Supporting information for manuscript

Highly efficient aqueous phase reduction of nitroarenes catalyzed by phosphine-decorated PEG-modified polymer immobilized ionic liquid stabilized PdNPs

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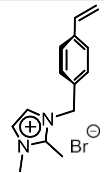
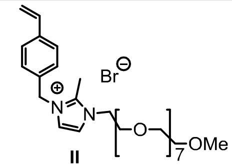
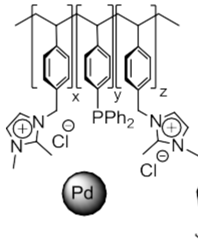
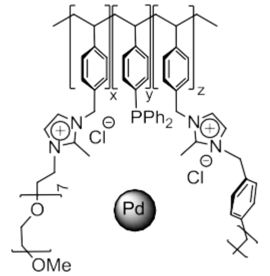
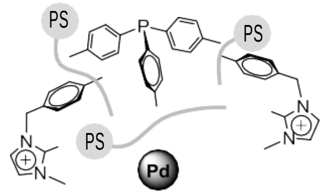
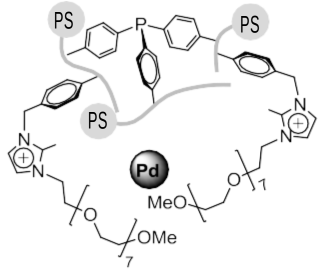
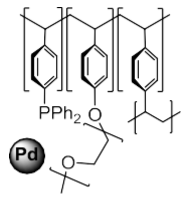
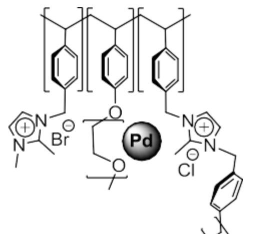
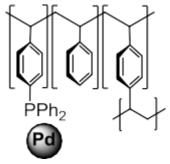
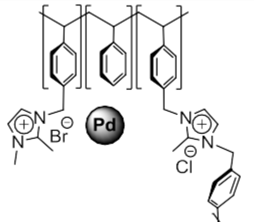
Contents

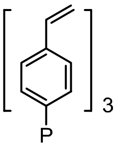
Experimental

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. Monomers 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (**I**) and 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride (**II**), polymers PPh_2-PIILP (**1a**) and PPh_2-PEGPIILP (**2a**), precursors $[PdCl_4]$@PPh_2-PIILP (**1b**) and $[PdCl_4]$@PPh_2-PEGPIILP (**2b**) and catalysts PdNP@PPh_2-PIILP (**1c**) and PdNP@PPh_2-PEGPIILP (**2c**) were prepared as previously described.[11] ^{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. X-ray photoelectron spectroscopy spectra were analysed using CasaXPS peak fitting software. The Pd 3d region was fitted using Gaussian/Lorentzian peak shapes with mixing ratio of 30:70, respectively, without imposing parameter constraints on the fwhm. The background was subtracted using the Shirley background subtraction algorithm. For X-ray photoelectron spectroscopy of Pd 3d, each electronic environment of Pd gives two components due to spin-orbit coupling: Pd $3d_{3/2}$ and Pd $3d_{5/2}$. 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. All FD-XAS measurements were carried out on the XMaS beamline (BM28) at the ESRF. Samples were deposited onto carbon tape, which was then mounted onto a stainless-steel sample holder. FD-XAS edge inflection points were obtained by fitting a smoothing spline to the measured spectrum, and taking the first derivative of the fitted spectrum. 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.

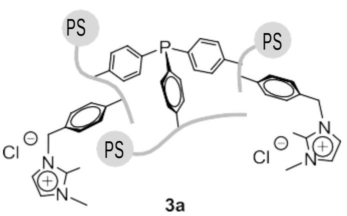
Table S1 Structures of Monomers and PIILP based Catalysts 1c-8c discussed in Table 3

 **I**	 **II**	
 PdNP@PPh$_2$-PIILP **1c**	 PdNP@PPh$_2$-PEGPIILP **2c**	 PdNP@PSty$_3$-PIILP **3c**
 PdNP@PSty$_3$-PEGPIILP **4c**	 PdNP@PPh$_2$-PEGstyrene **5c**	 PdNP@PEGPIILP **6c**
 PdNP@PPh$_2$-styrene **7c**	 PdNP@Sty-PIILP **8c**	

Synthesis of tris(4-vinylphenyl)phosphine. A round bottom flask was charged with Mg turnings (1.96 g, 81.7 mmol) suspended in anhydrous THF (25 mL). 1,2-dibromoethane (20 µL) was added in order to activate the Mg and the mixture was stirred for 10 min. After this, 4-chlorostyrene (7.49 g, 54.0 mmol) was added dropwise and the mixture was heated to 60°C and stirred for 4 hours. The mixture was then cooled to 0°C and PCl_3 (1.30 mL, 14.9 mmol) was added dropwise before stirring overnight at room temperature. After this time, the THF was removed from the mixture by vacuum distillation and to the resultant solid, degassed distilled water (20 mL) was added and the product was extracted with degassed diethyl ether (3 x 30 mL). The organic phases were then combined, dried over $MgSO_4$, filtered and the solvent was removed under vacuum to yield a white crystalline solid (3.16 g, 62 %). ^{31}P NMR (162 MHz, $CDCl_3$, δ): -6.65. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.08 (m, 12H), 6.67 – 6.60 (m, 3H), 5.67 (d, J = 16.8 Hz, 3H), 5.16 (d, J = 10.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 136.95, 135.61 (d, $J_{C\text{-}P}$ = 10.7 Hz, 3C), 135.63 (3C), 132.84 (d, $J_{C\text{-}P}$ = 19.6 Hz, 6C) 125.28 (d, $J_{C\text{-}P}$ = 7.13, 6C), 113.65 (3C).

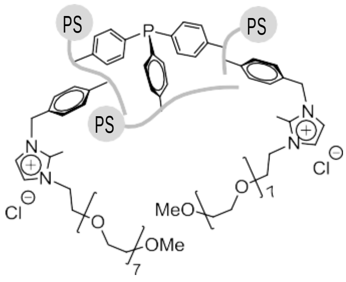


Synthesis of PSty$_3$-PIILP (3a). An oven-dried Schlenk was charged with tris(4-vinylphenyl)phosphine (4.0 g, 11.7 mmol), 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride (5.84 g, 23.50 mmol) and AIBN (0.157 g, 0.959 mmol) and dissolved in a mixture of anhydrous ethanol (30 mL) and anhydrous THF (50 mL) under a nitrogen atmosphere. The mixture was degassed using the freeze thaw method six times and then heated at reflux for four days. After this time, a further equivalent of AIBN (0.27 g, 1.64 mmol) was added, the degassing process repeated and the resulting mixture heated at reflux for one more day. The solvent was removed *in vacuo*, the resulting residue dissolved in dichloromethane (35 mL) and added dropwise to diethyl ether (350 mL) with vigorous stirring. The solution was stirred for 45 minutes and then allowed to settle, filtered and the solid washed with ether to afford **3a** as an off-white solid in 98% yield (9.75 g).



3a

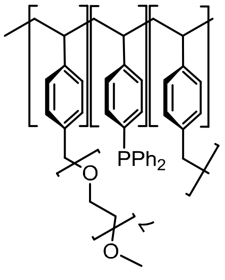
Synthesis of PSty$_3$-PEGPIILP (4a). An oven-dried Schlenk was charged with tris(4-vinylphenyl)phosphine (2.33 g, 6.88 mmol), 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride (7.77 g, 13.75 mmol) and AIBN (0.157 g, 0.959 mmol) and dissolved in a mixture of anhydrous ethanol (30 mL) and anhydrous THF (50 mL) under nitrogen atmosphere. The mixture was degassed using the freeze-thaw method six times and then heated at reflux for four days. After this time, a further equivalent of AIBN (0.157 g, 0.959 mmol) was added, the degassing procedure repeated and the resulting reaction mixture heated at reflux for a further 24 h. The solvent was removed *in vacuo* and the resulting residue



4a

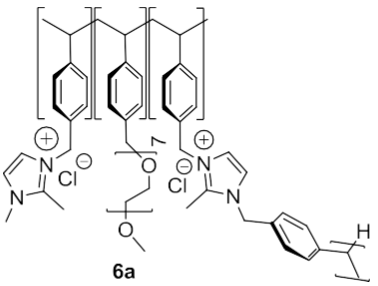
dissolved in dichloromethane (35 mL) and added dropwise to diethyl ether (350 mL) with vigorous stirring. The solution was allowed to stir for 45 minutes, left to settle, filtered and the resecting solid washed with diethyl ether to afford **4a** as an off-white solid in 91 % (9.0 g).

Synthesis of PPh$_2$PEG styrene (5a). 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 ^{o}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%).



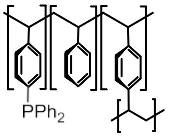
5a

Synthesis of PEGPIILP (6a). 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^{o}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%).



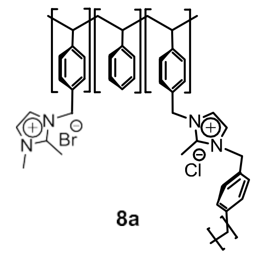
6a

Synthesis of PPh$_2$-polystyrene (7a). An oven-dried Schlenk was charged with diphenyl(4-vinylphenyl)phosphine (1.5 g, 5.2 mmol), styrene (1.1 mL , 9.7 mmol), divinylbenzene (104 µL, 0.73 mmol), AIBN (0.12 g, 0.74 mmol) and a mixture of anhydrous ethanol (30 mL) and anhydrous THF (40 mL) under a nitrogen atmosphere. The mixture was degassed using the freeze thaw method six times and then heated at reflux for 4 days. After this time, a further



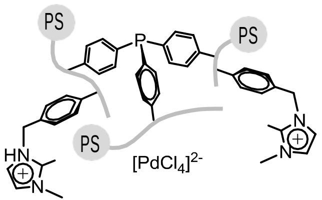
7a

equivalent of AIBN (0.12 g, 0.74 mmol) was added and the degassing process repeated before heating at reflux for a further 24 h. The solvent was removed *in vacuo* and the resulting residue was dissolved in dichloromethane (20 mL) and added dropwise to diethyl ether (350 mL) with rapid stirring. The solution was left to stir for 45 minutes, then left to settle filtered and the resulting solid washed with diethyl ether to afford **7a** as an off-white solid in 78 % yield (2.02 g).



8a

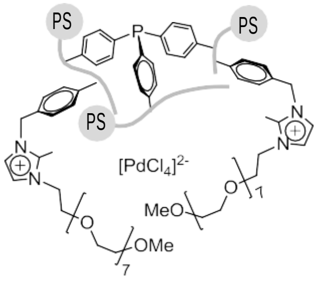
Synthesis of Styr-PIILP (8a). An oven-dried Schlenk was charged with 1,2-dimethyl-3-(4- vinylbenzyl)-1H-imidazol-3-ium chloride (3.17 g, 12.76 mmol), styrene (0.79 mL , 6.93 mmol), 2-methyl-1,3-bis(4-vinylbenzyl)-1H-imidazol-3-ium chloride (0.34 g, 0.97 mmol), AIBN (0.16 g, 0.97 mmol) and anhydrous ethanol (50 mL) under a nitrogen atmosphere. The mixture was degassed using the freeze thaw method six times and then heated at reflux for 4 days. After this time, a further equivalent of AIBN (0.16 g, 0.97 mmol) was added, the degassing process repeated and the mixture heated at reflux for a further 24 h. The solvent was removed *in vacuo* and the resulting residue was dissolved in dichloromethane (35 mL) and added dropwise to diethyl ether (350 mL) with vigorous stirring. The solution was left to stir for 45 minutes, then allowed to settle filtered and the isolated solid washed with diethyl ether to yield **8a** as an off-white solid in 96 % yield (4.06 g).



3b

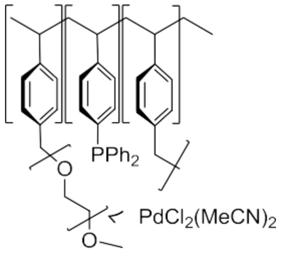
Synthesis of [PdCl$_4$]@PSty$_3$-PIILP (3b). A round bottomed flask charged with charged with palladium dichloride (0.3 g, 1.7 mmol), NaCl (2.2 g, 37.6 mmol) and water (45 mL) was heated to 80 °C for ca. 40 min to afford a clear deep red solution. The solution was allowed to cool to room temperature after which **3a** (1.42 g, 1.70 mmol) was added with the resulting red/orange mixture stirred vigorously for 12 hours. The precipitate was isolated by filtration through a frit and the resulting solid washed with distilled water (10 mL), ethanol (10 mL) and diethyl ether (10 mL) to yield **3b** as a red/brown powder (1.57 g, 82%). ICP-OES data: 3.2 wt% palladium and a palladium loading of 0.30 mmol g^{-1}.

Synthesis of [$PdCl_4$]@$PSty_3$-PEGPIILP (4b). A round bottomed flask charged with charged with palladium dichloride (0.3 g, 1.7 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 allowed to cool to room temperature after which **4a** (2.55 g, 1.70 mmol) was added and the resulting red/orange mixture stirred vigorously for 12 hours. The precipitate was isolated by filtration through a frit and the resulting solid washed with distilled water (10 mL), ethanol (10 mL) and diethyl ether (10 mL) to yield **4b** as a red/brown powder in 96% yield (2.87 g). ICP-OES data: 4.13 wt% palladium and a palladium loading of 0.39 mmol g^{-1}.



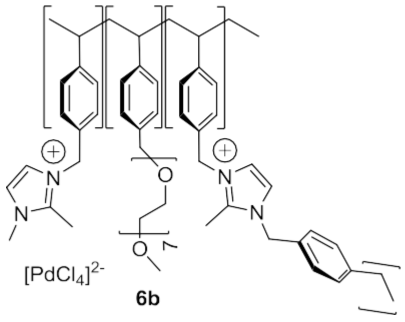
4b

Synthesis of $PdCl_2(MeCN)_2$@PPh_2PEGstyrene (5b). 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 mmolg^{-1}.



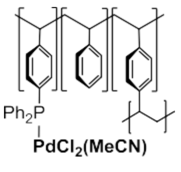
5b

Synthesis of [$PdCl_4$]@PEGPIILP (6b). 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 mmolg^{-1}.



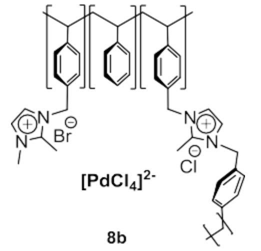
6b

Synthesis of [PdCl$_2$(MeCN)$_2$]@PPh$_2$-polystyrene (7b). A round-bottomed flask was charged with **7a** (0.51 g, 1.0 mmol) and suspended in anhydrous dichloromethane (8 mL). To this, was added a solution of PdCl$_2$(MeCN)$_2$ (0.28 g, 1.1 mmol) dissolved in anhydrous dichloromethane (5.0 mL) dropwise with rapid stirring over 5 min. resulting in the precipitation of an orange solid. The mixture was left to stir for 5 hours at room temperature after which time the solid was isolated by filtration and washed with dichloromethane (2 x 20 mL) to afford **7b** as a free-flowing orange solid in 70 % yield (0.53 g). ICP-OES data: 13.2 wt% palladium and a palladium loading of 1.24 mmol g^{-1}.



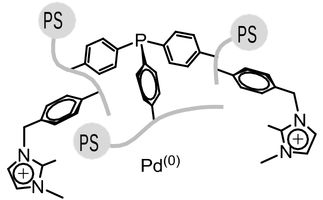
7b

Synthesis of [PdCl$_4$]@Styr-PIILP (8b). To a round-bottomed flask charged with a solution of Na$_2$[PdCl$_4$] (0.14 g, 0.48 mmol) in distilled water (15 mL) was added polymer **8a** (0.24 g, 0.43 mmol) in a single portion. The resulting red brown precipitate was left to stir for 5 hours at room temperature then isolated by filtration and washed with distilled water (2 x 5 mL), ethanol (2 x 5 mL) and diethyl ether (2 x 5 mL) to afford **8b** as a free flowing brick red powder in 73% yield (0.25 g). ICP-OES data: 22.2 wt% palladium and a palladium loading of 2.1 mmol g^{-1}.



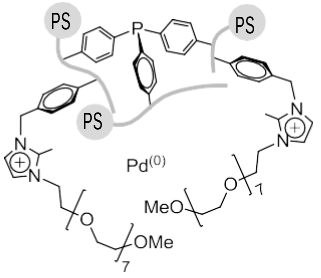
8b

Synthesis of PdNP@PSty$_3$-PIILP (3c). A round-bottom flask charged with **3b** (0.75 g, 0.69 mmol) and ethanol (20 mL) under a nitrogen atmosphere was cooled in an ice bath. A solution of NaBH$_4$ (0.18 g, 4.85 mmol) in water was added dropwise to the cooled mixture during which time the orange suspension rapidly turned black. The resulting reaction mixture was allowed to warm to room temperature and stirred overnight after which the product was precipitated by dropwise addition to a large excess (ca. 200 mL) of cold acetone with vigorous stirring. The solid was isolated by filtration dried and the resulting black solid was ground to a fine powder and washed with distilled water (10 mL) ethanol (10 mL) and diethyl ether (10 mL) to afford **3c** in 83% yield (0.77 g). ICP-OES data: 5.2 wt% palladium and a palladium loading of 0.48 mmol g^{-1}.



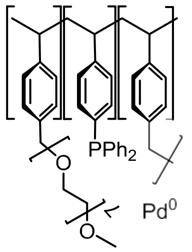
3c

Synthesis of PdNP@PSty$_3$-PEGPIILP (4c). A round bottom flask charged with **4b** (1.4 g, 0.8 mmol) and ethanol (20 ml) under a nitrogen atmosphere was cooled in an ice bath. A solution of NaBH$_4$ (0.21 g, 5.6 mmol) in water (2-3 ml) was added to the mixture slowly during which time the orange solution rapidly turned black. The resulting mixture was allowed to warm to room temperature and stirred overnight after which the product was precipitated by dropwise addition to a large excess (ca. 200 mL) of cold acetone with vigorous stirring. The solid was isolated by filtration, dried and the resulting black solid ground to a fine powder and washed with distilled water (10 mL) ethanol (10 mL) and diethyl ether (10 mL) to afford **4c** in 83% yield (1.17 g). ICP-OES data: 5.4 wt% palladium and a palladium loading of 0.51 mmol g^{-1}.



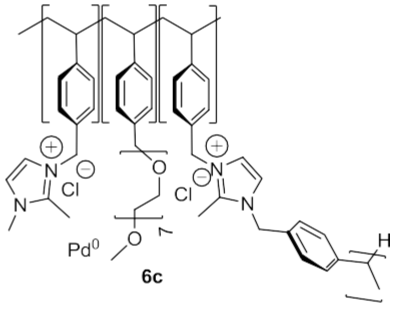
4c

Synthesis of PdNP@PPh$_2$PEGstyrene (5c). 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}.



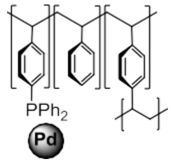
5c

Synthesis of PdNP@PEGPIILP (6c). 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}.



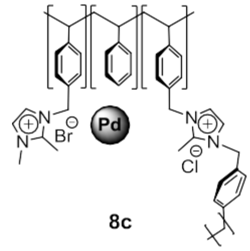
6c

Synthesis of PdNP@PPh$_2$-polystyrene (7c). A round bottomed flask was charged with **7b** (0.44 g, 0.57 mmol) and ethanol (10 mL) and the resulting suspension treated dropwise with a solution of $NaBH_4$ (0.15 g, 4.03 mmol) dissolved in distilled water (1 mL). The orange reaction mixture instantly turned black and was left to stir overnight at room temperature. The resulting black solution was then cooled to 0 °C and filtered to yield a black powder which was washed with distilled water (2 x 5 mL) ethanol (2 x 5 mL) and diethyl ether (2 x 5 mL) to afford **7c** as a fine black powder in 89% yield (0.31 g). ICP-OES data: 6.0 wt% palladium and a palladium loading of 0.57 mmol g^{-1}.



7c

Synthesis of PdNP@Styr-PIILP (8c). A round bottomed flask was charged with **8b** (0.55 g, 0.69 mmol) suspended in ethanol (15 mL) and treated dropwise over 5 min with a solution of $NaBH_4$ (0.18 g, 4.81 mmol) dissolved in distilled water (1.5 mL). The red brown solution instantly turned black and was then left to stir overnight at room temperature. After this time the solution was cooled to 0 °C, filtered and the resulting solid washed with distilled water (2 x 5 mL), ethanol (2 x 5 mL) and diethyl ether (2 x 5 mL) to afford **8c** as a fine black powder in 90% yield (0.41 g). ICP-OES data: 31.6 wt% palladium and a palladium loading of 3.0 mmol g^{-1}.



8c

General procedures for the catalytic reduction of nitroarenes with sodium borohydride

A Schlenk flask equipped with a magnetic stirrer was charged with catalyst (0.5 μmol, 0.05 mol%) and distilled water (2 mL). $NaBH_4$ (95.4 mg, 2.5 mmol) was added and the mixture stirred vigorously for 2 min during which time rapid evolution of gas was observed. The reaction was initiated by slow addition nitroarene (1 mmol) and the resulting yellow solution stirred at room temperature for two hours. The products were extracted into ethyl acetate (3 x 10 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to yield a yellow oil which was analysed by ^{1}H NMR using 1,4-dioxane as internal standard and GC analysis using n-decane as internal standard to quantify the composition of starting material and products.

General procedure for the catalytic hydrogenation of nitroarenes

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 and gas chromatography. 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 and GC to quantify the composition of starting material and products and to determine the selectivity; for each substrate tested an internal standard of decane was initially employed for the GC analysis to ensure mass balance. All ^{1}H NMR spectra were recorded using dioxane as internal standard 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. 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).

General procedure for the recycle sodium borohydride reductions

A Schlenk flask equipped with a magnetic stirrer was charged with catalyst (0.5 μmol, 0.05 mol%) and distilled water (2 mL). $NaBH_4$ (95.4 mg, 2.5 mmol) was added and the mixture stirred vigorously for 2 min during which time rapid evolution of gas was observed. The reaction was initiated by slow addition nitroarene (1.0 mmol) and the resulting yellow solution stirred at room temperature for two hours. The products were extracted into ethyl acetate (3 x 10 mL), dried over $MgSO_4$, filtered, the solvent removed under reduced pressure and the residue analysed by ^{1}H NMR using 1,4-dioxane as internal standard and GC analysis using *n*-decane as internal standard. The aqueous layer was then added back into the Schlenk flask, recharged with 1 mmol of aryl nitroarene and stirred for a further 2 h; this procedure was repeated 6 times.

Catalyst poisoning studies using pyridine

A Schlenk flask was charged with catalyst (0.05 mol%) and suspended in distilled water (7 mL). $NaBH_4$(0.336 g, 8.75 mmol) was added slowly and the mixture stirred rapidly for 2 min during which time there was rapid evolution of gas. After this, nitrobenzene (0.360 mL, 3.5 mmol) and 1,4-dioxane (0.298 mL, 3.5 mmol) were added slowly and the resulting yellow solution stirred at room temperature for two hours. Conversion and selectivity were analysed by ^{1}H NMR spectroscopy by sampling 50 μL portions at 20 minute intervals and extracting the product into ethyl acetate and dissolving the crude residue in d-chloroform (0.5 mL).

Continuous flow reduction of nitrobenzene

Solution reservoirs for the pumps were prepared by dissolving nitrobenzene (6.1555 g, 50 mmol) in ethanol (250 mL); and sodium borohydride (4.7288 g, 125 mmol) in 1M $NaOH_{(aq)}$ (250 mL). Reagents were pumped using JASCO PU980 dual piston HPLC pumps and pump streams were mixed using a Swagelok SS-100-3 tee-piece. The sodium borohydride solution was stirred on a hotplate. A 2.5 mL aluminium tube was packed with PdNP@PEGPPh$_2$ catalyst **2c** (92 mg, 3.8075 wt% Pd) and sand (3.915 g). The packed column was placed in an aluminium block, which was heated by nickel element inserts controlled using a Eurotherm temperature controller. The reactor was maintained under a fixed back pressure using an Upchurch Scientific 100 psi back pressure regulator. SS tubing (1/16" OD, 1/32" ID) was used throughout the reactor. A 0.5 mL aliquot was collected from the reactor outlet and diluted with 0.5 mL of a 0.02 M solution of 1,3,5-trimethoxybenzene in ethanol for HPLC analysis. HPLC analysis was performed on an Agilent 1100 series LC instrument using an Ascentis Express C18 reverse phase column (5 cm length, 4.6 mm ID and 2.7 μm particle size), a water/acetonitrile (A/B) mobile phase and a multiple wavelength detector. Quantitative analysis was conducted based on normalisation of response factors using 1,3,5-trimethoxybenzene as an internal standard. The method used was 10% to 90% B 12 mins, 90% to 10% B 0.1 min, 10% B 1 min, flow rate 1.5 mL min^{-1}, column temperature 20 °C.

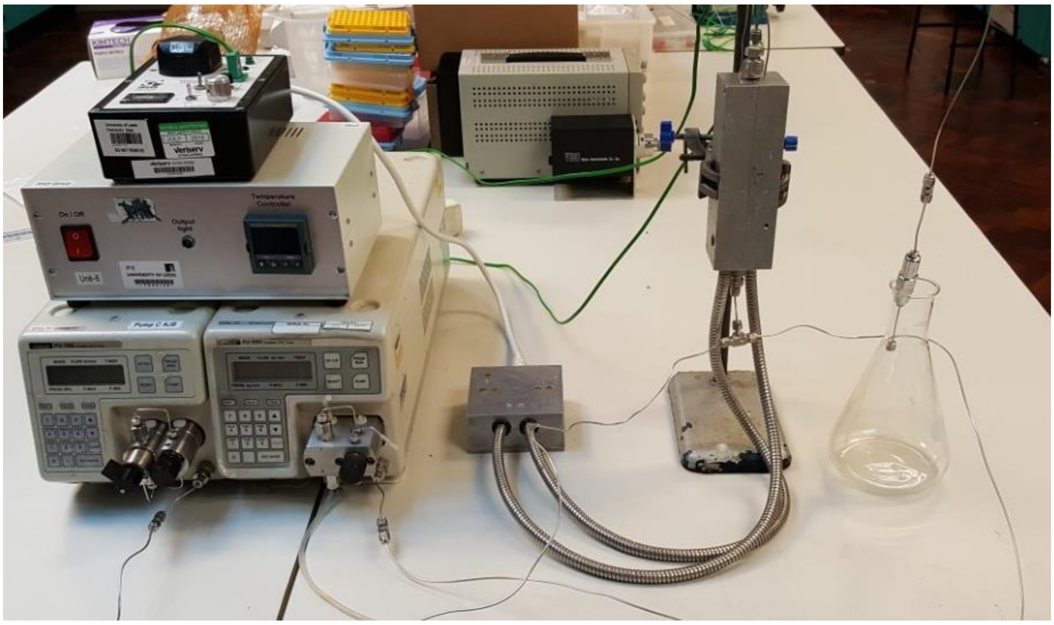


Figure 1. Photo of continuous flow reactor

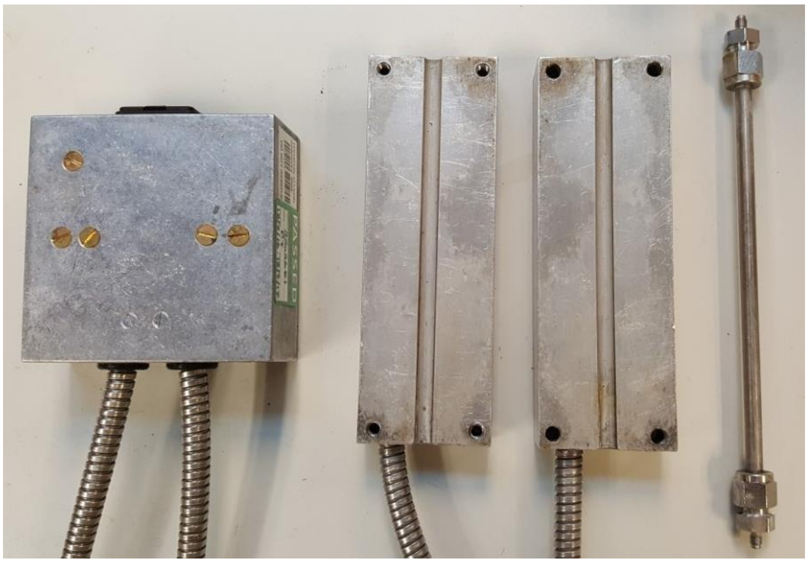


Figure 2. Photo of packed bed reactor (deconstructed)

Characterization Data for Polymers and Palladium Loaded Polymers

Figure S3 Solution ^{31}P NMR spectrum of PSty$_3$-PIILP (3a)

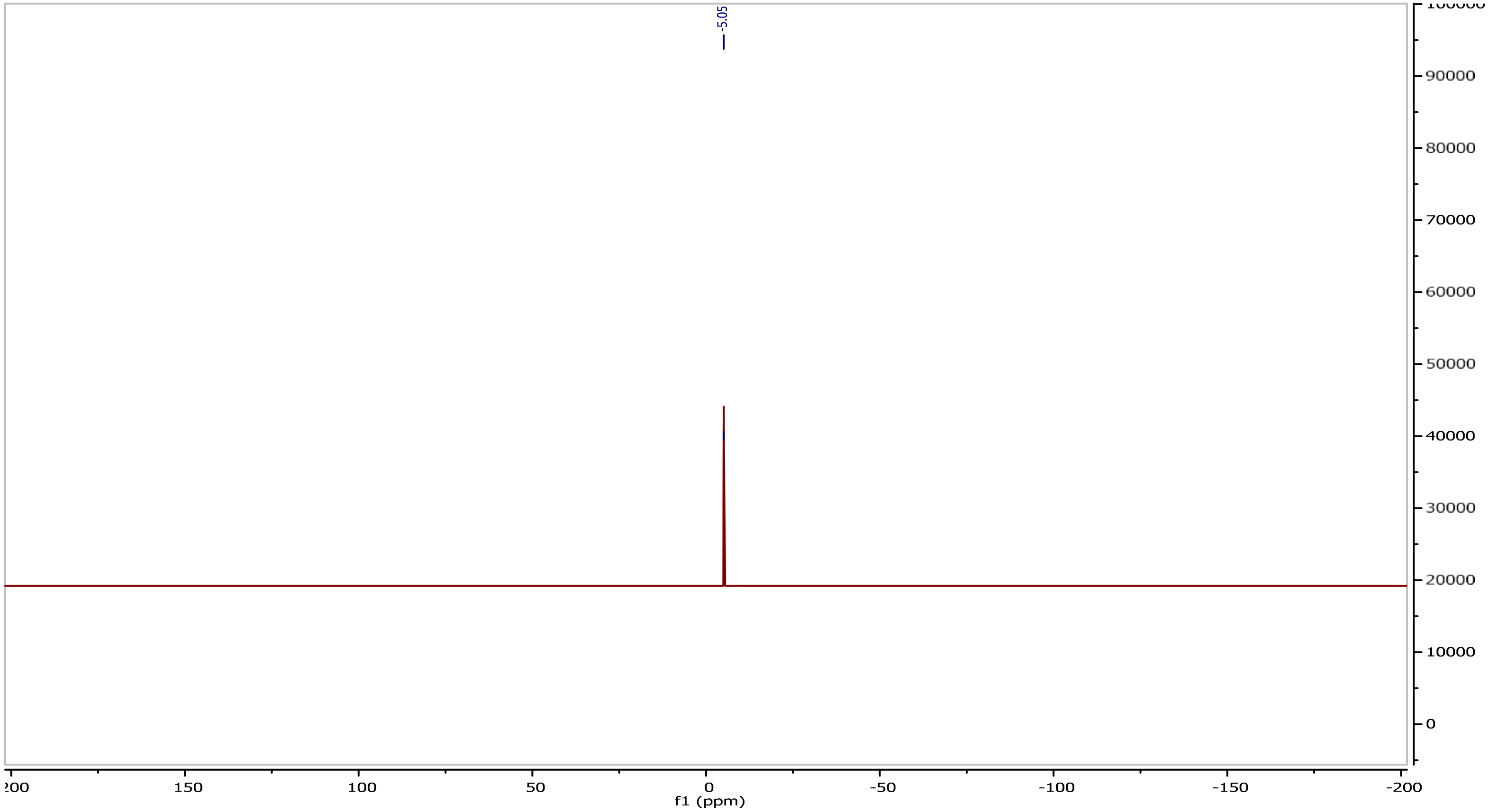
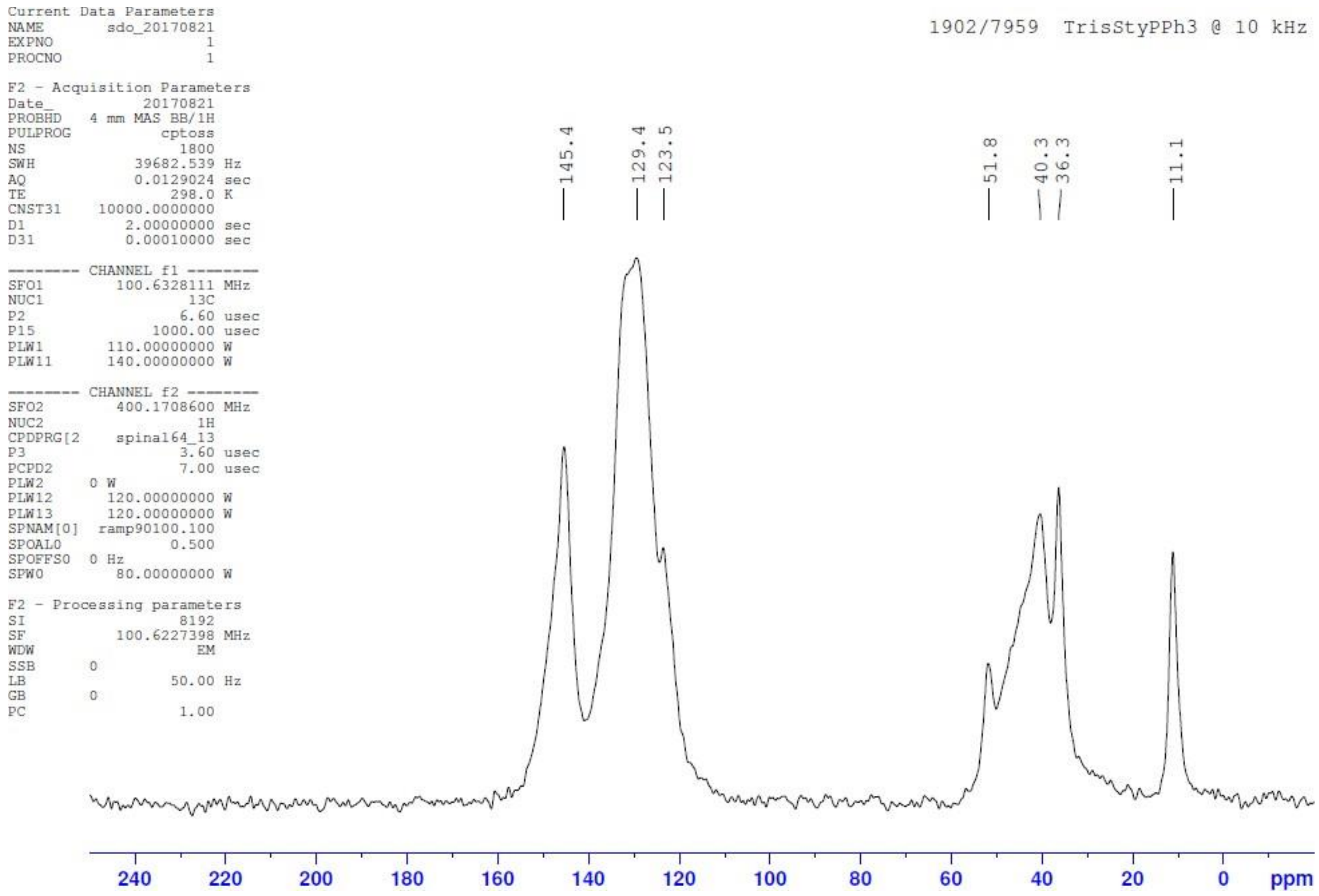


Figure S4 Solid state ^{13}C NMR spectrum of PSty$_3$-PIILP (3a)



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PROCNO                  1

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NS                   1800
SWH             39682.539 Hz
AQ              0.0129024 sec
TE                  298.0 K
CNST31    10000.0000000
D1             2.00000000 sec
D31            0.00010000 sec

======== CHANNEL f1 ========
SFO1          100.6328111 MHz
NUC1                  13C
P2                   6.60 usec
P15               1000.00 usec
PLW1         110.00000000 W
PLW11        140.00000000 W

======== CHANNEL f2 ========
SFO2          400.1708600 MHz
NUC2                   1H
CPDPRG[2      spinal64_13
P3                   3.60 usec
PCPD2                7.00 usec
PLW2      0 W
PLW12        120.00000000 W
PLW13        120.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0              0.500
SPOFFS0   0 Hz
SPW0          80.00000000 W

F2 - Processing parameters
SI                   8192
SF            100.6227398 MHz
WDW                    EM
SSB       0
LB                  50.00 Hz
GB        0
PC                   1.00
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Figure S5 SEM image of freshly prepared PSty$_3$-PIILP co-polymer (3a)

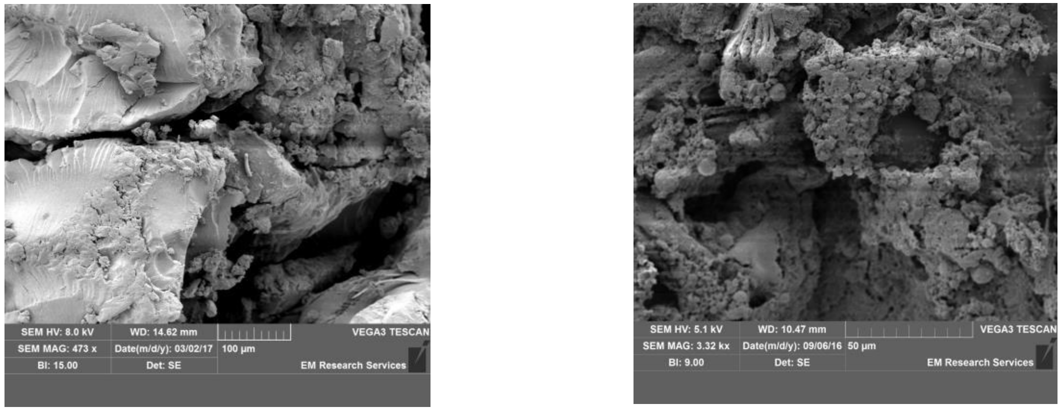


Figure S6 TGA curve for PSty$_3$-PIILP co-polymer (3a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

