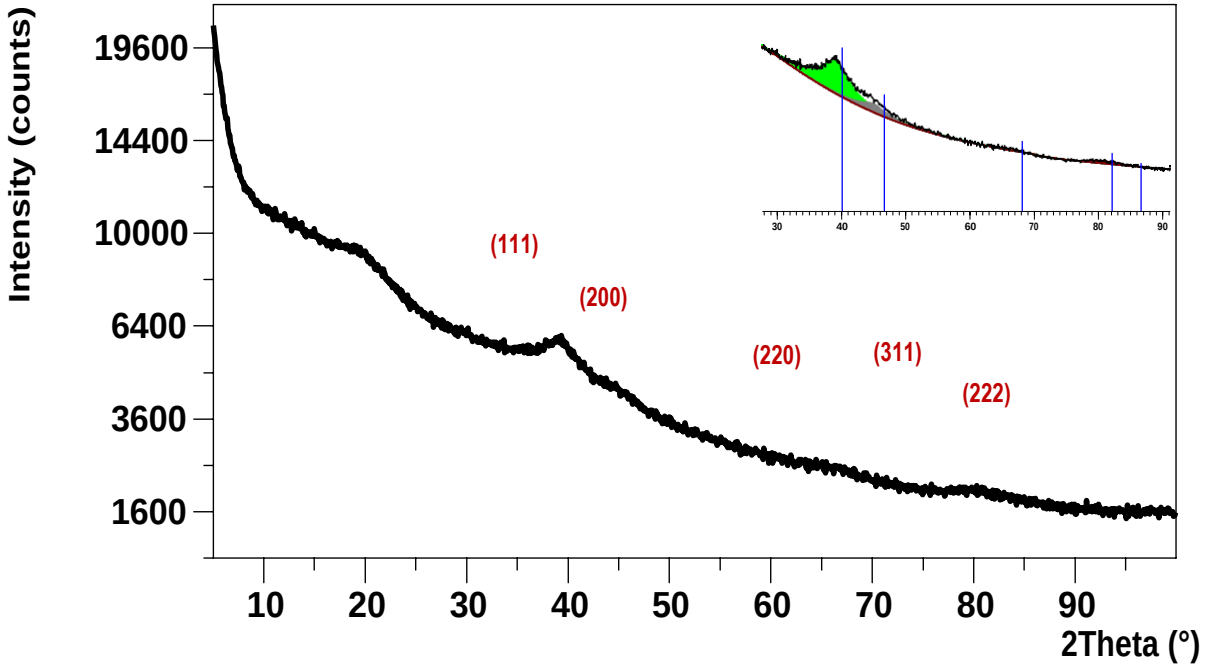


Figure S50 **Solid state ^{13}C NMR spectrum of PdNP@PPh_2-PEGPIILP (2c)**

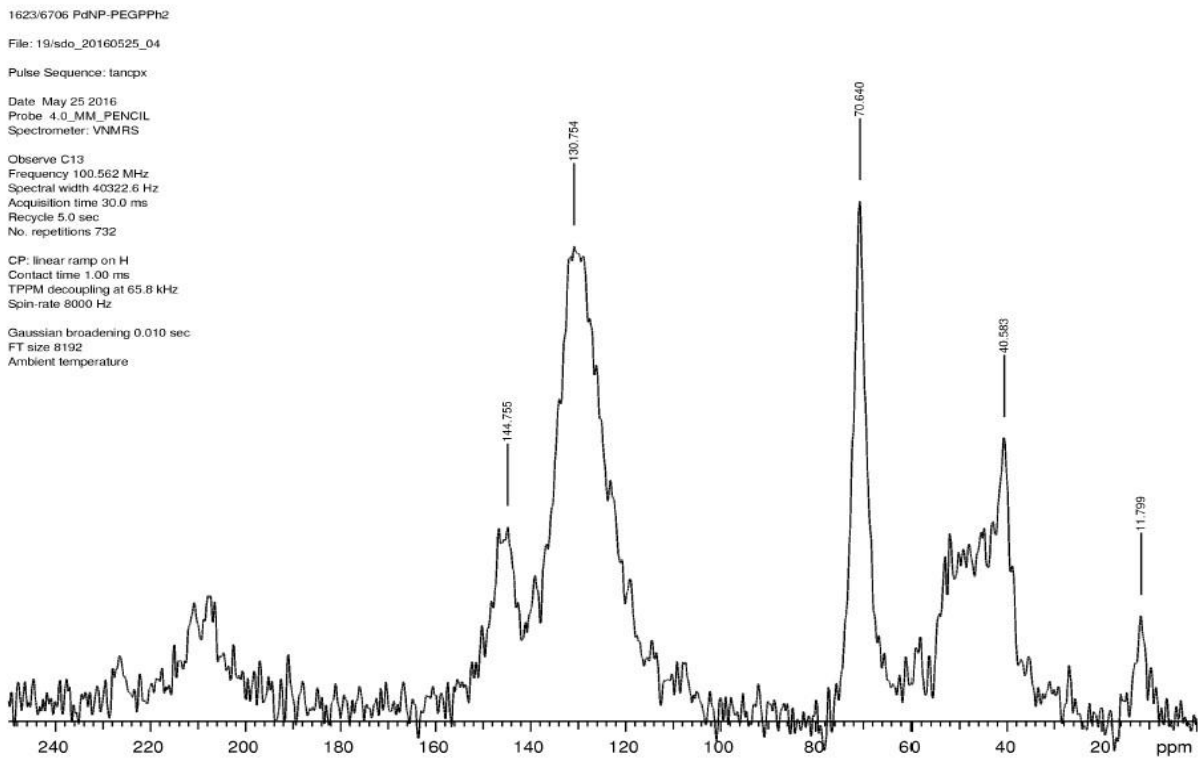


Figure S51 **Solid state ^{31}P NMR spectrum of PdNP@PPh_2-PEGPIILP (2c)**

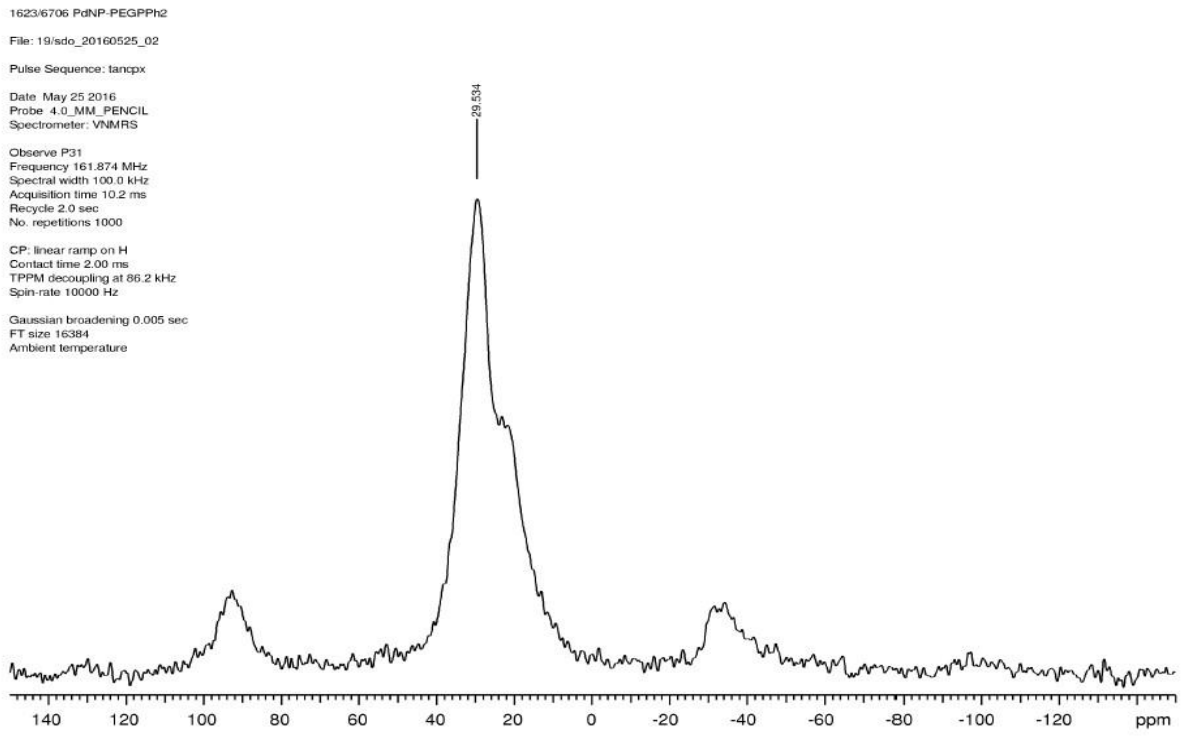
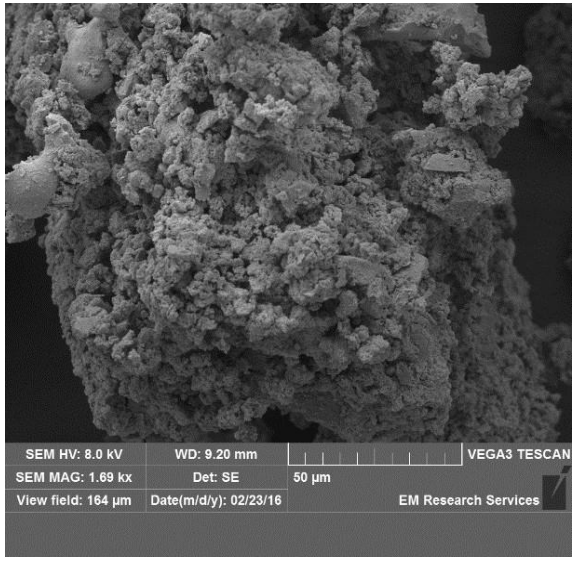


Figure S52 **SEM images of freshly prepared PdNP@PPh_2-PEGPIILP (2c)**



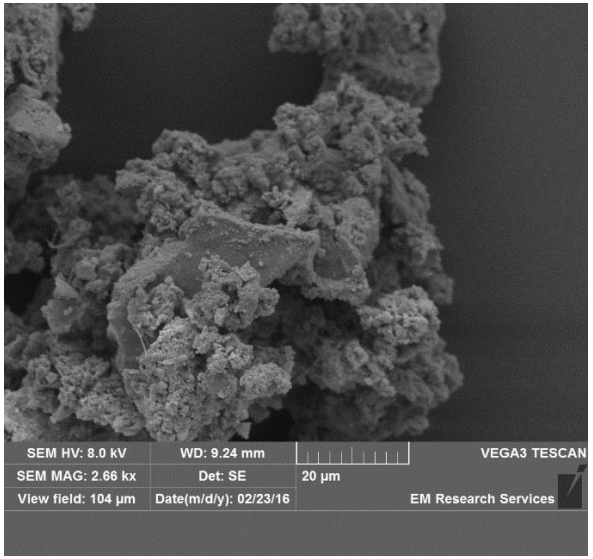


Figure S53 **FT-IR spectrum of freshly prepared PdNP@PPh_2-PEGPIILP (2c)**

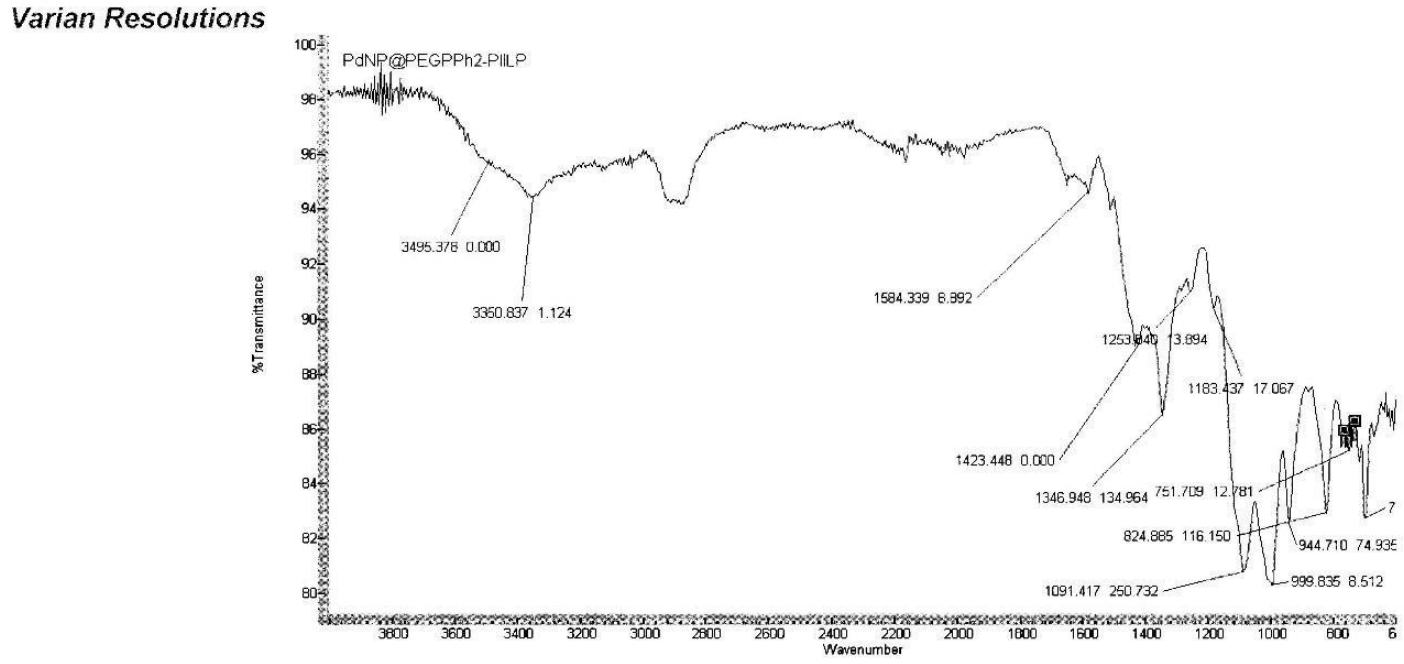


Figure S54 **Pd 3d core level XPS spectrum of PdNP@PPh_2-PEGPIILP (2c) referenced to the hydrocarbon C 1s**

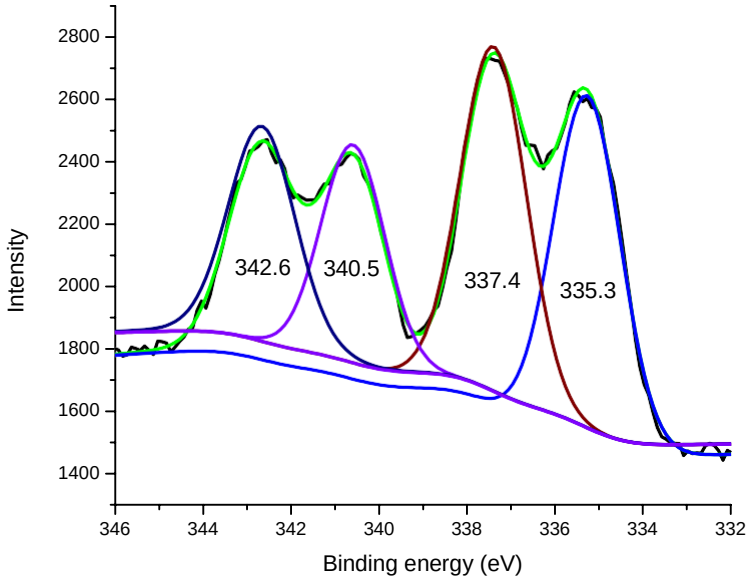


Figure S55 **(a-d) TEM image of PdNP@PPh_2-PEGPIILP (2c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)**

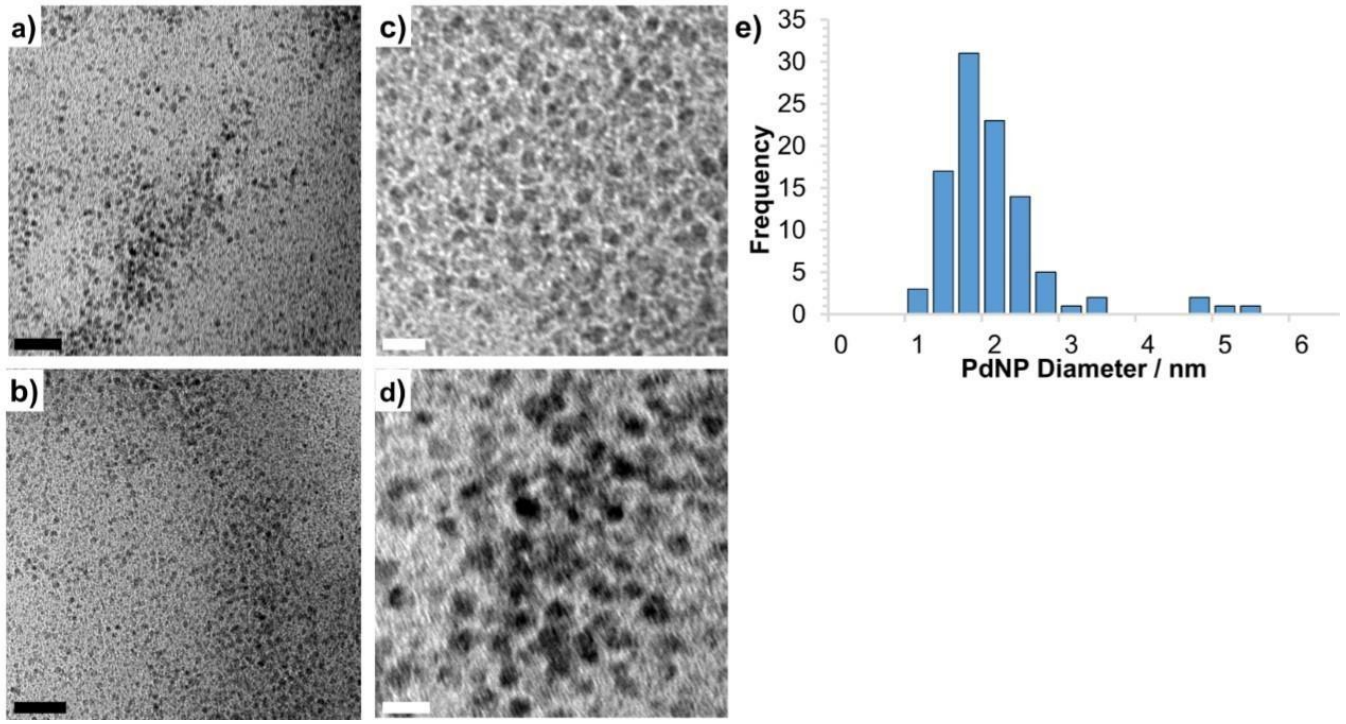
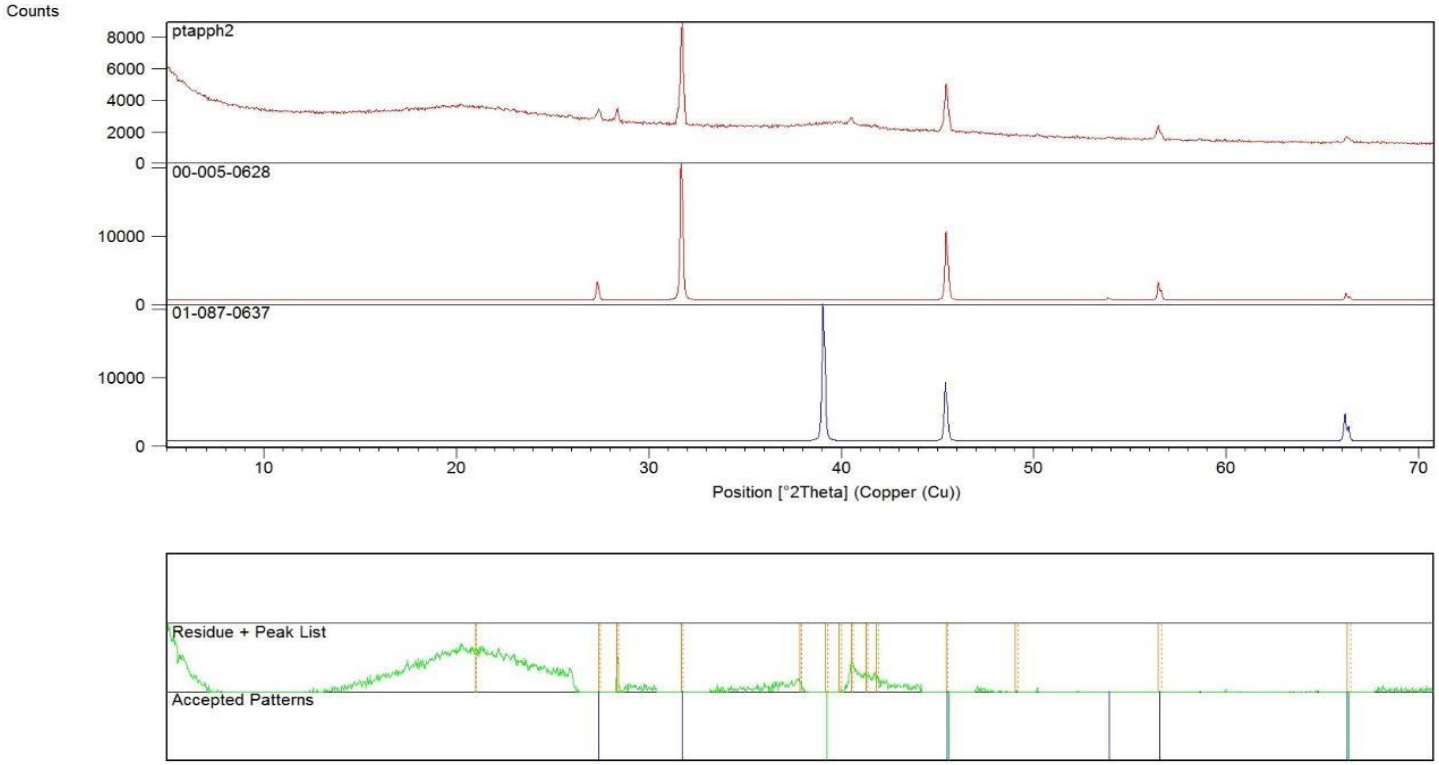


Figure S56 **X-ray powder diffraction pattern of PdNP@PPh_2-PEGPIILP (2c)**



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_2PEGstyrene (3c)**

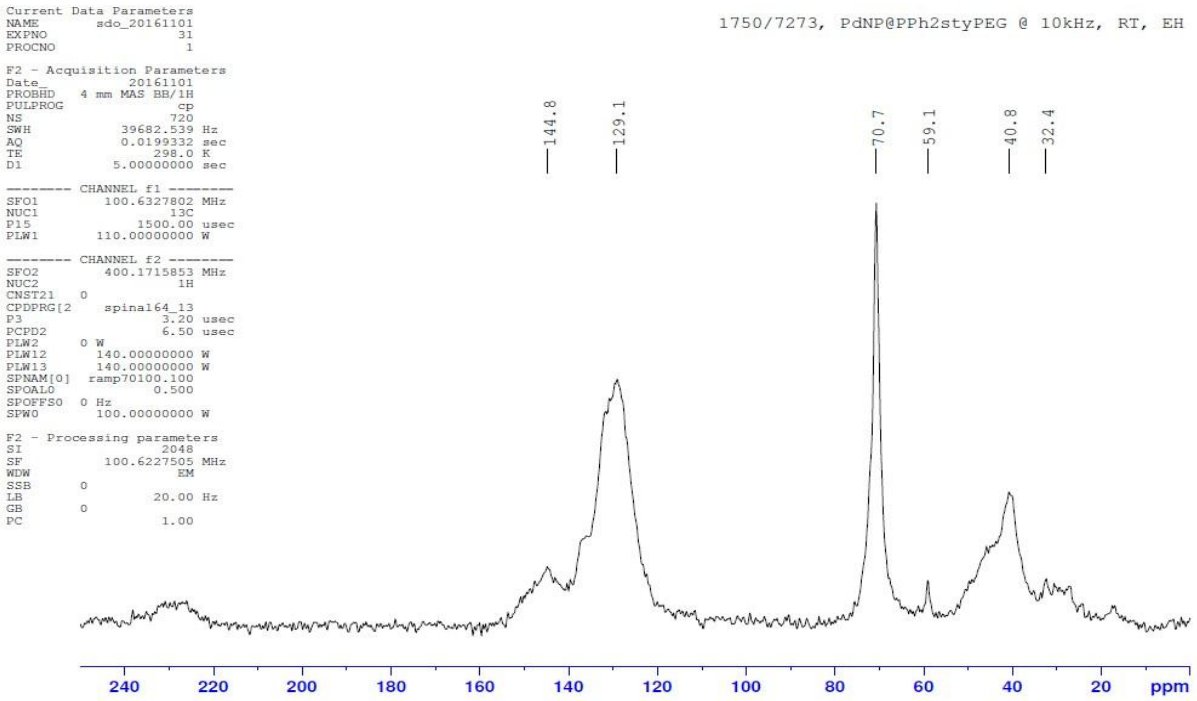


Figure S58 **Solid state ^{31}P NMR spectrum of PdNP@PPh_2PEGstyrene (3c)**

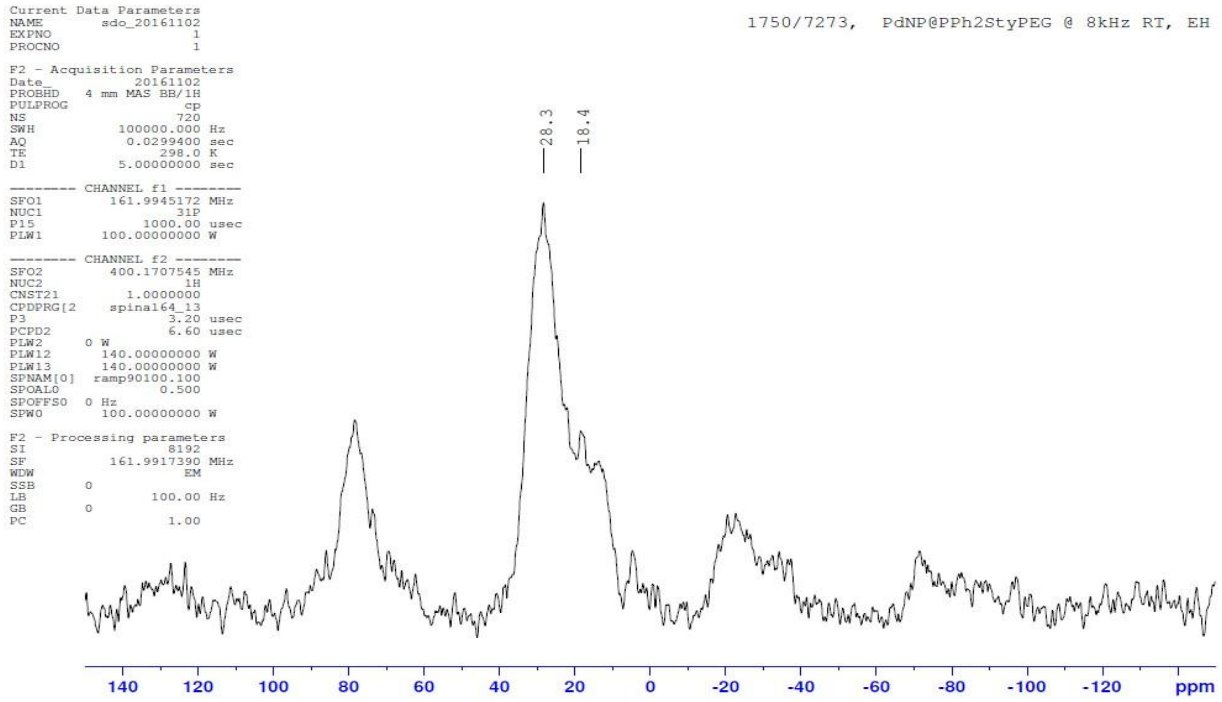
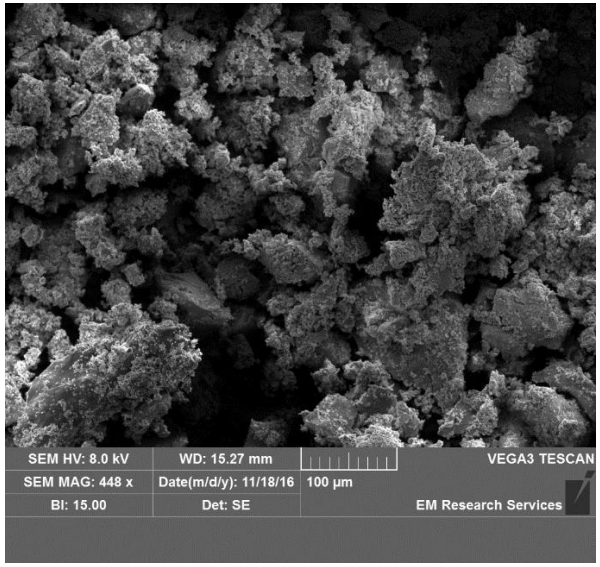