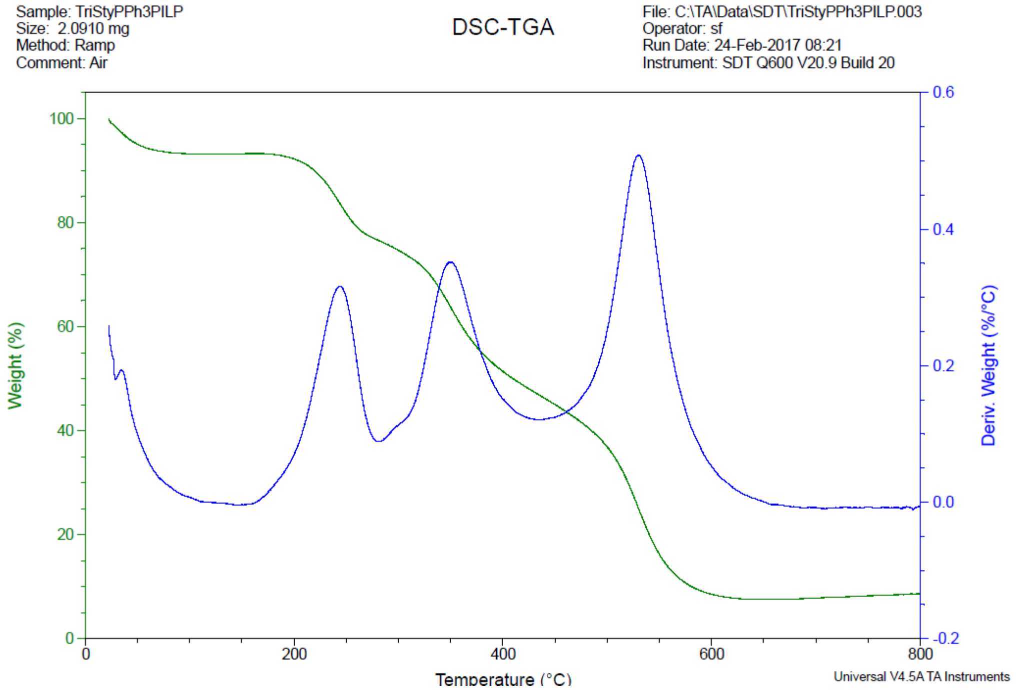


Figure S7 FT-IR spectrum of freshly prepared PSty$_3$-PIILP co-polymer (3a)

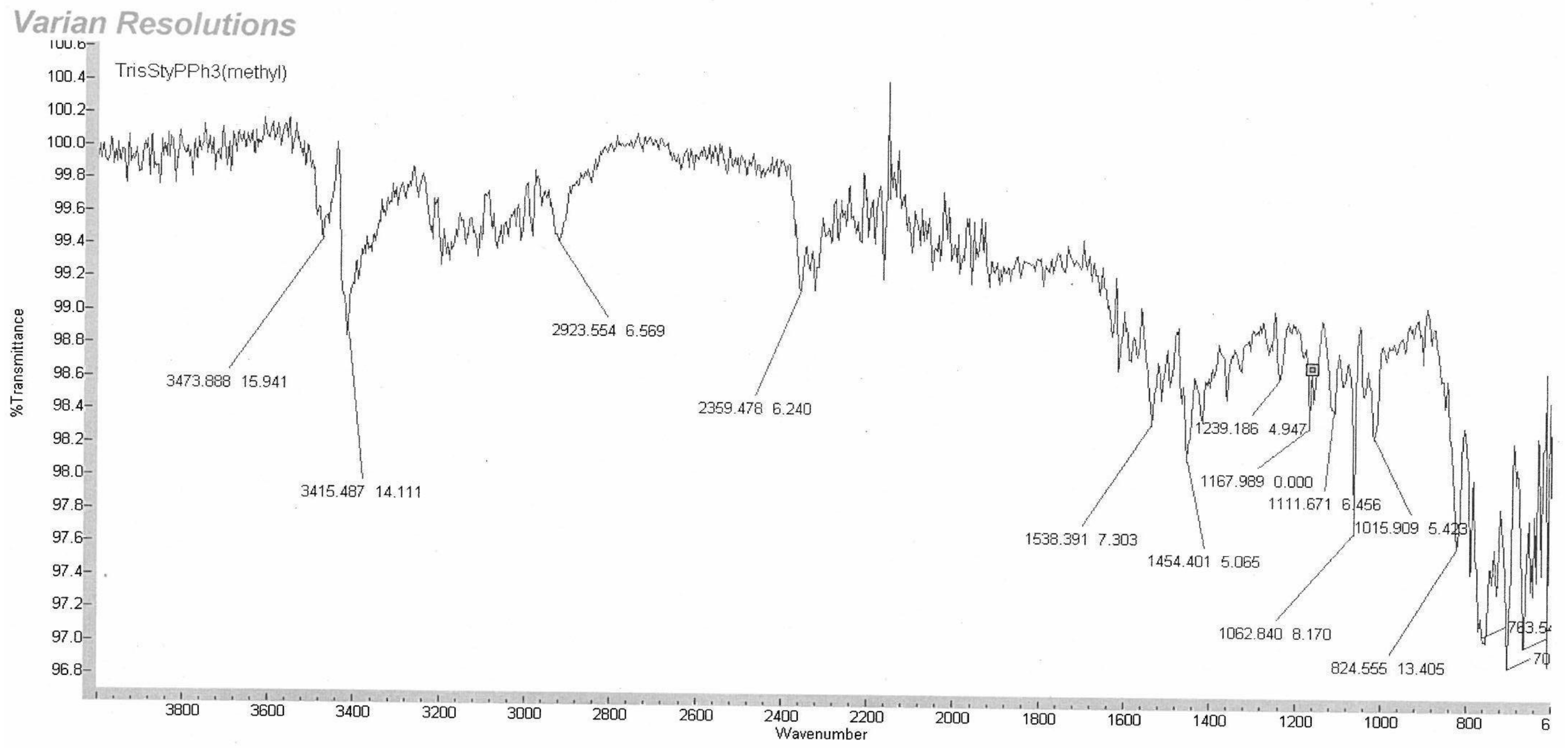
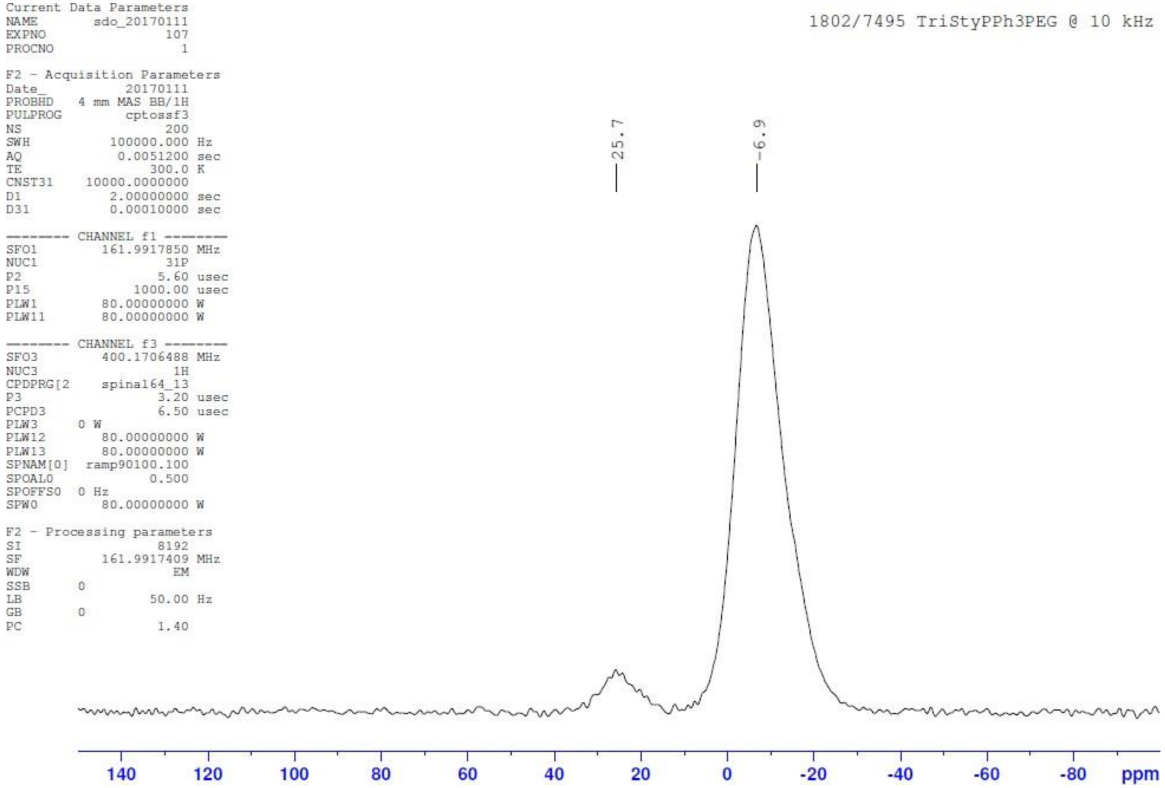


Figure S8 Solid State ^{31}P NMR spectrum of PSty$_3$-PEGPIILP (4a)



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PROCNO                 1

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NS                   200
SWH          100000.000 Hz
AQ            0.0051200 sec
TE                300.0 K
CNST31   10000.0000000
D1           2.00000000 sec
D31          0.00010000 sec

======== CHANNEL f1 ========
SFO1        161.9917850 MHz
NUC1                31P
P2                 5.60 usec
P15             1000.00 usec
PLW1        80.00000000 W
PLW11       80.00000000 W

======== CHANNEL f3 ========
SFO3        400.1706488 MHz
NUC3                 1H
CPDPRG[2    spinal64_13
P3                 3.20 usec
PCPD3              6.50 usec
PLW3      0 W
PLW12       80.00000000 W
PLW13       80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                  8192
SF          161.9917409 MHz
WDW                   EM
SSB       0
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GB        0
PC                  1.40
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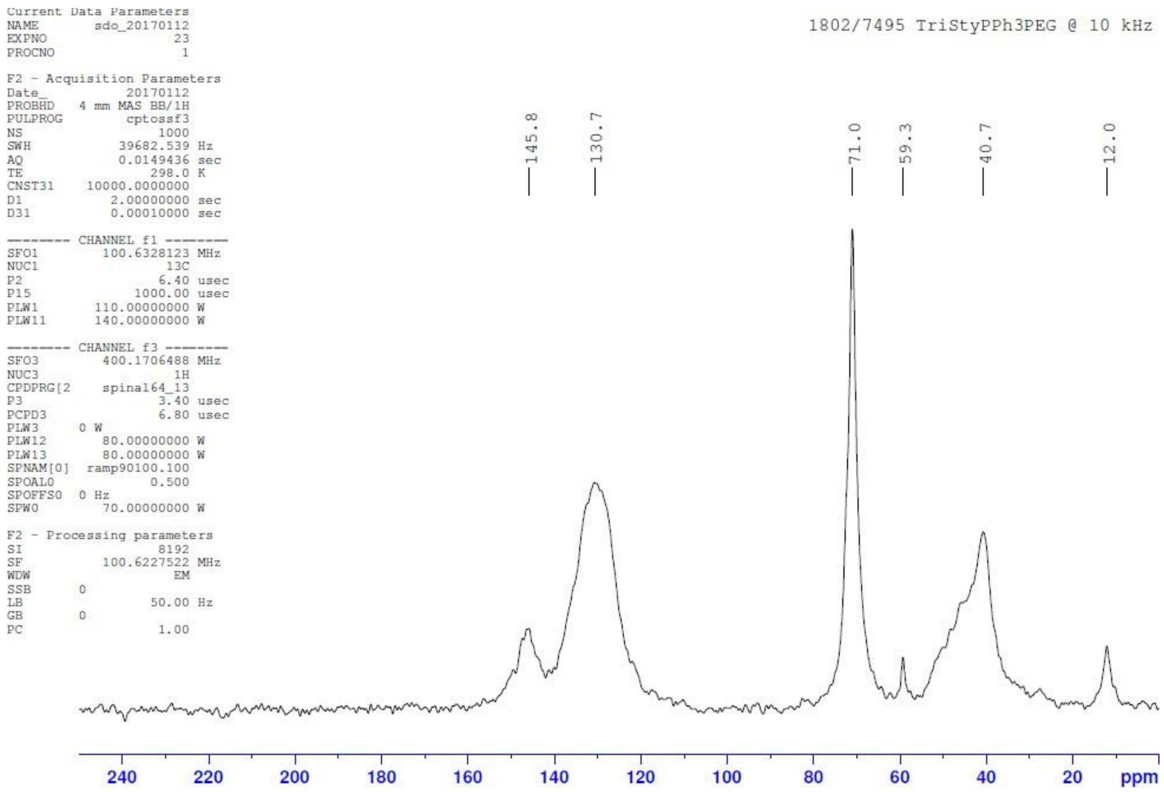
Figure S9 Solid state ^{13}C NMR spectrum of $PSty_3$-PEGPIILP (4a)



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PROCNO                 1

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PULPROG         cptossf3
NS                  1000
SWH            39682.539 Hz
AQ             0.0149436 sec
TE                 298.0 K
CNST31    10000.0000000
D1            2.00000000 sec
D31           0.00010000 sec

-------- CHANNEL f1 --------
SFO1         100.6328123 MHz
NUC1                 13C
P2                  6.40 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

-------- CHANNEL f3 --------
SFO3         400.1706488 MHz
NUC3                  1H
CPDPRG[2     spinal64_13
P3                  3.40 usec
PCPD3               6.80 usec
PLW3     0 W
PLW12        80.00000000 W
PLW13        80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0  0 Hz
SPW0         70.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227522 MHz
WDW                   EM
SSB      0
LB                 50.00 Hz
GB       0
PC                  1.00
```

Figure S10 SEM image of freshly prepared PSty$_3$-PEGPIILP co-polymer (4a)

Figure S11 TGA curve for PSty$_3$-PEGPIILP co-polymer (4a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

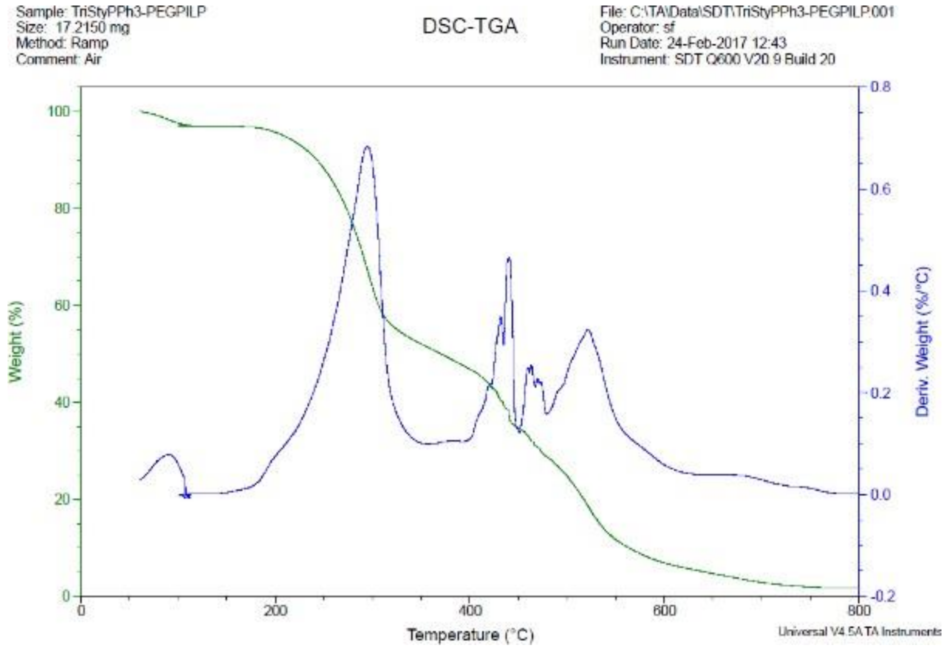


Figure S12 FT-IR spectrum of freshly prepared PSty$_3$-PEGPIILP co-polymer (4a)

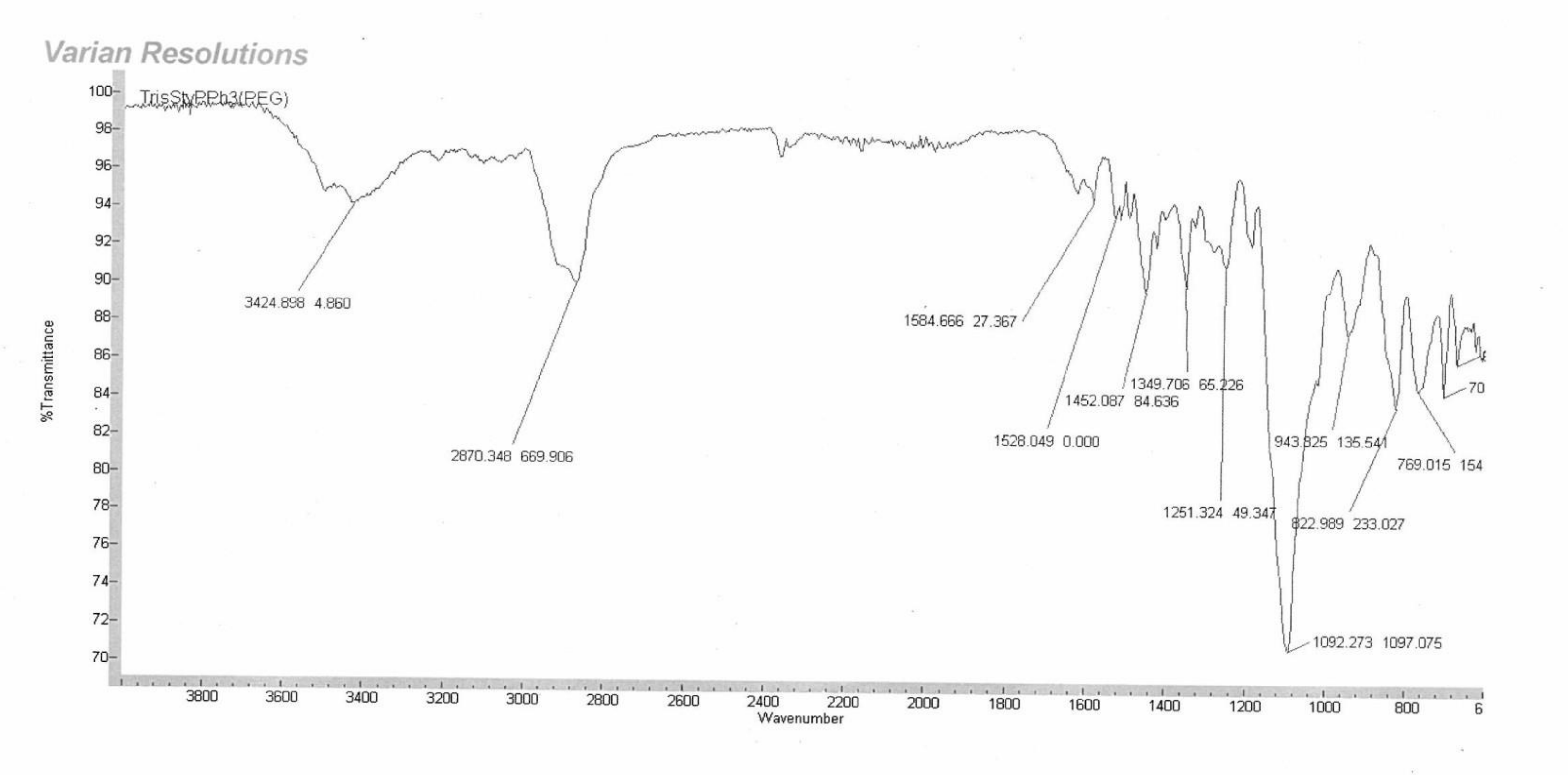


Figure S13 ^{1}H NMR spectrum of PPh$_2$PEGstyrene (5a)

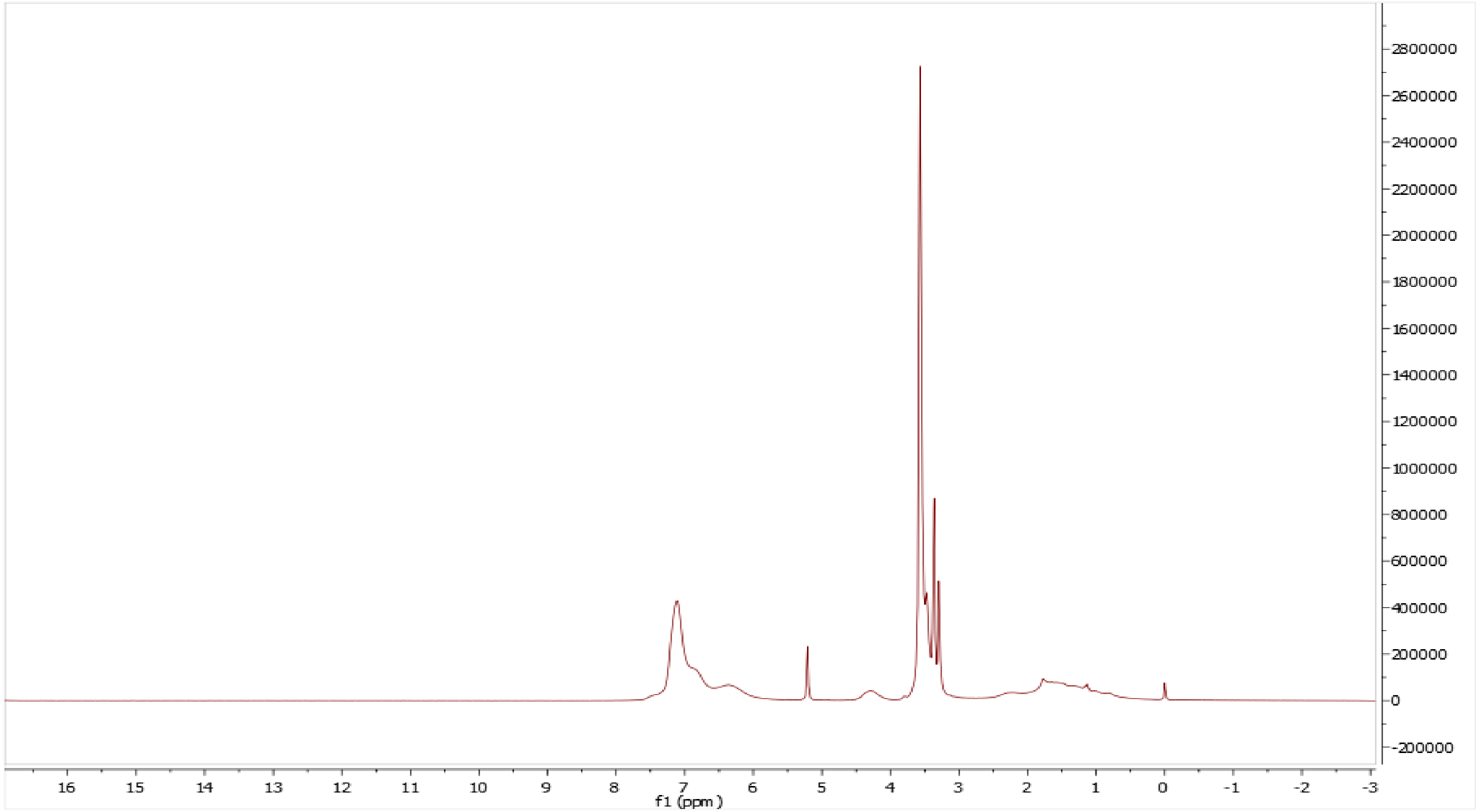
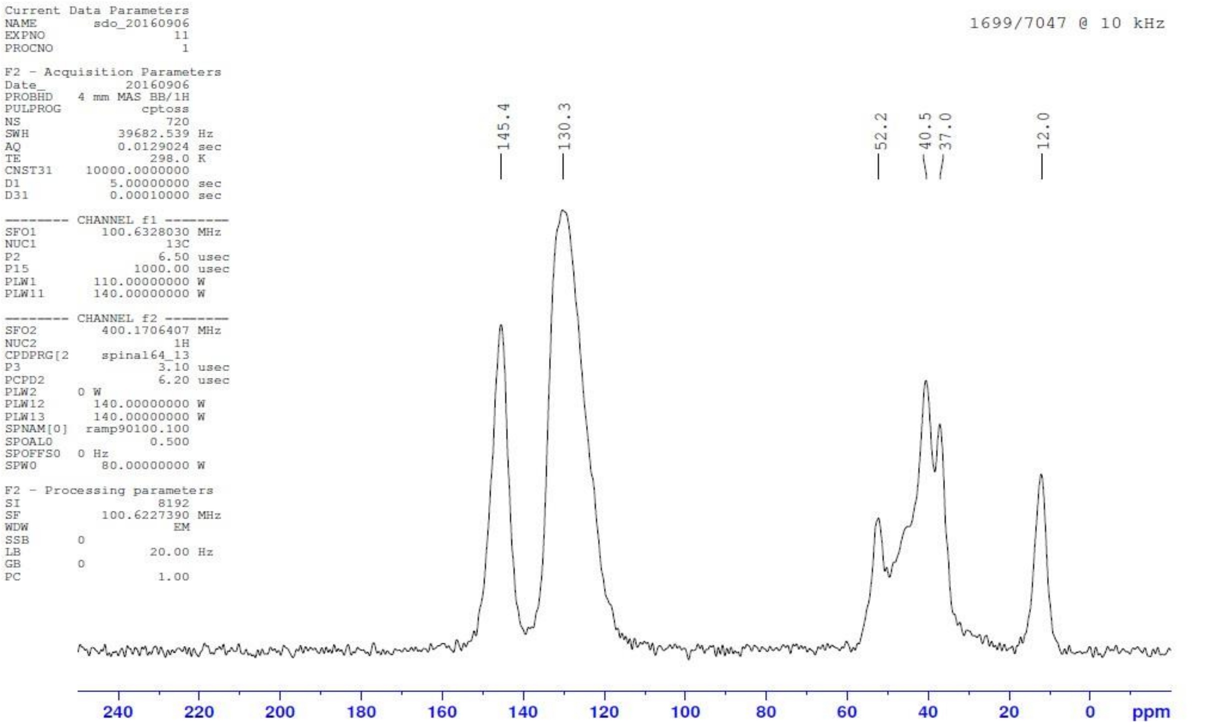


Figure S14 Solid state ^{13}C NMR spectrum of PPh_2PEGstyrene (5a)



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PROCNO                 1

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PULPROG           cptoss
NS                   720
SWH            39682.539 Hz
AQ             0.0129024 sec
TE                 298.0 K
CNST31     10000.0000000
D1            5.00000000 sec
D31           0.00010000 sec

======== CHANNEL f1 ========
SFO1         100.6328030 MHz
NUC1                 13C
P2                  6.50 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

======== CHANNEL f2 ========
SFO2         400.1706407 MHz
NUC2                  1H
CPDPRG[2     spinal64_13
P3                  3.10 usec
PCPD2               6.20 usec
PLW2      0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0         80.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227390 MHz
WDW                   EM
SSB       0
LB                 20.00 Hz
GB        0
PC                  1.00
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Figure S15 **Solid state ^{31}P NMR spectrum of PPh_2PEGstyrene (5a)**

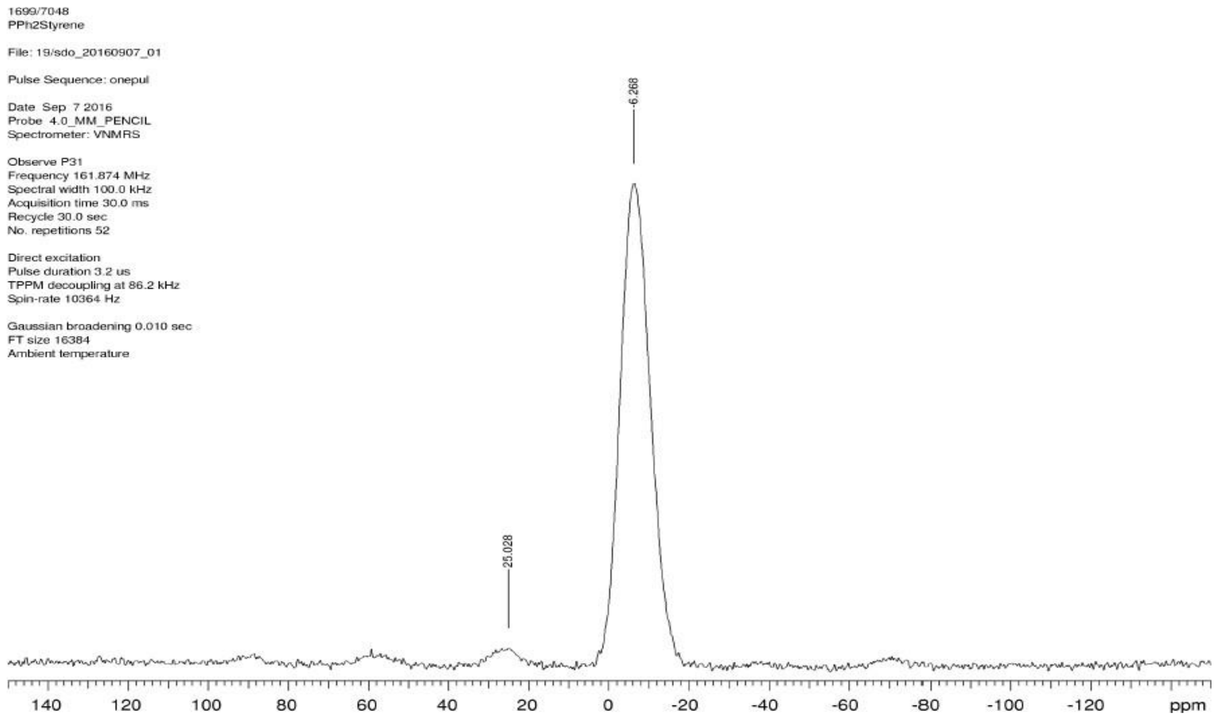


Figure S16 SEM images of freshly prepared PPh_2PEGstyrene (5a)

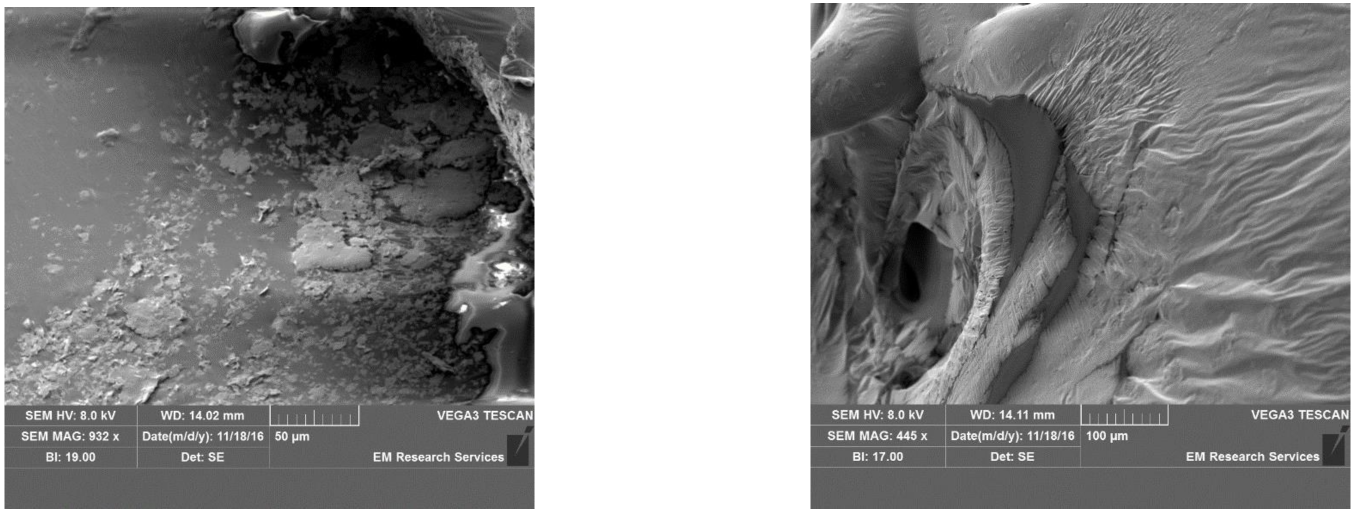


Figure S17 TGA curve for PPh_2PEGstyrene (5a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

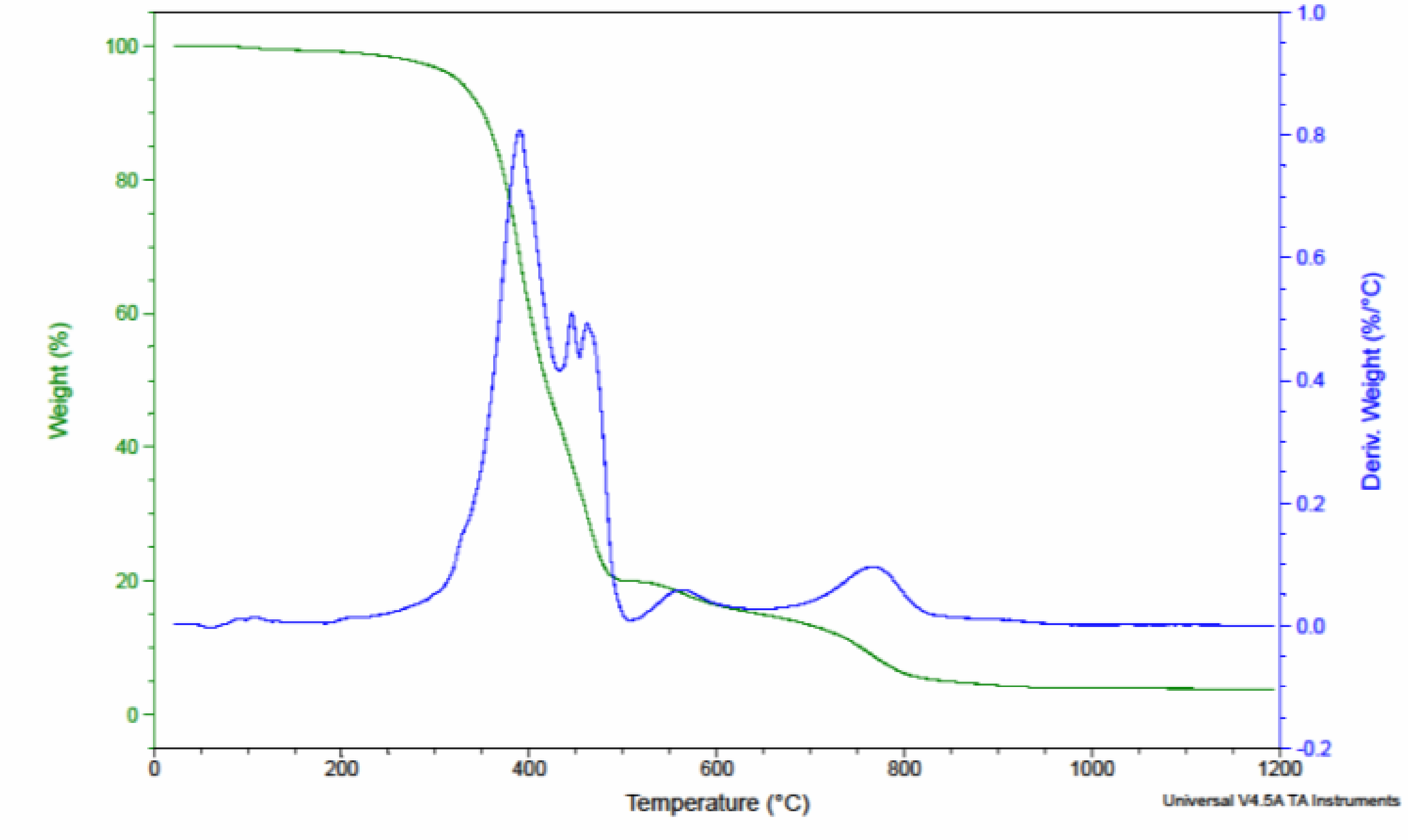


Figure S18 FT-IR spectrum of freshly prepared $PPh_2PEGstyrene$ (5a)

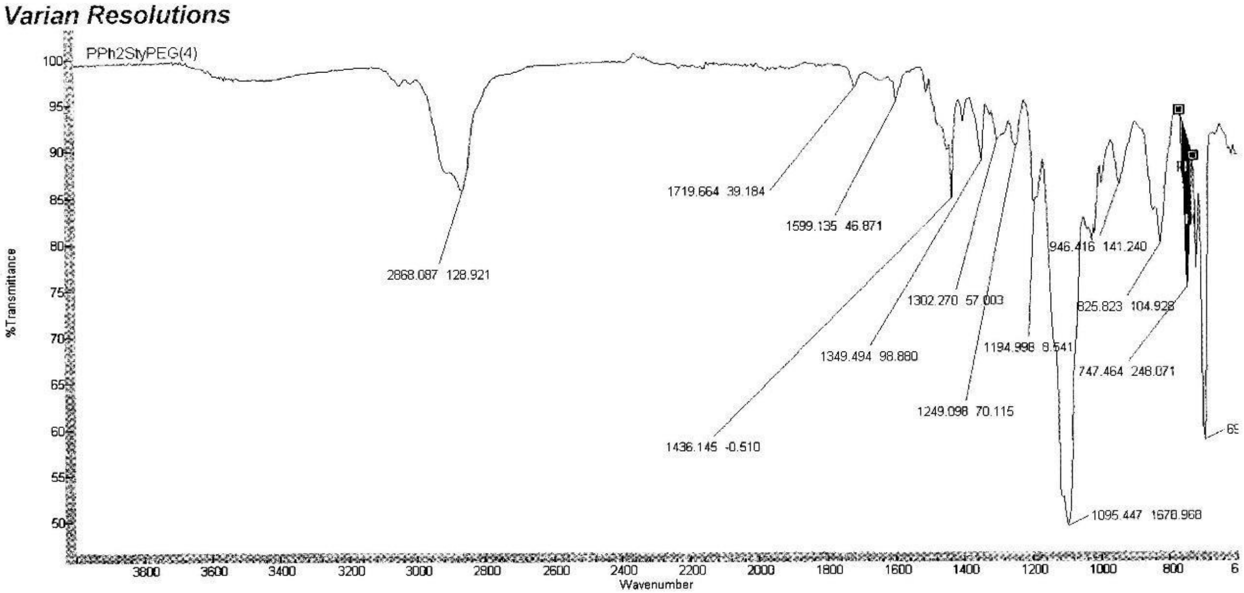


Figure S19 ^{1}H NMR spectrum of PEGPIILP co-polymer (6a)

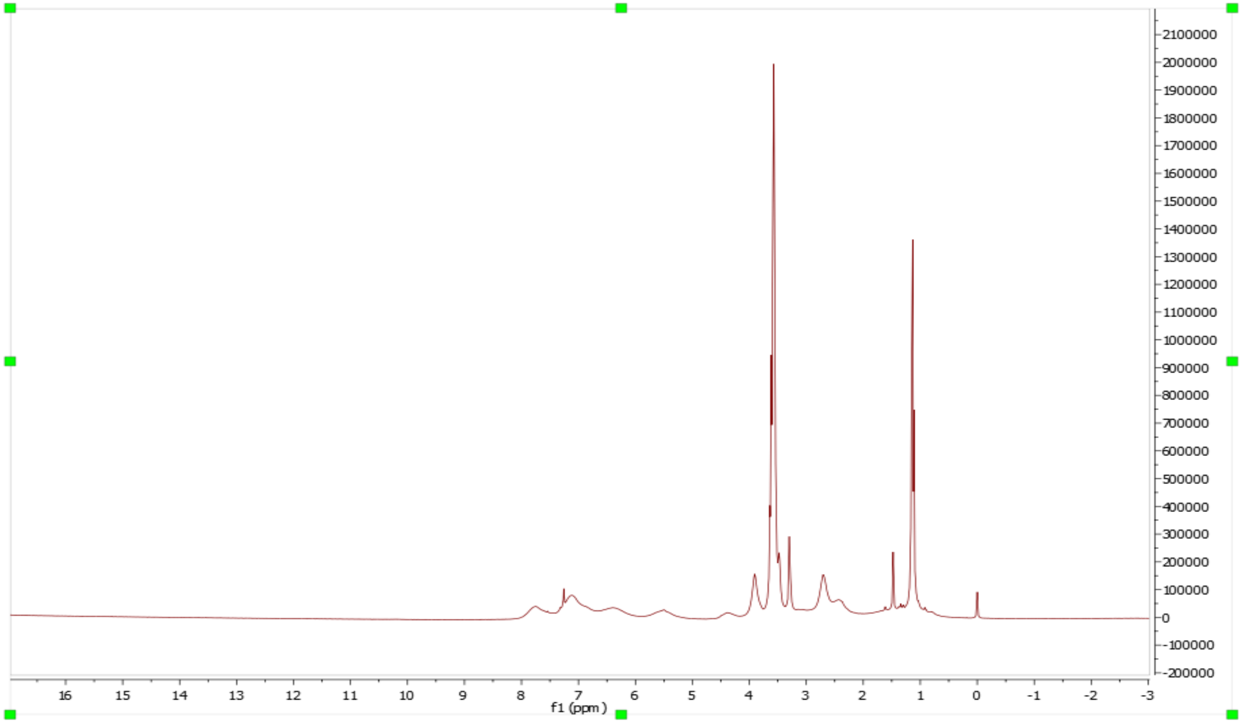
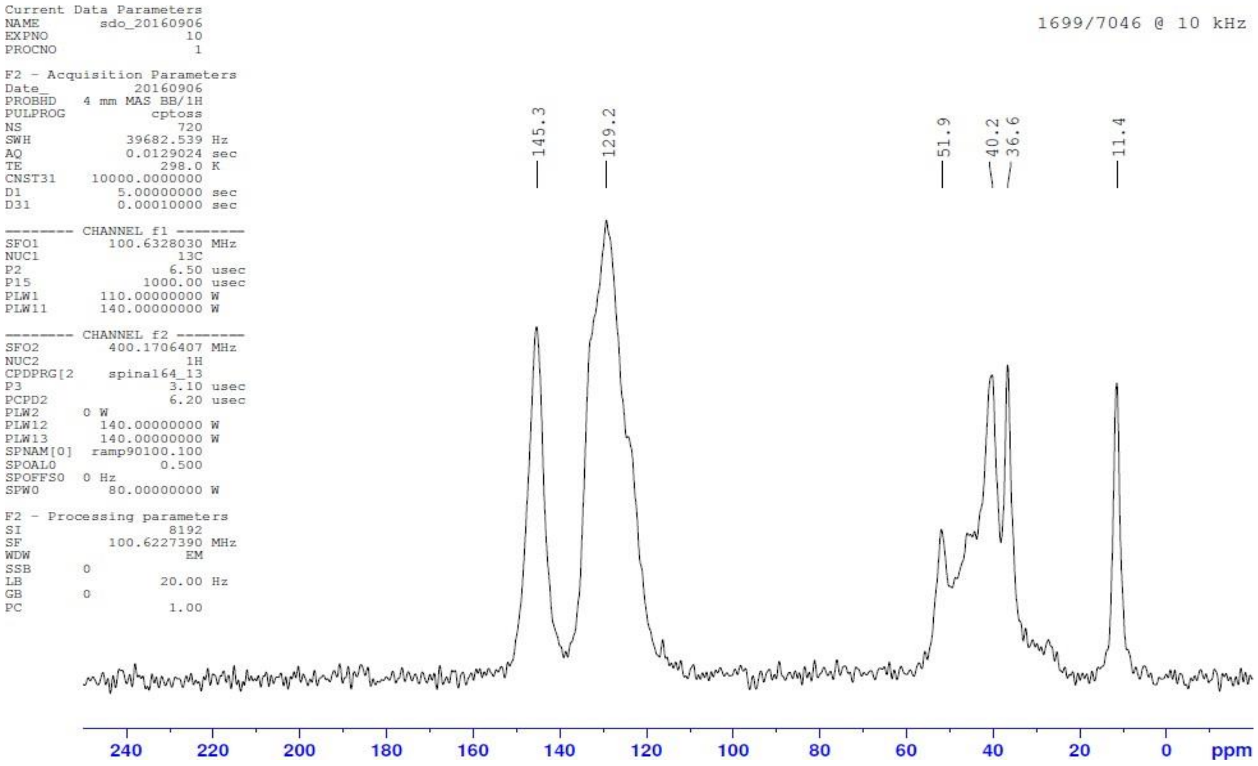


Figure S20 Solid state ^{13}C NMR spectrum of PEGPIILP co-polymer (6a)



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PROCNO                 1

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SWH            39682.539 Hz
AQ             0.0129024 sec
TE                 298.0 K
CNST31     10000.0000000
D1            5.00000000 sec
D31           0.00010000 sec

-------- CHANNEL f1 --------
SFO1         100.6328030 MHz
NUC1                 13C
P2                  6.50 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

-------- CHANNEL f2 --------
SFO2         400.1706407 MHz
NUC2                  1H
CPDPRG[2    spinal64_13
P3                  3.10 usec
PCPD2               6.20 usec
PLW2      0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0         80.00000000 W

F2 - Processing parameters
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SF           100.6227390 MHz
WDW                   EM
SSB       0
LB                 20.00 Hz
GB        0
PC                  1.00
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Figure S21 SEM images offreshly prepared PEGPIILP co-polymer (6a)

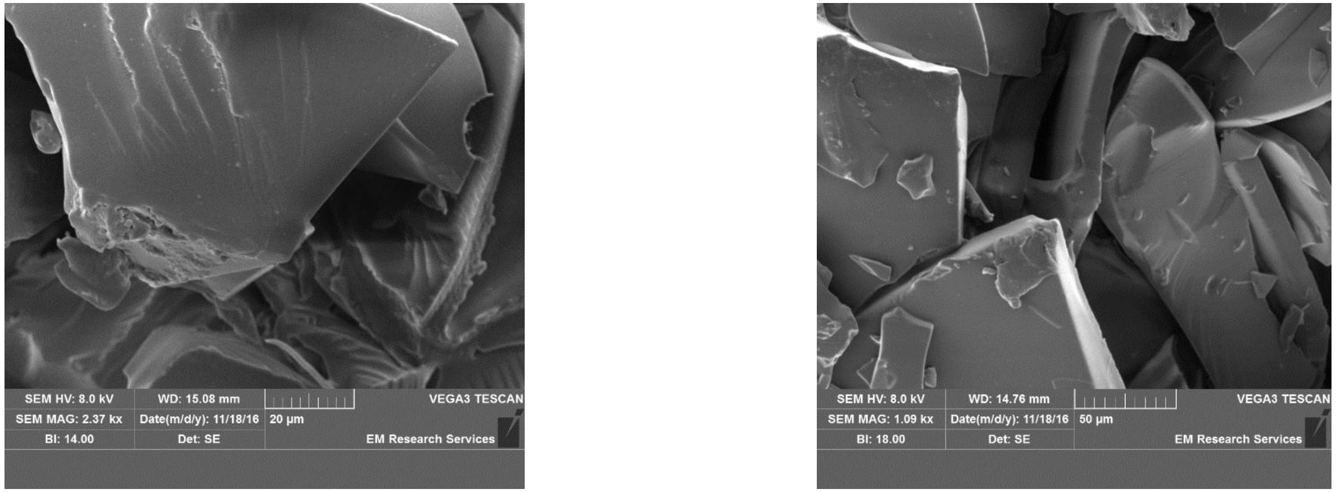


Figure S22 TGA curve for PEGPIILP copolymer (6a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

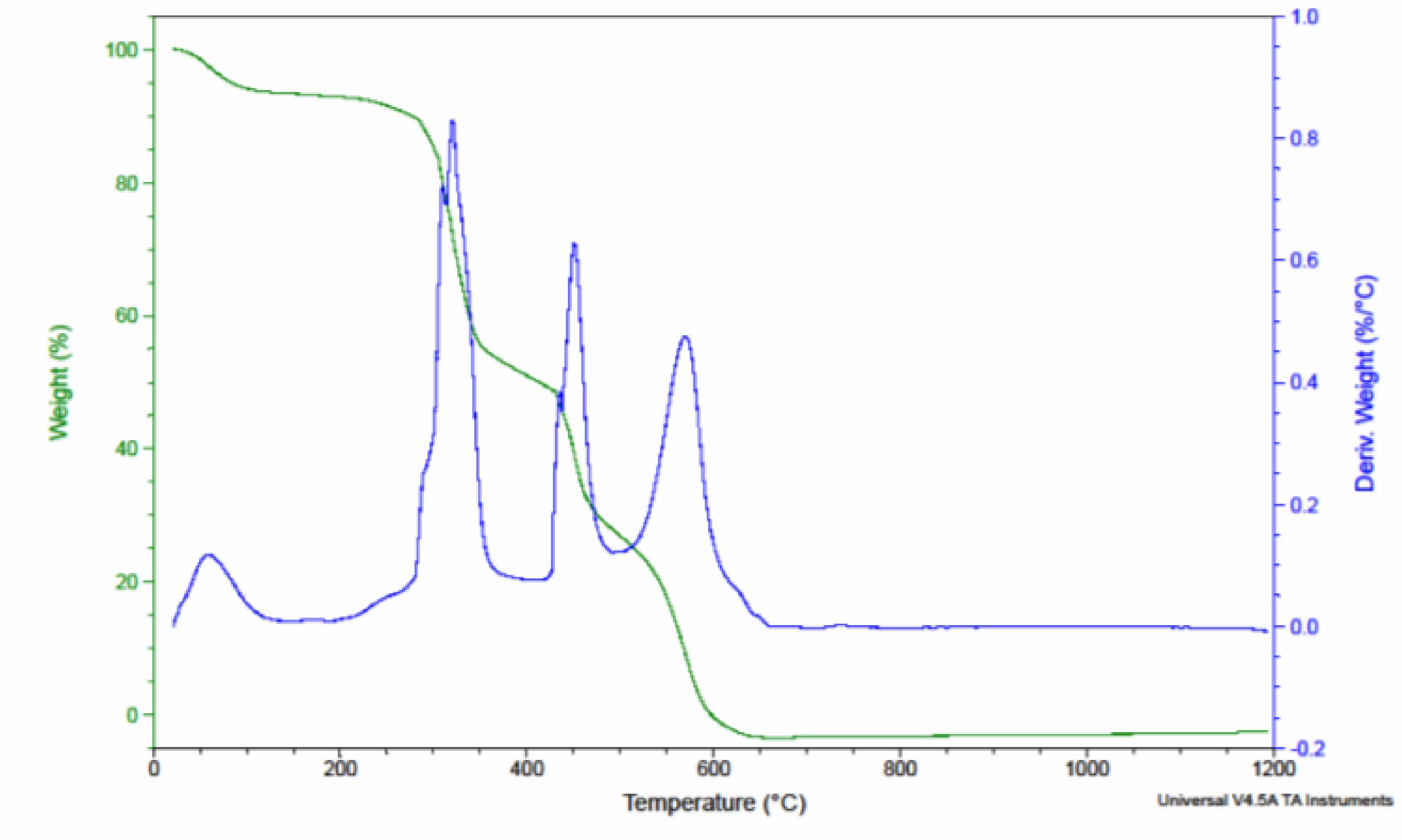


Figure S23 FT-IR spectrum of freshly prepared PEGPIILP co-polymer (6a)

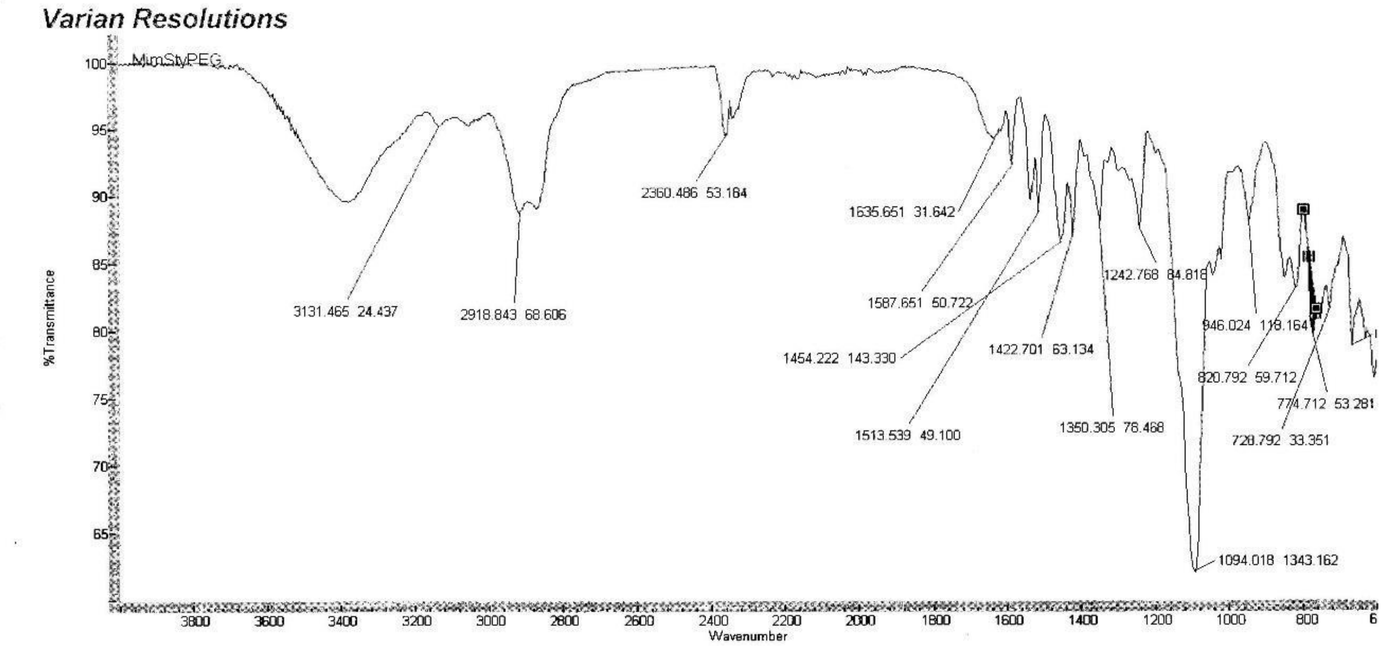


Figure S24 Solution ^{1}H NMR spectrum of PPh$_2$-polystyrene (7a)

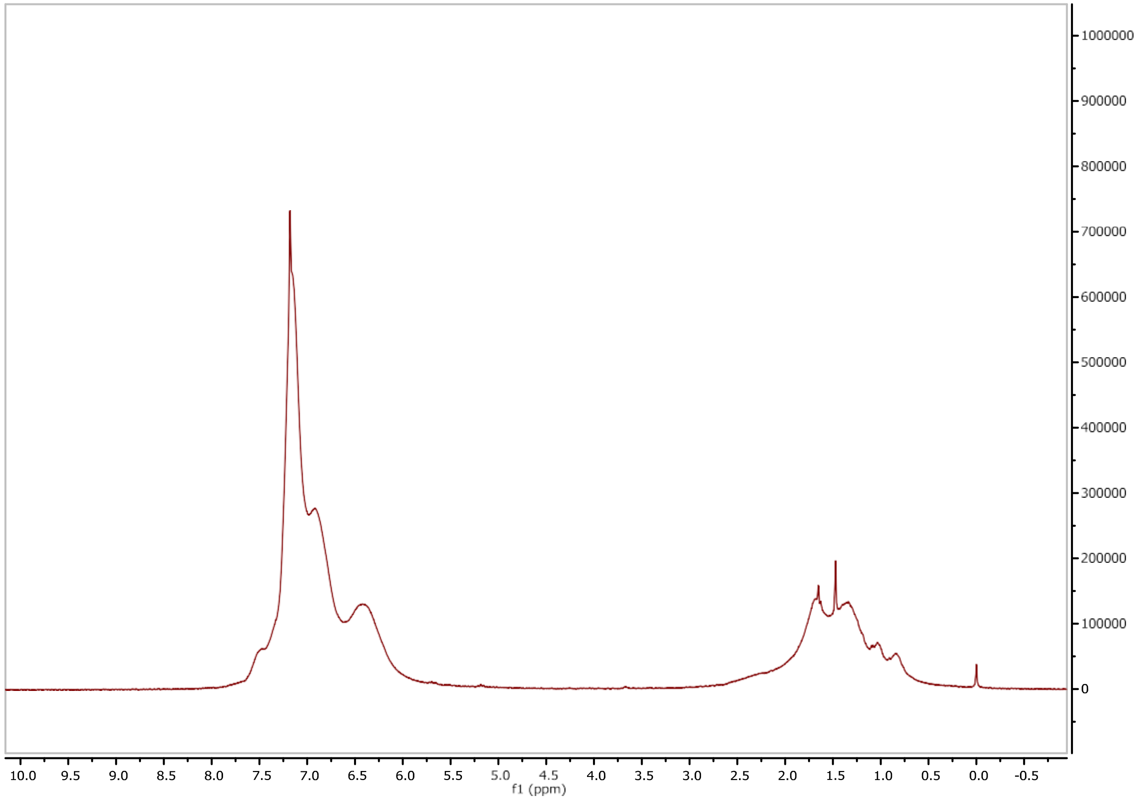


Figure S25 Solid state ^{31}P NMR spectrum of PPh_2-polystyrene (7a)

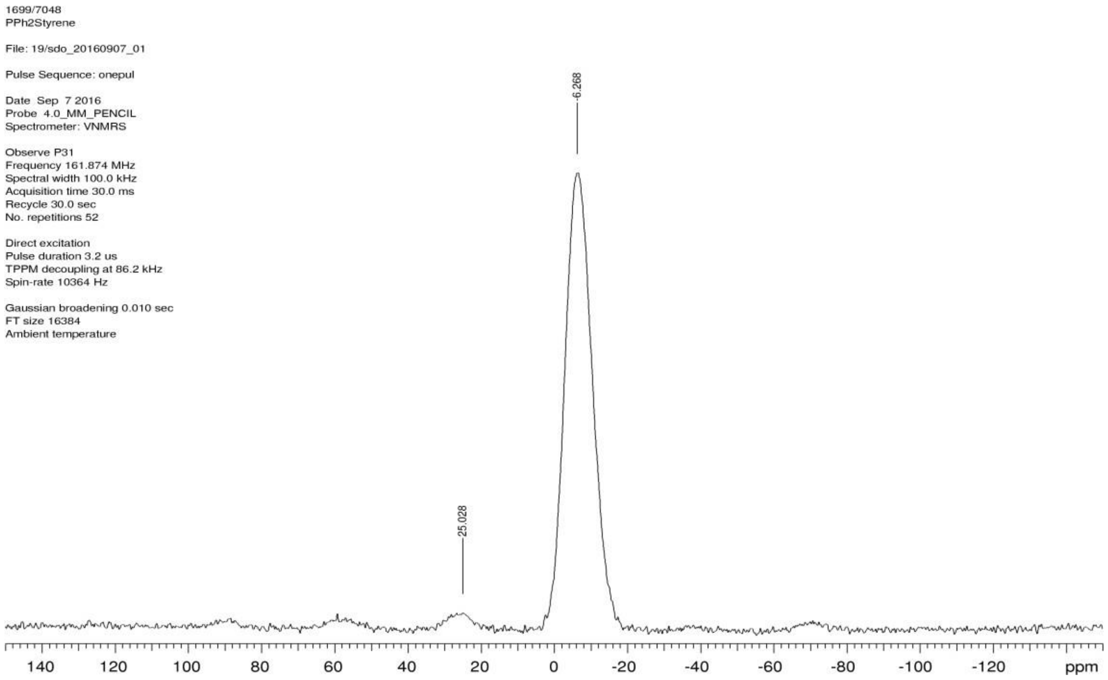
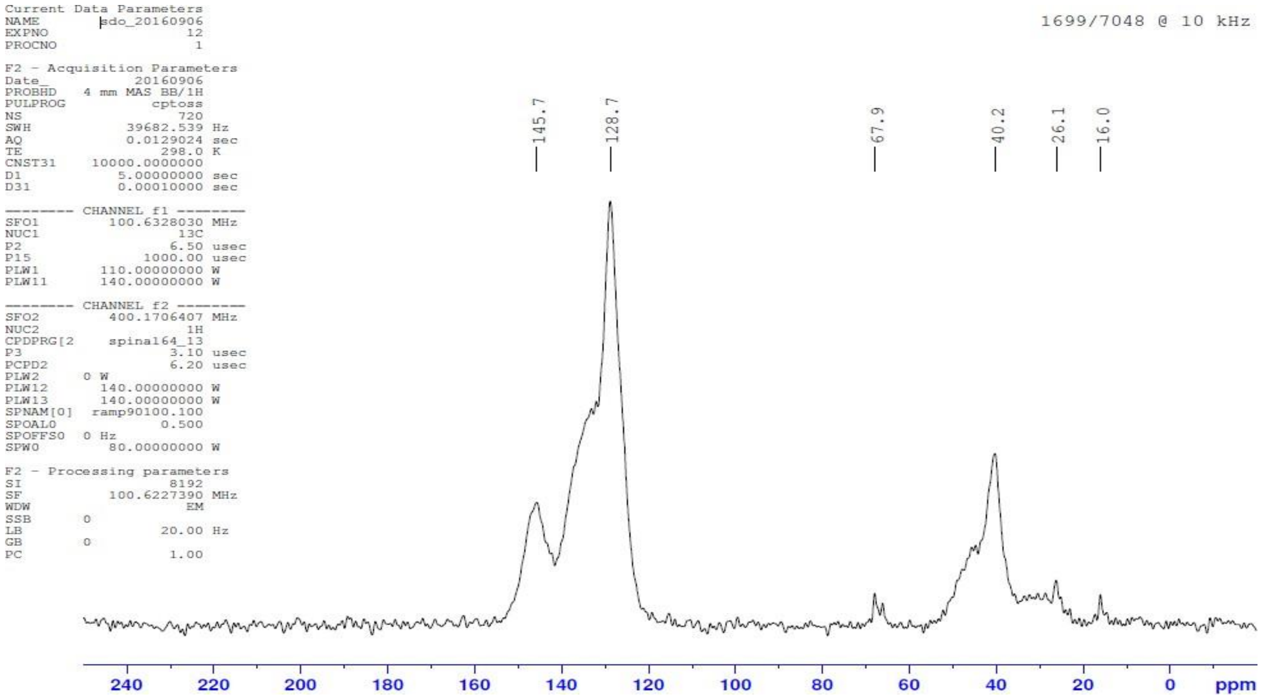


Figure S26 Solid state ^{13}C NMR spectrum of PPh_2-polystyrene (7a)



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SWH              39682.539 Hz
AQ               0.0129024 sec
TE                   298.0 K
CNST31     10000.0000000
D1              5.00000000 sec
D31             0.00010000 sec

-------- CHANNEL f1 --------
SFO1           100.6328030 MHz
NUC1                   13C
P2                    6.50 usec
P15                1000.00 usec
PLW1          110.00000000 W
PLW11         140.00000000 W

-------- CHANNEL f2 --------
SFO2           400.1706407 MHz
NUC2                    1H
CPDPRG[2      spinal64_13
P3                    3.10 usec
PCPD2                 6.20 usec
PLW2      0 W
PLW12         140.00000000 W
PLW13         140.00000000 W
SPNAM[0]    ramp90100.100
SPOAL0               0.500
SPOFFS0   0 Hz
SPW0           80.00000000 W

F2 - Processing parameters
SI                    8192
SF             100.6227390 MHz
WDW                     EM
SSB       0
LB                   20.00 Hz
GB        0
PC                    1.00
```

Figure S27 SEM images of freshly prepared PPh_2-polystyrene (7a)

Figure S28 TGA curve for PPh$_2$-polystyrene (7a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

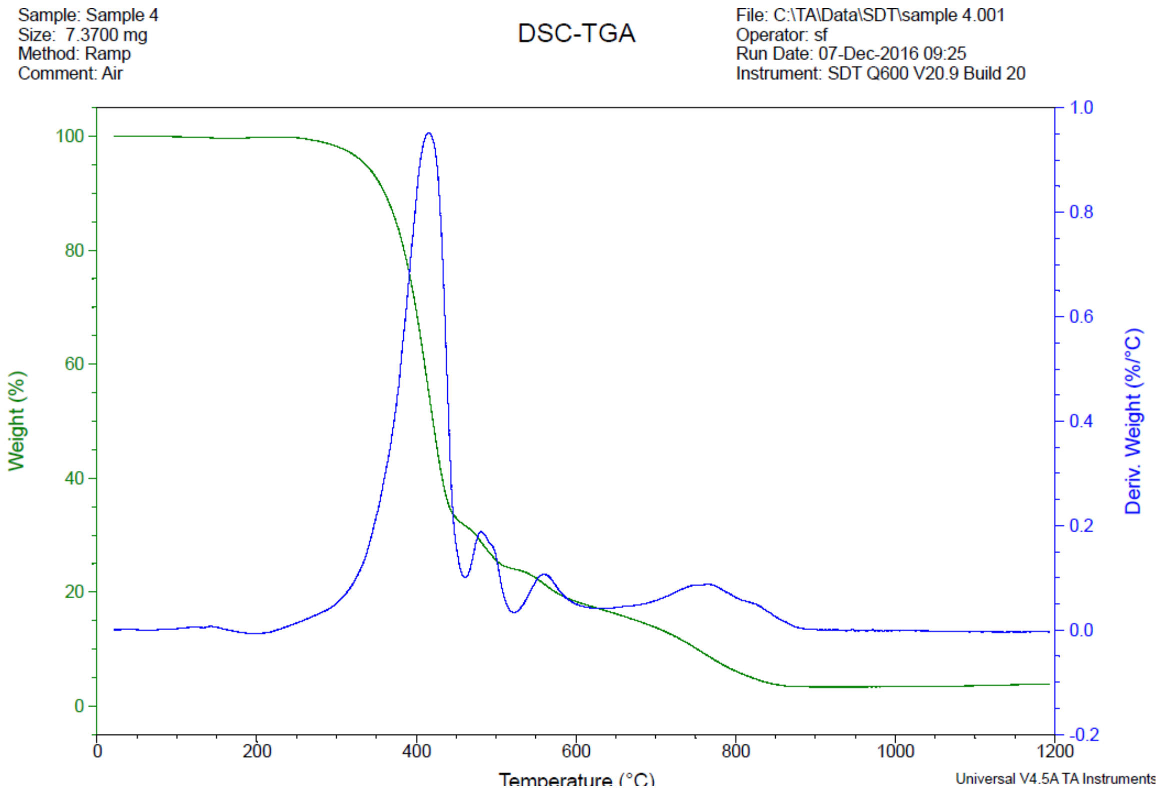


Figure S29 FT-IR spectrum of freshly prepared PPh$_2$-polystyrene (7a)

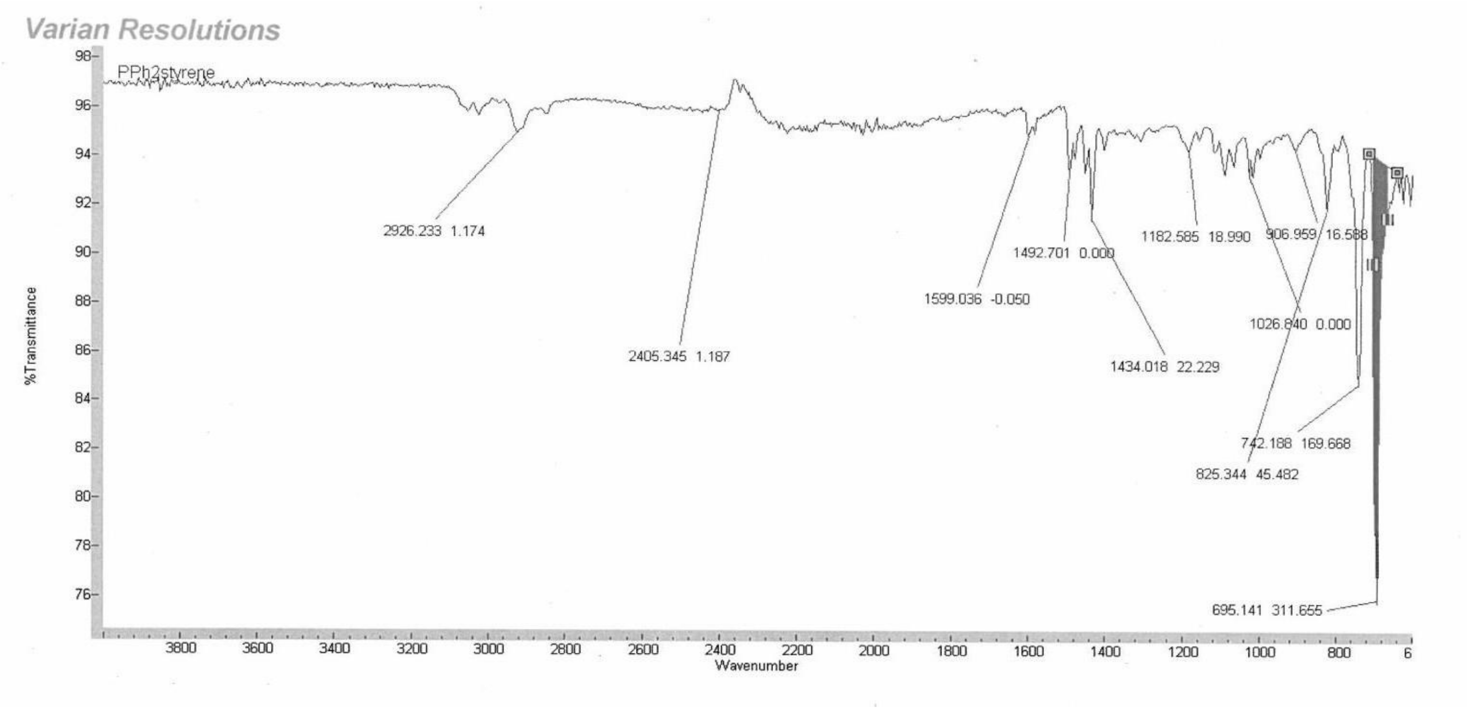


Figure S30 Solution ^{1}H NMR spectrum of Styr-PIILP (8a)

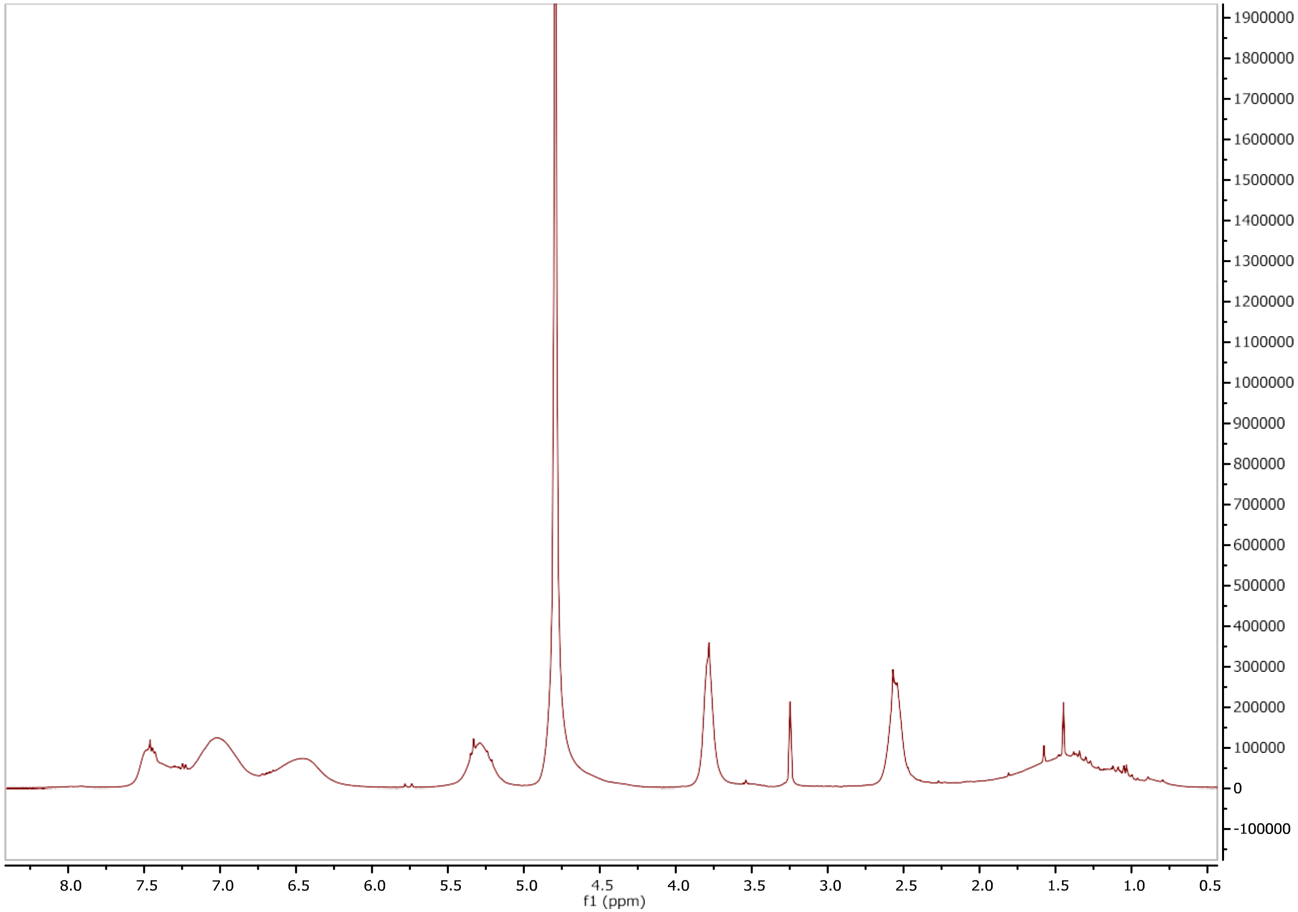
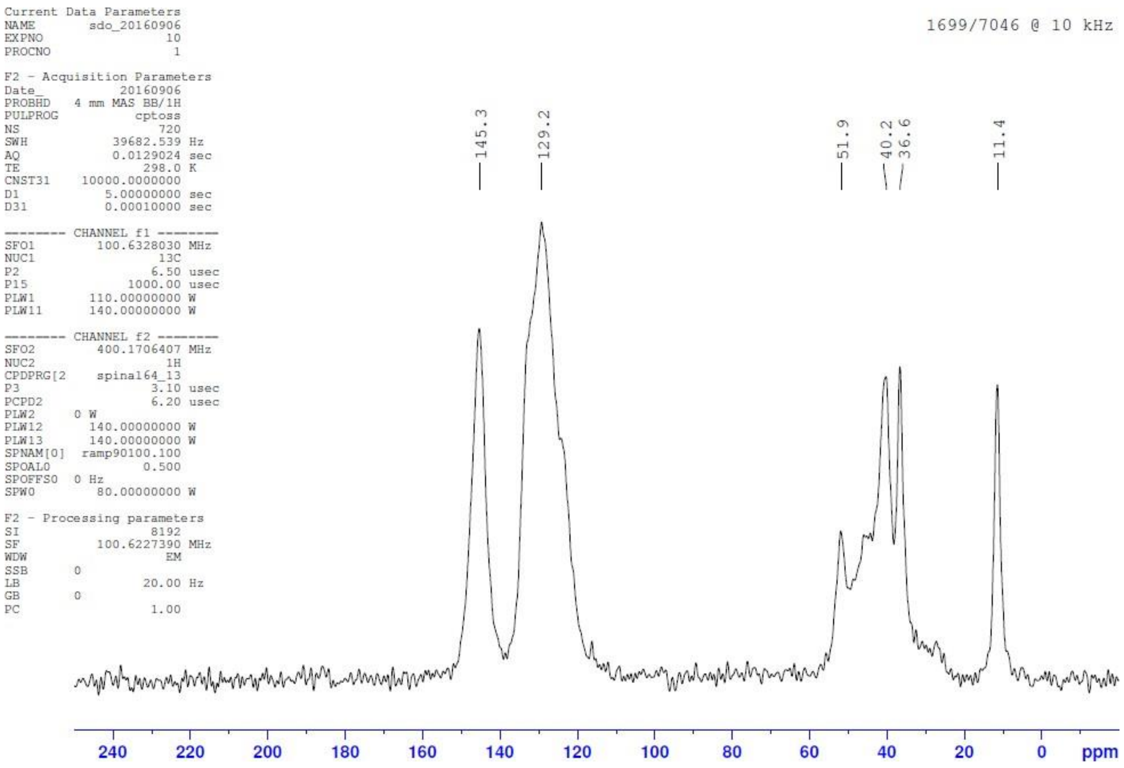


Figure S31 Solid state ^{13}C NMR spectrum of Styr-PIILP (8a)



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Current Data Parameters
NAME        sdo_20160906
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160906
PROBHD   4 mm MAS BB/1H
PULPROG           cptoss
NS                   720
SWH            39682.539 Hz
AQ             0.0129024 sec
TE                 298.0 K
CNST31   10000.0000000
D1            5.00000000 sec
D31           0.00010000 sec

-------- CHANNEL f1 --------
SFO1         100.6328030 MHz
NUC1                 13C
P2                  6.50 usec
P15              1000.00 usec
PLW1       110.00000000 W
PLW11      140.00000000 W