Figure S59 **SEM images of freshly prepared PdNP@PPh$_2$PEGstyrene (3c)**



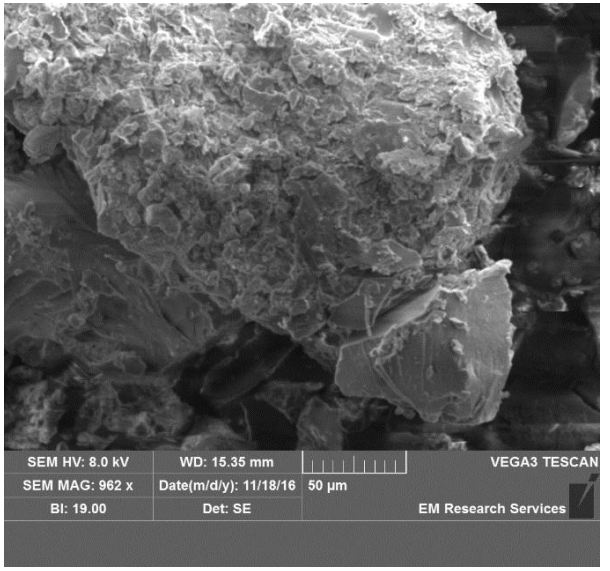


Figure S60 **FT-IR spectrum of freshly prepared PdNP@PPh$_2$PEGstyrene (3c)**

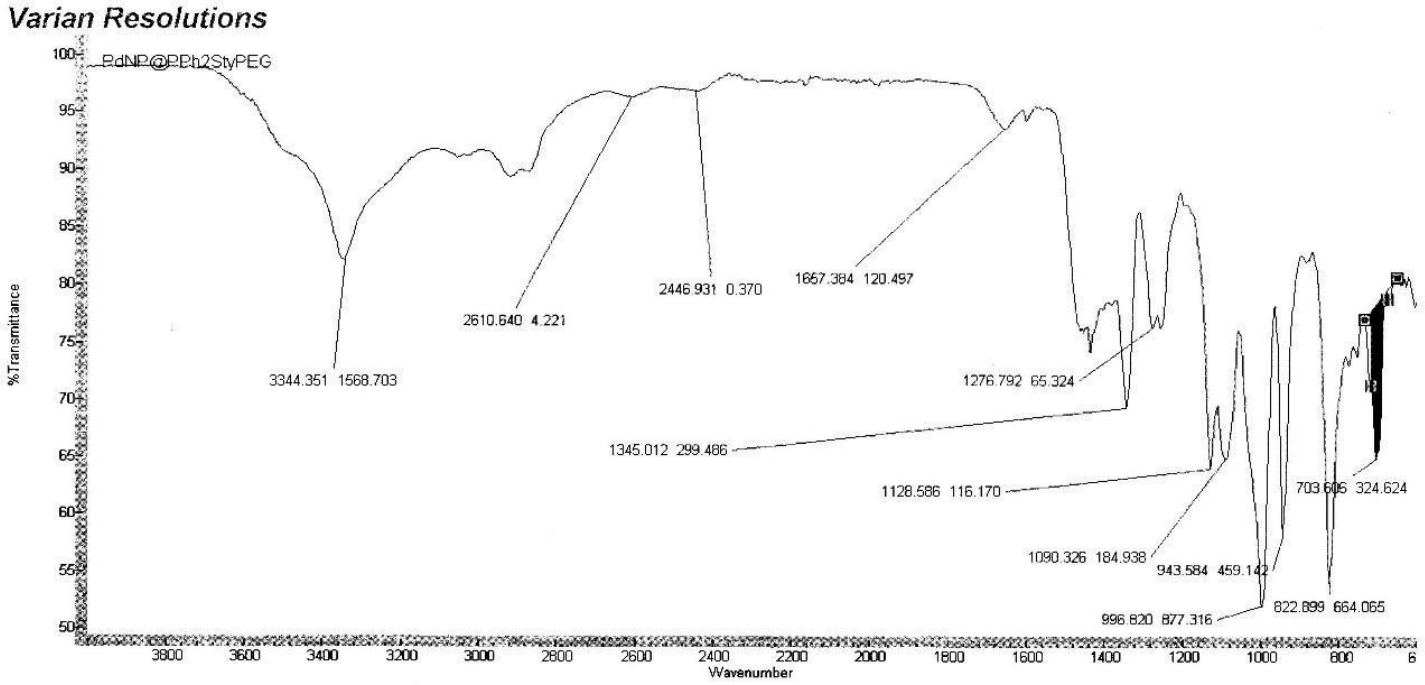


Figure S61 **Pd 3d core level XPS spectrum of PdNP@PPh$_2$PEGstyrene (3c) referenced to the hydrocarbon C 1s**

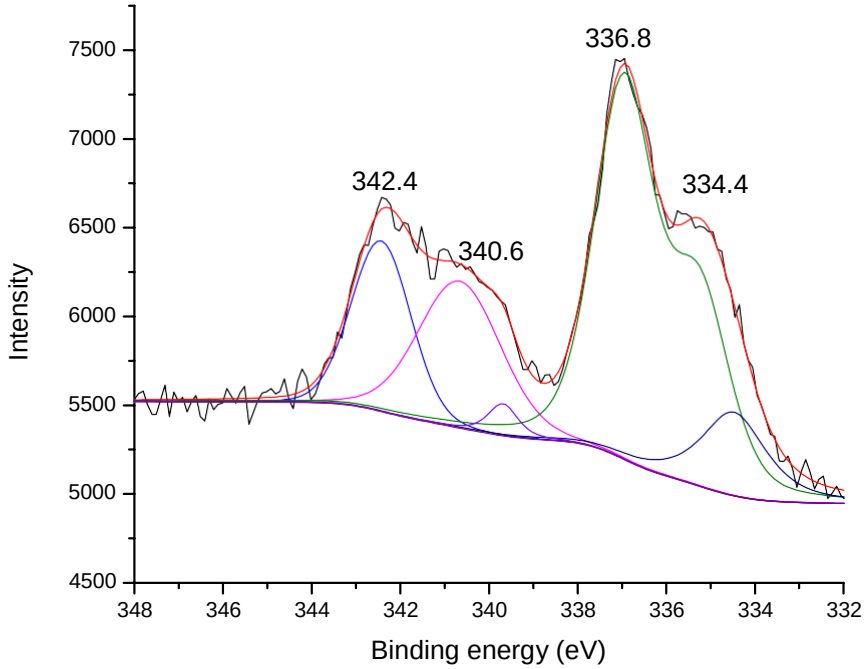


Figure S62 **(a-d) TEM image of PdNP@PPh$_2$PEGstyrene (3c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)**

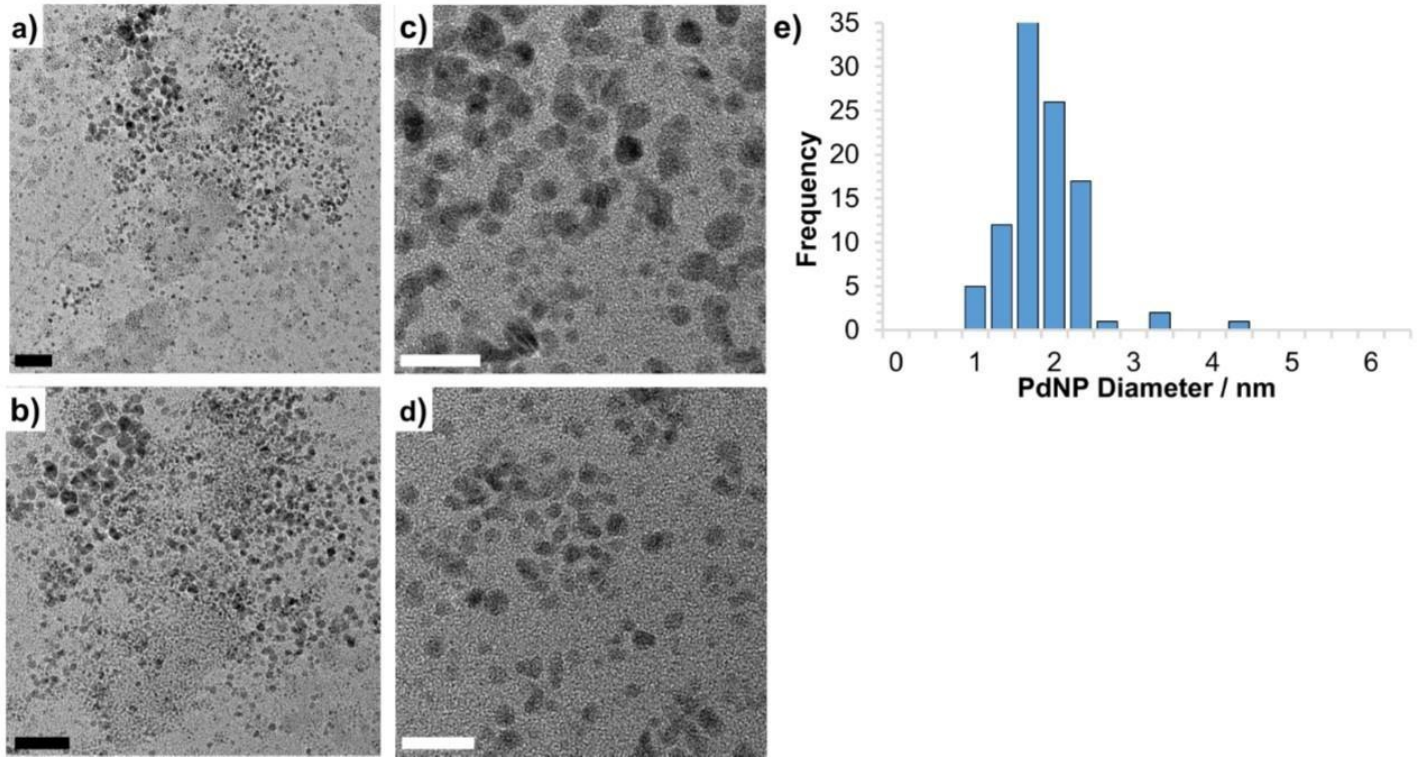


Figure S63 Solid state ^{13}C NMR spectrum of PdNP@PEGPIILP (4c)

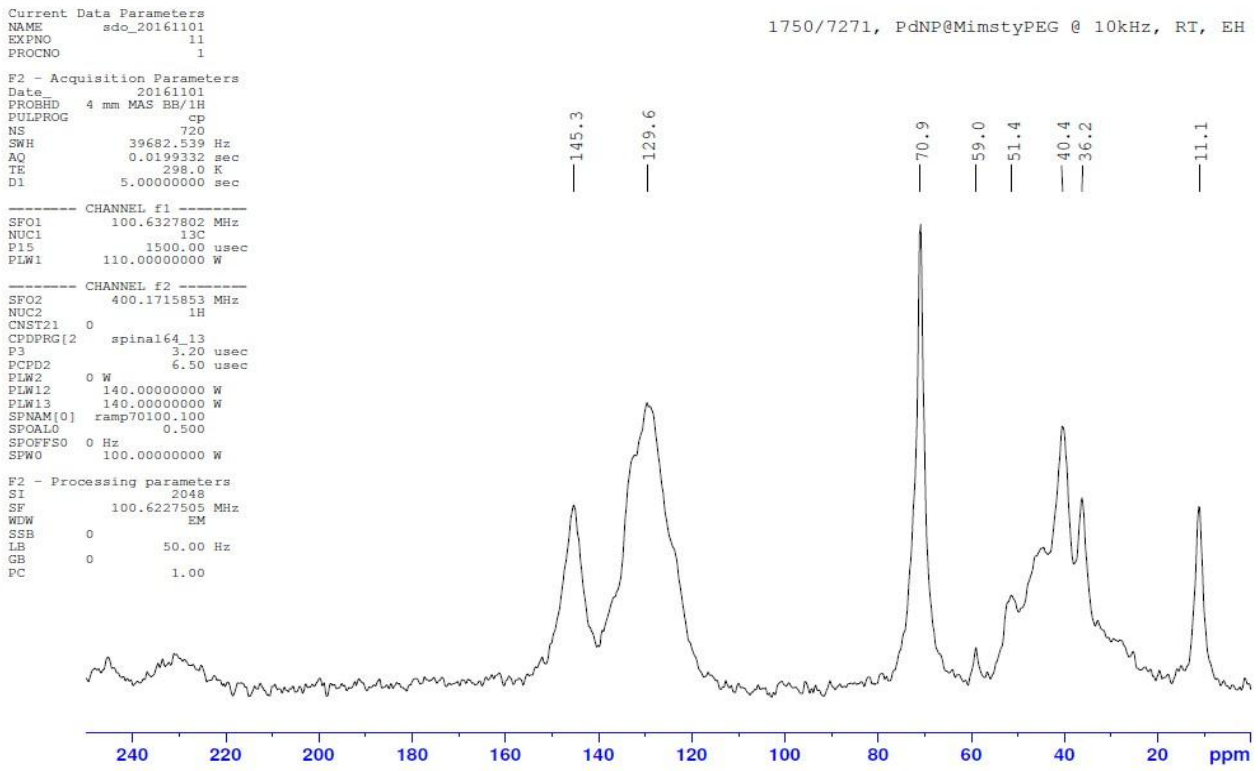
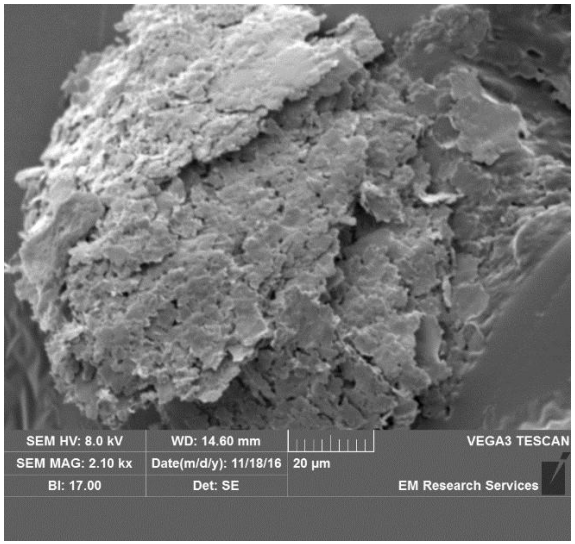


Figure S64 SEM images of freshly prepared PdNP@PEGPIILP (4c)



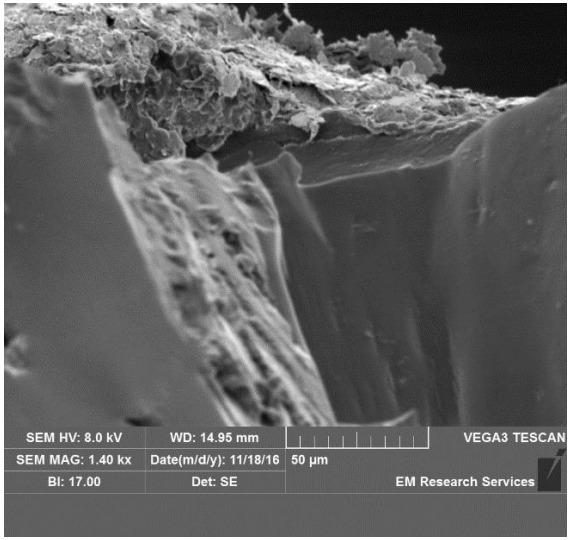


Figure S65 FT-IR spectrum of freshly prepared PdNP@PEGPIILP (4c)