-------- CHANNEL f2 --------
SFO2         400.1706407 MHz
NUC2                  1H
CPDPRG[2     spinal64_13
P3                  3.10 usec
PCPD2               6.20 usec
PLW2      0 W
PLW12      140.00000000 W
PLW13      140.00000000 W
SPNAM[0]   ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227390 MHz
WDW                   EM
SSB       0
LB                 20.00 Hz
GB        0
PC                  1.00
```

Figure S32 SEM images of freshly prepared Styr-PIILP (8a)

Figure S33 TGA curve for Styr-PIILP (8a); wt% v temperature (green) and (b) derivative wt% v temperature (blue). Heating rate of 10 °C min^{-1} in air

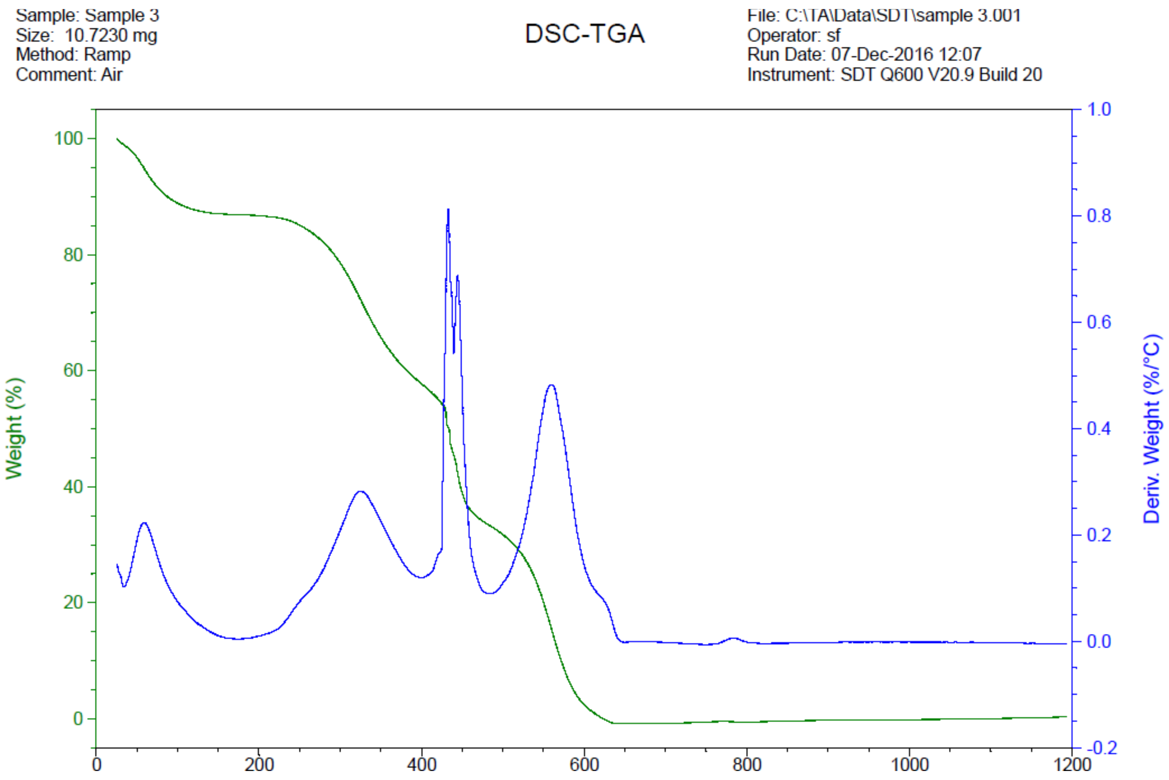


Figure S34 FT-IR spectrum of freshly prepared Styr-PIILP (8a)

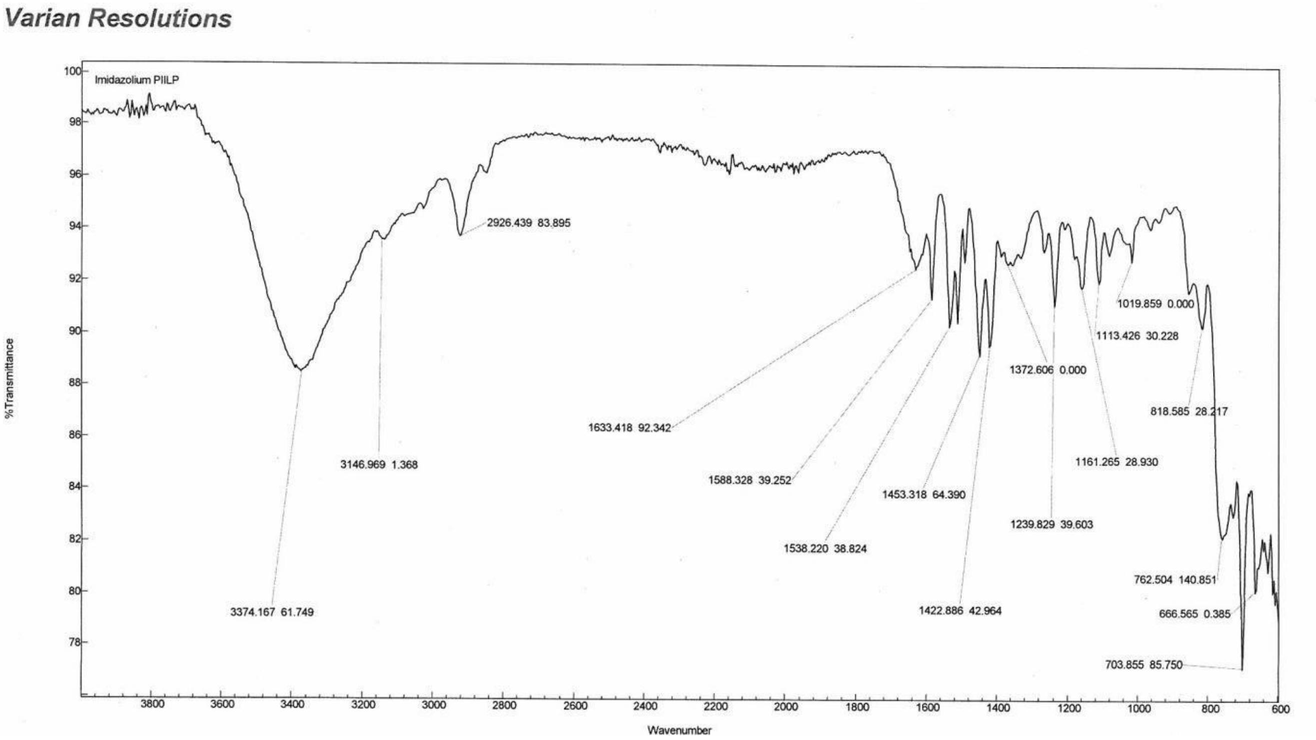
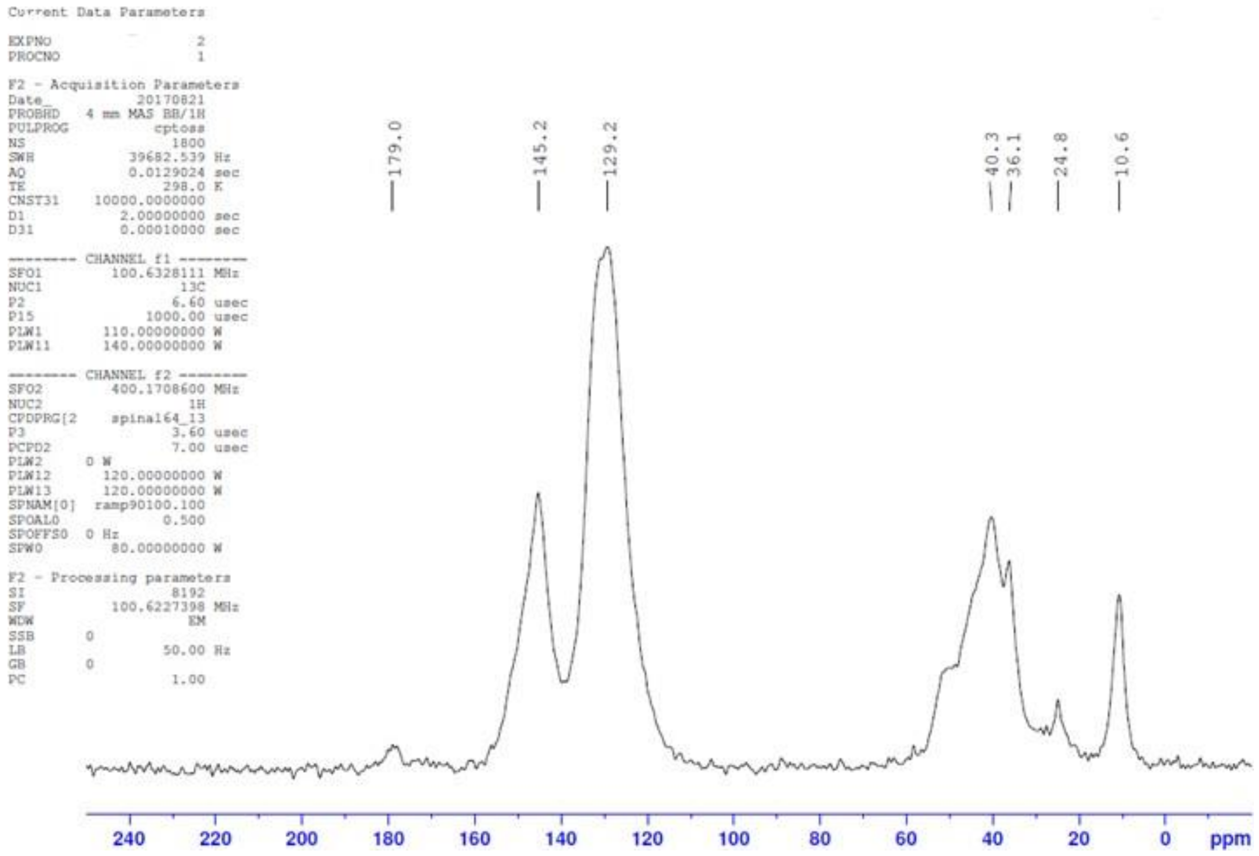


Figure S35 Solid state ^{13}C NMR spectrum of $[PdCl_4]@PSty_3$-PIILP (3b)



```
Current Data Parameters

EXPNO                 2
PROCNO                1

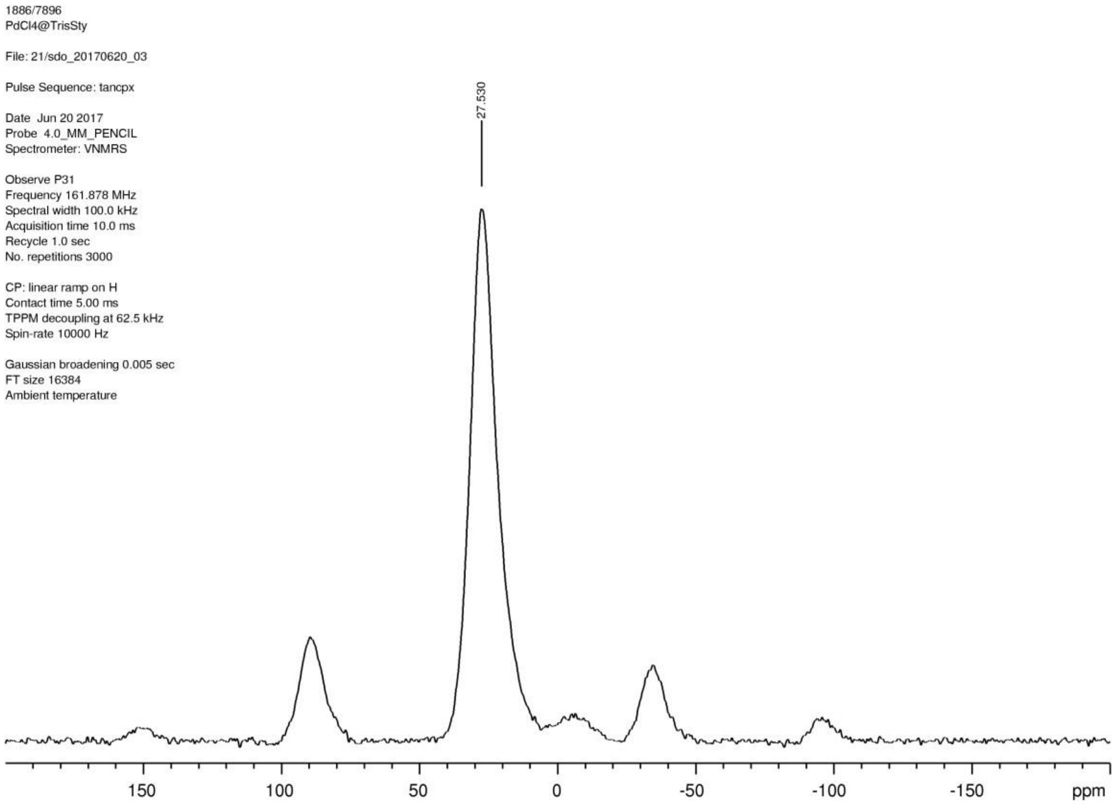
F2 - Acquisition Parameters
Date_          20170821
PROBHD   4 mm MAS BB/1H
PULPROG          cptoss
NS                 1800
SWH           39682.539 Hz
AQ            0.0129024 sec
TE                298.0 K
CNST31    10000.0000000
D1           2.00000000 sec
D31          0.00010000 sec

-------- CHANNEL f1 --------
SFO1        100.6328111 MHz
NUC1                13C
P2                 6.60 usec
P15             1000.00 usec
PLW1       110.00000000 W
PLW11      140.00000000 W

-------- CHANNEL f2 --------
SFO2        400.1708600 MHz
NUC2                 1H
CPDPRG[2     spinal64_13
P3                 3.60 usec
PCPD2              7.00 usec
PLW2      0 W
PLW12      120.00000000 W
PLW13      120.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0            0.500
SPOFFS0   0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                 8192
SF          100.6227398 MHz
WDW                  EM
SSB       0
LB                50.00 Hz
GB        0
PC                 1.00
```

Figure S36 Solid state ^{31}P NMR spectrum of $[PdCl_4]$@PSty$_3$-PIILP (3b)


1886/7896
PdCl4@TrisSty

File: 21/sdo_20170620_03

Pulse Sequence: tancpx

Date Jun 20 2017
Probe 4.0_MM_PENCIL
Spectrometer: VNMRS

Observe P31
Frequency 161.878 MHz
Spectral width 100.0 kHz
Acquisition time 10.0 ms
Recycle 1.0 sec
No. repetitions 3000

CP: linear ramp on H
Contact time 5.00 ms
TPPM decoupling at 62.5 kHz
Spin-rate 10000 Hz

Gaussian broadening 0.005 sec
FT size 16384
Ambient temperature

$[PdCl_4]$@PSty$_3$-PEGPIILP– ^{31}P shows almost all phosphine is coordinated to Pd, small amount (6%) of uncoordinated phosphine (*)

Figure S37 SEM images of freshly prepared $[PdCl_4]@PSty_3$-PIILP (3b)

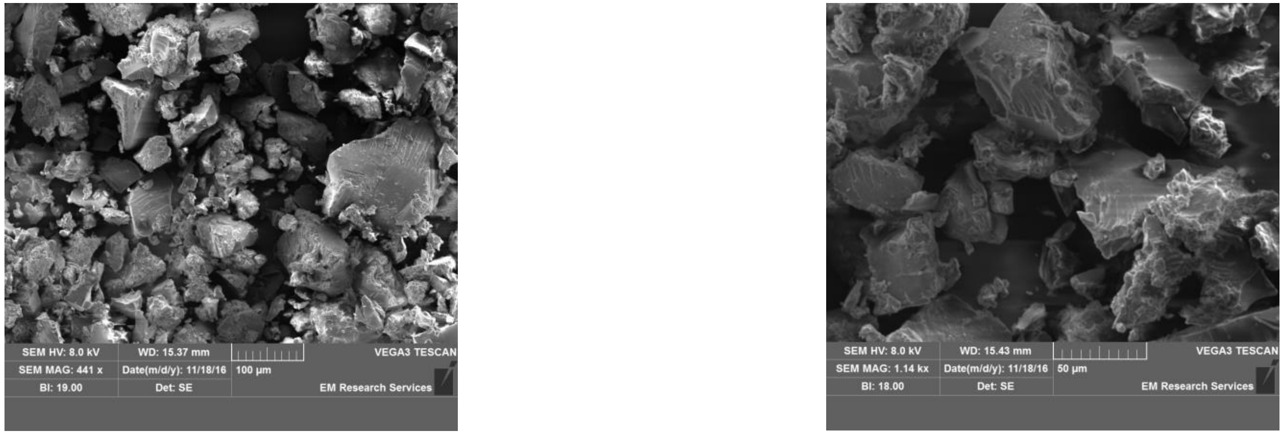


Figure S38 FT-IR spectrum of freshly prepared [$PdCl_4$]@$PSty_3$-PIILP (3b)

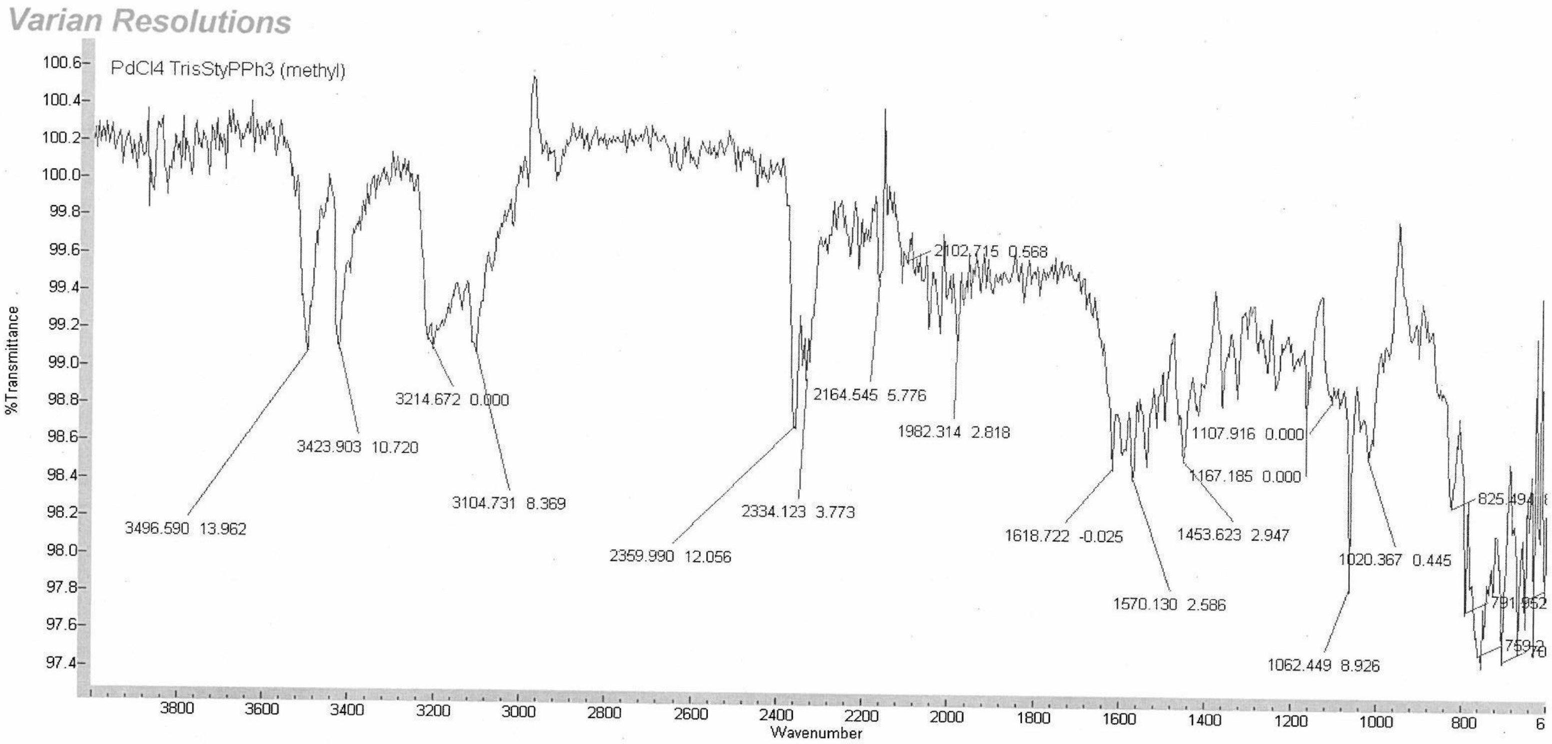


Figure S39 Pd 3d core level XPS spectrum of $[PdCl_4]$@PSty$_3$-PIILP (3b) referenced to the hydrocarbon C 1s

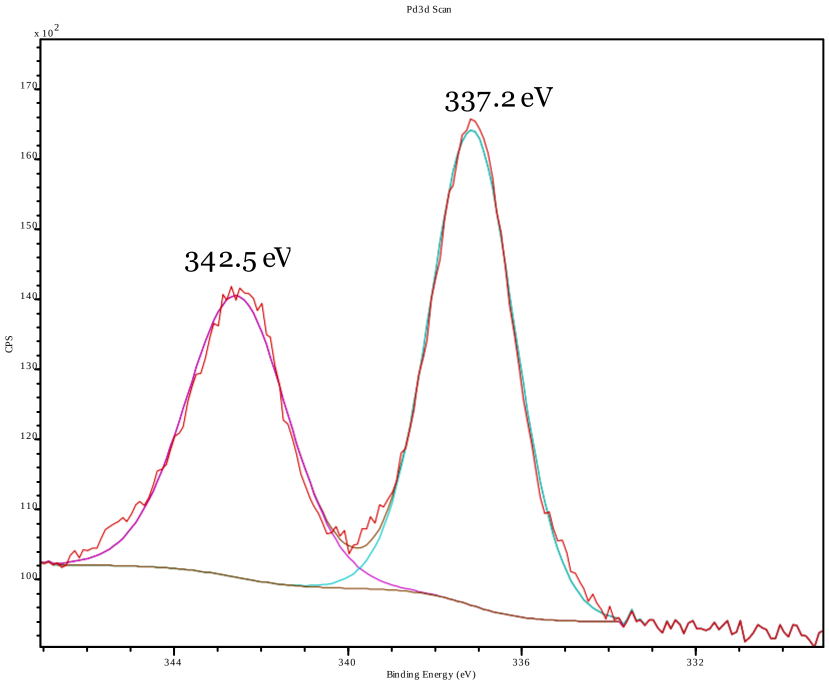
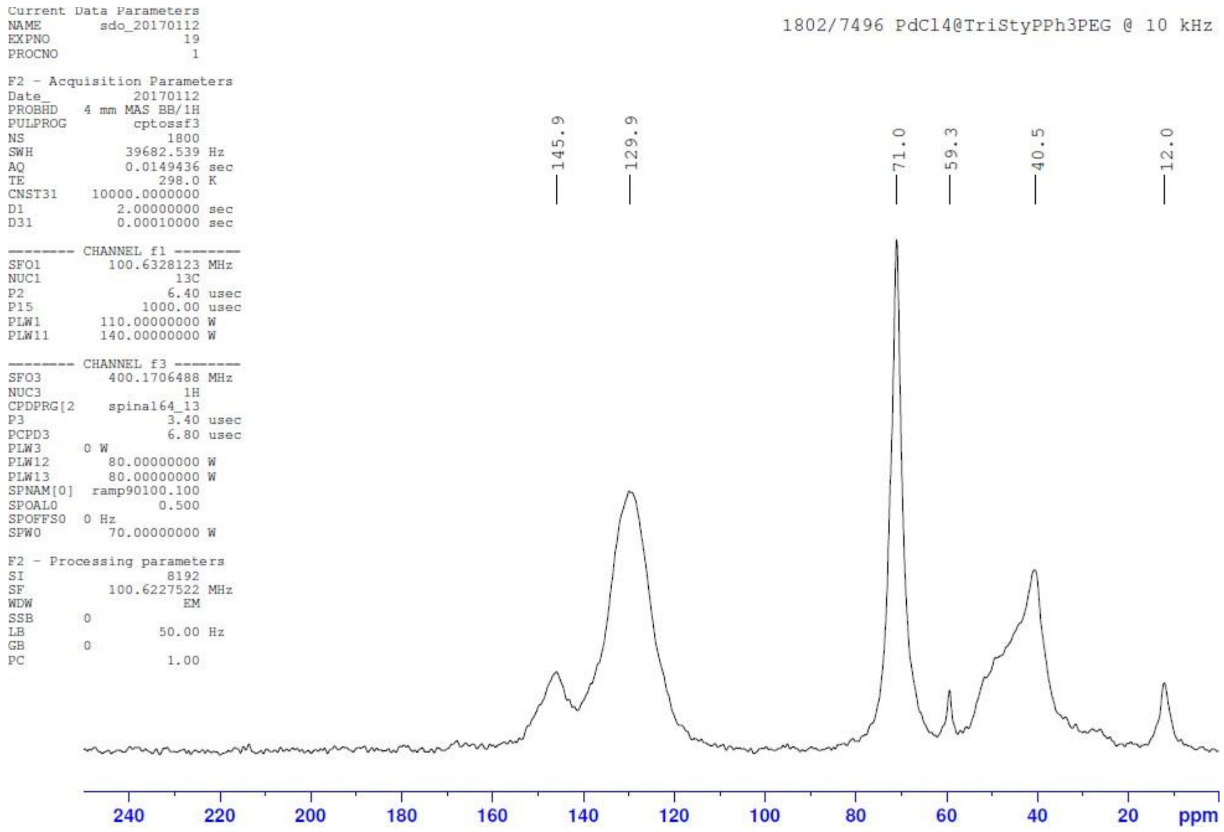


Figure S40 Solid state ^{13}C NMR spectrum of $[PdCl_4]$@PSty$_3$-PEGPIILP (4b)



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Current Data Parameters
NAME        sdo_20170112
EXPNO                 19
PROCNO                 1

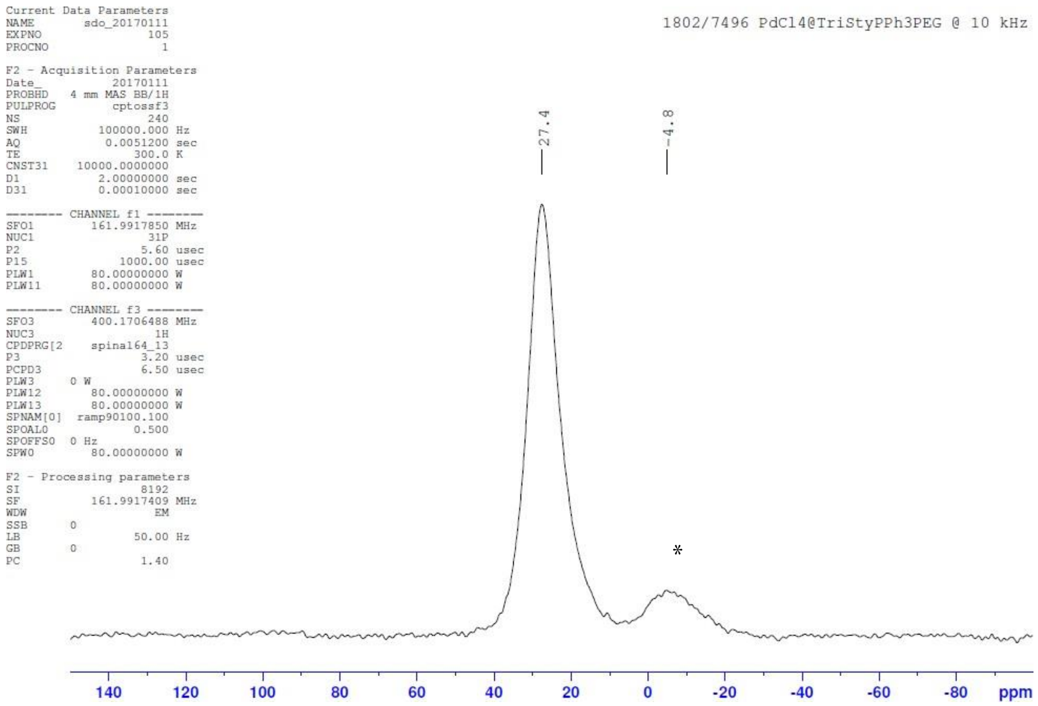
F2 - Acquisition Parameters
Date_           20170112
PROBHD   4 mm MAS BB/1H
PULPROG         cptossf3
NS                  1800
SWH          39682.539 Hz
AQ           0.0149436 sec
TE               298.0 K
CNST31    10000.0000000
D1          2.00000000 sec
D31         0.00010000 sec

======== CHANNEL f1 ========
SFO1       100.6328123 MHz
NUC1                 13C
P2                  6.40 usec
P15              1000.00 usec
PLW1      110.00000000 W
PLW11     140.00000000 W

======== CHANNEL f3 ========
SFO3       400.1706488 MHz
NUC3                  1H
CPDPRG[2     spinal64_13
P3                  3.40 usec
PCPD3               6.80 usec
PLW3      0 W
PLW12      80.00000000 W
PLW13      80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0       70.00000000 W

F2 - Processing parameters
SI                  8192
SF         100.6227522 MHz
WDW                   EM
SSB       0
LB                 50.00 Hz
GB        0
PC                  1.00
```

Figure S41 Solid state ^{31}P NMR spectrum of [PdCl$_4$]@PSty$_3$-PEGPIILP (4b)



```
Current Data Parameters
NAME       sdo_20170111
EXPNO               105
PROCNO                1

F2 - Acquisition Parameters
Date_          20170111
PROBHD   4 mm MAS BB/1H
PULPROG        cptossf3
NS                  240
SWH          100000.000 Hz
AQ            0.0051200 sec
TE                300.0 K
CNST31    10000.0000000
D1           2.00000000 sec
D31          0.00010000 sec

======== CHANNEL f1 ========
SFO1        161.9917850 MHz
NUC1                31P
P2                 5.60 usec
P15             1000.00 usec
PLW1        80.00000000 W
PLW11       80.00000000 W

======== CHANNEL f3 ========
SFO3        400.1706488 MHz
NUC3                 1H
CPDPRG[2    spinal64_13
P3                 3.20 usec
PCPD3              6.50 usec
PLW3     0 W
PLW12       80.00000000 W
PLW13       80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0            0.500
SPOFFS0  0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                 8192
SF          161.9917409 MHz
WDW                  EM
SSB      0
LB                50.00 Hz
GB       0
PC                 1.40
```

[PdCl$_4$]@PSty$_3$-PEGPIILP– ^{31}P shows almost all phosphine is coordinated to Pd, small amount (14%) of uncoordinated phosphine (*)

Figure S42 SEM images of freshly prepared [$PdCl_4$]@$PSty_3$-PEGPIILP (4b)

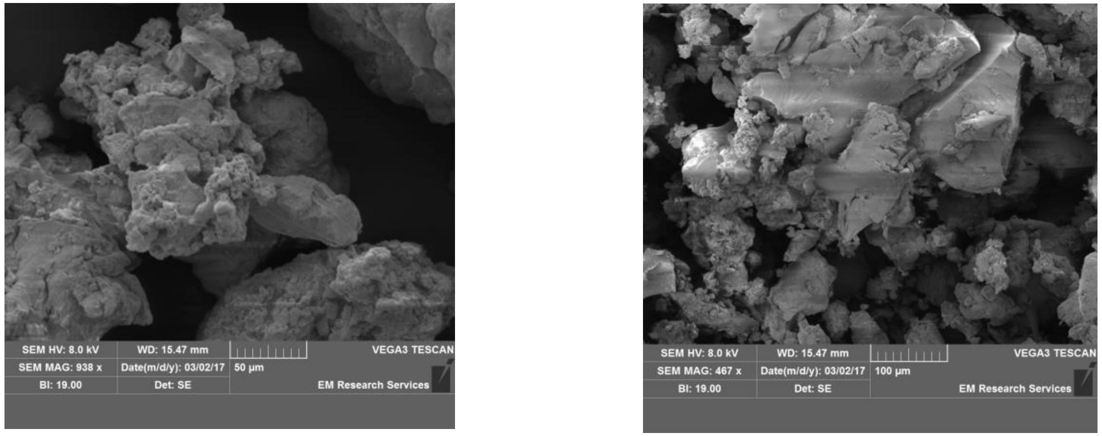


Figure S43 FT-IR spectrum of freshly prepared [$PdCl_4$]@$PSty_3$-PEGPIILP (4b)

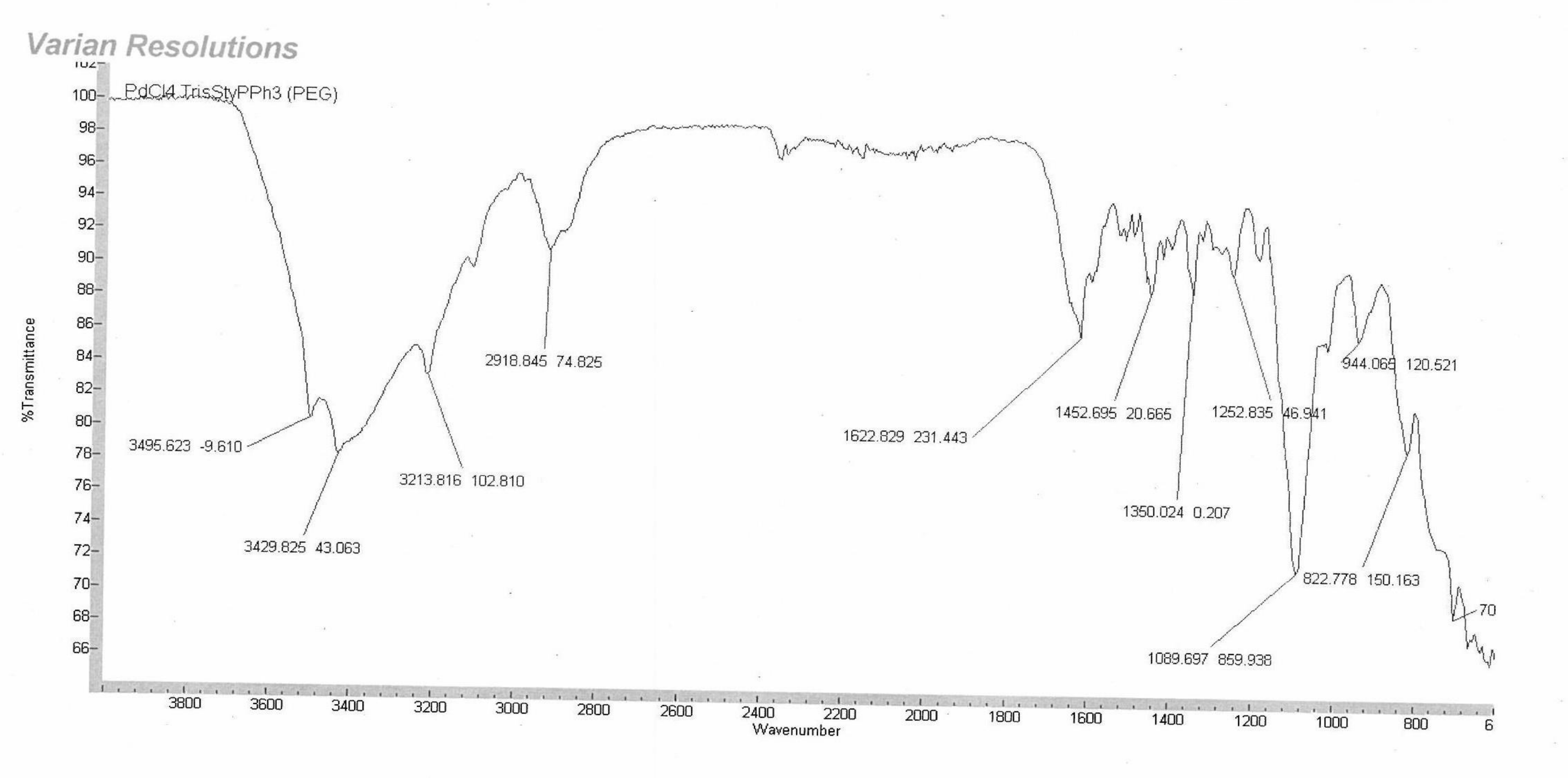


Figure S44 **Pd 3d core level XPS spectrum of [PdCl$_4$]@PSty$_3$-PEGPIILP (4b) referenced to the hydrocarbon C 1s**

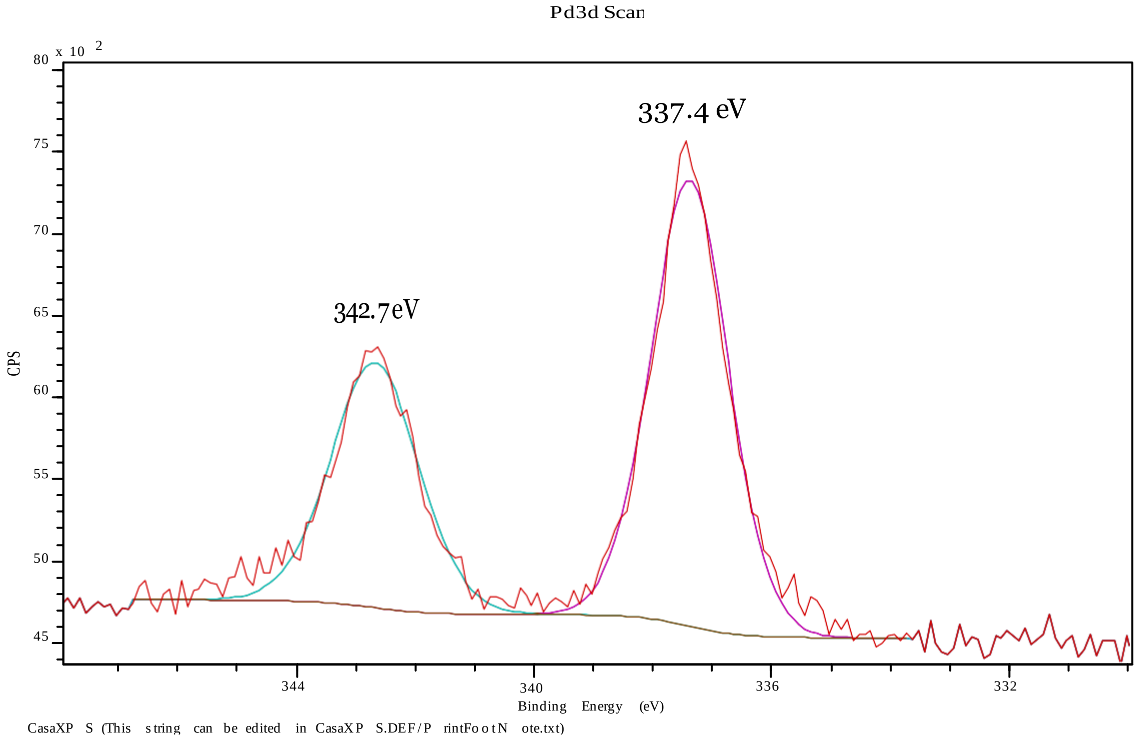
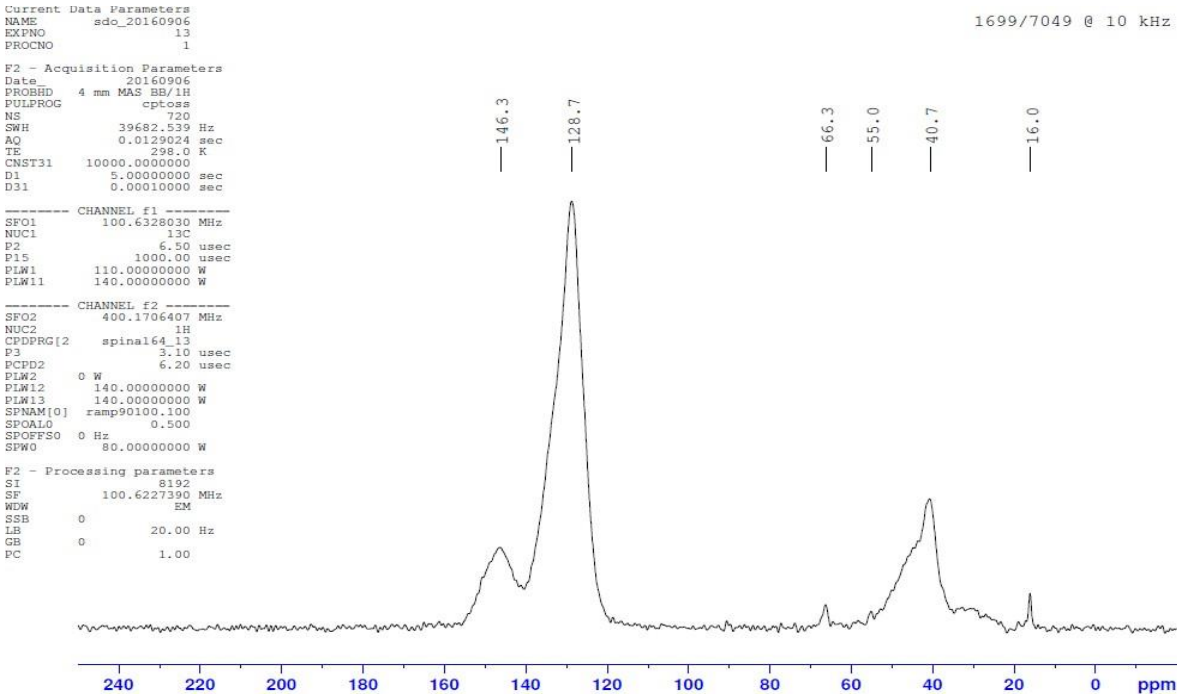


Figure S45 Solid state ^{13}C NMR spectrum of $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (5b)



```
Current Data Parameters
NAME          sdo_20160906
EXPNO                   13
PROCNO                   1

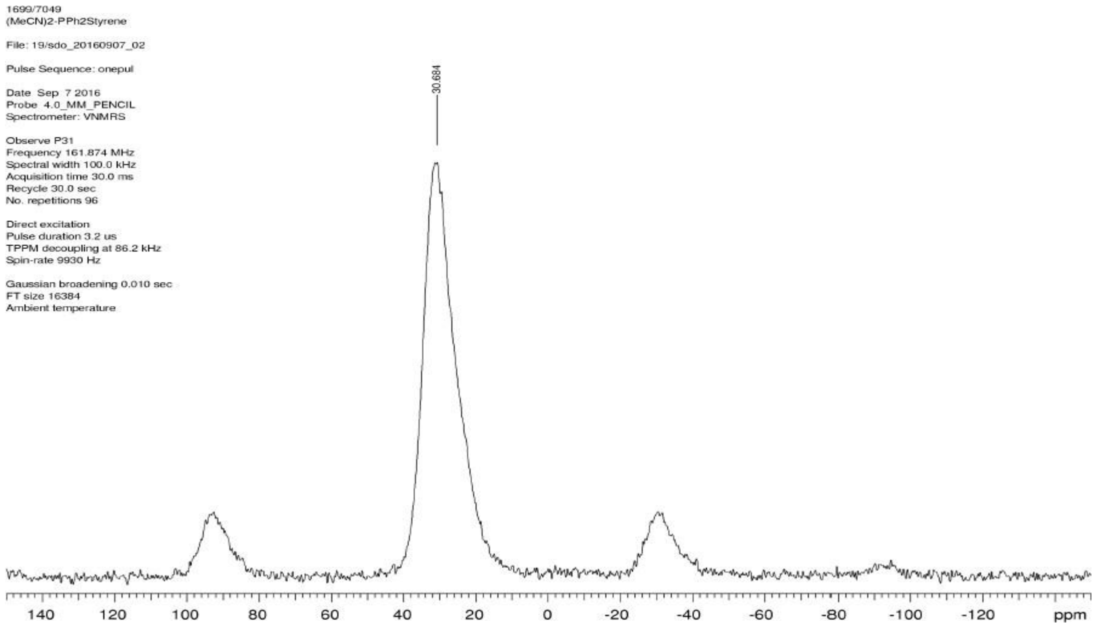
F2 - Acquisition Parameters
Date_             20160906
PROBHD   4 mm MAS BB/1H
PULPROG             cptoss
NS                     720
SWH              39682.539 Hz
AQ               0.0129024 sec
TE                   298.0 K
CNST31     10000.0000000
D1              5.00000000 sec
D31             0.00010000 sec

======== CHANNEL f1 ========
SFO1           100.6328030 MHz
NUC1                   13C
P2                    6.50 usec
P15                1000.00 usec
PLW1          110.00000000 W
PLW11         140.00000000 W

======== CHANNEL f2 ========
SFO2           400.1706407 MHz
NUC2                    1H
CPDPRG[2     spinal64_13
P3                    3.10 usec
PCPD2                 6.20 usec
PLW2      0 W
PLW12         140.00000000 W
PLW13         140.00000000 W
SPNAM[0]   ramp90100.100
SPOAL0               0.500
SPOFFS0   0 Hz
SPW0           80.00000000 W

F2 - Processing parameters
SI                    8192
SF             100.6227390 MHz
WDW                     EM
SSB       0
LB                   20.00 Hz
GB        0
PC                    1.00
```

Figure S46 **Solid state ^{31}P NMR spectrum of $[PdCl_2(MeCN)_2]$@PPh_2PEGstyrene (5b)**



1699/7049
(MeCN)2-PPh2Styrene

File: 19/sdo_20160907_02

Pulse Sequence: onepul

Date Sep 7 2016
Probe 4.0_MM_PENCIL
Spectrometer: VNMRS

Observe P31
Frequency 161.874 MHz
Spectral width 100.0 kHz
Acquisition time 30.0 ms
Recycle 30.0 sec
No. repetitions 96

Direct excitation
Pulse duration 3.2 us
TPPM decoupling at 86.2 kHz
Spin-rate 9930 Hz

Gaussian broadening 0.010 sec
FT size 16384
Ambient temperature

Figure S47 SEM images of freshly prepared [$PdCl_2(MeCN)_2$]@PPh_2PEGstyrene (5b)

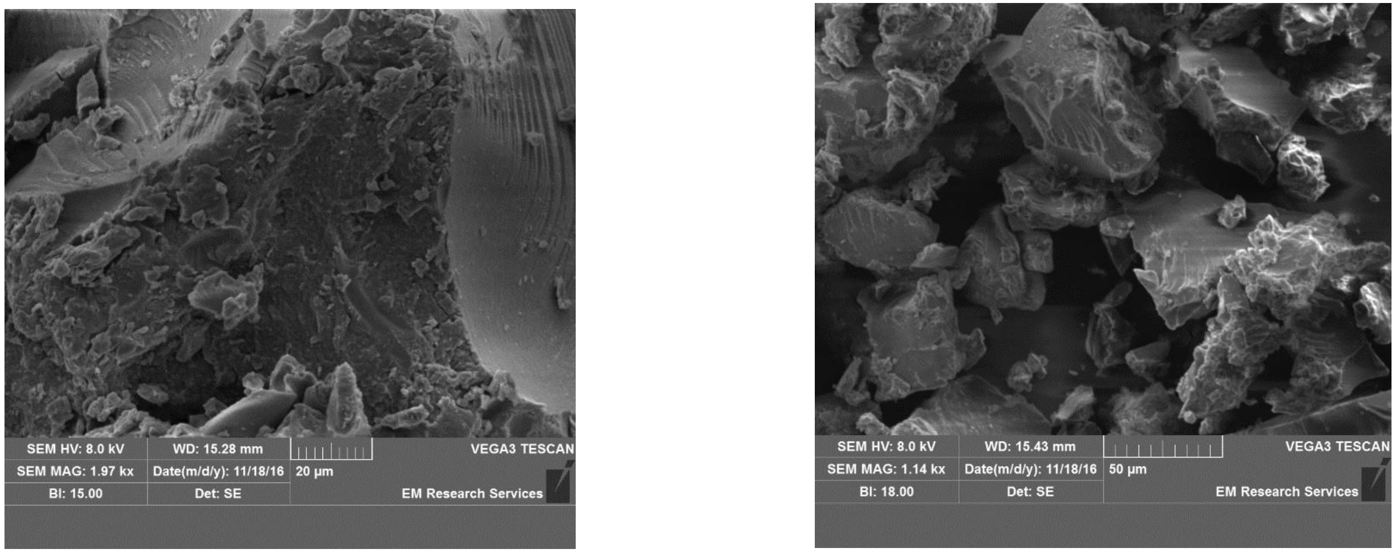


Figure S48 FT-IR spectrum of freshly prepared [PdCl$_2$(MeCN)$_2$]@PPh$_2$PEGstyrene (5b)

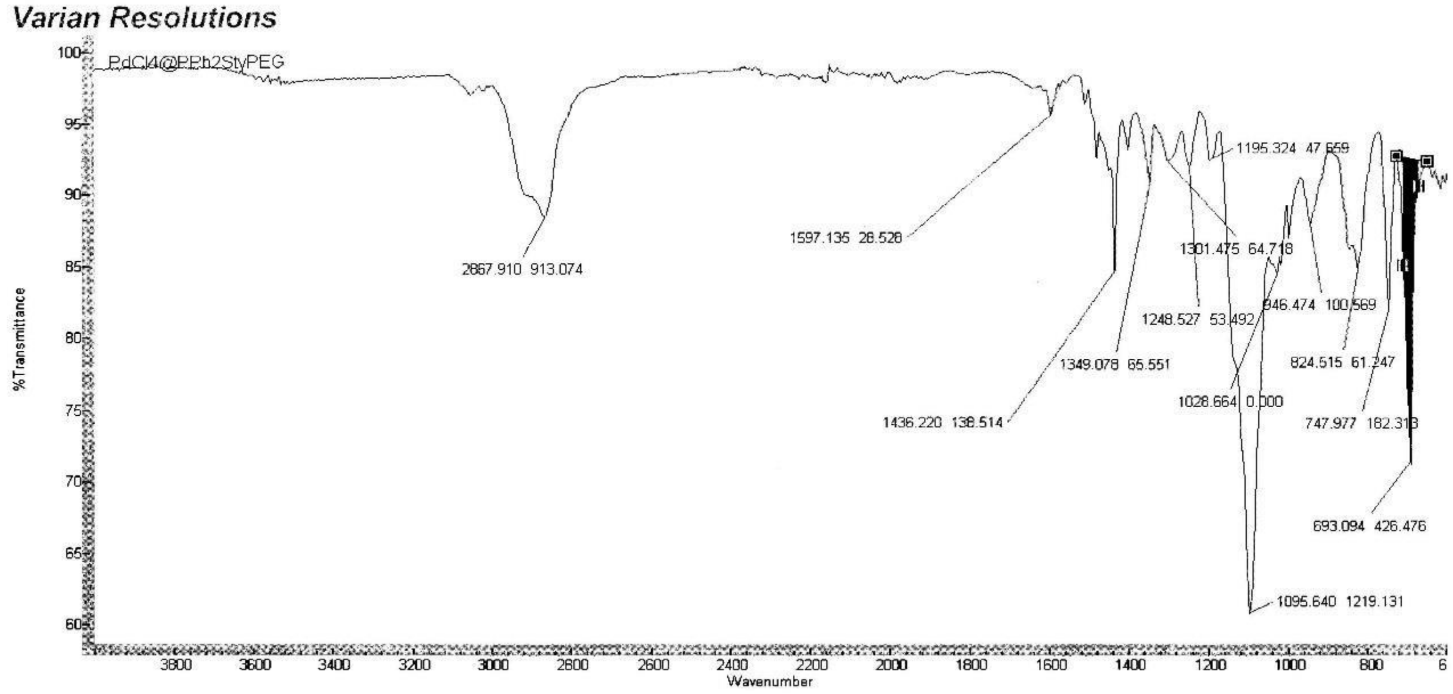


Figure S49 Pd 3d core level XPS spectrum of [$PdCl_2(MeCN)_2$]@PPh_2PEGstyrene (5b) referenced to the hydrocarbon C 1s

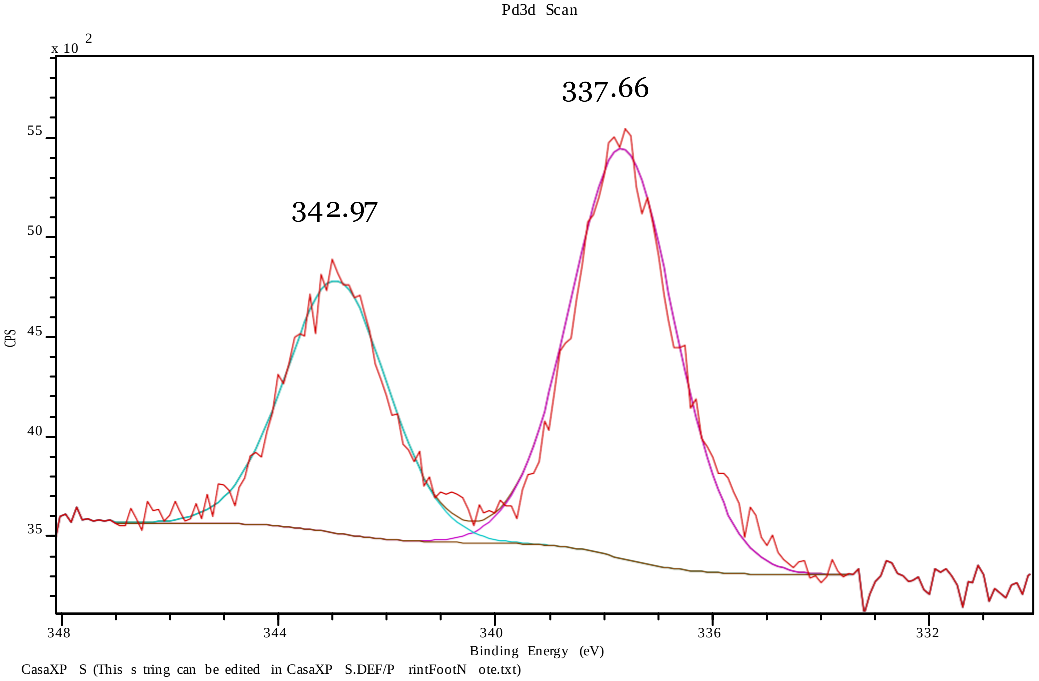
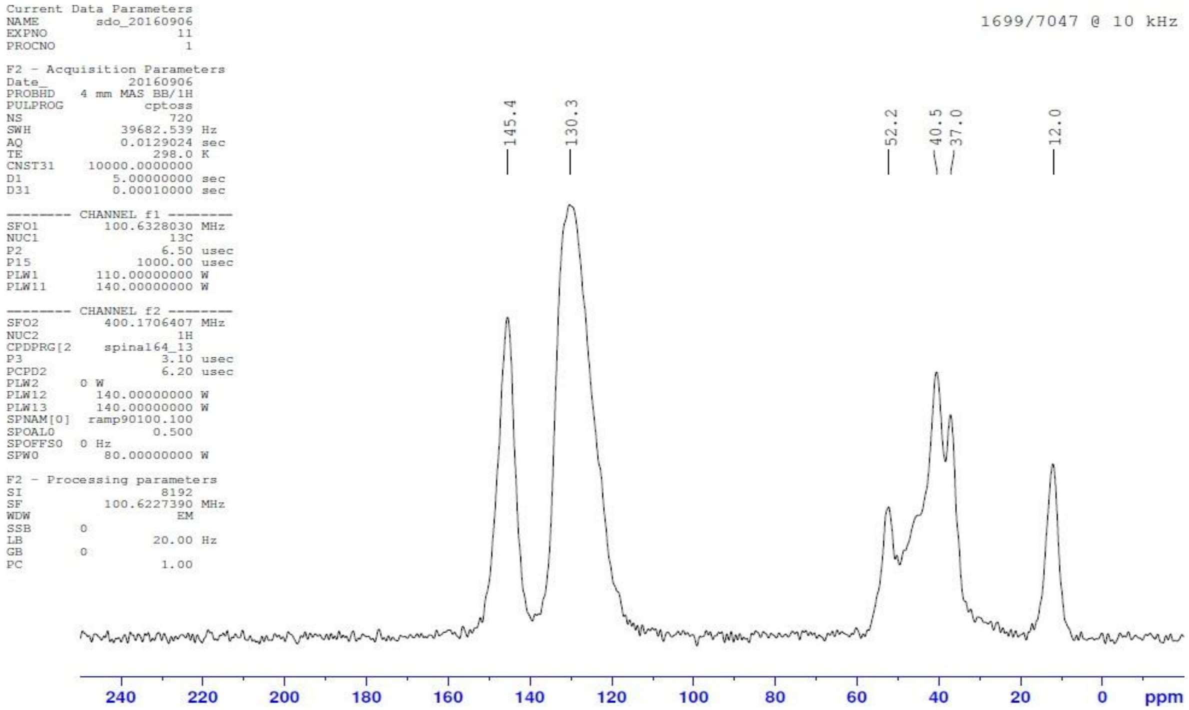


Figure S50 **Solid state ^{13}C NMR spectrum of [PdCl$_4$]@PEGPIILP (6b)**



```
Current Data Parameters
NAME        sdo_20160906
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160906
PROBHD    4 mm MAS BB/1H
PULPROG           cptoss
NS                   720
SWH            39682.539 Hz
AQ             0.0129024 sec
TE                 298.0 K
CNST31     10000.0000000
D1            5.00000000 sec
D31           0.00010000 sec

-------- CHANNEL f1 --------
SFO1         100.6328030 MHz
NUC1                 13C
P2                  6.50 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

-------- CHANNEL f2 --------
SFO2         400.1706407 MHz
NUC2                  1H
CPDPRG[2     spinal64_13
P3                  3.10 usec
PCPD2               6.20 usec
PLW2       0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0    0 Hz
SPW0         80.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227390 MHz
WDW                   EM
SSB        0
LB                 20.00 Hz
GB         0
PC                  1.00
```

Figure S51 SEM images of freshly prepared [PdCl$_4$]@PEGPIILP (6b)

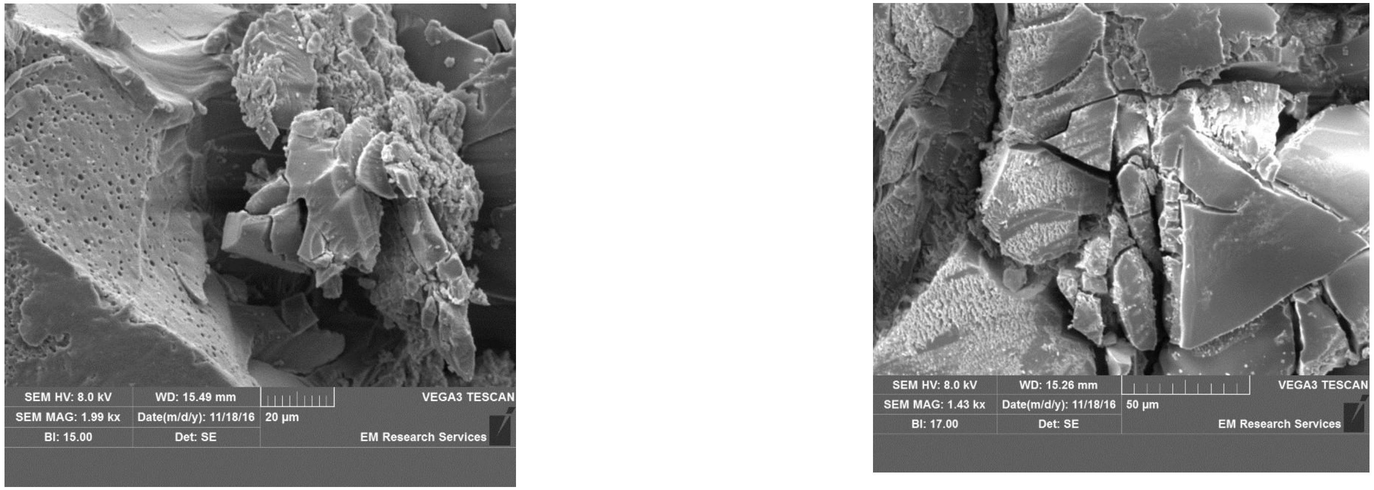


Figure S52 FT-IR spectrum of freshly prepared [PdCl$_4$]@PEGPIILP (6b)

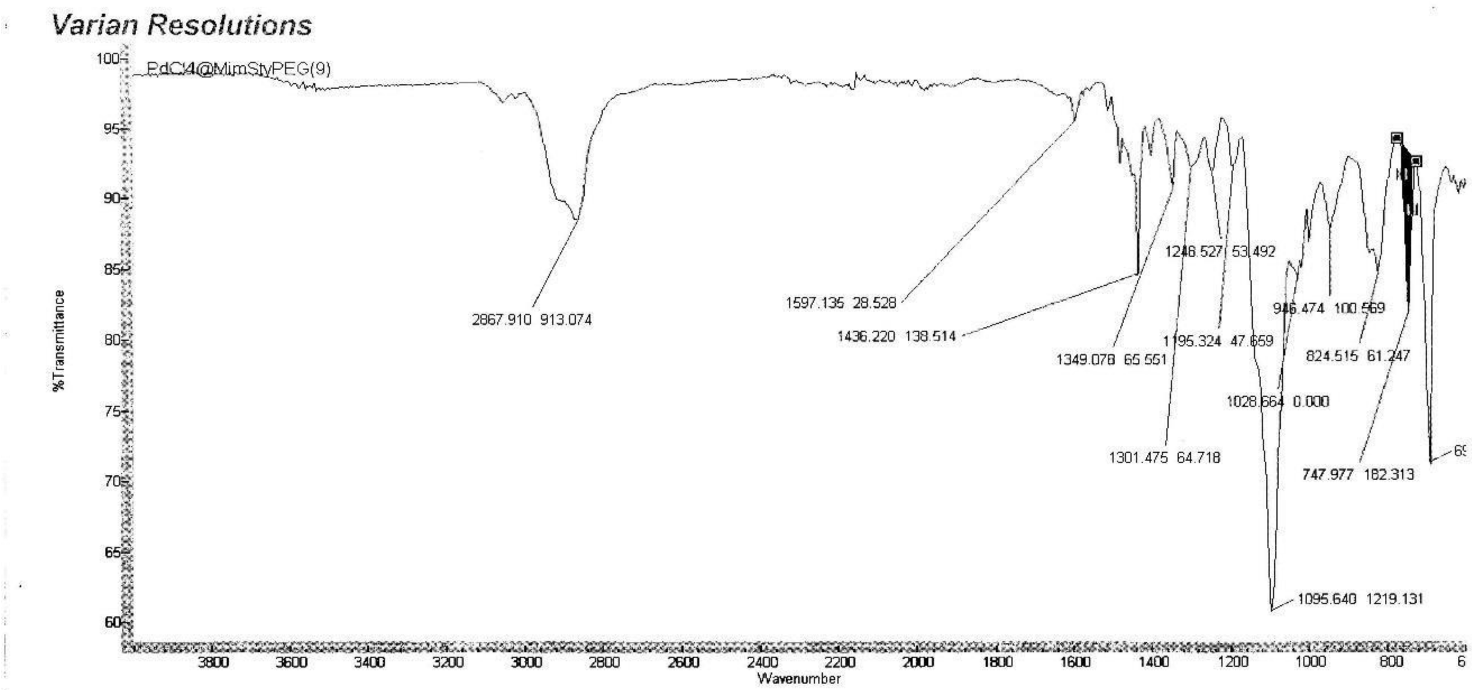


Figure S53 Pd 3d core level XPS spectrum of [PdCl$_4$]@PEGPIILP (6b) referenced to the hydrocarbon C 1s

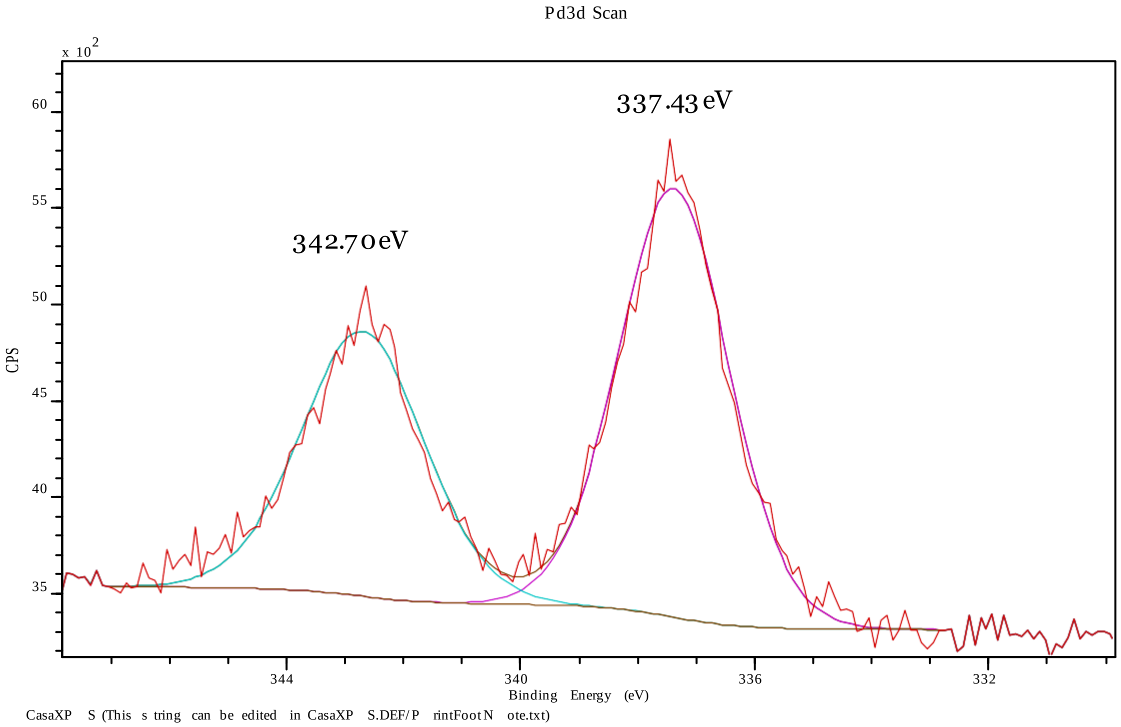
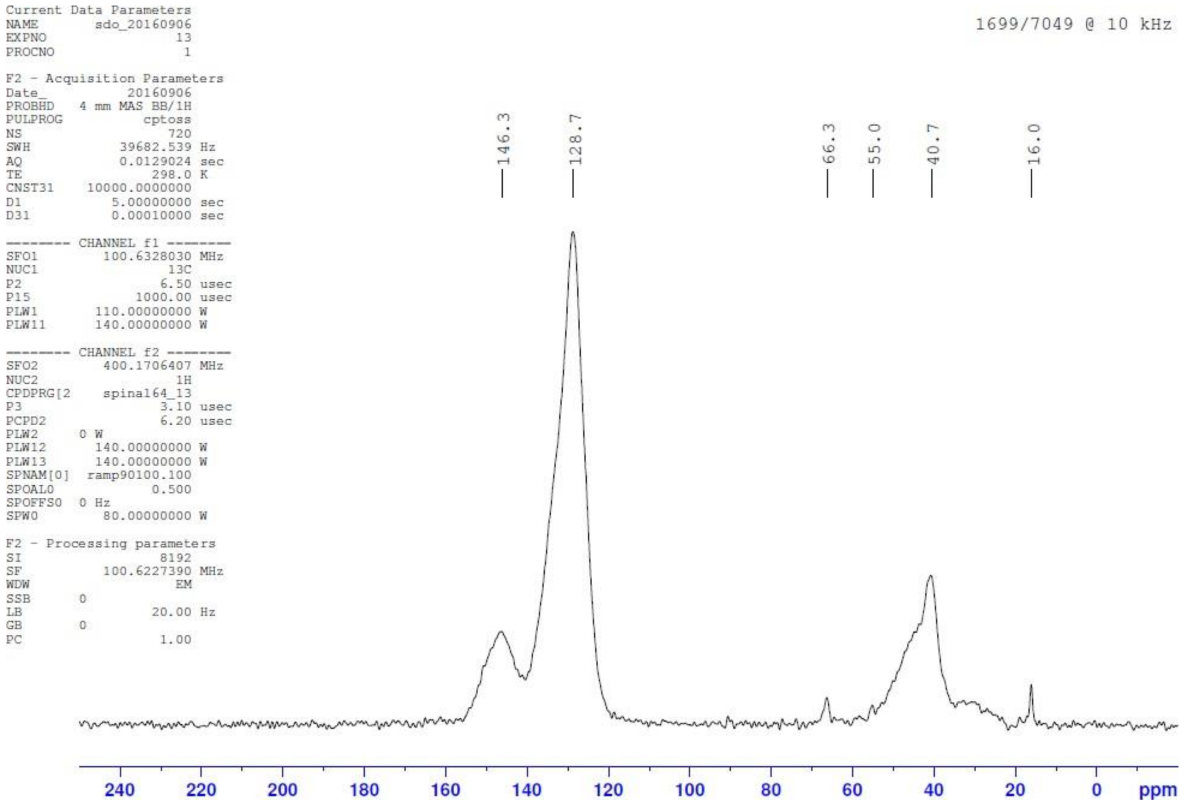


Figure S54 Solid state ^{13}C NMR spectrum of $[PdCl_2(MeCN)_2]$@PPh_2-polystyrene (7b)



```
Current Data Parameters
NAME       sdo_20160906
EXPNO                13
PROCNO                1

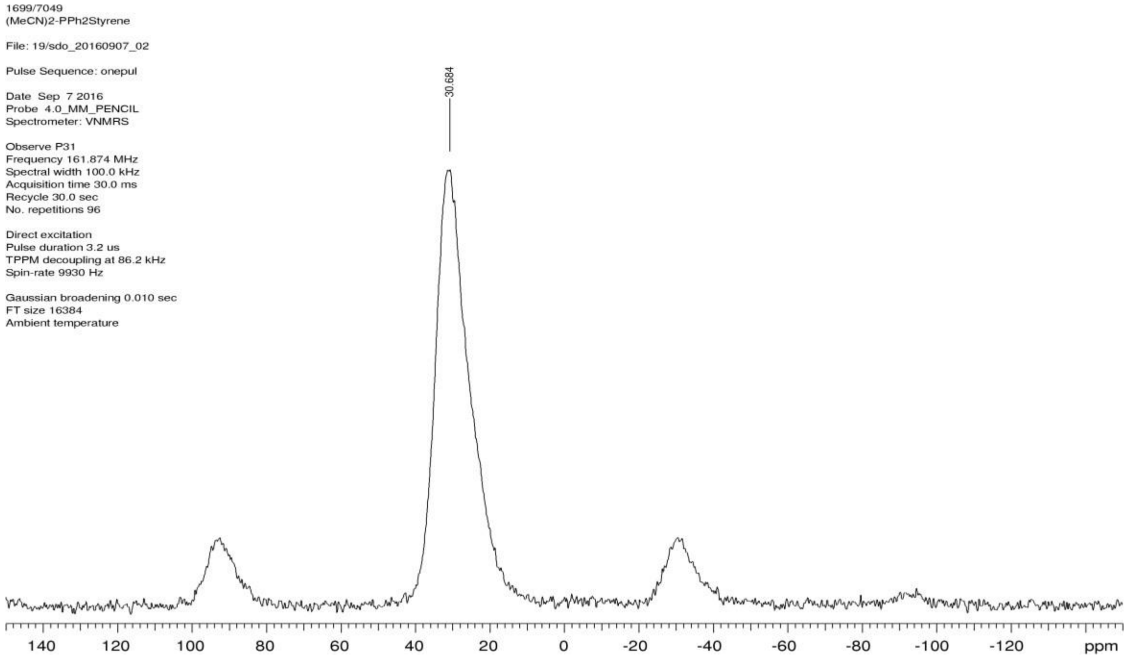
F2 - Acquisition Parameters
Date_          20160906
PROBHD   4 mm MAS BB/1H
PULPROG          cptoss
NS                  720
SWH           39682.539 Hz
AQ            0.0129024 sec
TE                298.0 K
CNST31    10000.0000000
D1           5.00000000 sec
D31          0.00010000 sec

-------- CHANNEL f1 --------
SFO1        100.6328030 MHz
NUC1                13C
P2                 6.50 usec
P15             1000.00 usec
PLW1       110.00000000 W
PLW11      140.00000000 W

-------- CHANNEL f2 --------
SFO2        400.1706407 MHz
NUC2                 1H
CPDPRG[2    spinal64_13
P3                 3.10 usec
PCPD2              6.20 usec
PLW2      0 W
PLW12      140.00000000 W
PLW13      140.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0            0.500
SPOFFS0   0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                 8192
SF          100.6227390 MHz
WDW                  EM
SSB       0
LB                20.00 Hz
GB        0
PC                 1.00
```

Figure S55 **Solid state ^{31}P NMR spectrum of [$PdCl_2(MeCN)_2$]@PPh_2-polystyrene (7b)**


1699/7049
(MeCN)2-PPh2Styrene

File: 19/sdo_20160907_02

Pulse Sequence: onepul

Date Sep 7 2016
Probe 4.0_MM_PENCIL
Spectrometer: VNMRS

Observe P31
Frequency 161.874 MHz
Spectral width 100.0 kHz
Acquisition time 30.0 ms
Recycle 30.0 sec
No. repetitions 96

Direct excitation
Pulse duration 3.2 us
TPPM decoupling at 86.2 kHz
Spin-rate 9930 Hz

Gaussian broadening 0.010 sec
FT size 16384
Ambient temperature

Figure S56 SEM images of freshly prepared $[PdCl_2(MeCN)_2]$@PPh_2-polystyrene (7b)

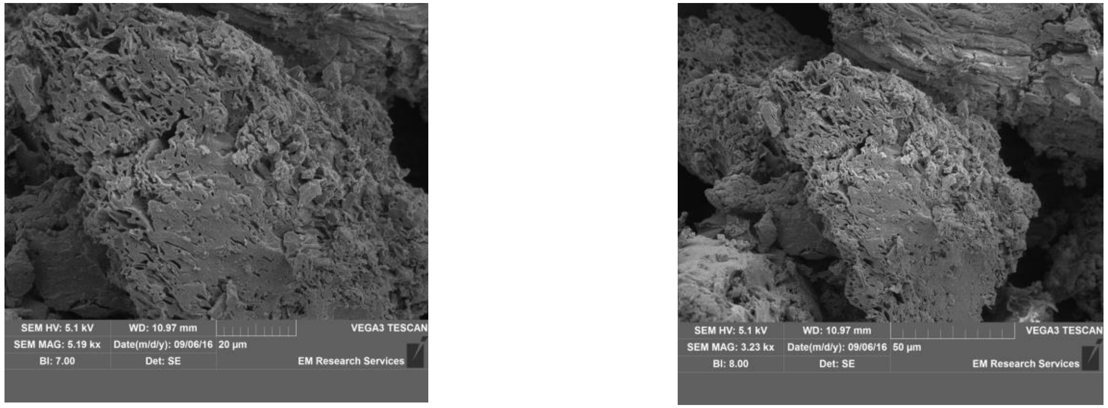


Figure S57 **FT-IR spectrum offreshly prepared [$PdCl_2(MeCN)_2$]@PPh_2-polystyrene (7b)**

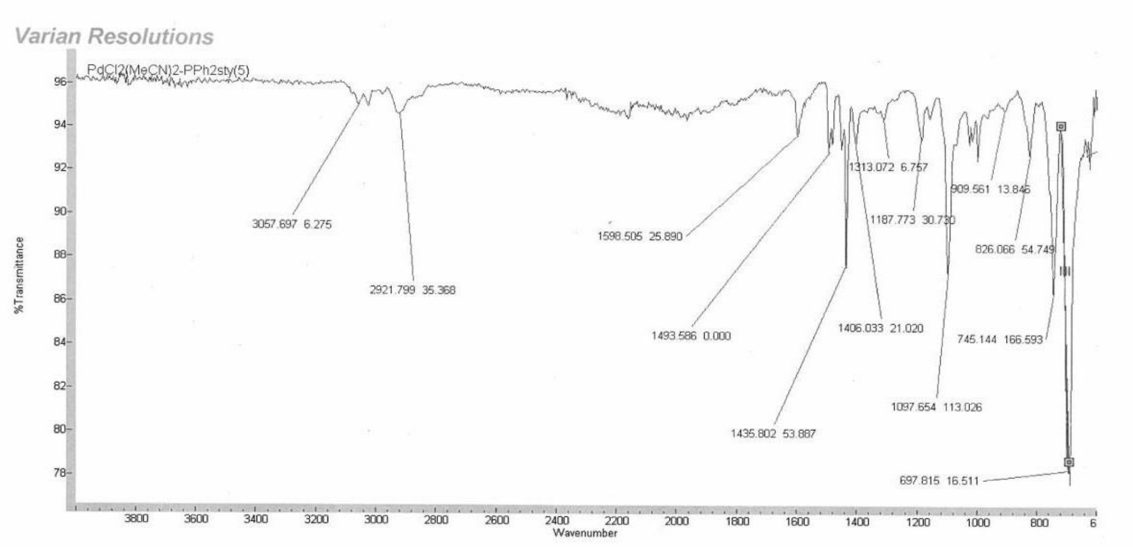


Figure S58 Pd 3d core level XPS spectrum of [$PdCl_2(MeCN)_2$]@PPh_2-polystyrene (7b) referenced to the hydrocarbon C 1s

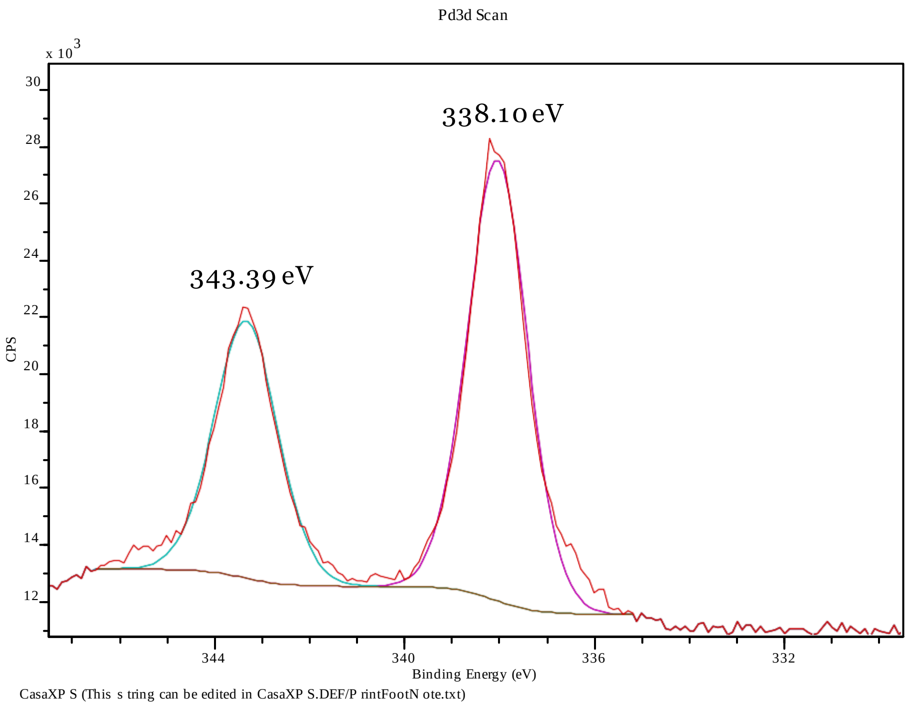
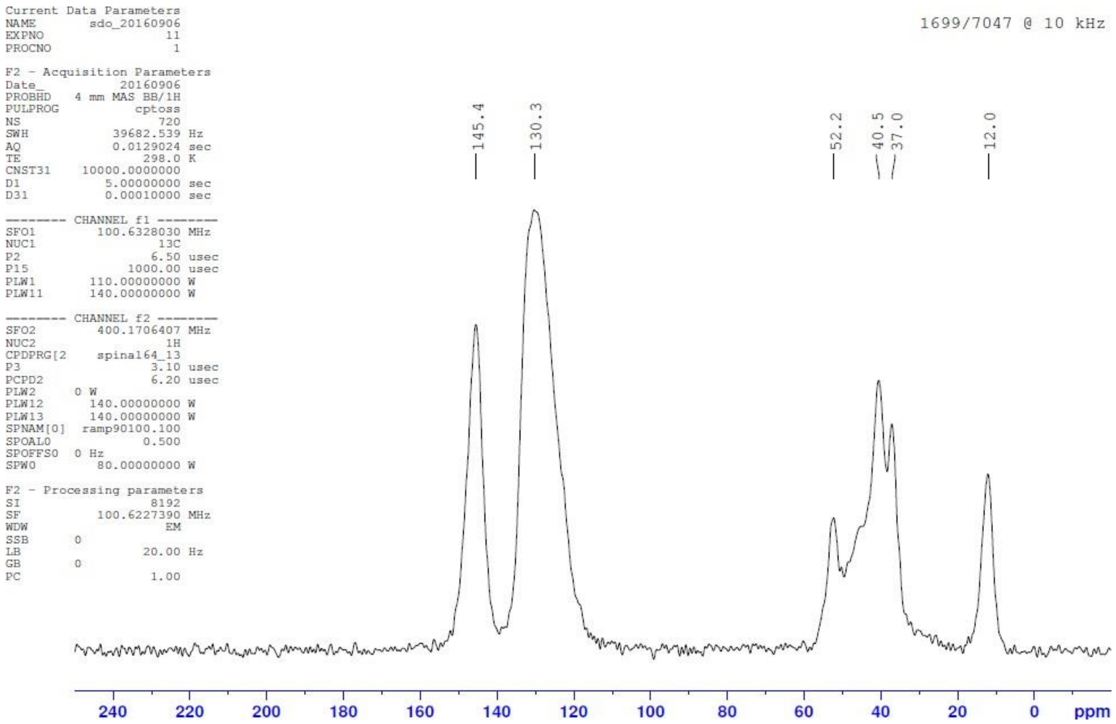


Figure S59 Solid state ^{13}C NMR spectrum of [PdCl$_4$]@Styr-PIILP (8b)



```
Current Data Parameters
NAME        sdo_20160906
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160906
PROBHD   4 mm MAS BB/1H
PULPROG           cptoss
NS                   720
SWH            39682.539 Hz
AQ             0.0129024 sec
TE                 298.0 K
CNST31     10000.0000000
D1            5.00000000 sec
D31           0.00010000 sec

-------- CHANNEL f1 --------
SFO1         100.6328030 MHz
NUC1                 13C
P2                  6.50 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

-------- CHANNEL f2 --------
SFO2         400.1706407 MHz
NUC2                  1H
CPDPRG[2     spinal64_13
P3                  3.10 usec
PCPD2               6.20 usec
PLW2      0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0         80.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227390 MHz
WDW                   EM
SSB       0
LB                 20.00 Hz
GB        0
PC                  1.00
```

Figure S60 SEM images offreshly prepared [$PdCl_4$]@Styr-PIILP (8b)