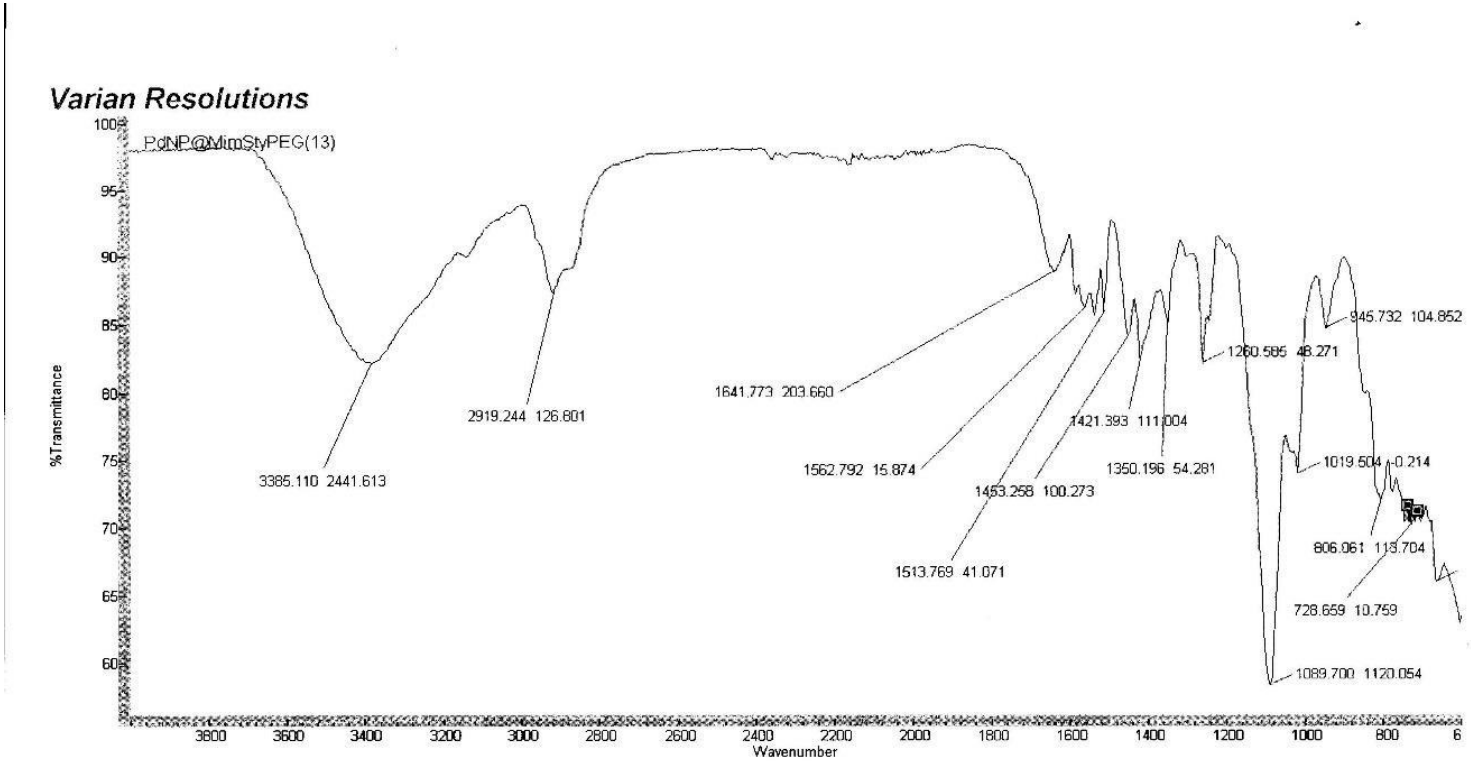


Figure S66 **(a-d) TEM image of PdNP@PEGPIILP (4c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)**

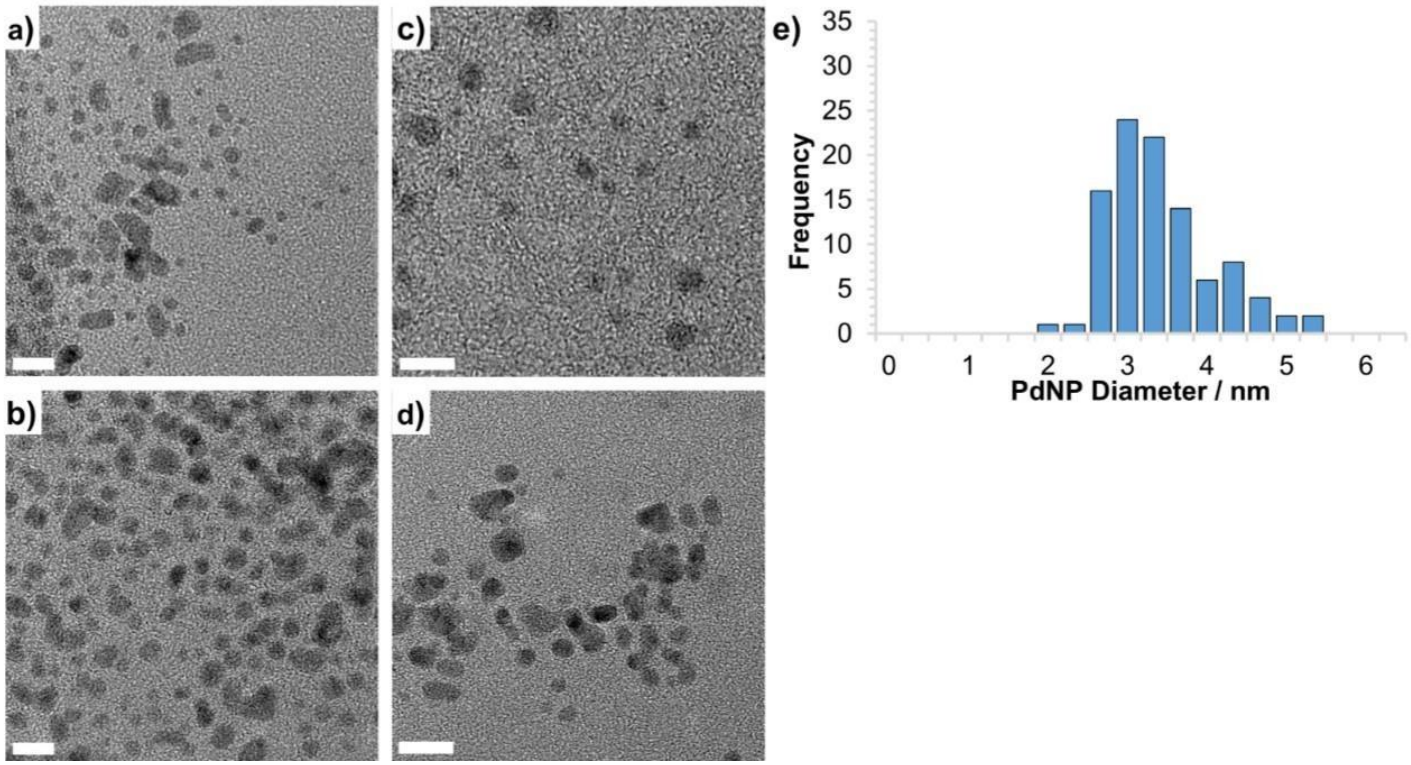
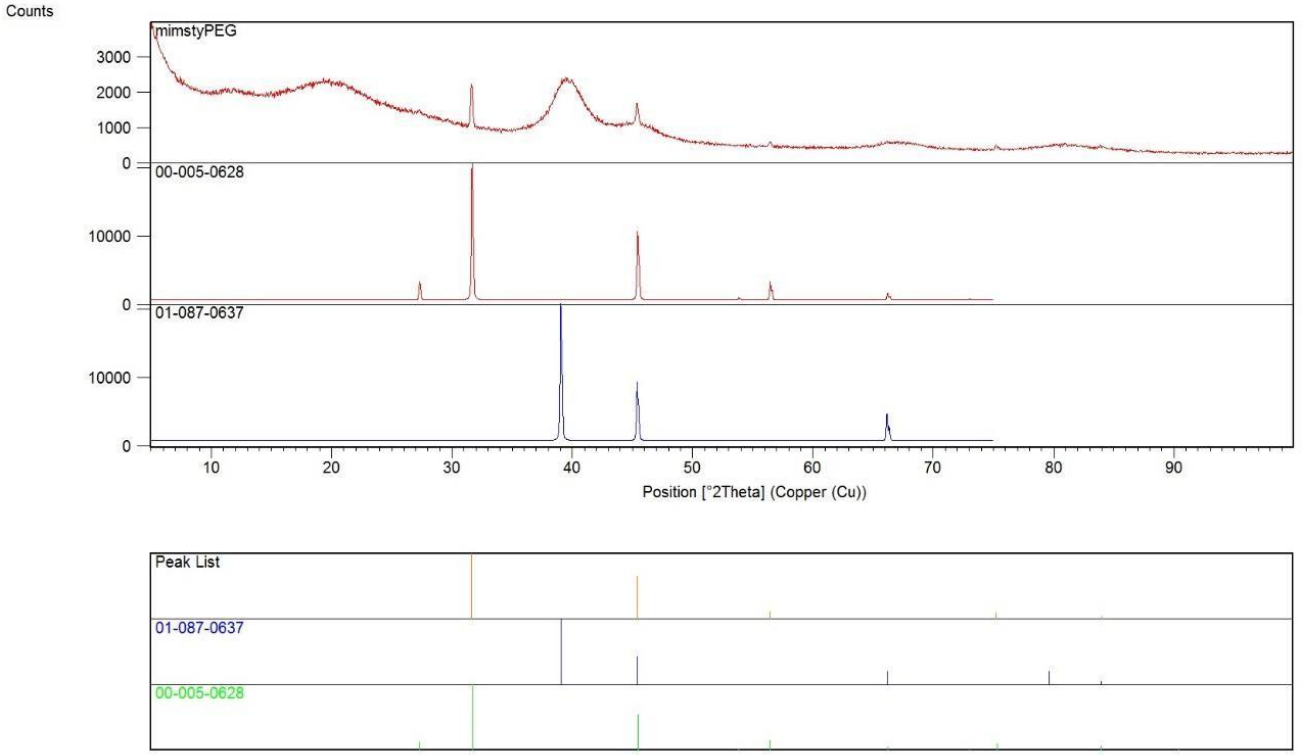


Figure S67 X-ray powder diffraction pattern of PdNP@PEGPIILP (4c)



XRD scattering patter 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

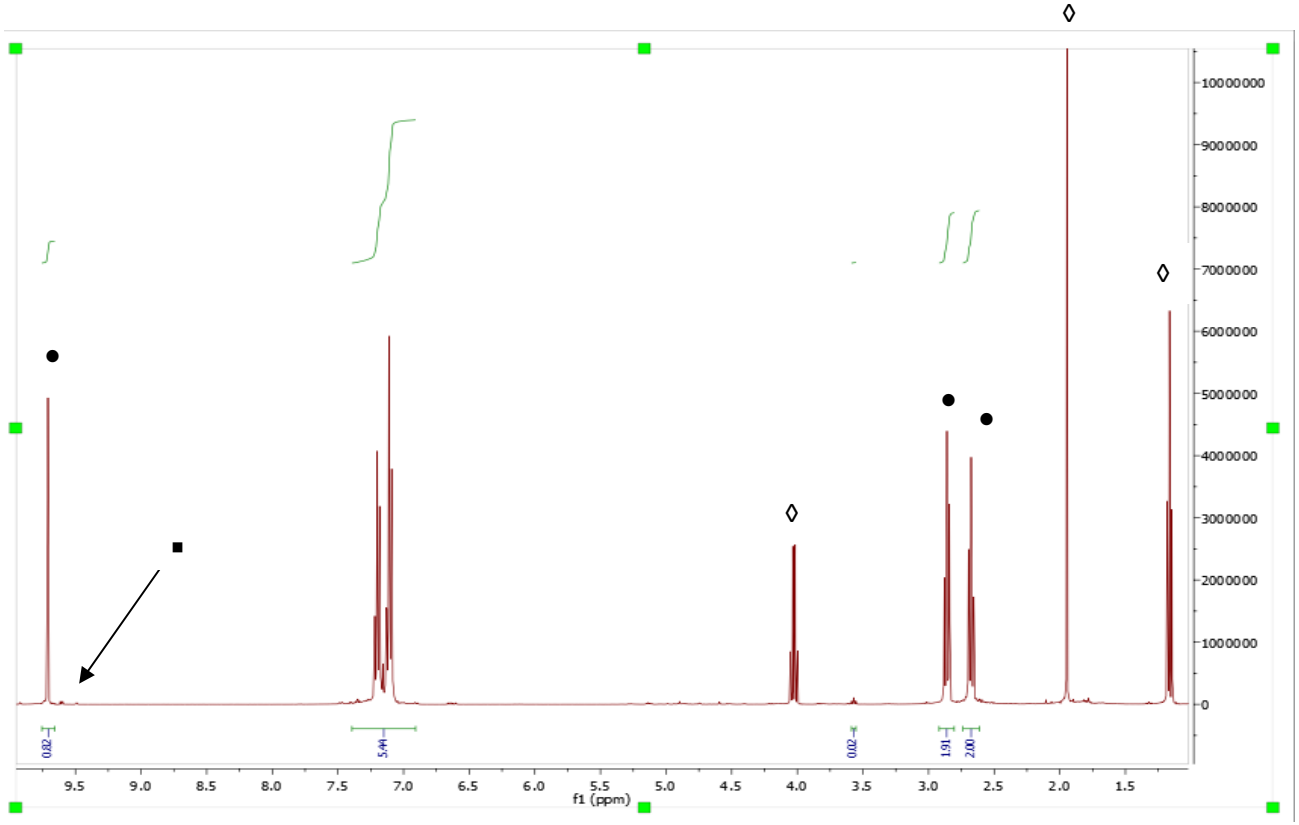


Figure S69 Sample ^{1}H NMR spectrum for calculating selectivity from the hydrogenation of trans-2-pentenal[2]

Sample spectrum used to determine selectivity; ● trans-2-pentenal, ◊ pentan-1-ol

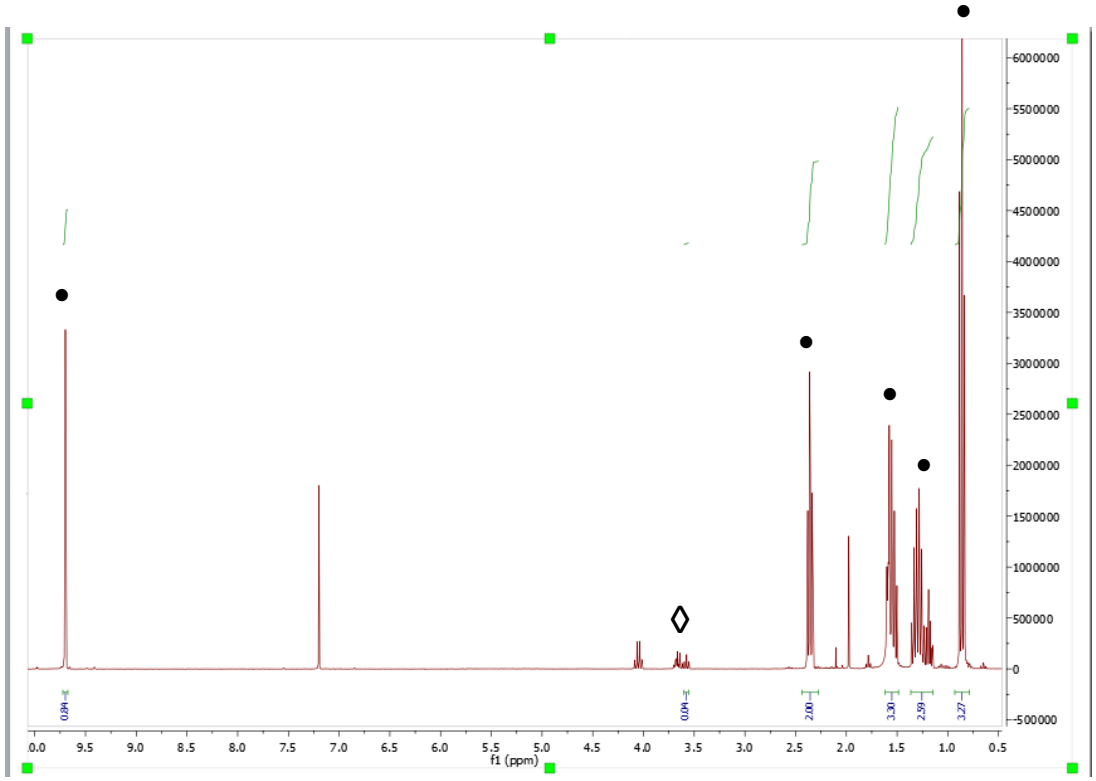


Figure S70 Sample ^{1}H NMR spectrum for calculating the selectivity from the hydrogenation of 3-(furan-2-yl)acrolein[3]

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

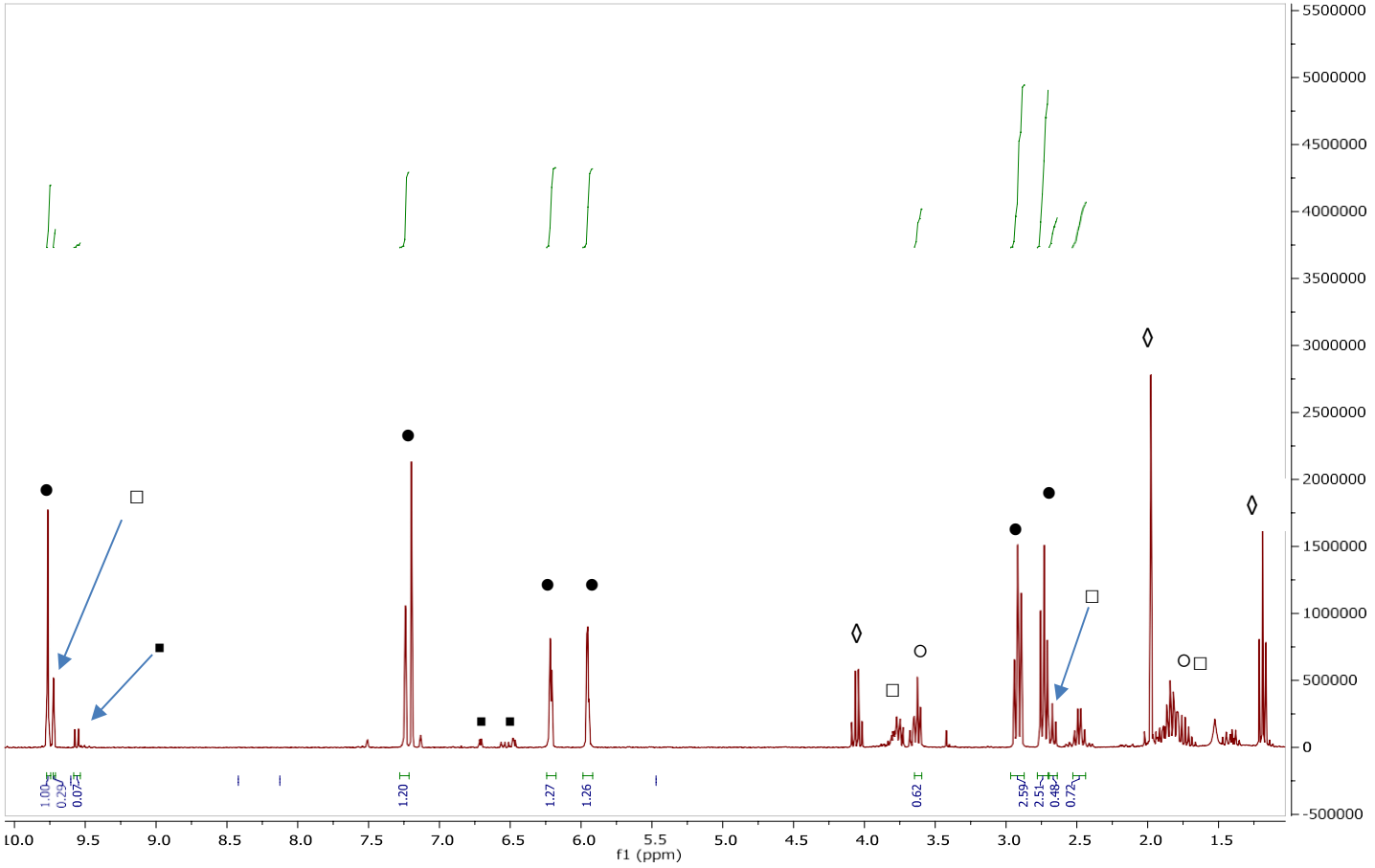


Figure S71 Sample ^{1}H NMR spectrum for calculating the selectivity from the hydrogenation of 2,6,6-trimethyl-2- cyclohexene-1,4- dione[4]

Sample spectrum used to determine selectivity; ▪ 2,6,6-trimethyl-2- cyclohexene-1,4- dione, ● 2,6,6-trimethyl-1,4-cyclohexanedione (levodione), □ 4-hydroxy-3,3,5-trimethylcyclohexanone, ◊ 4-hydroxy-3,5,5-trimethyl-cyclohex-2-enone.

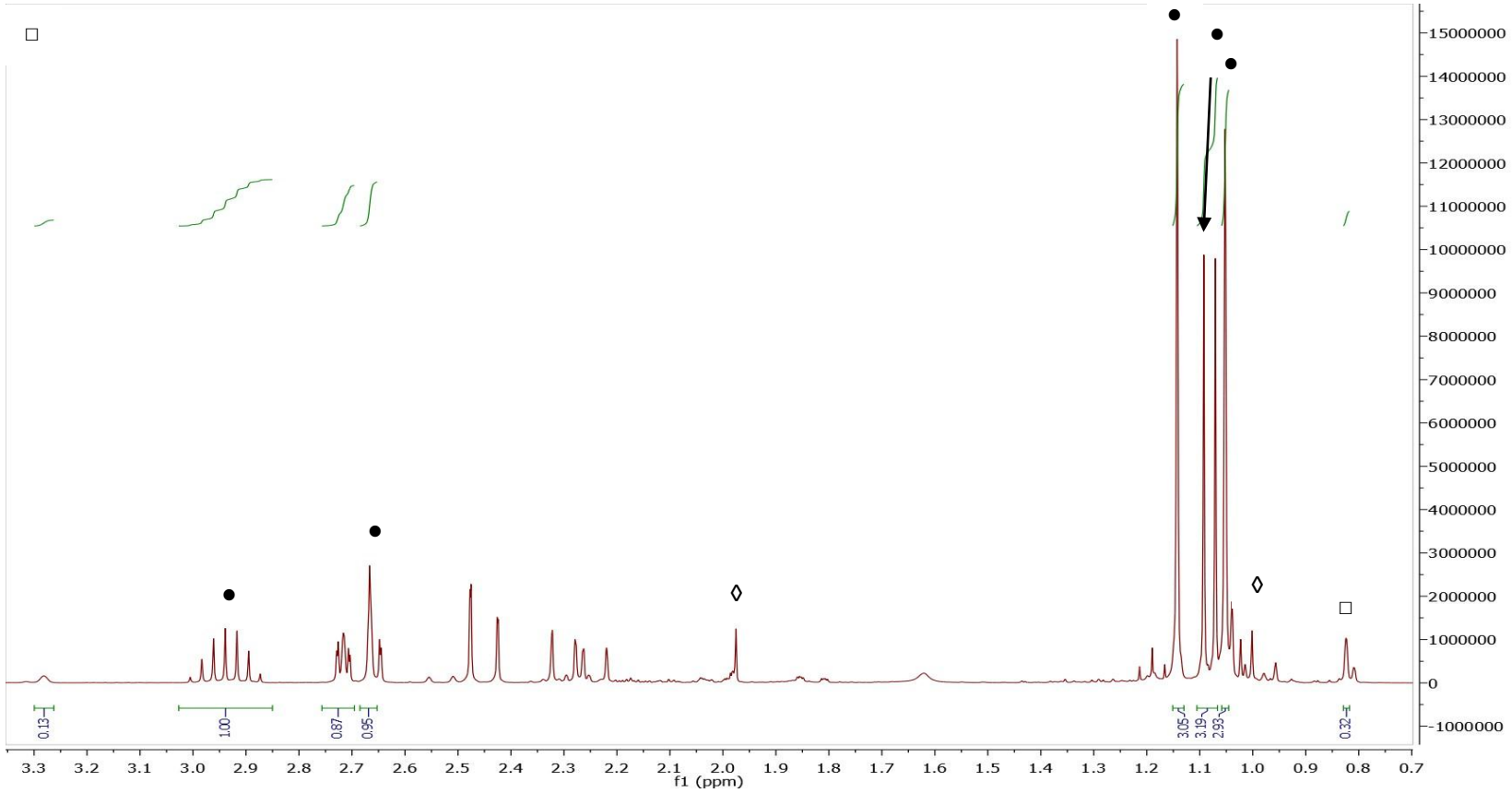


Figure S72 Sample ^{1}H NMR spectrum for calculating the selectivity from the hydrogenation of *trans*-4-phenyl-3-buten-2-one[5]

Sample spectrum used to determine selectivity; ● 4-phenylbutan-2-one, ◊ ethyl acetate, □ ethanol

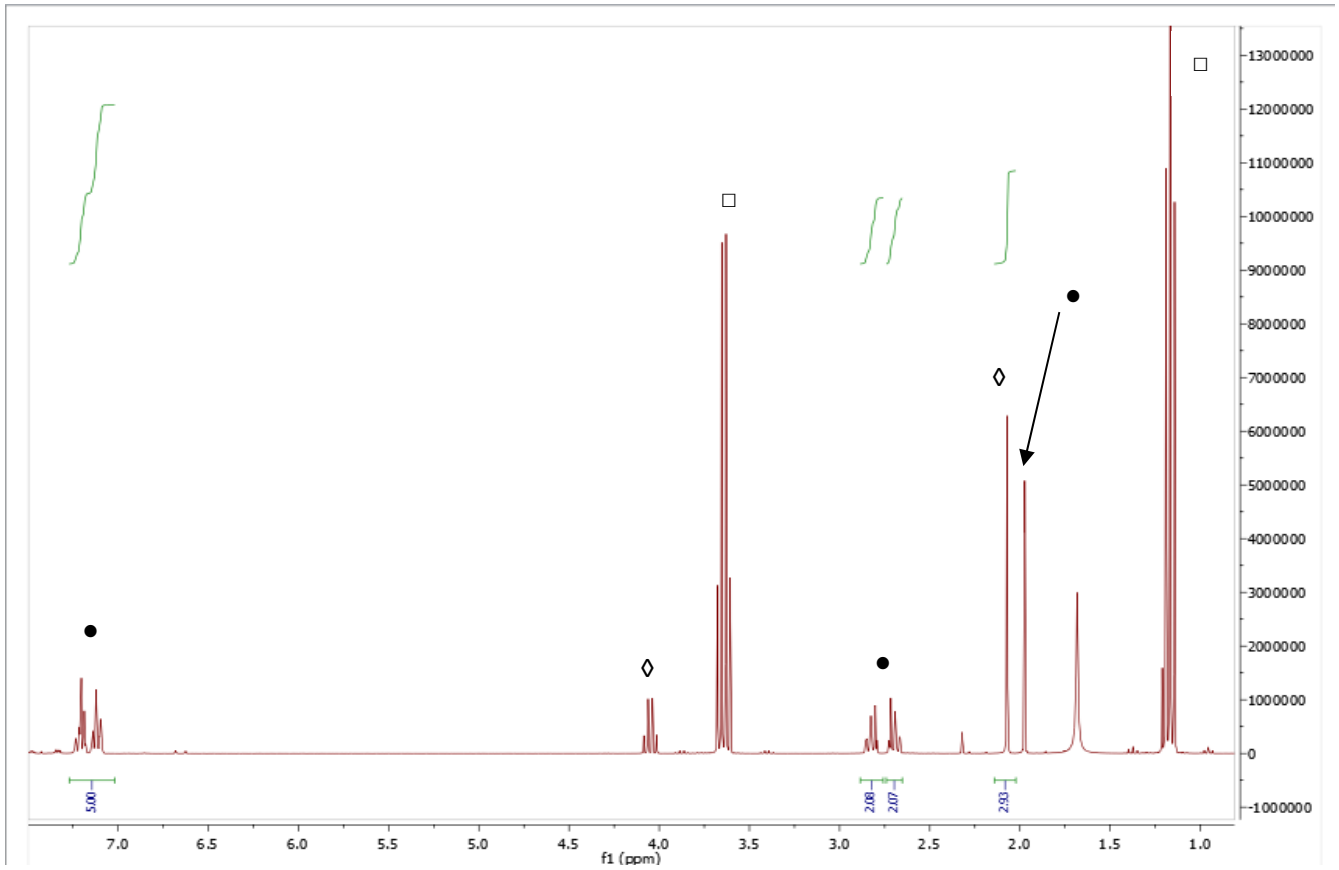


Figure S73 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of *trans*-chalcone[6]