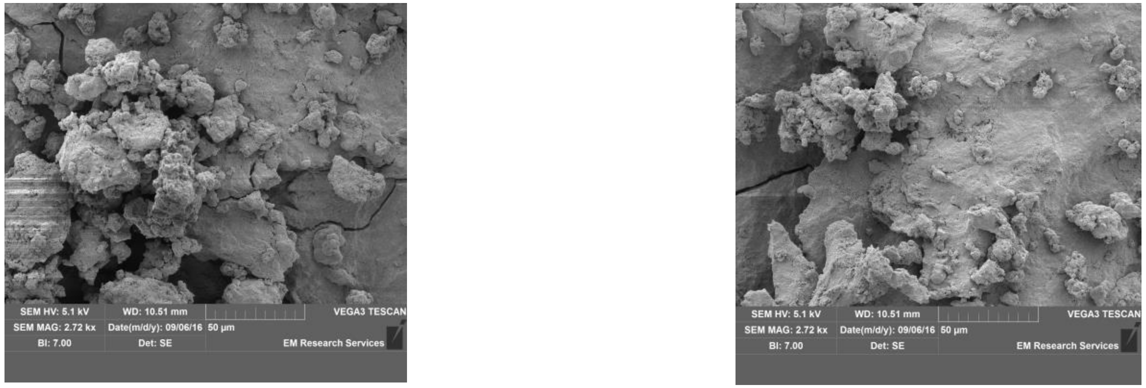


Figure S61 FT-IR spectrum of freshly prepared [PdCl$_4$]@Styr-PIILP (8b)

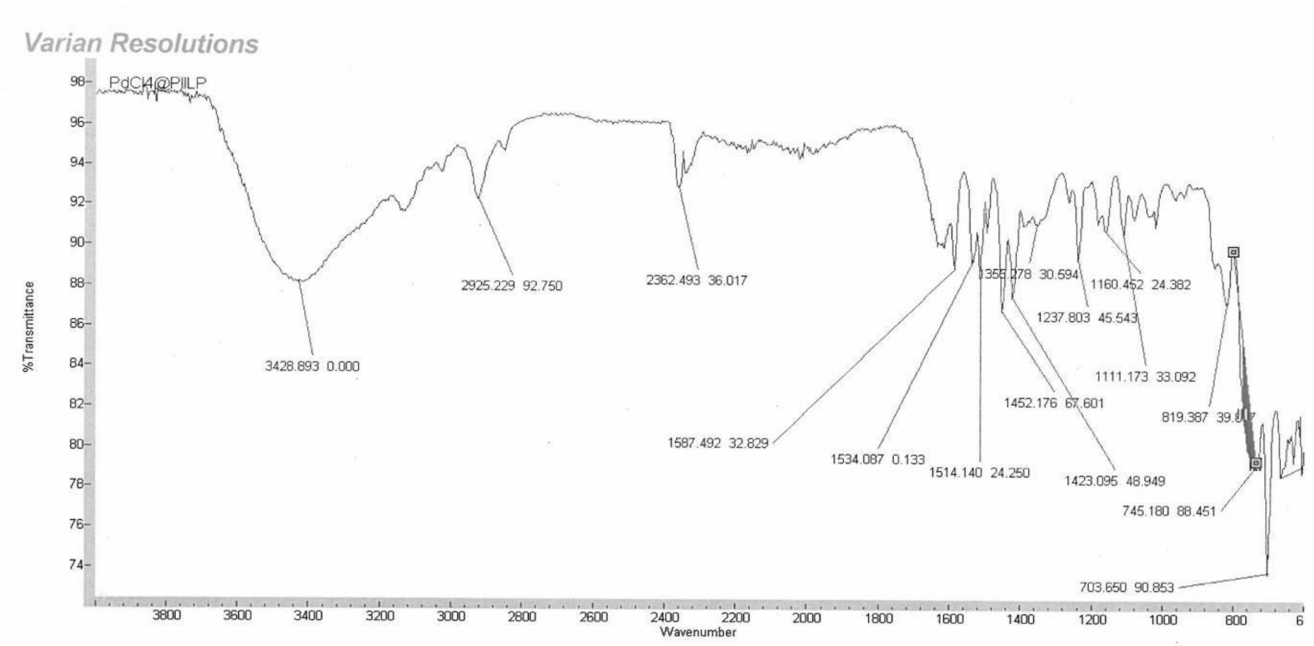


Figure S62 Pd 3d core level XPS spectrum of [PdCl$_4$]@Styr-PIILP (8b) referenced to the hydrocarbon C 1s

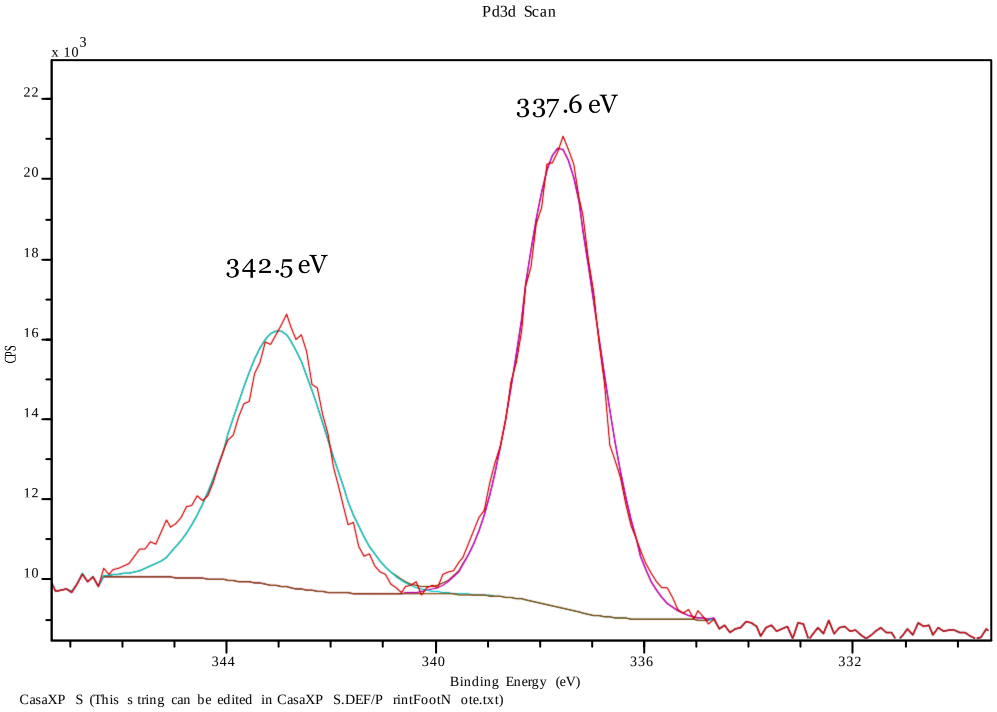
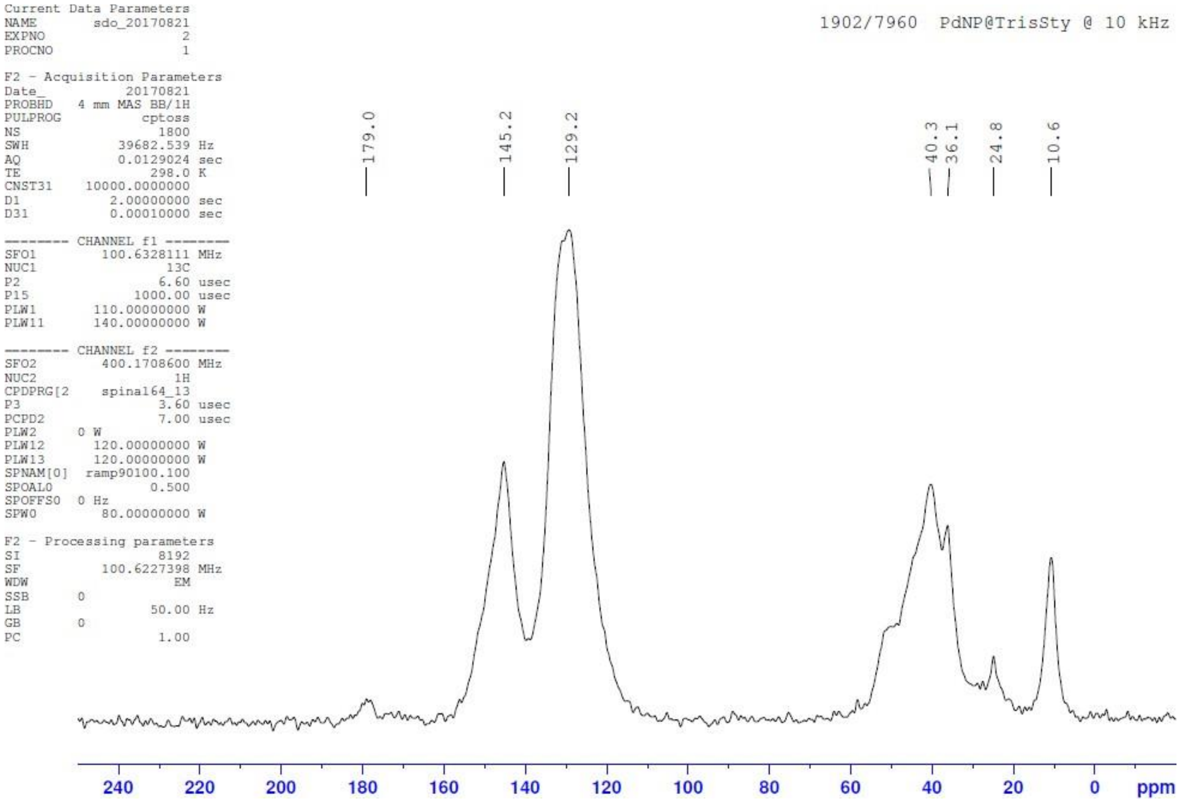


Figure S63 Solid state ^{13}C NMR spectrum of PdNP@PSty$_3$-PIILP (3c)



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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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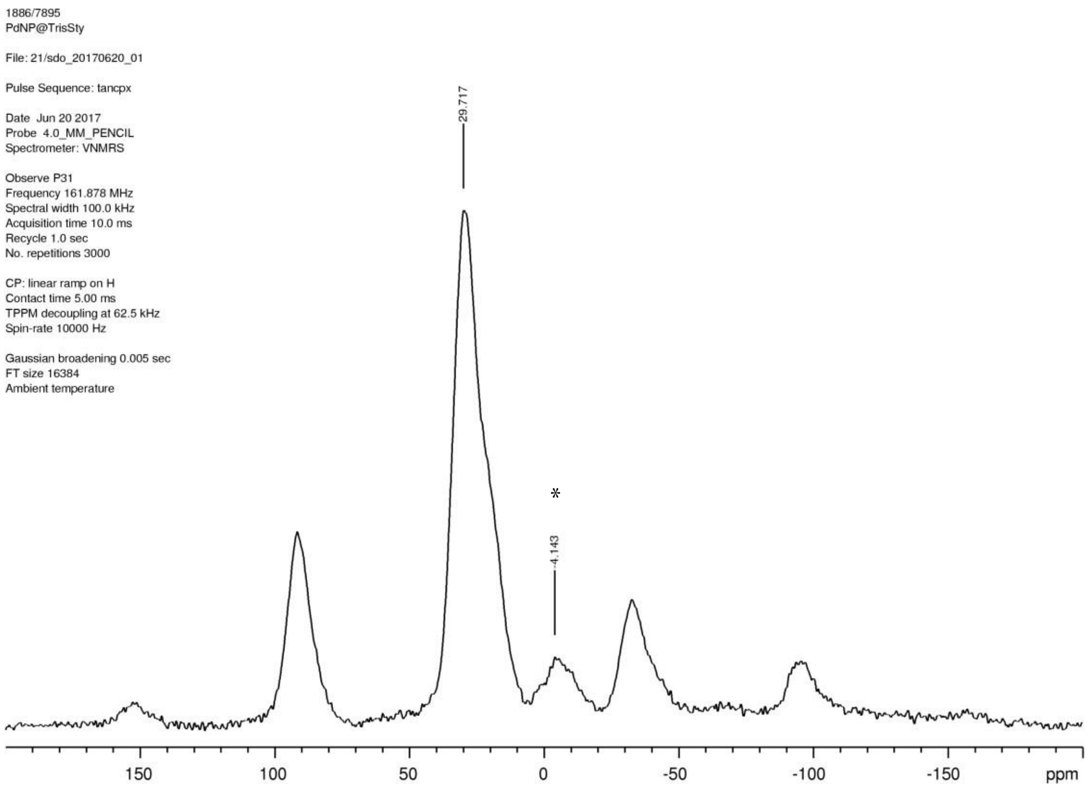
PULPROG          cptoss
NS                 1800
SWH           39682.539 Hz
AQ            0.0129024 sec
TE                298.0 K
CNST31    10000.0000000
D1           2.00000000 sec
D31          0.00010000 sec

-------- CHANNEL f1 --------
SFO1        100.6328111 MHz
NUC1                13C
P2                 6.60 usec
P15             1000.00 usec
PLW1       110.00000000 W
PLW11      140.00000000 W

-------- CHANNEL f2 --------
SFO2        400.1708600 MHz
NUC2                 1H
CPDPRG[2    spinal64_13
P3                 3.60 usec
PCPD2              7.00 usec
PLW2      0 W
PLW12      120.00000000 W
PLW13      120.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0            0.500
SPOFFS0   0 Hz
SPW0        80.00000000 W

F2 - Processing parameters
SI                 8192
SF          100.6227398 MHz
WDW                  EM
SSB       0
LB                50.00 Hz
GB        0
PC                 1.00
```

Figure S64 **Solid state ^{31}P NMR spectrum of PdNP@PSty$_3$-PIILP (3c)**



* Uncoordinated phosphine

Figure S65 SEM images of freshly prepared PdNP@PSty$_3$-PIILP (3c)

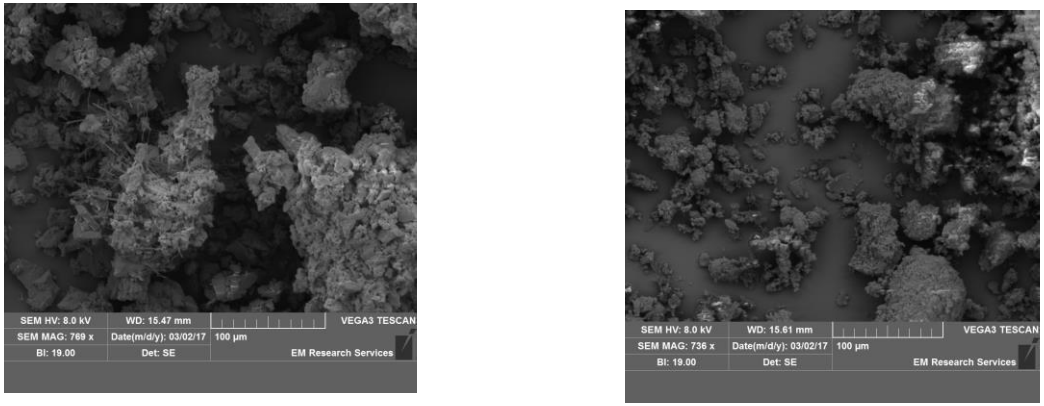


Figure S66 FT-IR spectrum of freshly prepared PdNP@PSty$_3$-PIILP (3c)

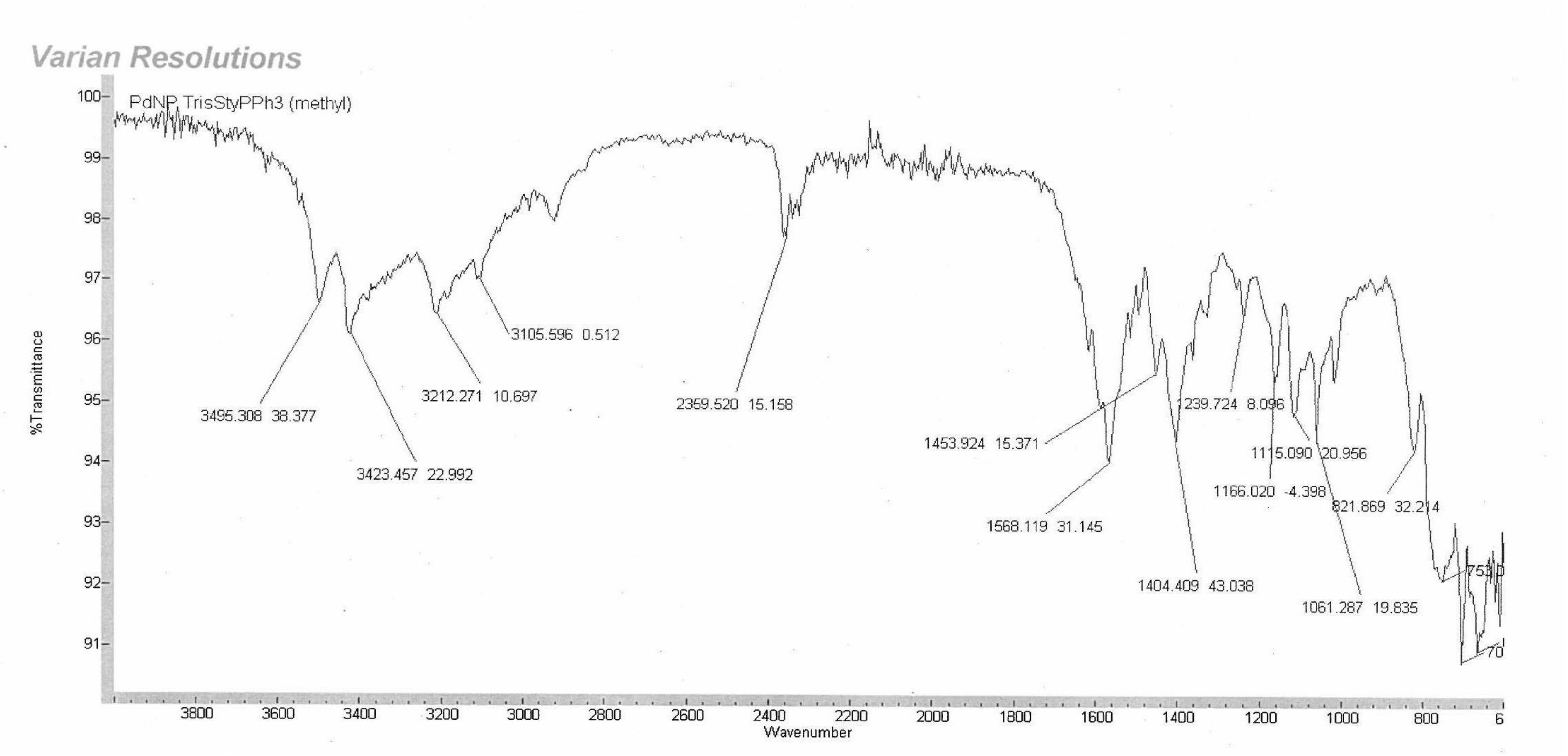


Figure S67 Pd 3d core level XPS spectrum of PdNP@PSty$_3$-PIILP (3c) referenced to the hydrocarbon C 1s

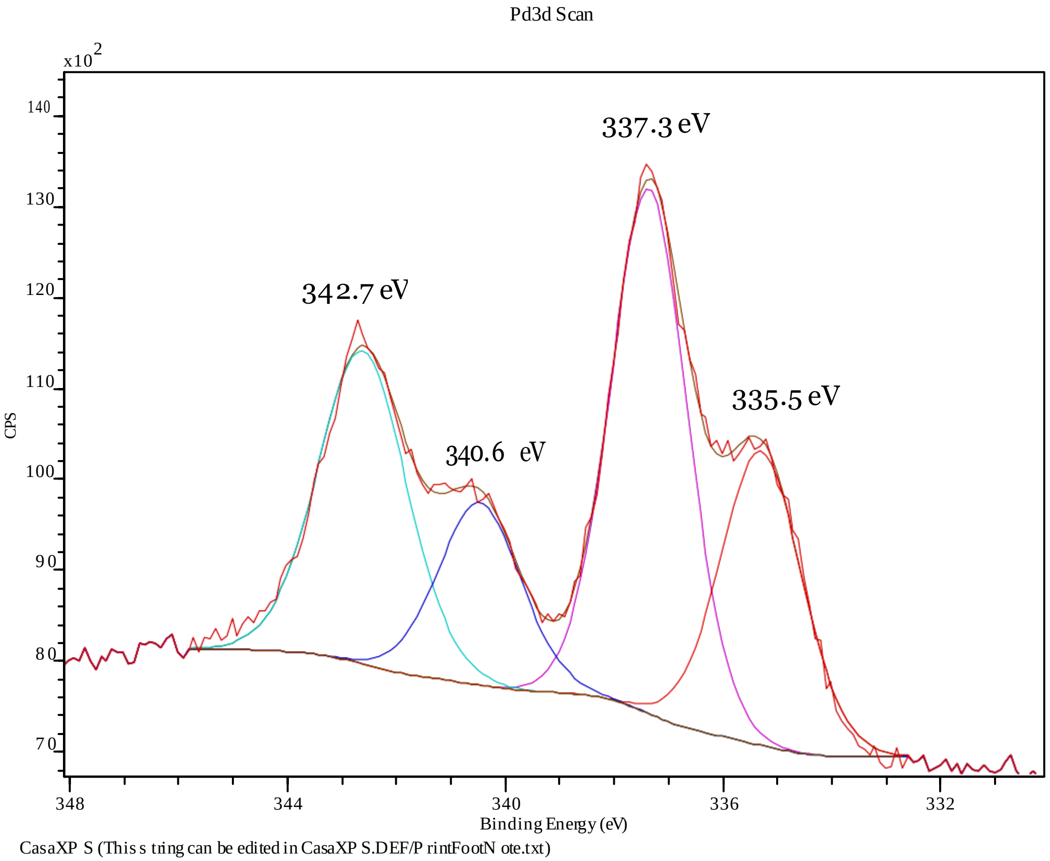


Figure S68 (a-b) TEM images of PdNP@PSty$_3$-PIILP (3c), (c) histogram of particle size (diameter, nm). Scale bars are 20 nm (black) and 5 nm (white)

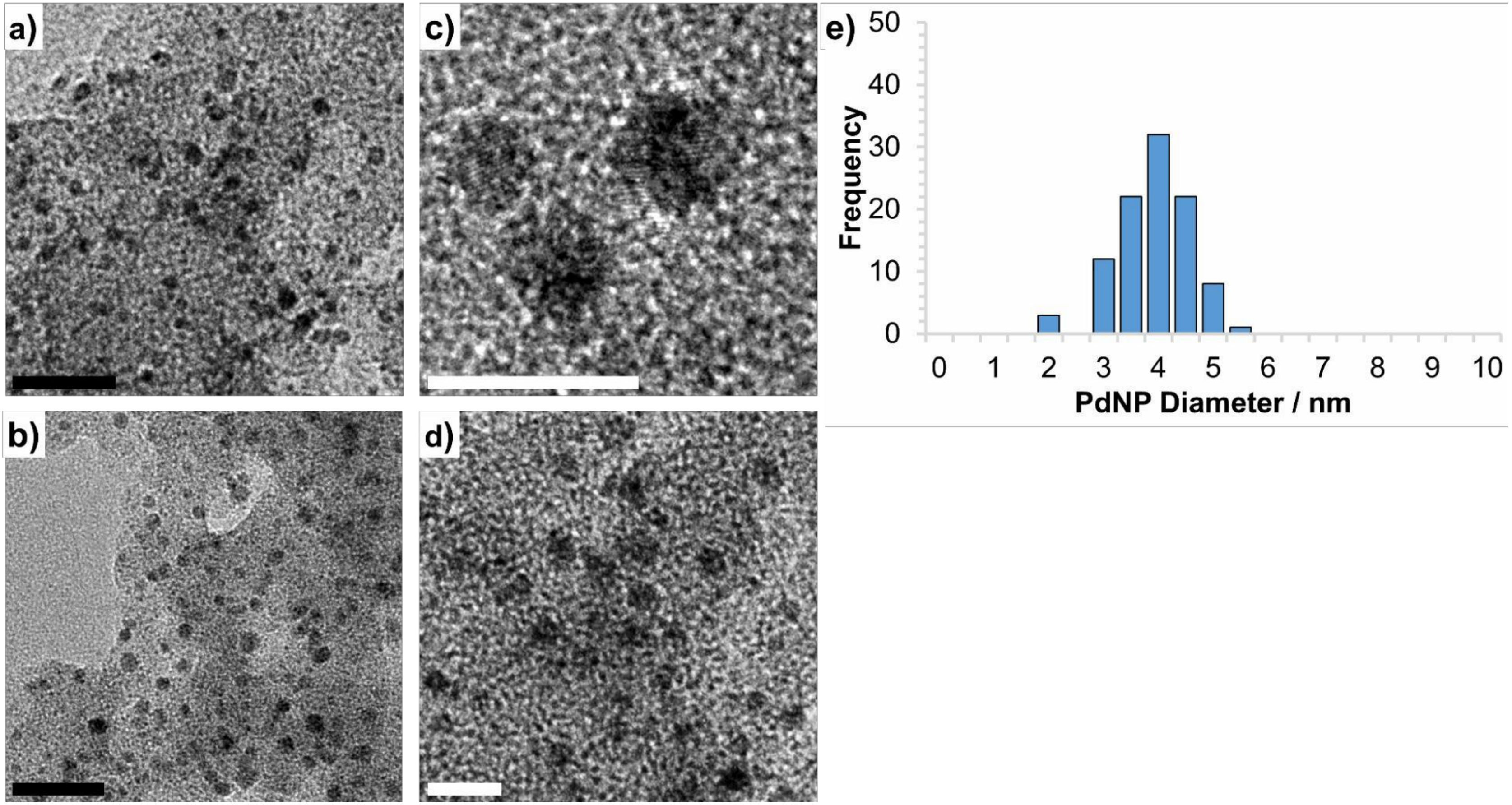


Figure S69 Powder X-ray Diffraction Pattern of PdNP@PSty$_3$-PIILP (3c)

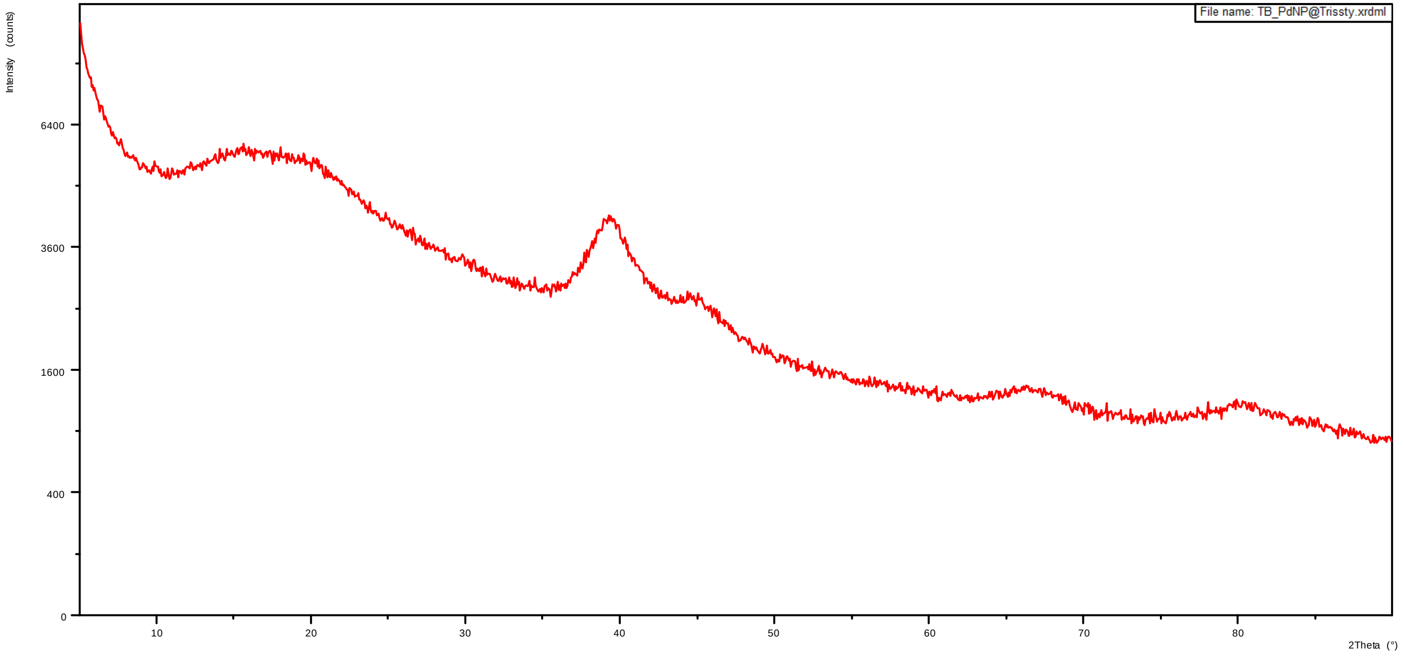
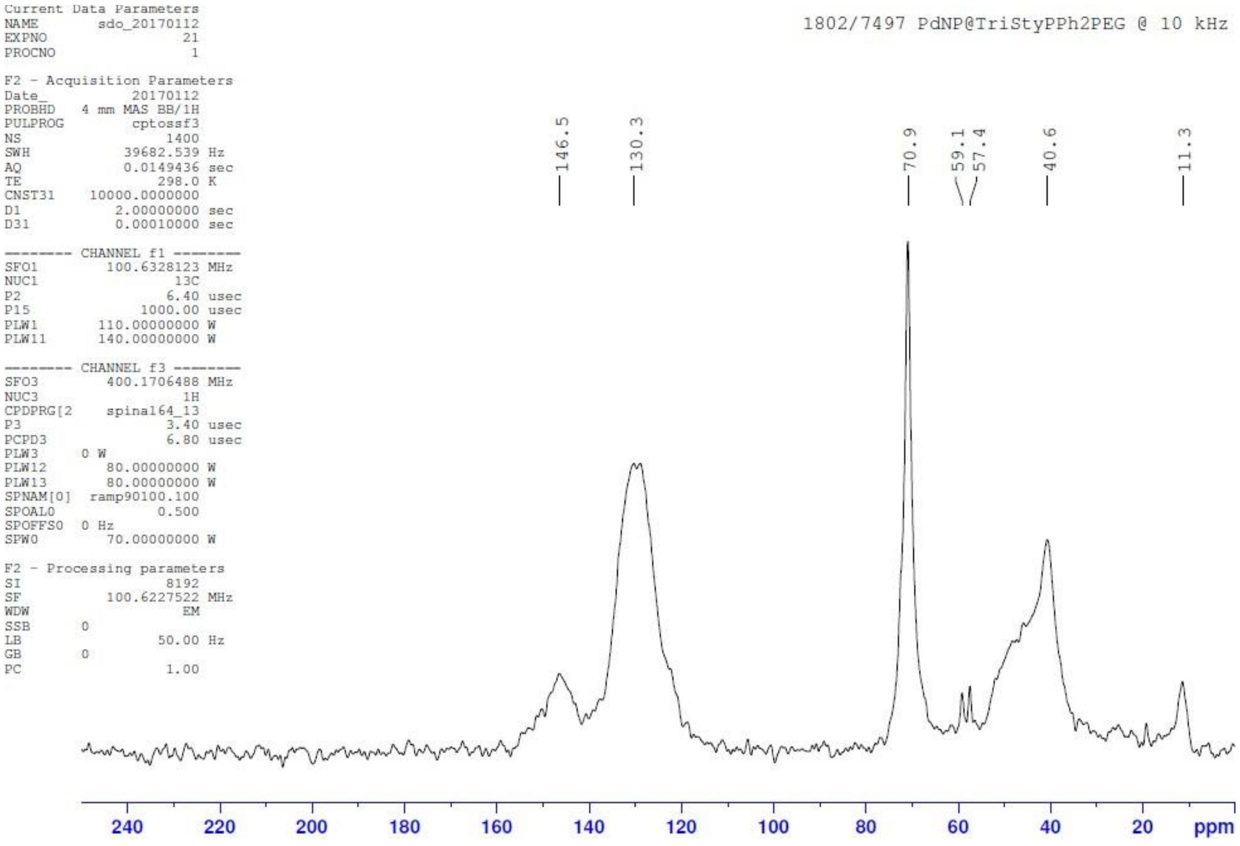


Figure S70 Solid state ^{13}C NMR spectrum of PdNP@PSty$_3$-PEGPIILP (4c)



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Current Data Parameters
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EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
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PULPROG         cptossf3
NS                  1400
SWH            39682.539 Hz
AQ             0.0149436 sec
TE                 298.0 K
CNST31     10000.0000000
D1            2.00000000 sec
D31           0.00010000 sec

======== CHANNEL f1 ========
SFO1         100.6328123 MHz
NUC1                 13C
P2                  6.40 usec
P15              1000.00 usec
PLW1        110.00000000 W
PLW11       140.00000000 W

======== CHANNEL f3 ========
SFO3         400.1706488 MHz
NUC3                  1H
CPDPRG[2     spinal64_13
P3                  3.40 usec
PCPD3               6.80 usec
PLW3      0 W
PLW12        80.00000000 W
PLW13        80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0         70.00000000 W

F2 - Processing parameters
SI                  8192
SF           100.6227522 MHz
WDW                   EM
SSB       0
LB                 50.00 Hz
GB        0
PC                  1.00
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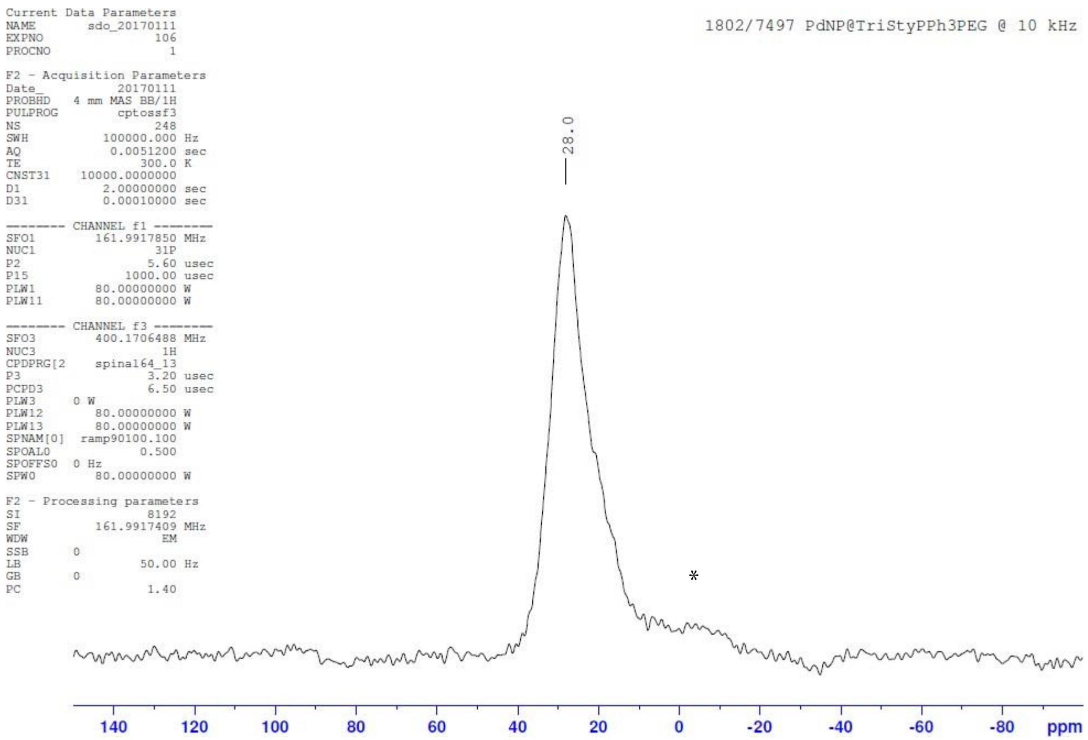
Figure S71 Solid state ^{31}P NMR spectrum of PdNP@PSty$_3$-PEGPIILP (4c)



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Current Data Parameters
NAME         sdo_20170111
EXPNO                 106
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170111
PROBHD   4 mm MAS BB/1H
PULPROG          cptossf3
NS                    248
SWH            100000.000 Hz
AQ              0.0051200 sec
TE                  300.0 K
CNST31   10000.0000000
D1             2.00000000 sec
D31            0.00010000 sec

======== CHANNEL f1 ========
SFO1          161.9917850 MHz
NUC1                  31P
P2                   5.60 usec
P15               1000.00 usec
PLW1          80.00000000 W
PLW11         80.00000000 W

======== CHANNEL f3 ========
SFO3          400.1706488 MHz
NUC3                   1H
CPDPRG[2      spinal64_13
P3                   3.20 usec
PCPD3                6.50 usec
PLW3     0 W
PLW12         80.00000000 W
PLW13         80.00000000 W
SPNAM[0]  ramp90100.100
SPOAL0              0.500
SPOFFS0  0 Hz
SPW0          80.00000000 W

F2 - Processing parameters
SI                   8192
SF            161.9917409 MHz
WDW                    EM
SSB      0
LB                  50.00 Hz
GB       0
PC                   1.40
```

* Uncoordinated phosphine

Figure S72 SEM images of freshly prepared PdNP@PSty$_3$-PEGPIILP (4c)

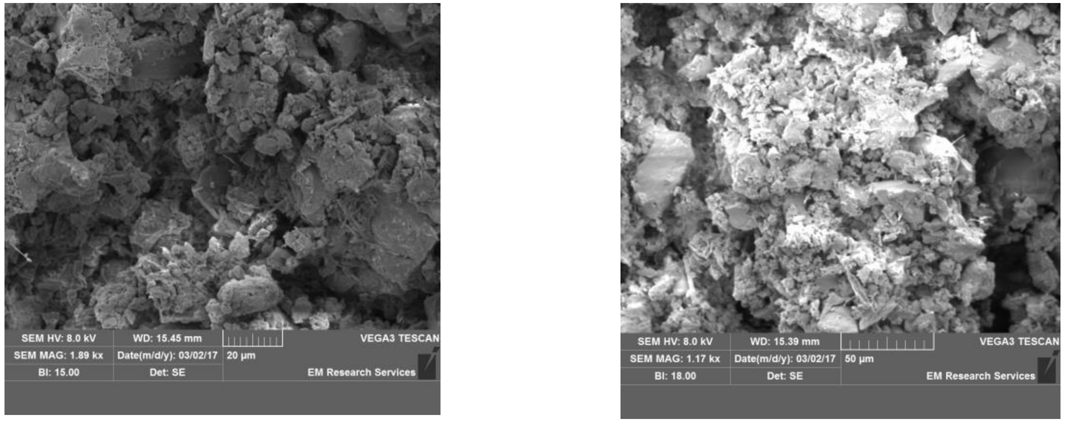


Figure S73 FT-IR spectrum of freshly prepared PdNP@PSty$_3$-PEGPIILP (4c)