Sample spectrum used to determine selectivity; ● 1,3-diphenylpropan-1-one

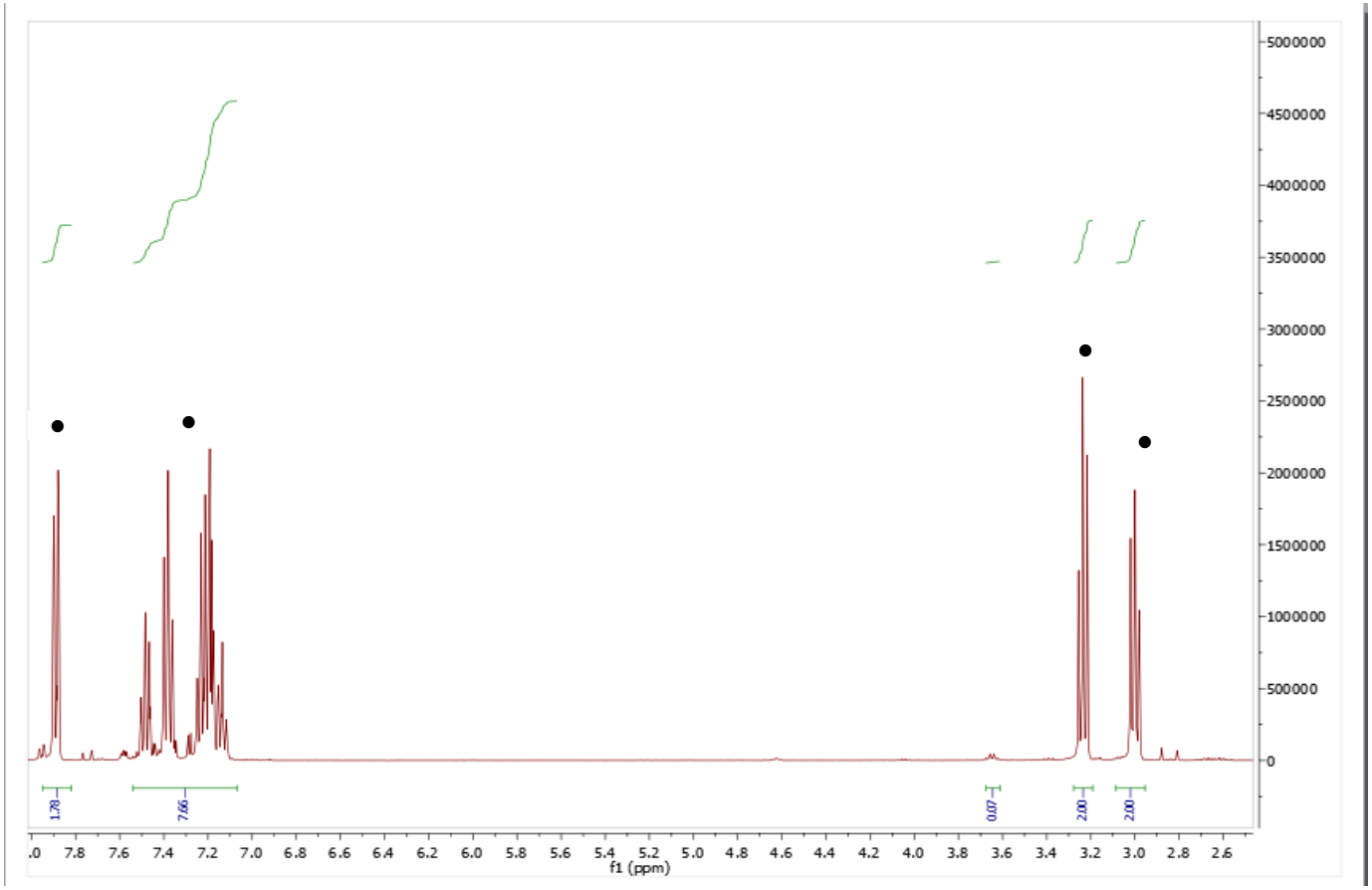


Figure S74 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of citral[7]

Sample spectrum used to determine selectivity; ● 3,7-dimethyl-oct-6-enal, ◊ ethyl acetate

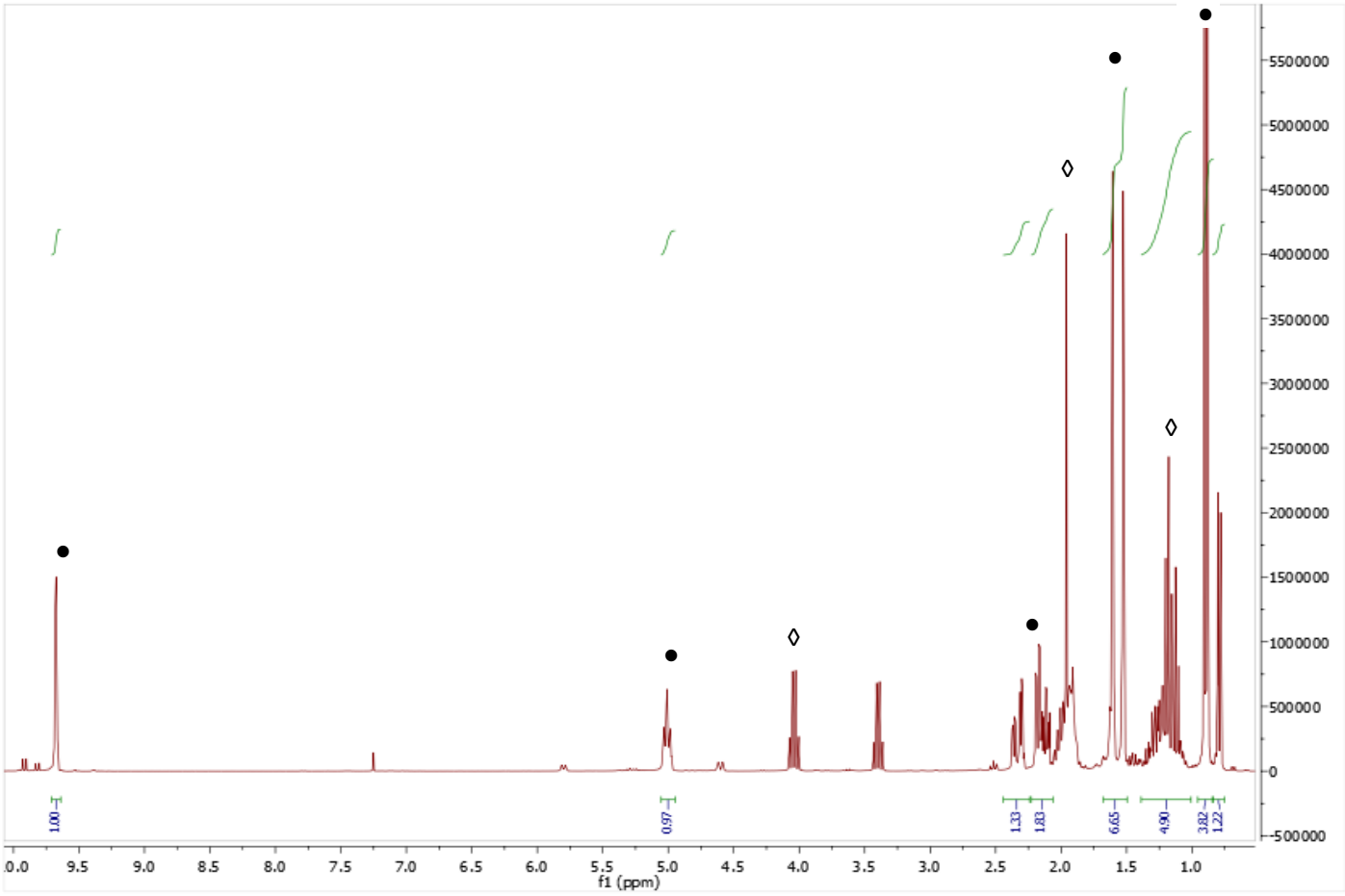


Figure S75 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of cyclohexenone[8]

Sample spectrum used to determine selectivity; ● cyclohexanone, ◊ ethyl acetate

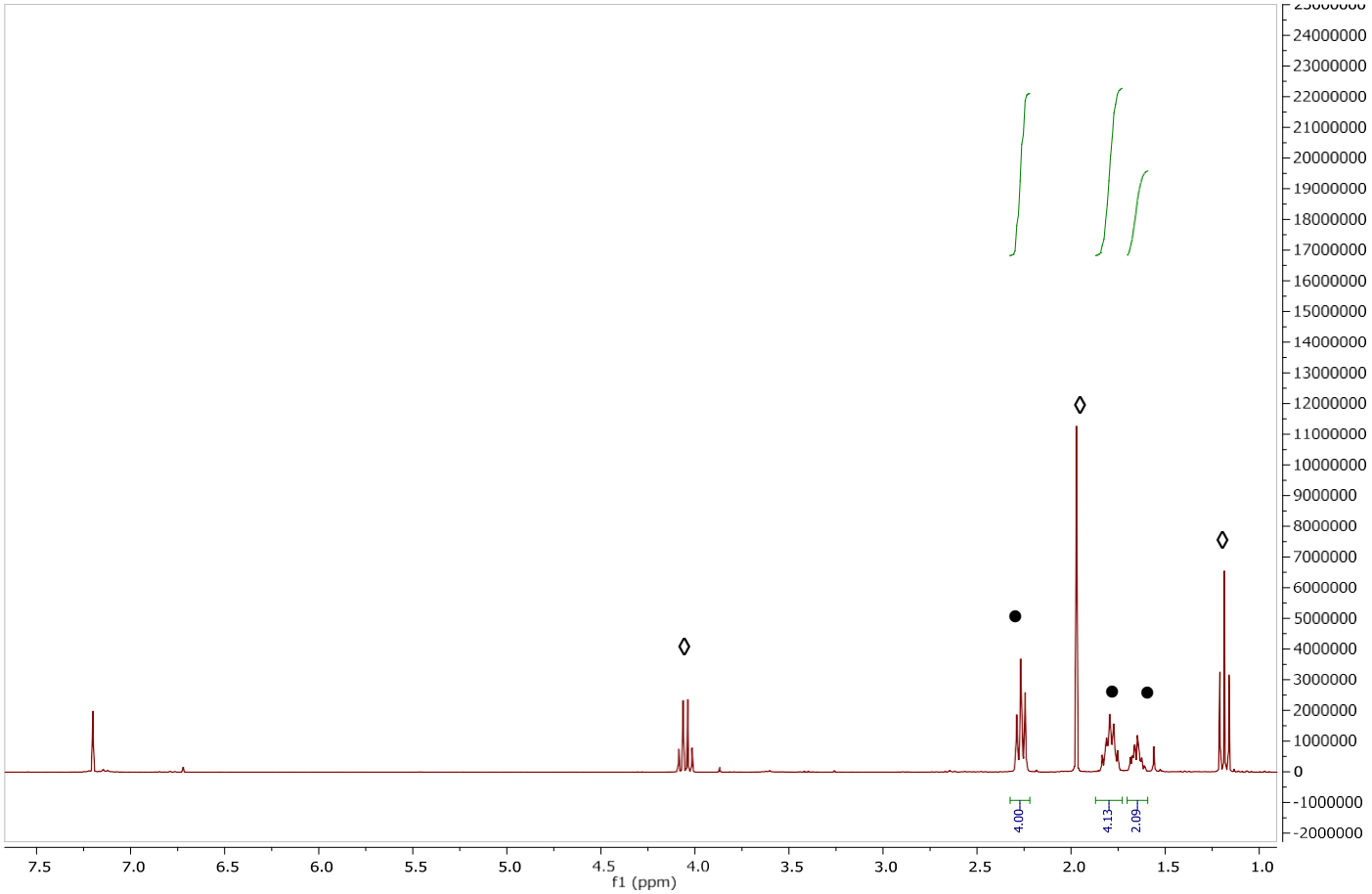


Figure S76 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of trans-4-methoxycinnamaldehyde[9]

Sample spectrum used to determine selectivity; ▪ trans-4-methoxycinnamaldehyde, ● 3-(4-methoxyphenyl)propionaldehyde,

○ 3-(4-dimethylaminophenyl)-propan-1-ol, ◊ ethyl acetate

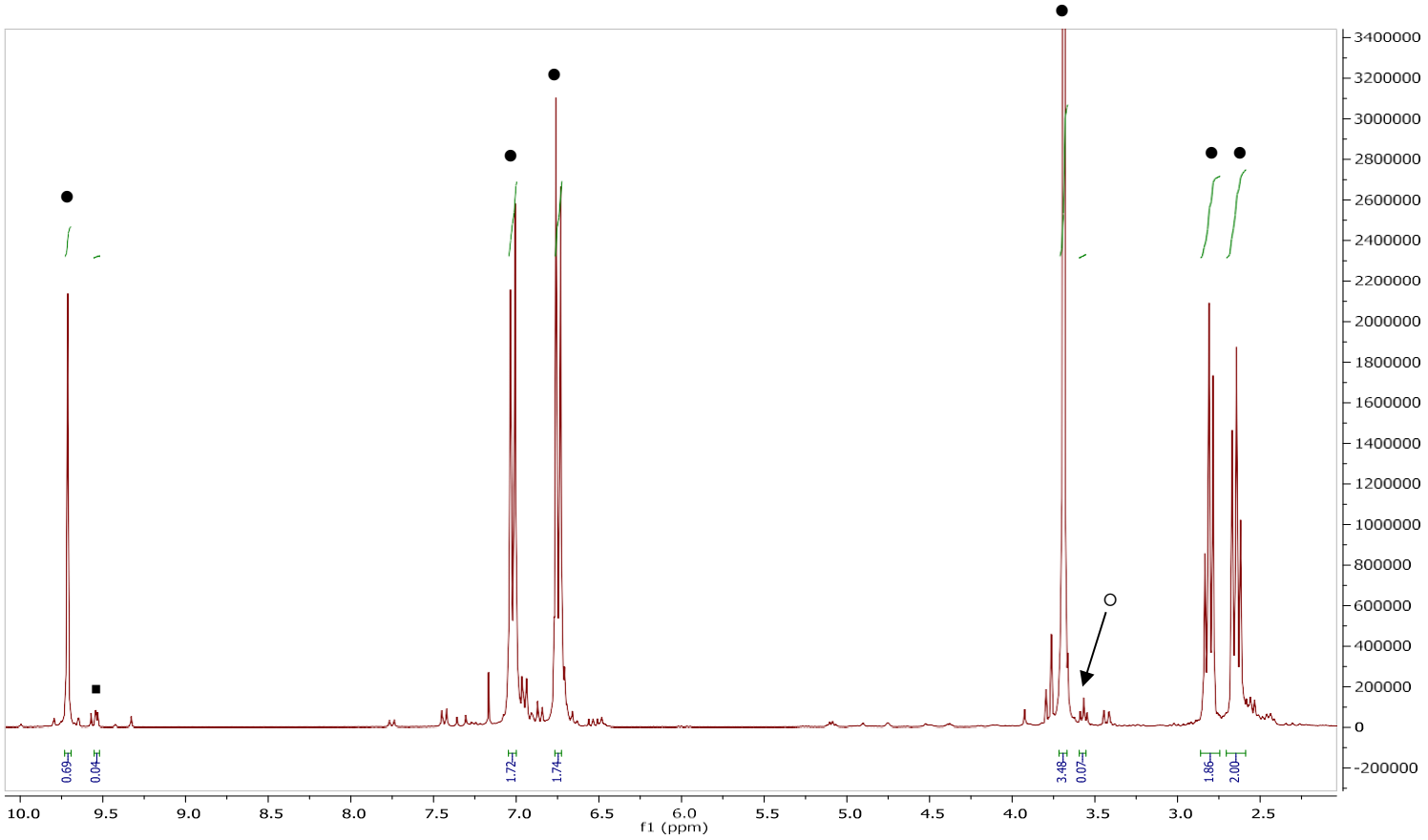


Figure S77 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of cinnamonitrile[10]