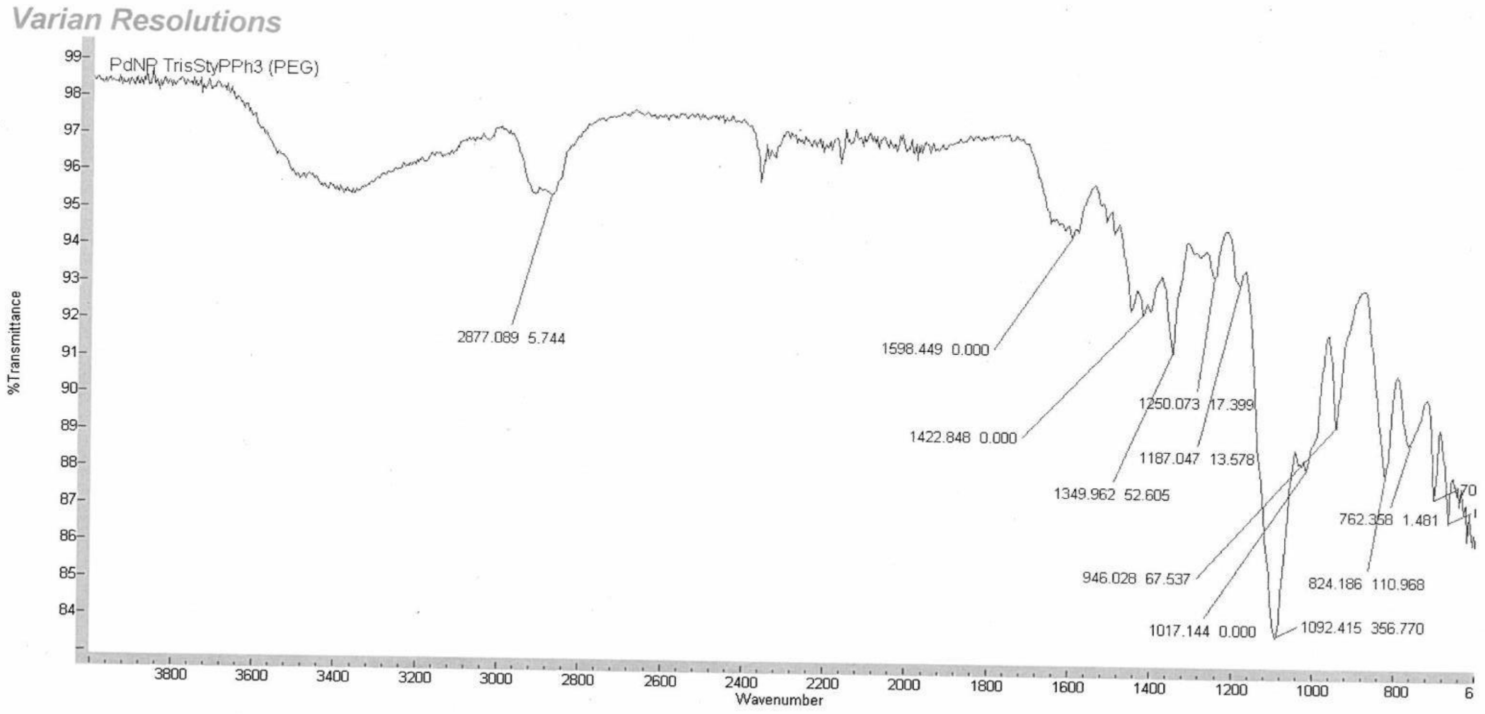


Figure S74 Pd 3d core level XPS spectrum of PdNP@PSty$_3$-PEGPIILP (4c) referenced to the hydrocarbon C 1s

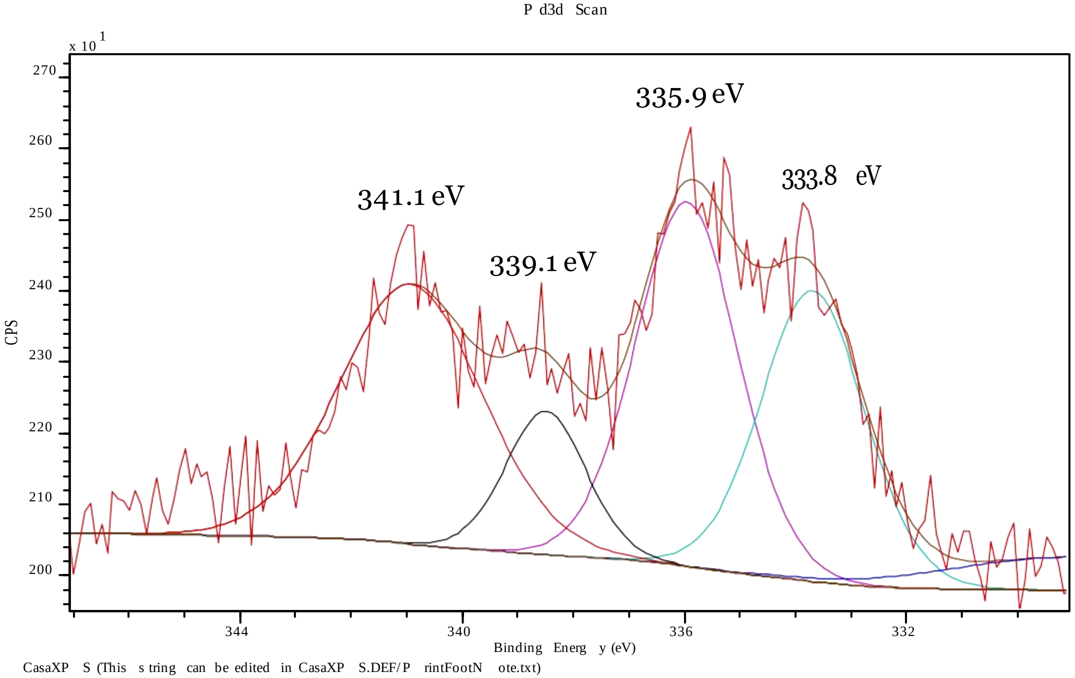


Figure S75 (a-b) TEM images of PdNP@PSty$_3$-PEGPIILP (4c) and (c) histogram of particle size (diameter, nm). Scale bars are 20 nm (black) and 5 nm (white)

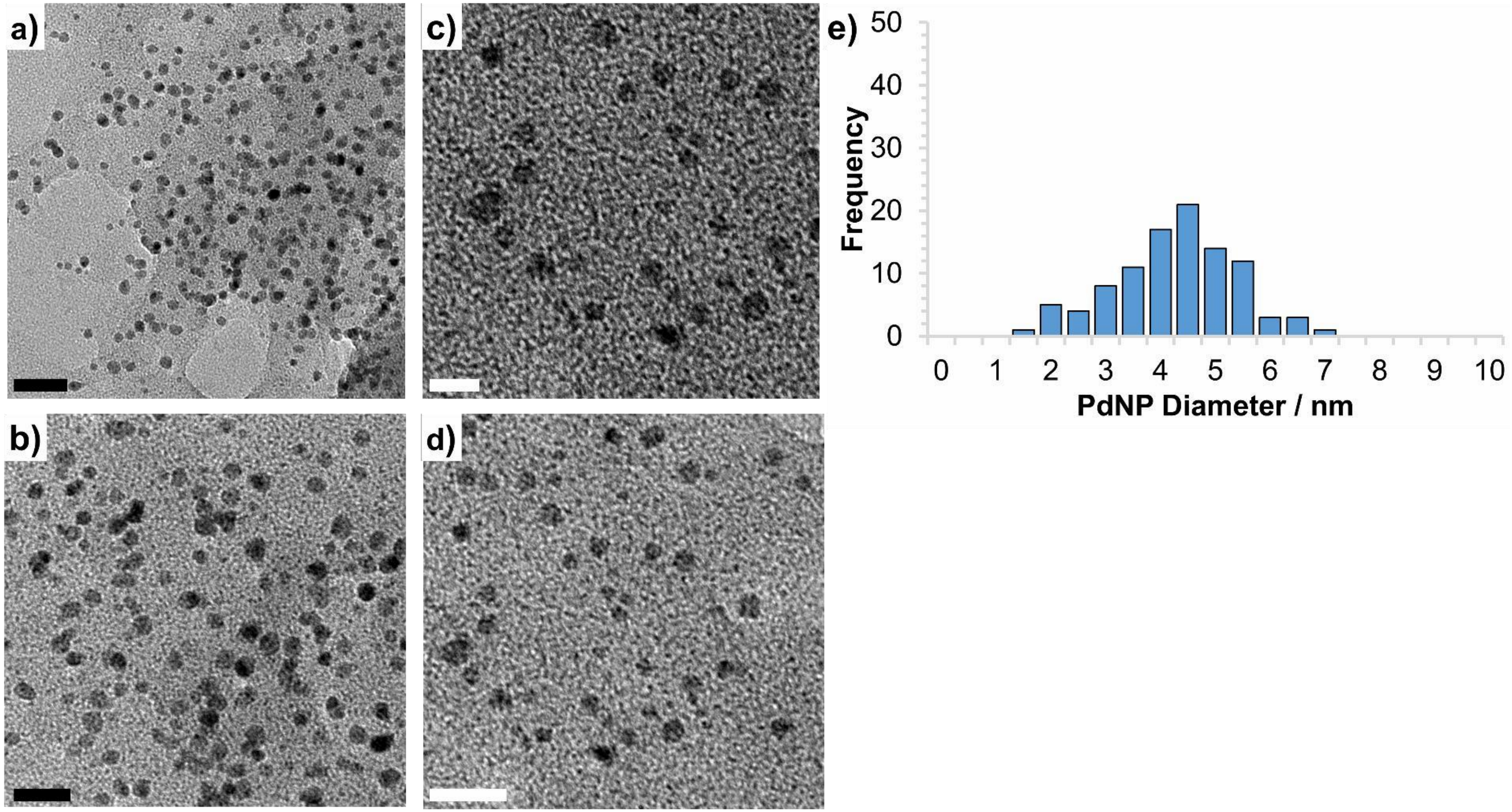


Figure S76 Powder X-ray Diffraction Pattern of PdNP@PSty$_3$-PEGPIILP (4c)

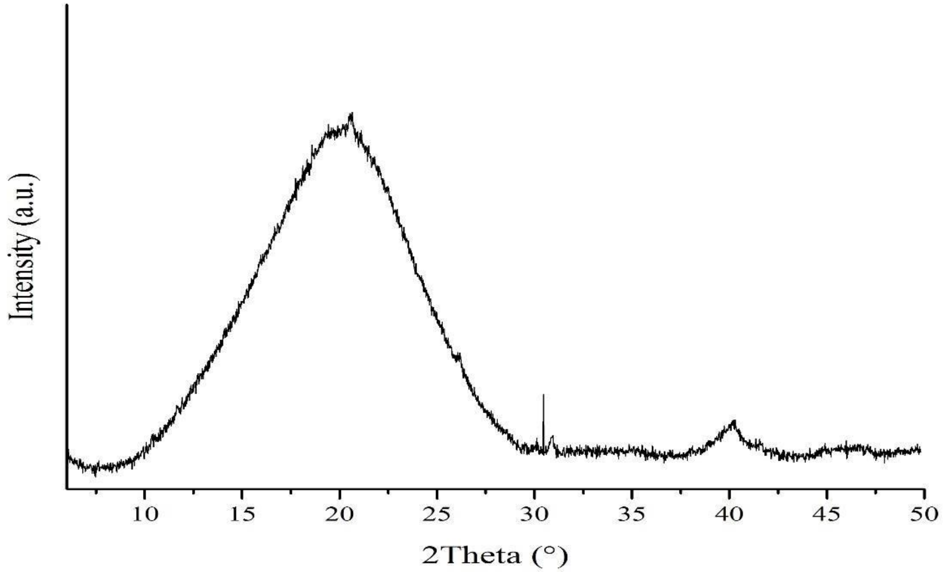
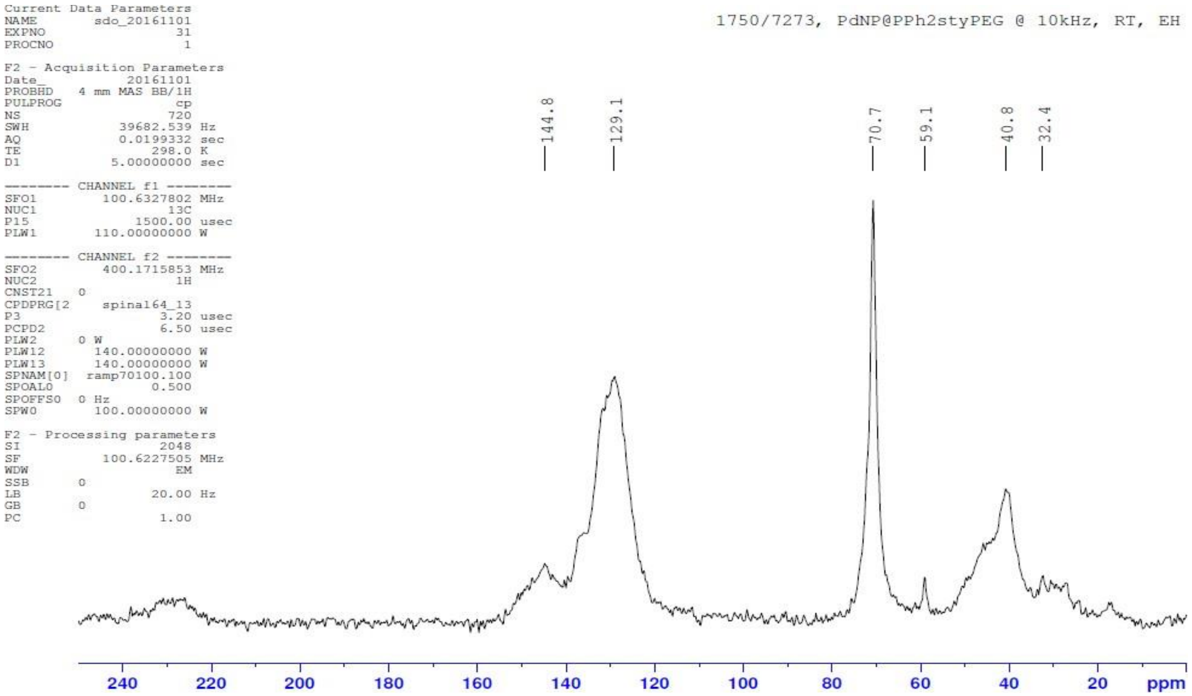


Figure S77 Solid state ^{13}C NMR spectrum ofPdNP@PPh$_2$PEGstyrene (5c)



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Current Data Parameters
NAME          sdo_20161101
EXPNO                   31
PROCNO                   1

F2 - Acquisition Parameters
Date_             20161101
PROBHD   4 mm MAS BB/1H
PULPROG                 cp
NS                     720
SWH             39682.539 Hz
AQ              0.0199332 sec
TE                  298.0 K
D1             5.00000000 sec

-------- CHANNEL f1 --------
SFO1          100.6327802 MHz
NUC1                   13C
P15               1500.00 usec
PLW1         110.00000000 W

-------- CHANNEL f2 --------
SFO2          400.1715853 MHz
NUC2                    1H
CNST21    0
CPDPRG[2       spinal64_13
P3                   3.20 usec
PCPD2                6.50 usec
PLW2      0 W
PLW12        140.00000000 W
PLW13        140.00000000 W
SPNAM[0]  ramp70100.100
SPOAL0               0.500
SPOFFS0   0 Hz
SPW0         100.00000000 W

F2 - Processing parameters
SI                    2048
SF            100.6227505 MHz
WDW                     EM
SSB       0
LB                  20.00 Hz
GB        0
PC                   1.00
```

Figure S78 Solid state ^{31}P NMR spectrum of PdNP@PPh$_2$PEG styrene (5c)

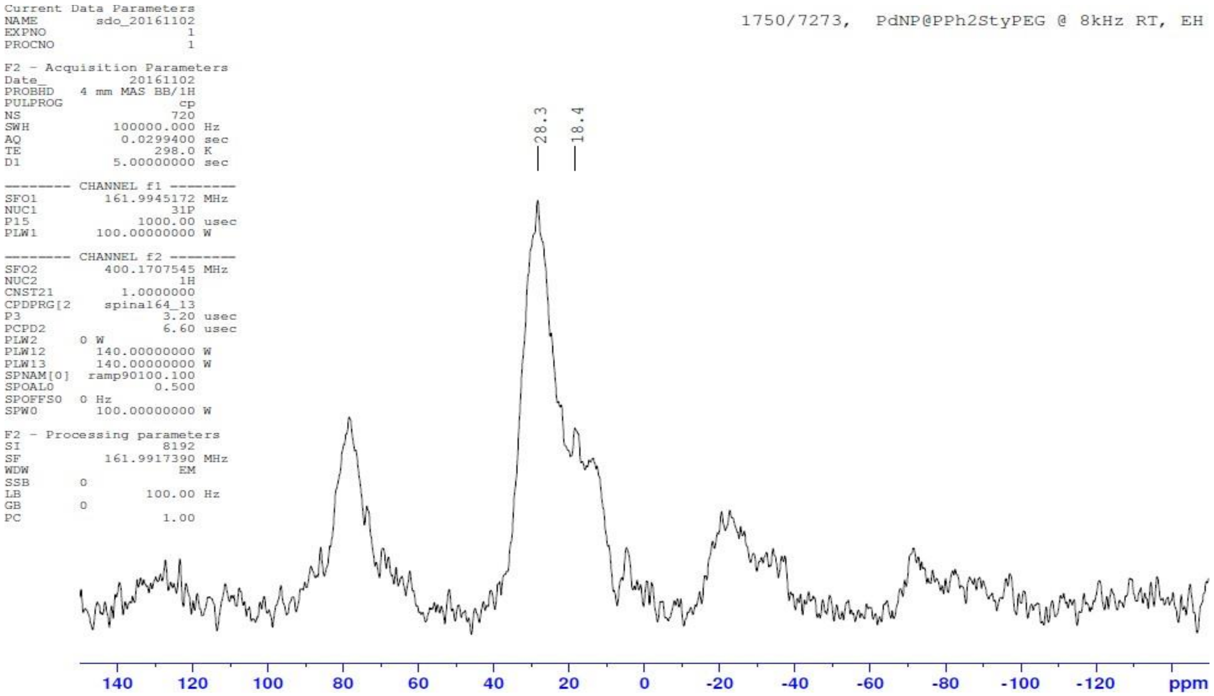


Figure S79 SEM images of freshly prepared PdNP@PPh$_2$PEGstyrene (5c)

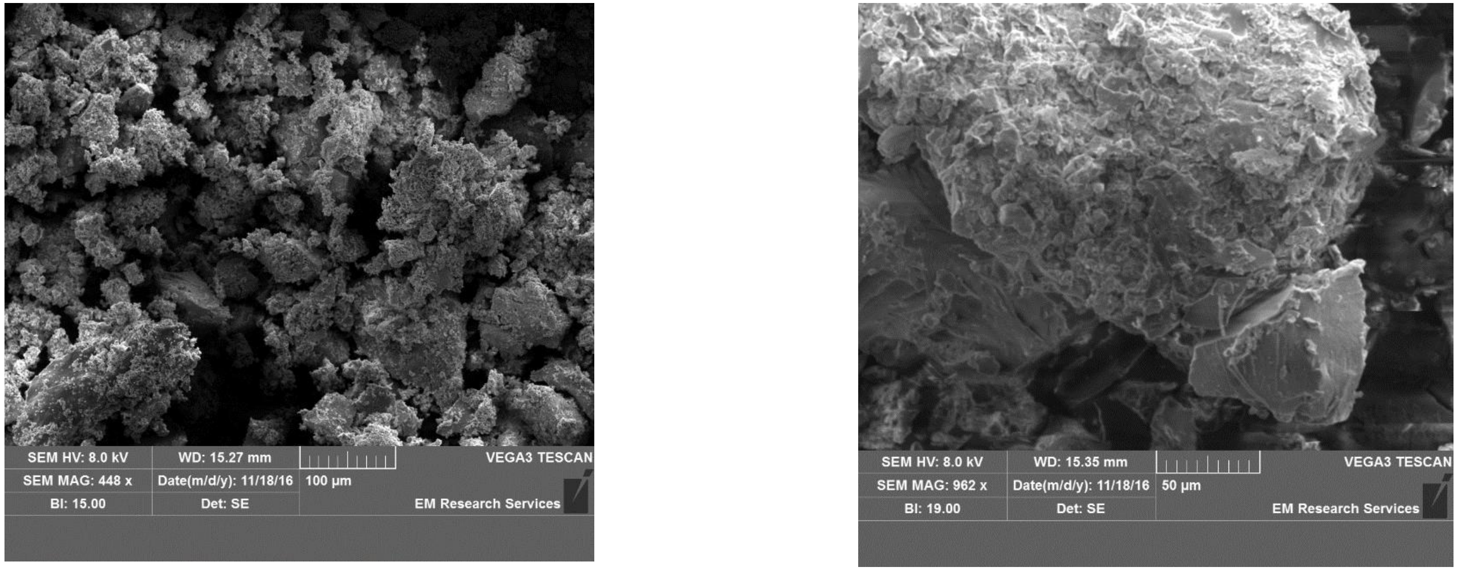


Figure S80 FT-IR spectrum of freshly prepared PdNP@PPh$_2$PEGstyrene (5c)

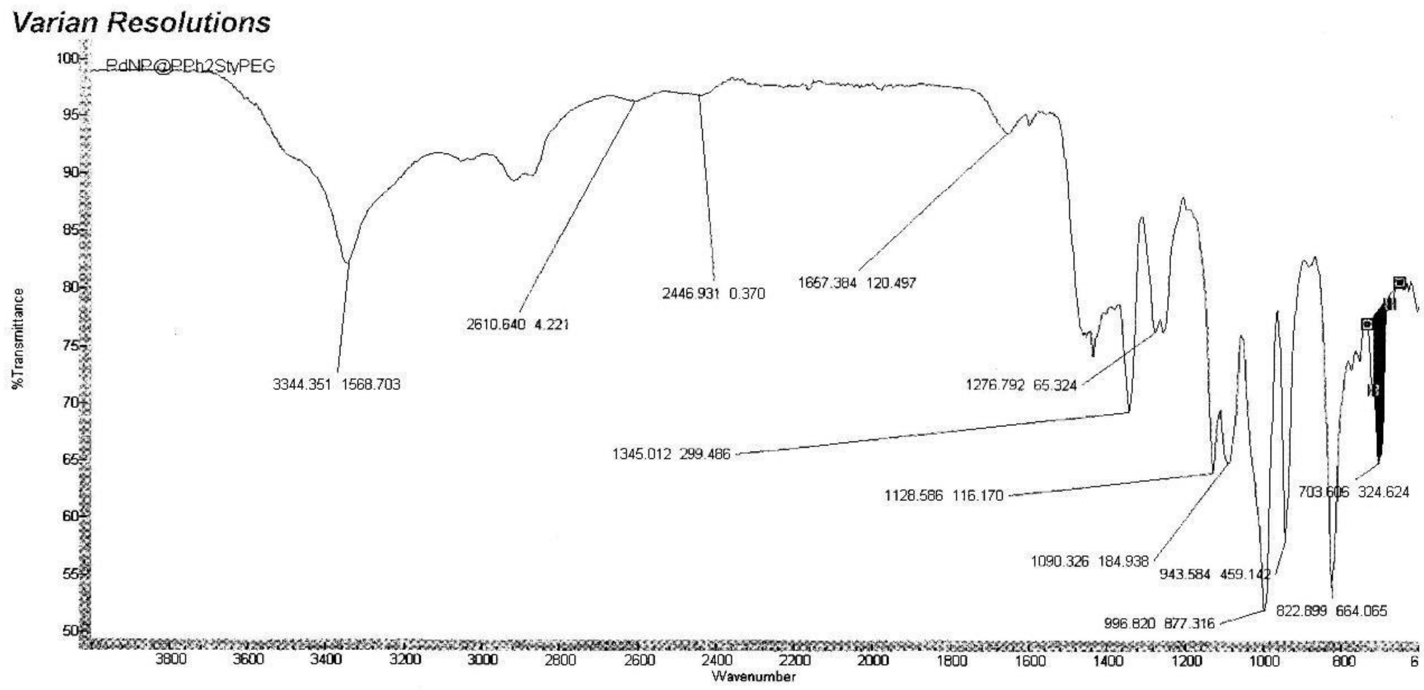


Figure S81 Pd 3d core level XPS spectrum of PdNP@PPh$_2$PEGstyrene (5c) referenced to the hydrocarbon C 1s

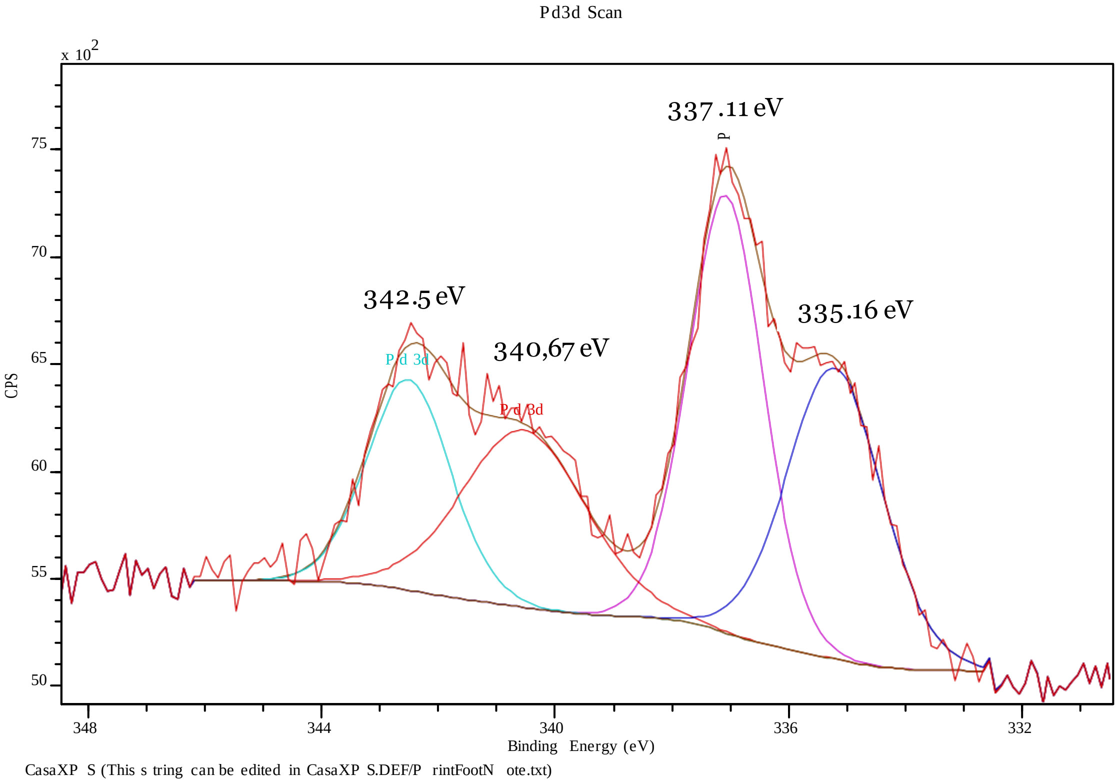


Figure S82 (a-d) TEM image of PdNP@PPh_2PEGstyrene (5c) and (e) histogram of particle size (diameter, nm). Scale bars are 25 nm (black) and 5 nm (white)

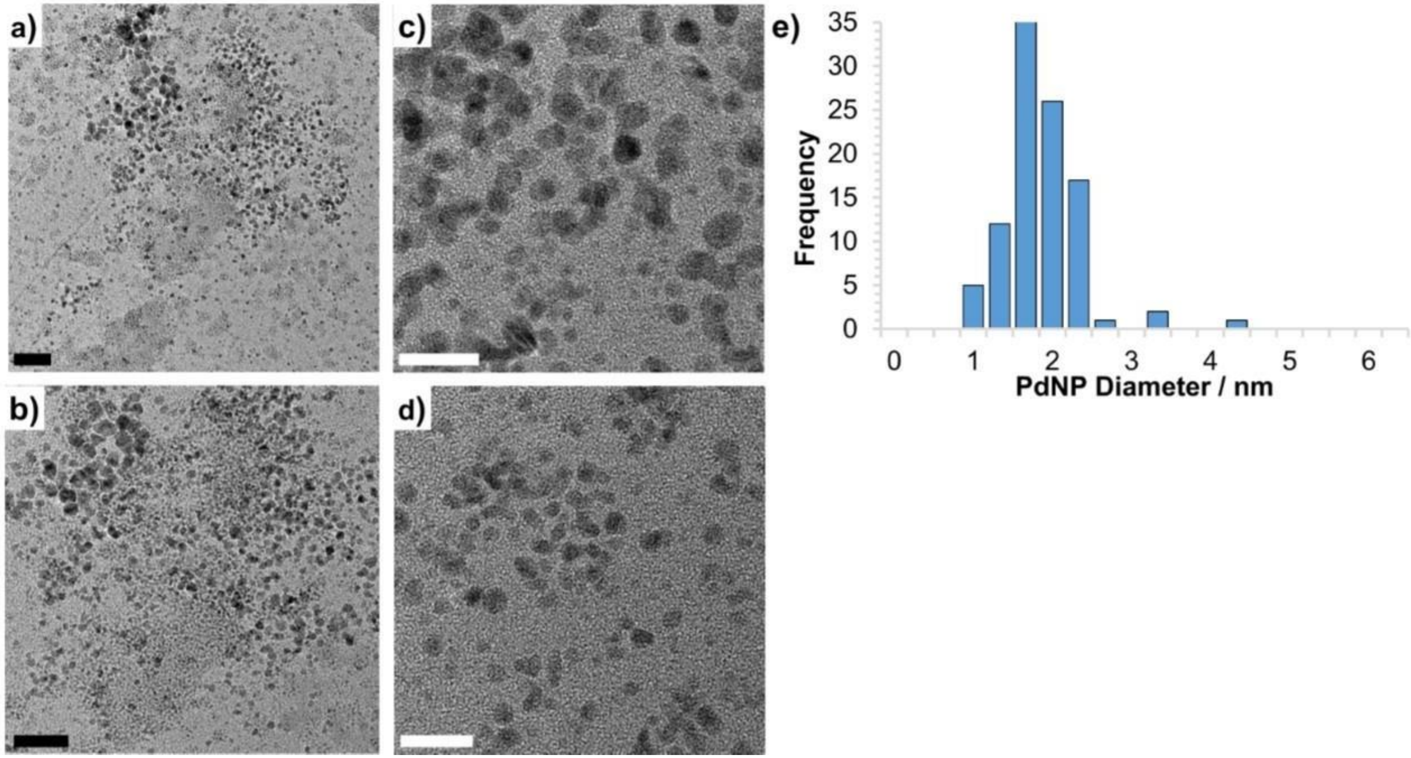


Figure S83 Powder X-ray Diffraction Pattern of PdNP@PPh$_2$PEGstyrene (5c)

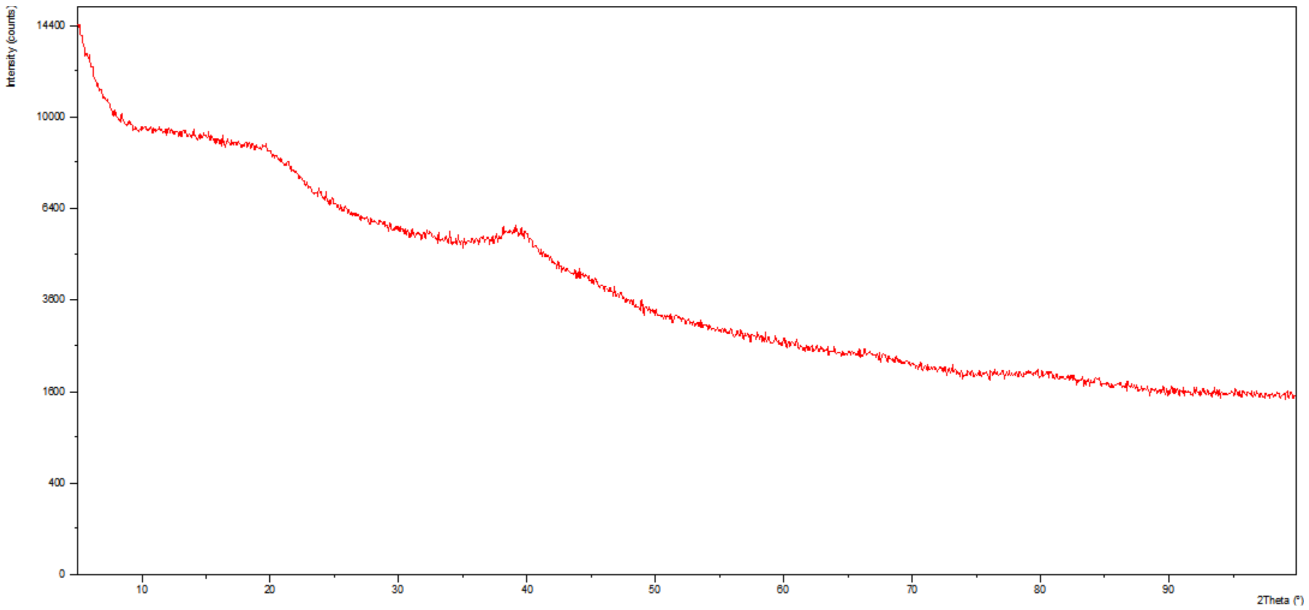
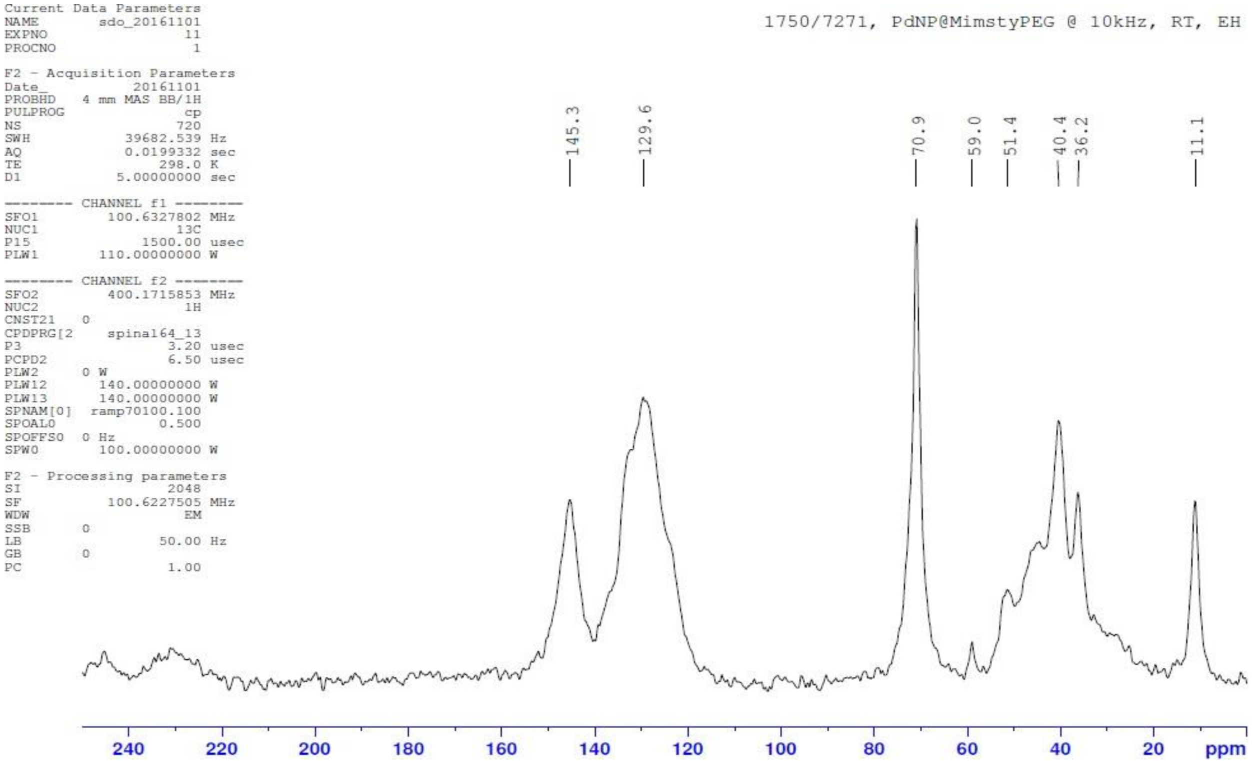


Figure S84 Solid state ^{13}C NMR spectrum ofPdNP@PEGPIILP (6c)



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Current Data Parameters
NAME        sdo_20161101
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161101
PROBHD   4 mm MAS BB/1H
PULPROG               cp
NS                   720
SWH            39682.539 Hz
AQ             0.0199332 sec
TE                 298.0 K
D1            5.00000000 sec

======== CHANNEL f1 ========
SFO1         100.6327802 MHz
NUC1                 13C
P15              1500.00 usec
PLW1        110.00000000 W

======== CHANNEL f2 ========
SFO2         400.1715853 MHz
NUC2                  1H
CNST21    0
CPDPRG[2      spinal64_13
P3                  3.20 usec
PCPD2               6.50 usec
PLW2      0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]  ramp70100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0        100.00000000 W

F2 - Processing parameters
SI                  2048
SF           100.6227505 MHz
WDW                   EM
SSB       0
LB                 50.00 Hz
GB        0
PC                  1.00
```

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

Figure S85 SEM images of freshly prepared PdNP@PEGPIILP (6c)

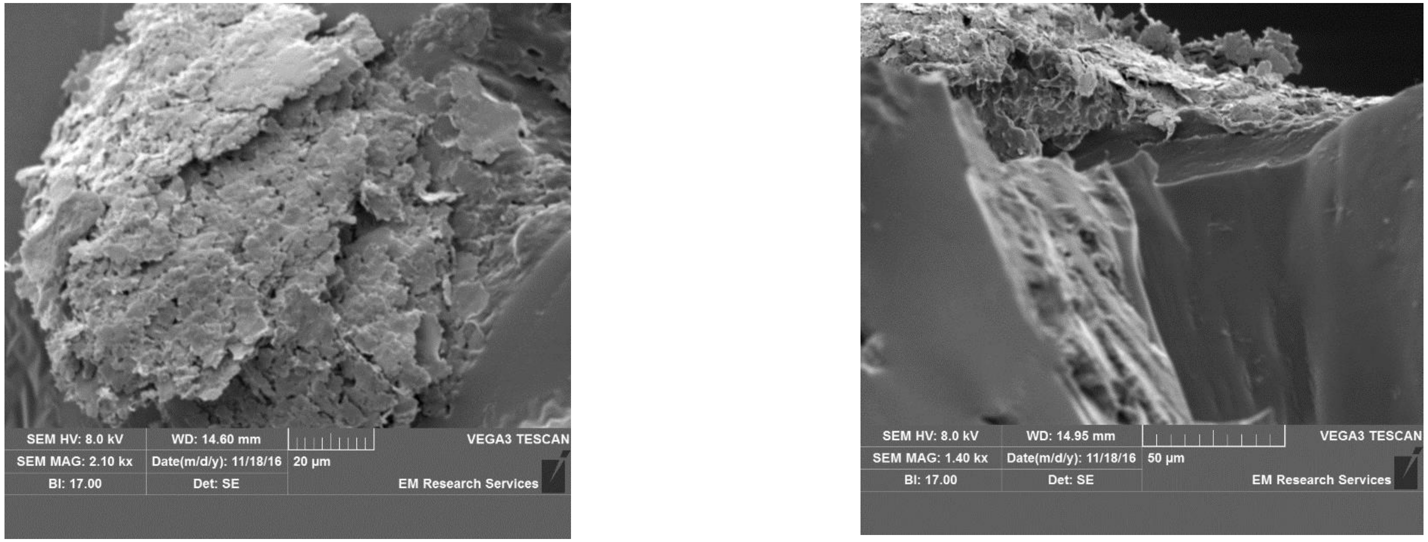


Figure S86 FT-IR spectrum of freshly prepared PdNP@PEGPIILP (6c)