Sample spectrum used to determine selectivity; ▪ cinnamonitrile, ● 3-phenylpropan-1-amine, ◊ ethyl acetate

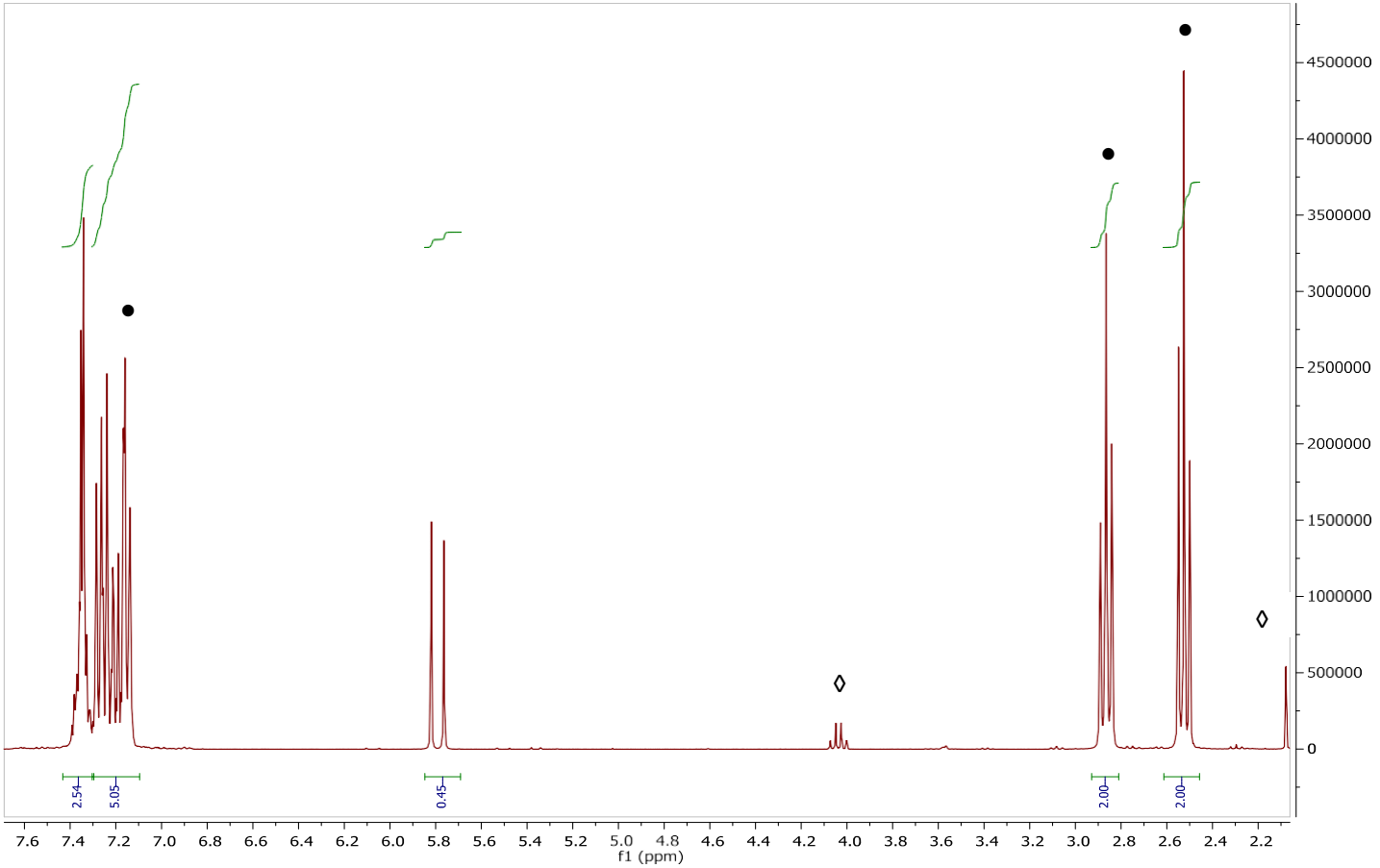


Figure S78 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of 4-dimethylaminocinnamaldehyde[11]

Sample spectrum used to determine selectivity; ▪ 4-dimethylaminocinnamaldehyde, ● 3-(4-dimethylaminophenyl)propionaldehyde, ○ 3-(4-dimethylaminophenyl)-propan-1-ol, ◊ ethyl acetate

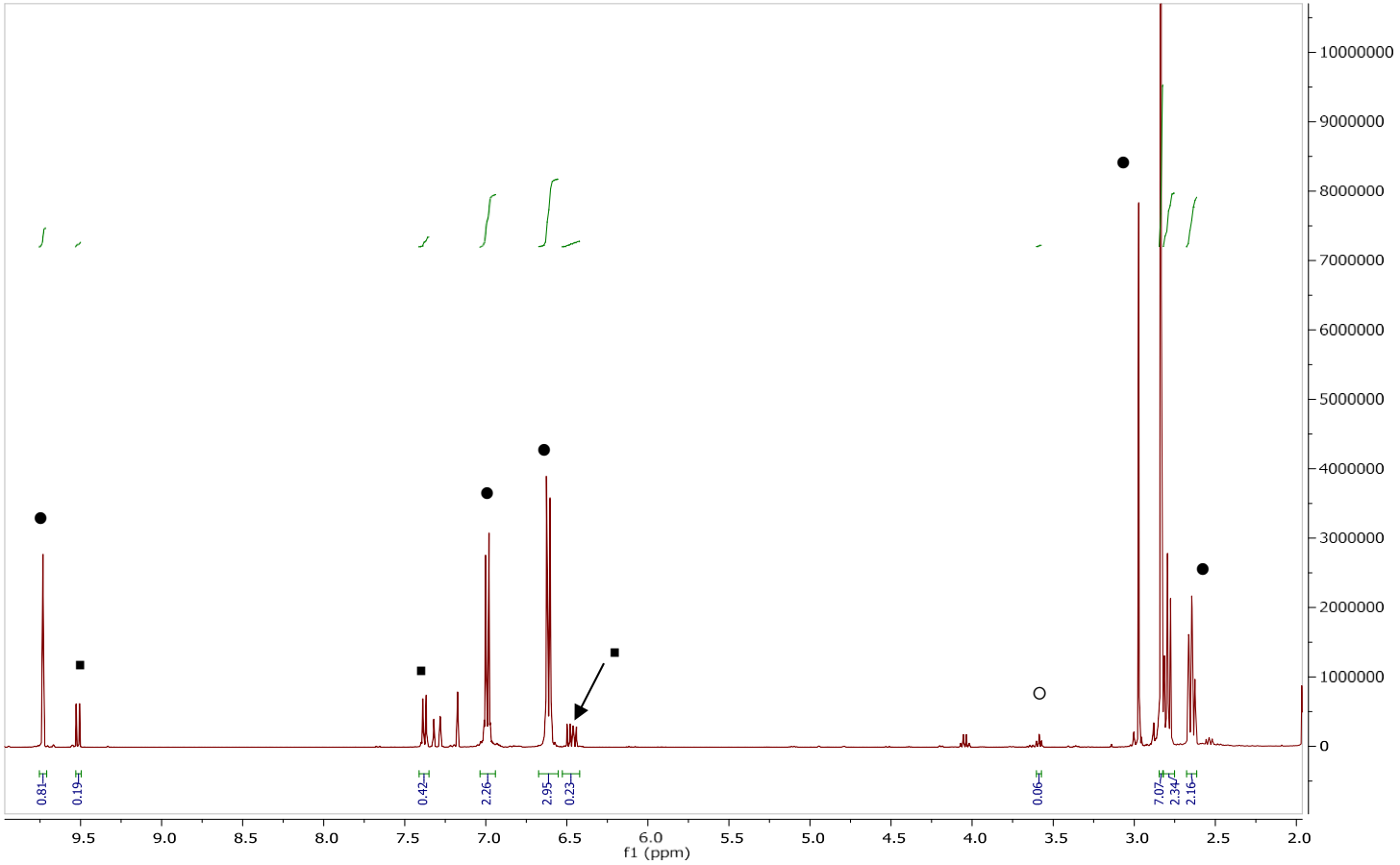


Figure S79 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of ethyl cinnamate[12]

Sample spectrum used to determine selectivity; ▪ ethyl cinnamate, ● ethyl 3-phenylpropionate, ◊ ethyl acetate

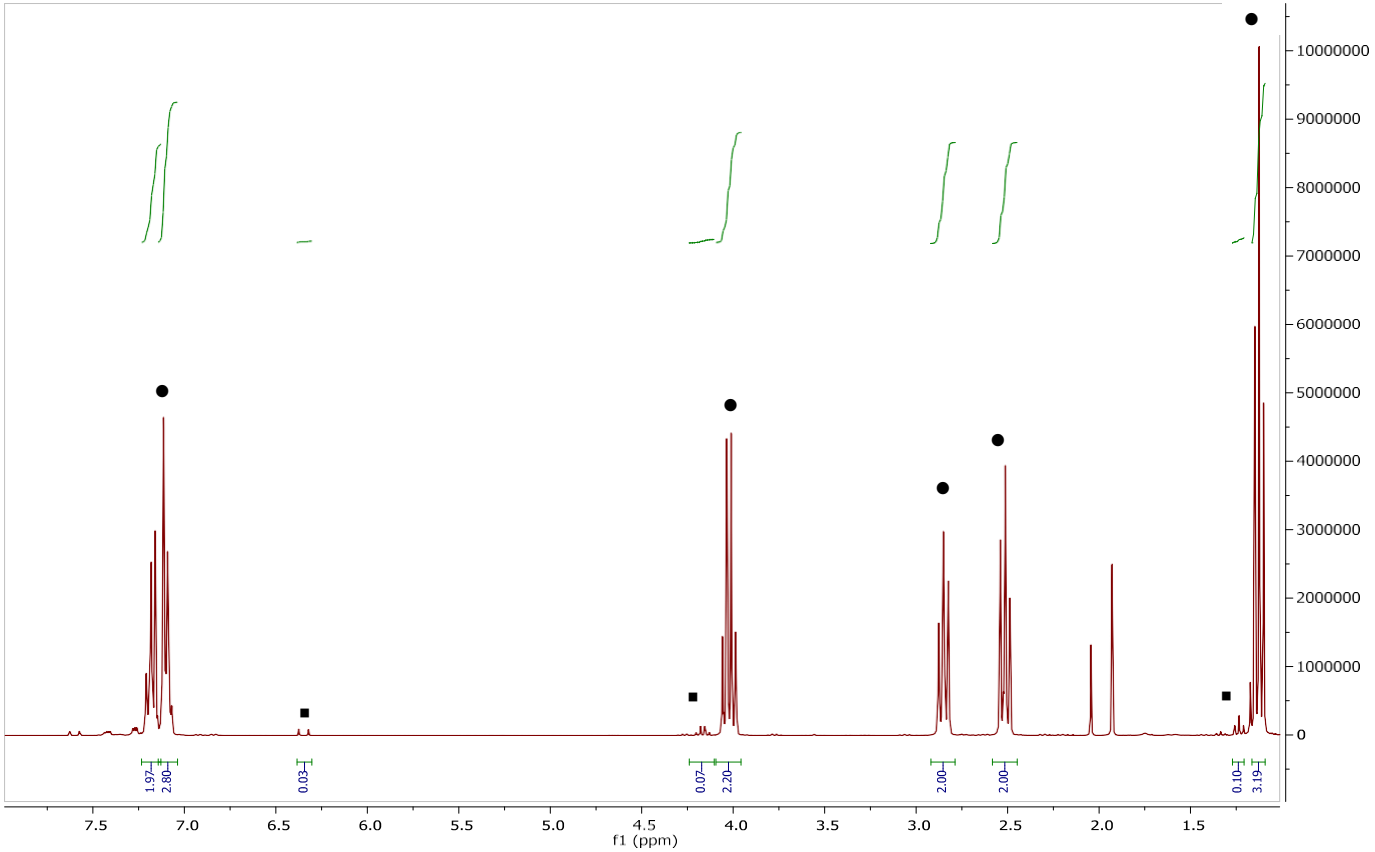


Figure S80 Sample ^{1}H NMR spectrum for calculating the selectivity for the hydrogenation of 3-methyl-2-butenal[13]

Sample spectrum used to determine selectivity; ● 3-methylbutyrylaldehyde, ◊ ethyl acetate; water

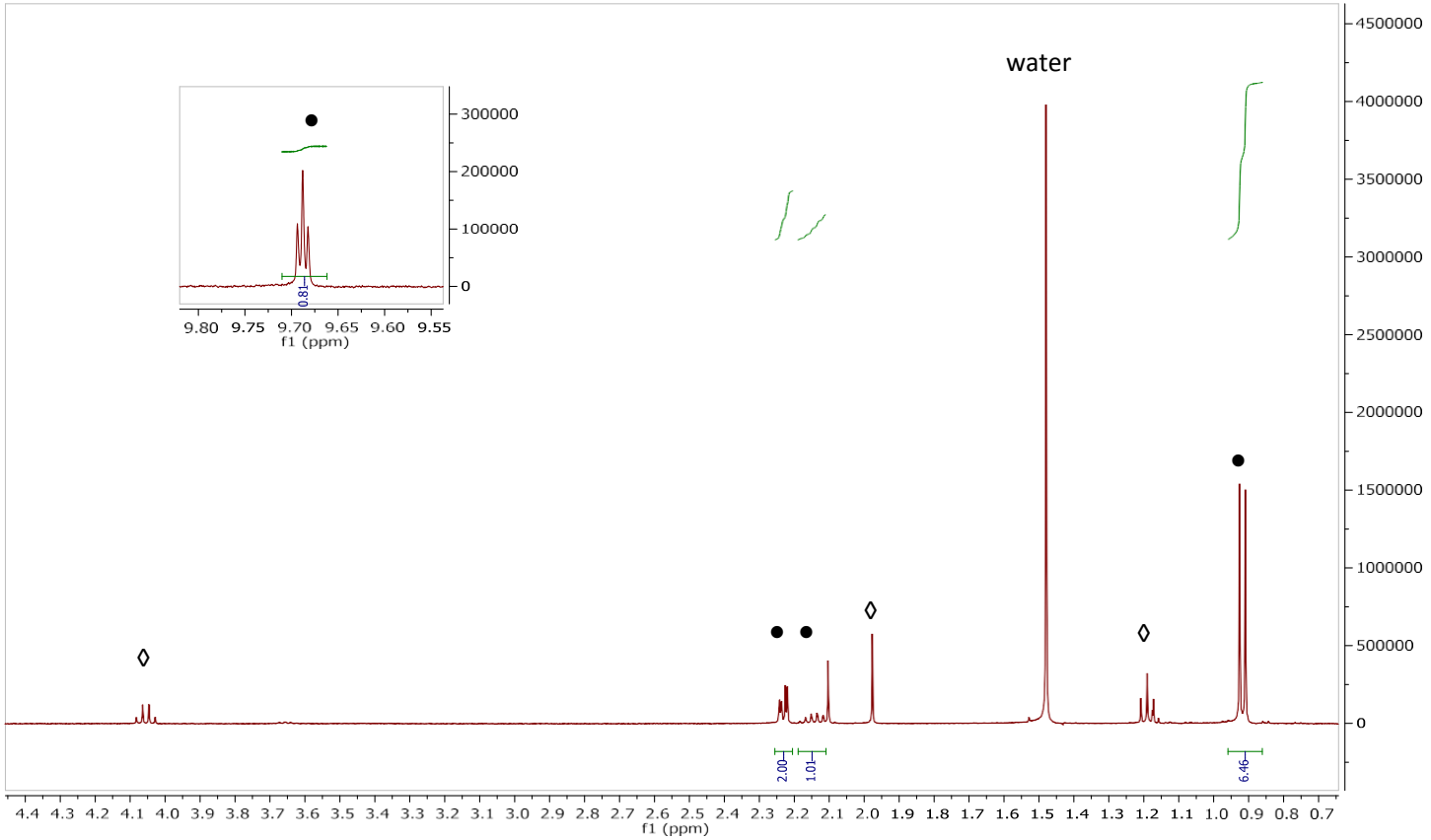
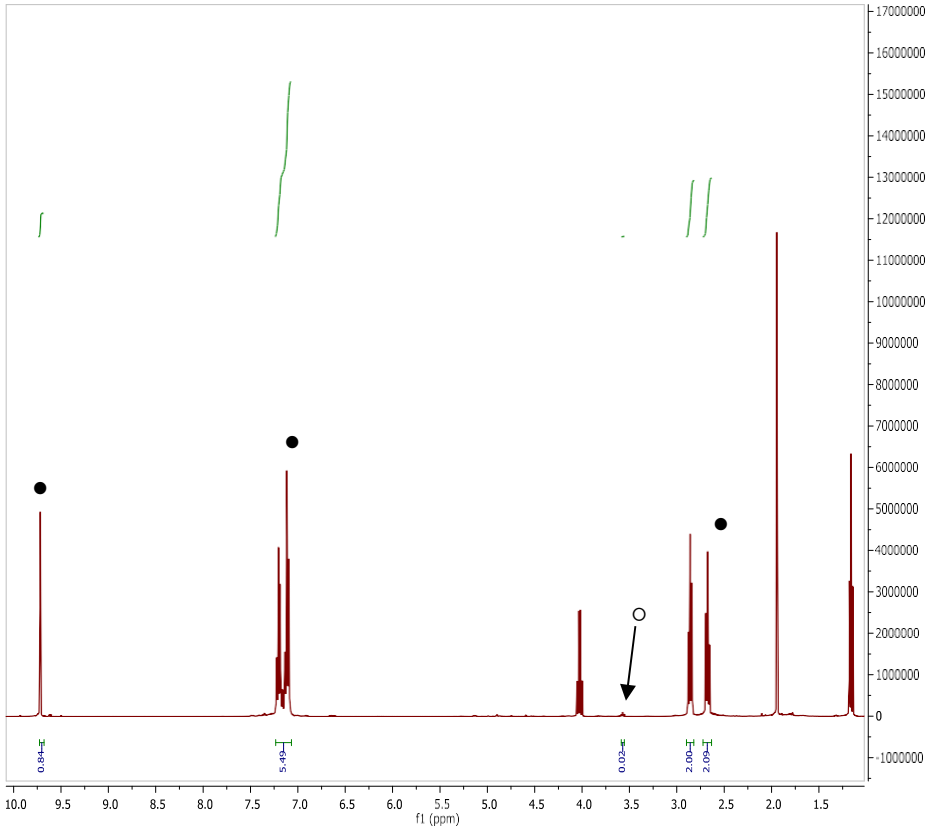


Figure S81 Comparison of the ^{1}H NMR spectrum and GC trace of the reaction mixtures obtained from the hydrogenation of cinnamaldehyde using catalyst 2a and showing a reliable correlation at high conversion and selectivity (100 conversion, 99% selectivity). (a) ^{1}H NMR spectrum, (b) GC trace

(a)

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



(b)

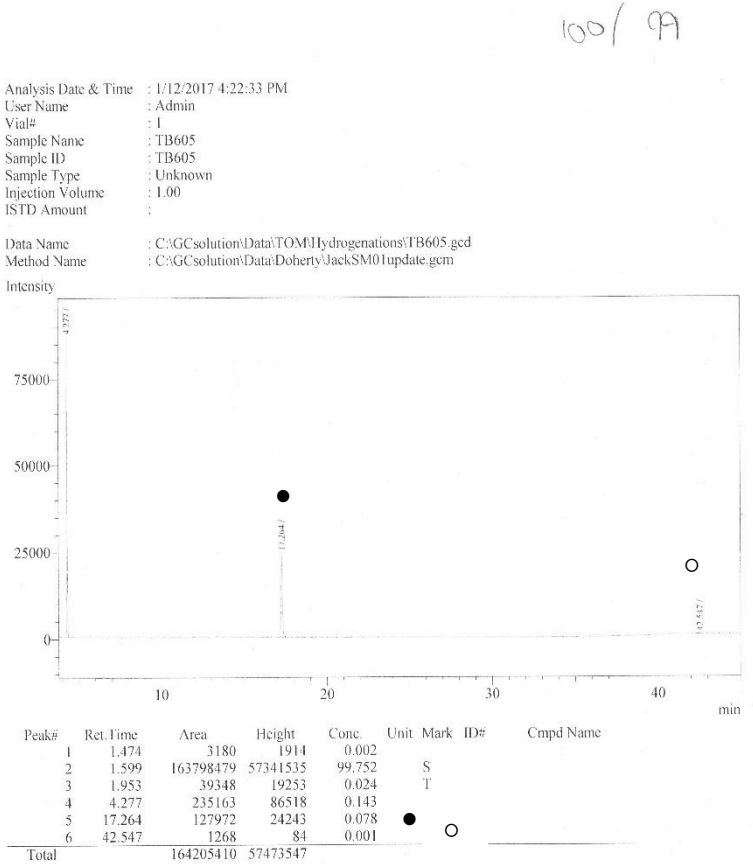
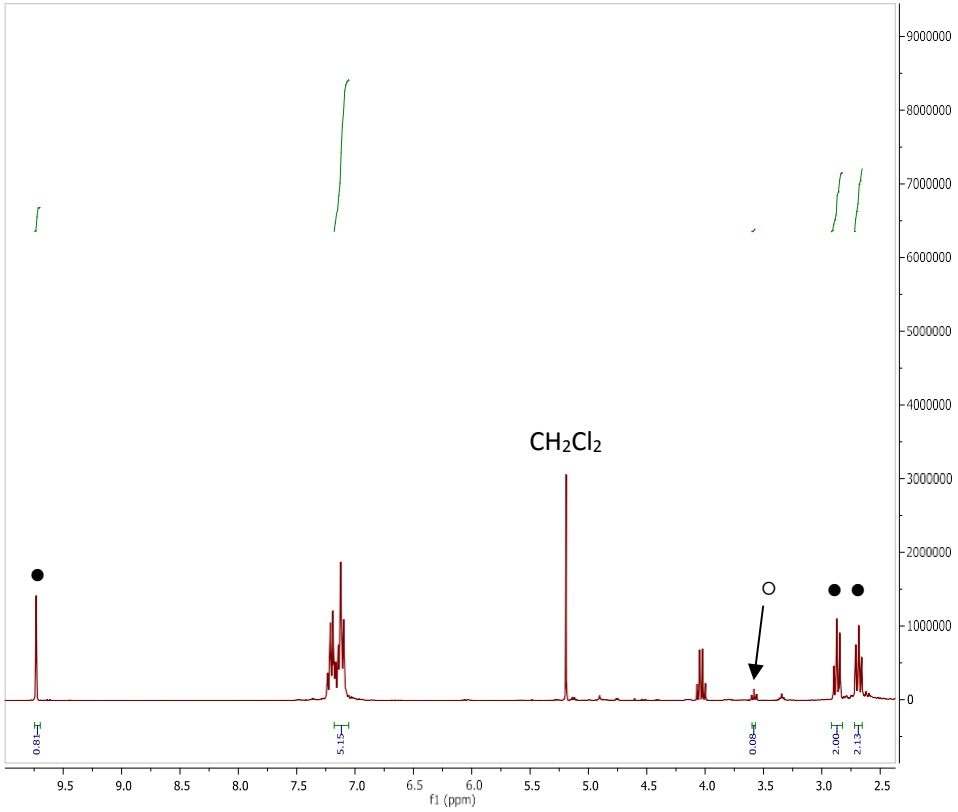


Figure S82 Comparison of the ^{1}H NMR spectrum and GC trace of the reaction mixtures obtained from the hydrogenation of cinnamaldehyde s using catalyst 2a and showing a reliable correlation at high conversion and reduced selectivity when the reaction was conducted with less than one equivalent of base (100% conversion, 96% selectivity). (a) ^{1}H NMR spectrum, (b) GC trace

(a)

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

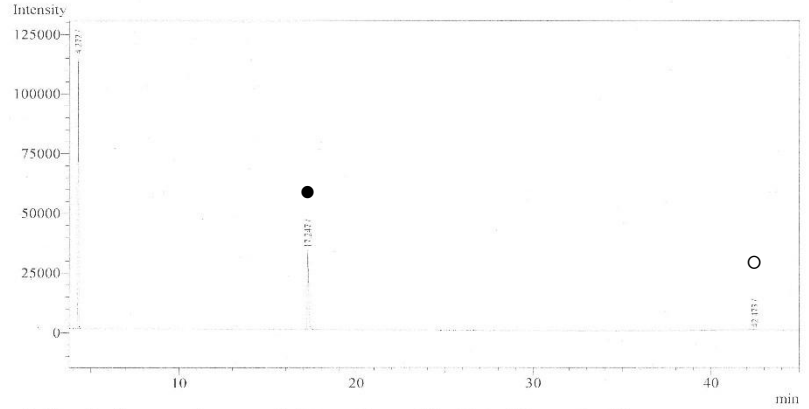


(b)

100 / 96

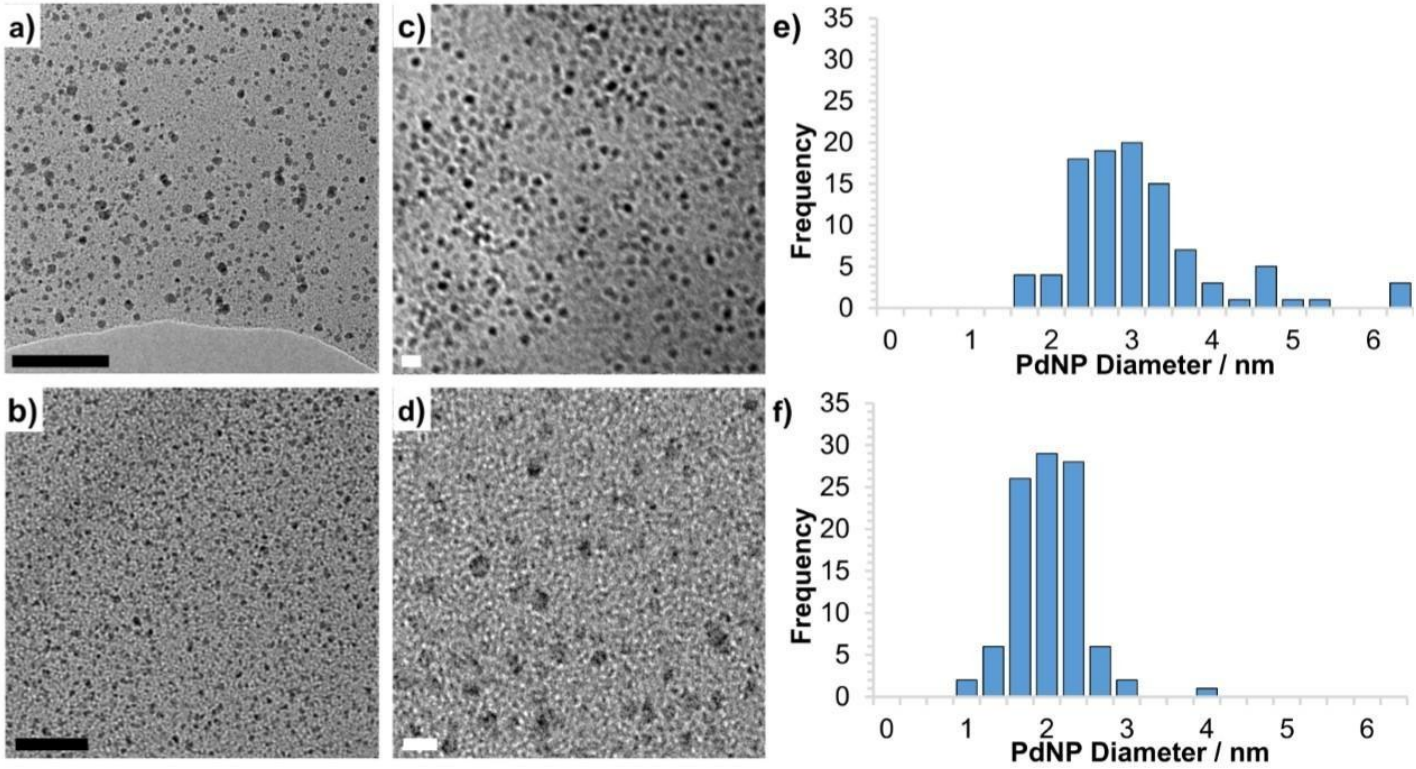
Analysis Date & Time : 1/13/2017 2:29:32 PM
User Name : Admin
Vial# : 1
Sample Name : TB605.3
Sample ID : TB605.3
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

Data Name : C:\GCsolution\Data\TOM\Hydrogenations\TB605.3.gcd
Method Name : C:\GCsolution\Data\Doherty\JackSM01update.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.423	3237683	2381249	1.911				
2	1.597	165626382	57617326	97.754		SV		
3	1.845	27688	11044	0.016		T		
4	1.952	40649	20189	0.024		T		
5	3.746	1169	407	0.001		TV		
6	4.272	307234	113874	0.181				
7	17.247	182893	33397	0.108		S		
8	42.473	7844	223	0.005				
Total		169431542	60177709					

Figure S823 **(a-d) TEM images of PdNP@PPh_2-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)**



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