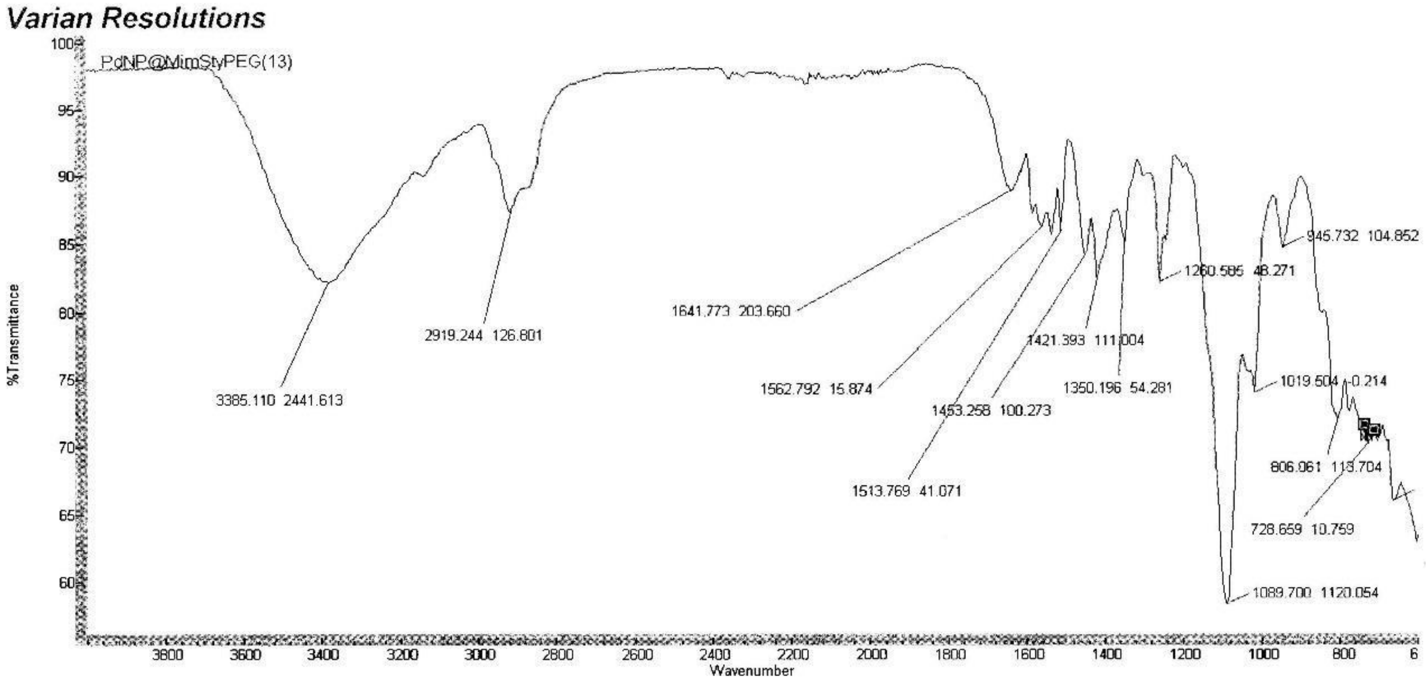
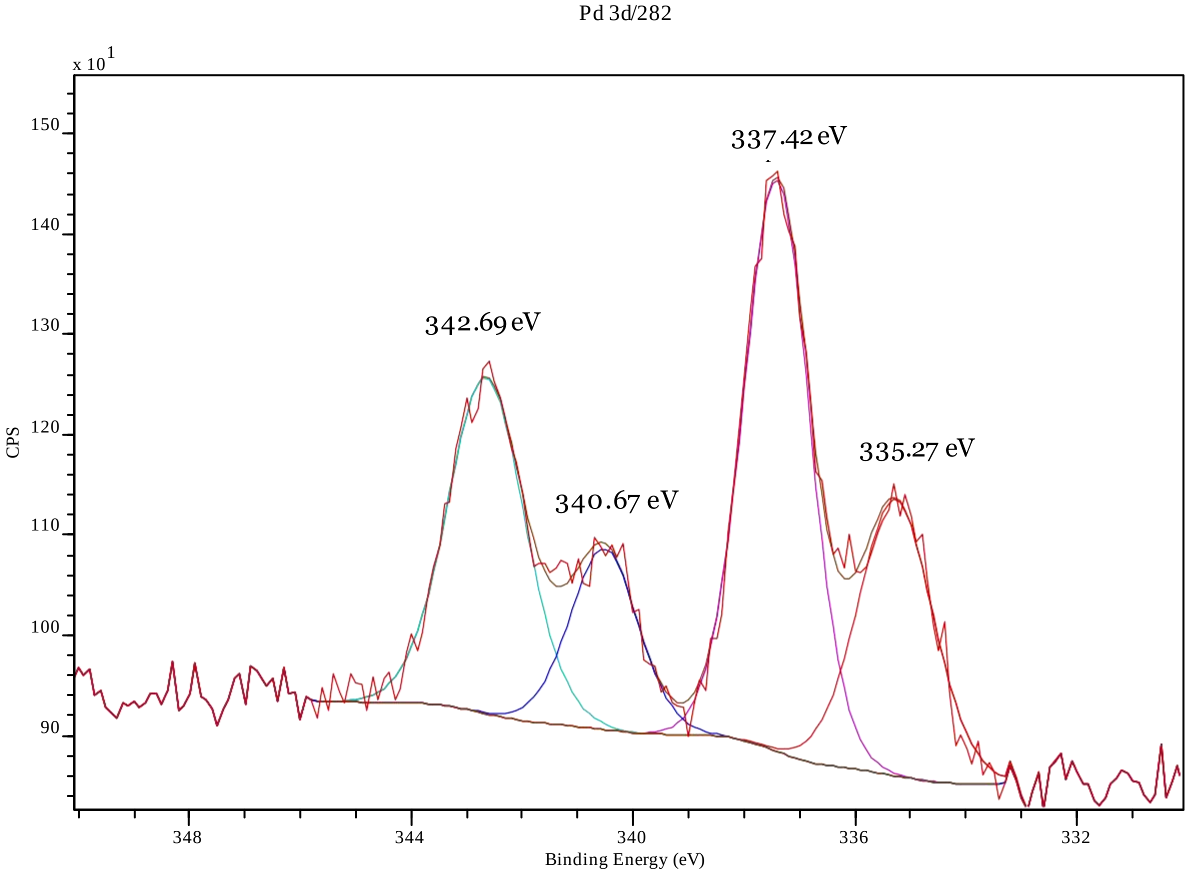


Figure S87 Pd 3d core level XPS spectrum of PdNP@PEGPIILP (6c) referenced to the hydrocarbon C 1s



CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

Figure S88 (a-d) TEM image of PdNP@PEGPIILP (6c) and (e) histogram of particle size (diameter, nm). Scale bars are 5 nm (white)

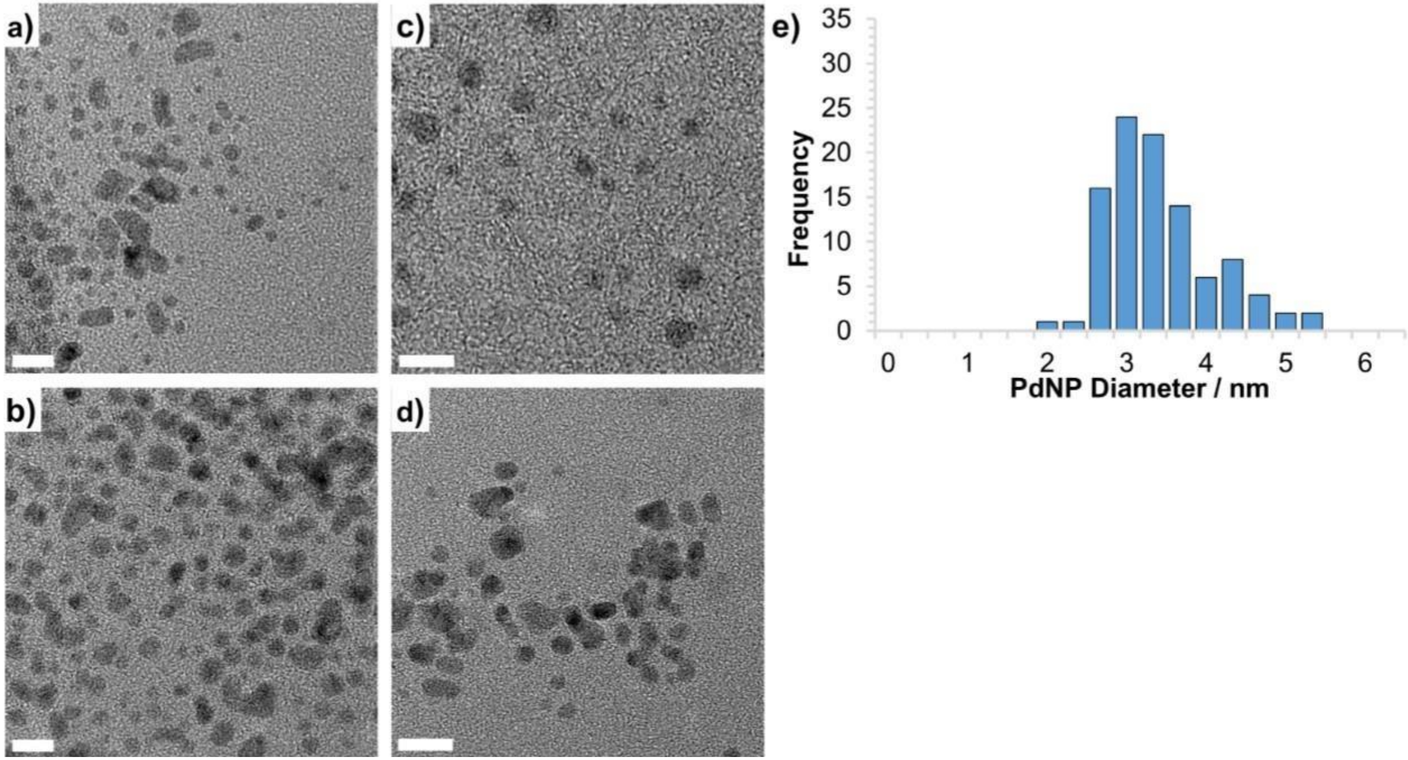


Figure S89 Powder X-ray Diffraction Pattern of PdNP@PEGPIILP (6c)

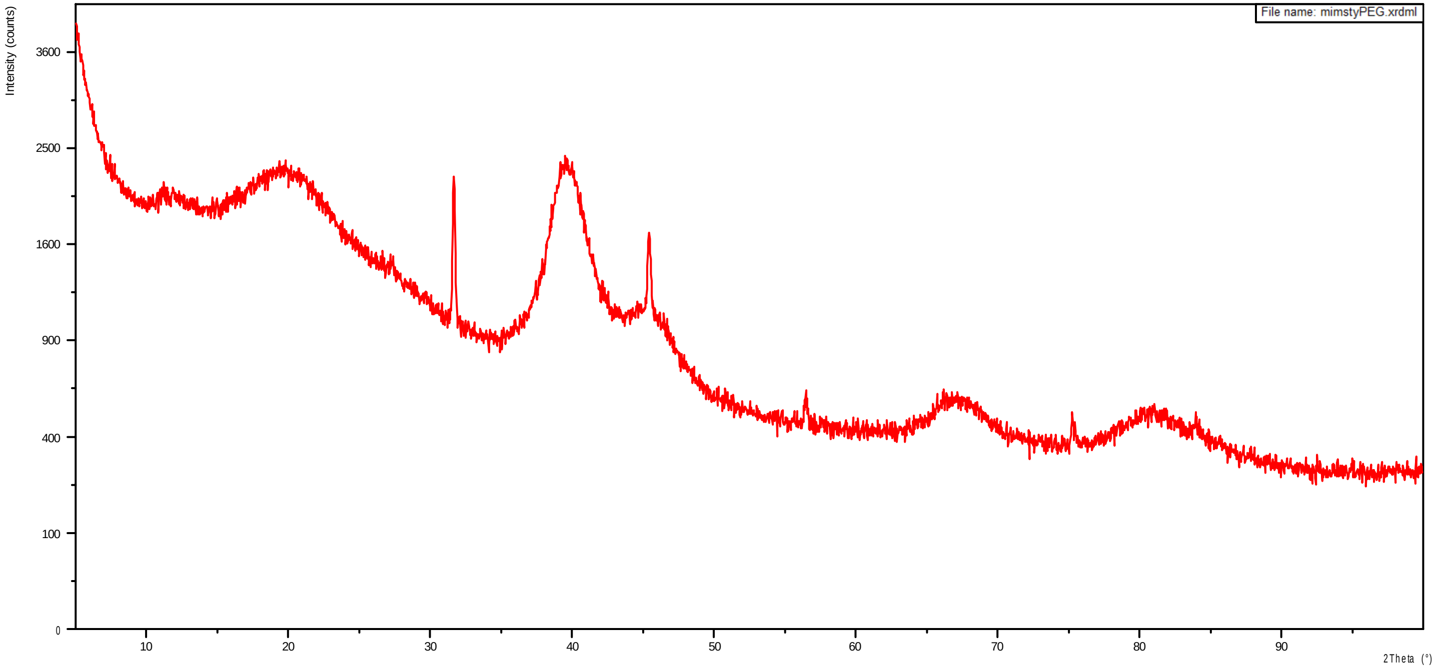
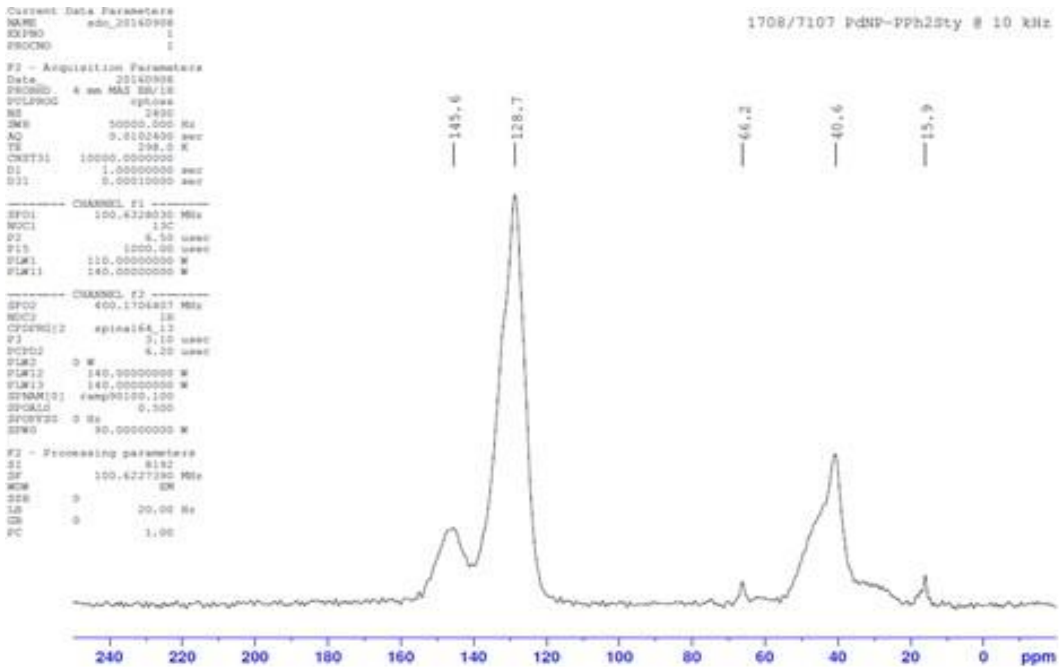


Figure S90 Solid state ^{13}C NMR spectrum of PdNP@PPh$_2$-polystyrene (7c)



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Current Data Parameters
NAME          edn_20160908
EXPNO                    1
PROCNO                   1

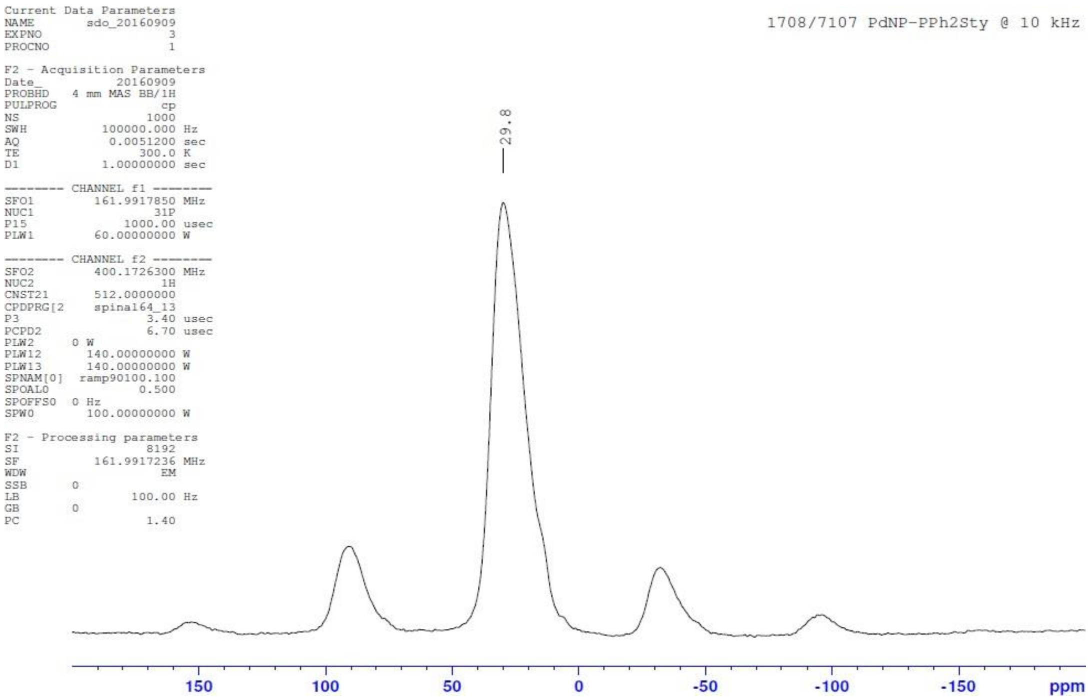
F2 - Acquisition Parameters
Date_             20160908
PROBHD    4 mm MAS BB/1H
PULPROG             cptoss
NS                    2400
SWH             50000.000 Hz
AQ              0.0102400 sec
TE                  298.0 K
CNST31     10000.0000000
D1             1.00000000 sec
D31            0.00010000 sec

======== CHANNEL f1 ========
SFO1          100.6328030 MHz
NUC1                   13C
P2                    6.50 usec
P15                1000.00 usec
PLW1         110.00000000 W
PLW11        140.00000000 W

======== CHANNEL f2 ========
SFO2          400.1704807 MHz
NUC2                    1H
CPDPRG[2     spinal64_13
P3                    3.10 usec
PCPD2                 6.20 usec
PLW2      0 W
PLW12        140.00000000 W
PLW13        140.00000000 W
SPNAM[0]   ramp90100.100
SPOAL0               0.500
SPOFFS0   0 Hz
SPW0          90.00000000 W

F2 - Processing parameters
SI                    8192
SF            100.6227290 MHz
WDW                     EM
SSB       0
LB                   20.00 Hz
GB        0
PC                    1.00
```

Figure S91 Solid state ^{31}P NMR spectrum of PdNP@PPh$_2$-polystyrene (7c)



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Current Data Parameters
NAME        sdo_20160909
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160909
PROBHD   4 mm MAS BB/1H
PULPROG               cp
NS                  1000
SWH           100000.000 Hz
AQ             0.0051200 sec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
SFO1         161.9917850 MHz
NUC1                 31P
P15              1000.00 usec
PLW1         60.00000000 W

======== CHANNEL f2 ========
SFO2         400.1726300 MHz
NUC2                  1H
CNST21       512.0000000
CPDPRG[2     spinal64_13
P3                  3.40 usec
PCPD2               6.70 usec
PLW2      0 W
PLW12       140.00000000 W
PLW13       140.00000000 W
SPNAM[0]   ramp90100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0        100.00000000 W

F2 - Processing parameters
SI                  8192
SF           161.9917236 MHz
WDW                   EM
SSB       0
LB                100.00 Hz
GB        0
PC                  1.40
```

Figure S92 SEM images of freshly prepared PdNP@PPh_2-polystyrene (7c)

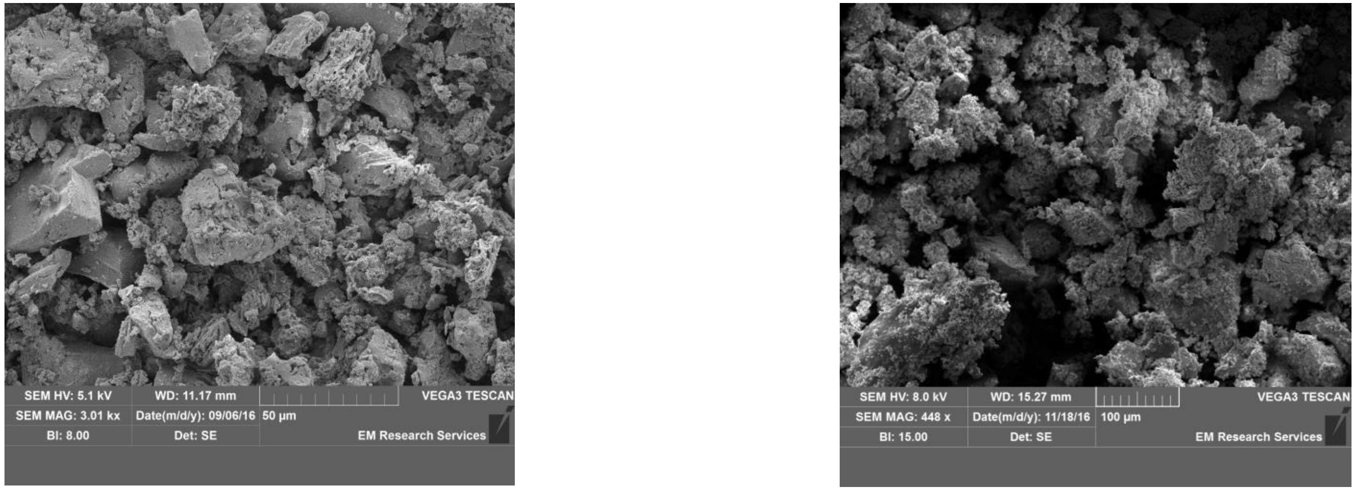


Figure S93 FT-IR spectrum of freshly prepared PdNP@PPh$_2$-polystyrene (7c)

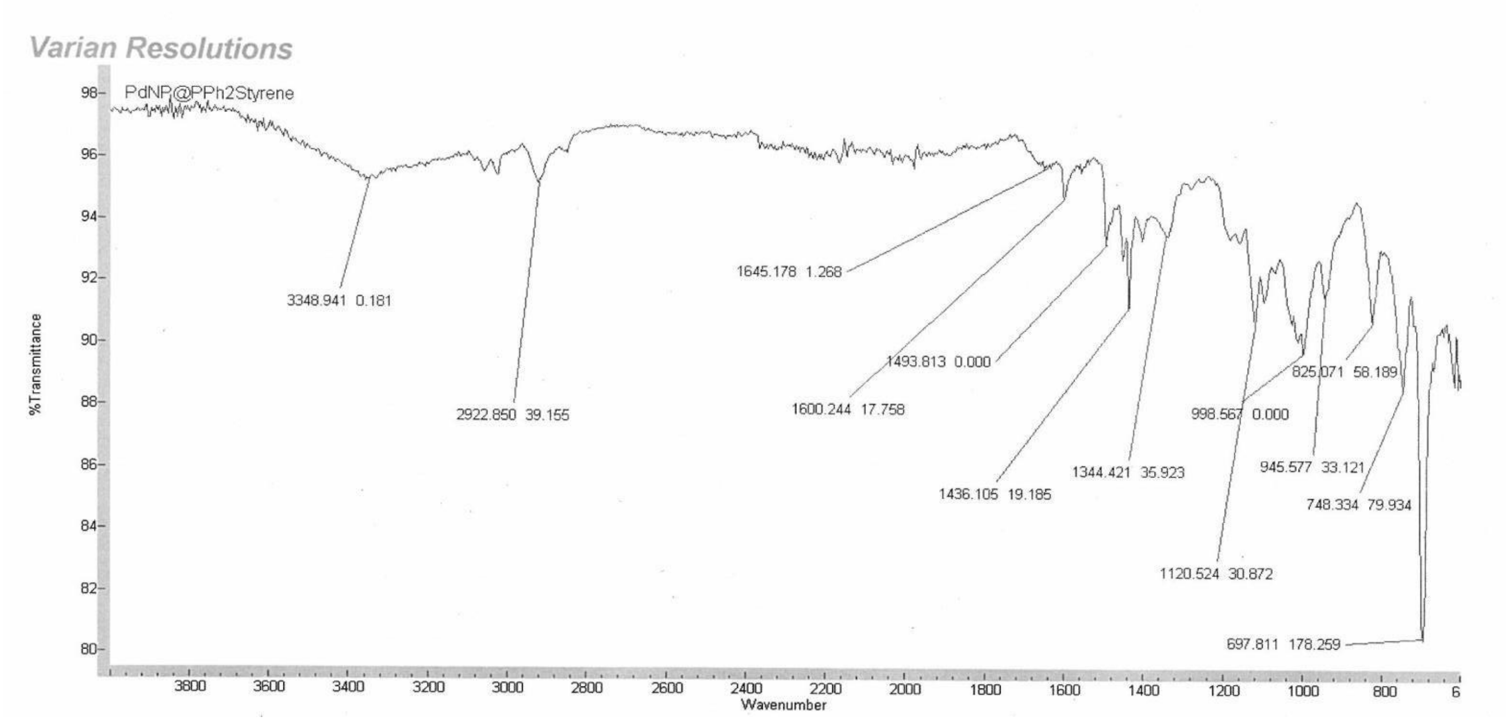


Figure S94 Pd 3d core level XPS spectrum of PdNP@PPh$_2$-polystyrene (7c) referenced to the hydrocarbon C 1s

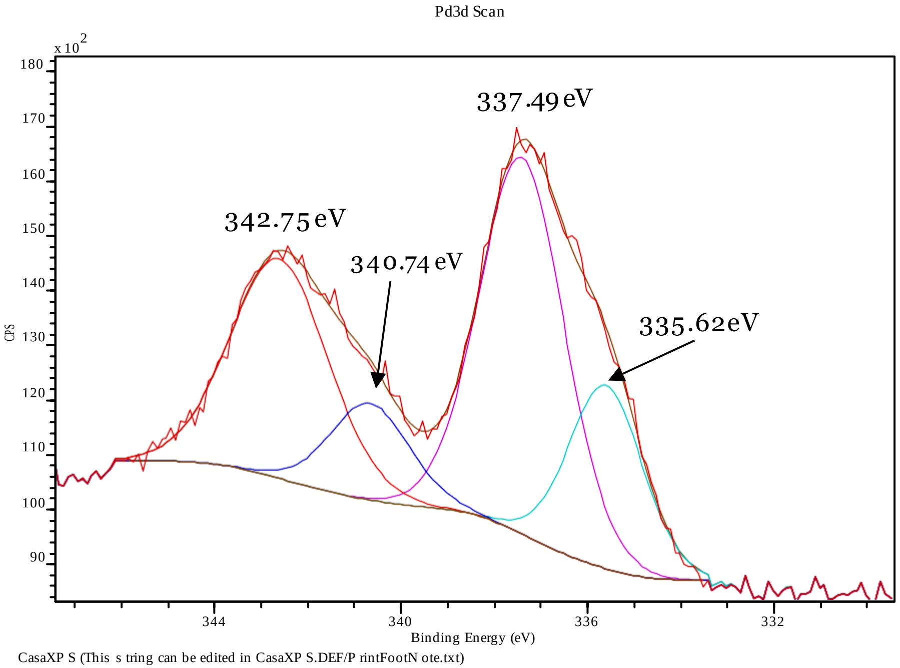


Figure S95 (a-d) TEM images of PdNP@PPh$_2$-polystyrene (7c) and e) histogram showing the distribution of particle sizes (average NP diameter = 1.39 ± 0.19 nm). Scale bars 25 nm (black) and 5 nm (white).

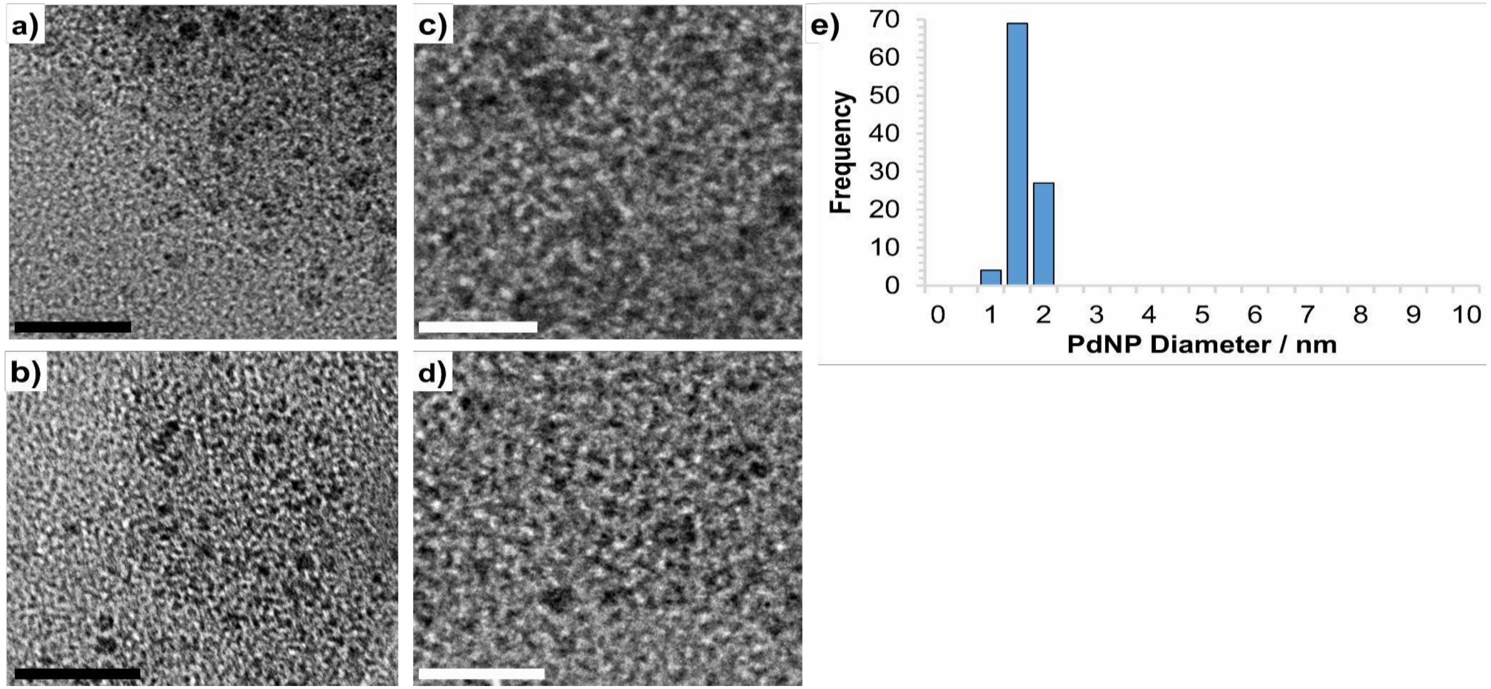


Figure S96 Powder X-ray Diffraction Pattern of PdNP@PPh_2-polystyrene (7c)

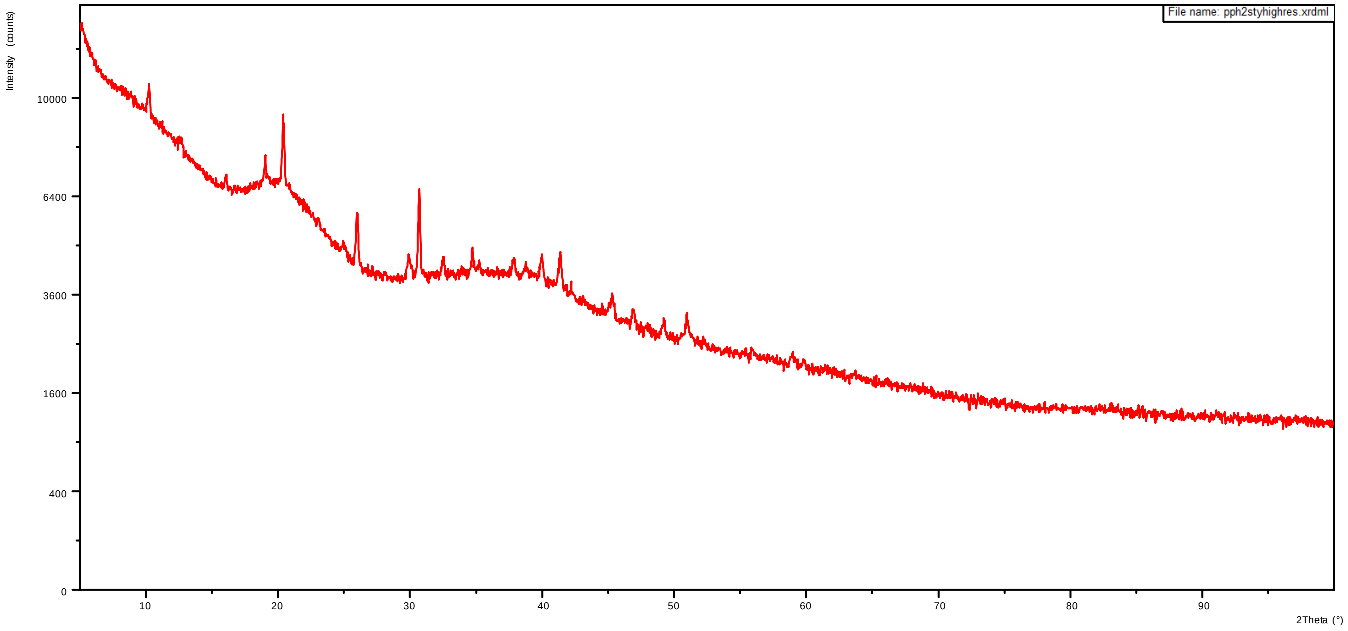
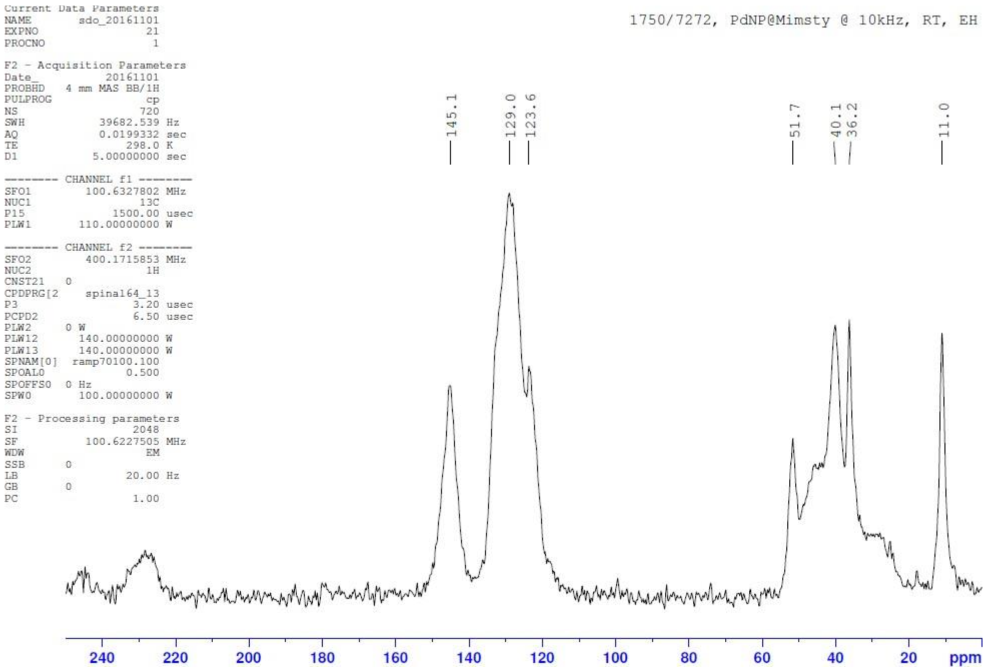


Figure S97 Solid state ^{13}C NMR spectrum of PdNP@Styr-PIILP (8c)



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Current Data Parameters
NAME        sdo_20161101
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161101
PROBHD   4 mm MAS BB/1H
PULPROG               cp
NS                   720
SWH           39682.539 Hz
AQ            0.0199332 sec
TE                298.0 K
D1           5.00000000 sec

-------- CHANNEL f1 --------
SFO1        100.6327802 MHz
NUC1                 13C
P15             1500.00 usec
PLW1       110.00000000 W

-------- CHANNEL f2 --------
SFO2        400.1715853 MHz
NUC2                  1H
CNST21    0
CPDPRG[2     spinal64_13
P3                 3.20 usec
PCPD2              6.50 usec
PLW2      0 W
PLW12      140.00000000 W
PLW13      140.00000000 W
SPNAM[0]  ramp70100.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0       100.00000000 W

F2 - Processing parameters
SI                  2048
SF          100.6227505 MHz
WDW                   EM
SSB       0
LB                 20.00 Hz
GB        0
PC                  1.00
```

1750/7272, PdNP@Mimsty @ 10kHz, RT, EH

Figure S98 SEM images of freshly prepared PdNP@Styr-PIILP (8c)

Figure S99 FT-IR spectrum of freshly prepared PdNP@Styr-PIILP (8c)

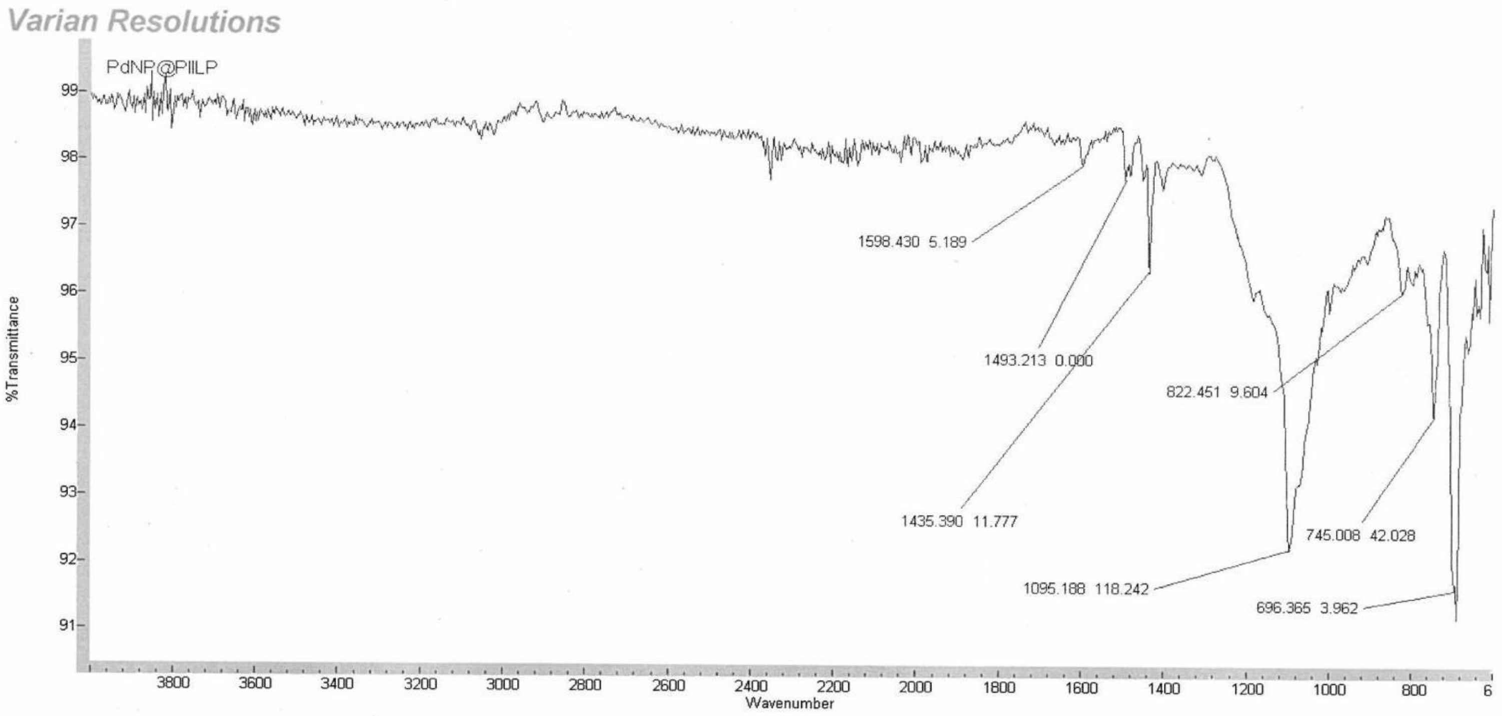


Figure S100 Pd 3d core level XPS spectrum of PdNP@Styr-PIILP (8c) referenced to the hydrocarbon C1s

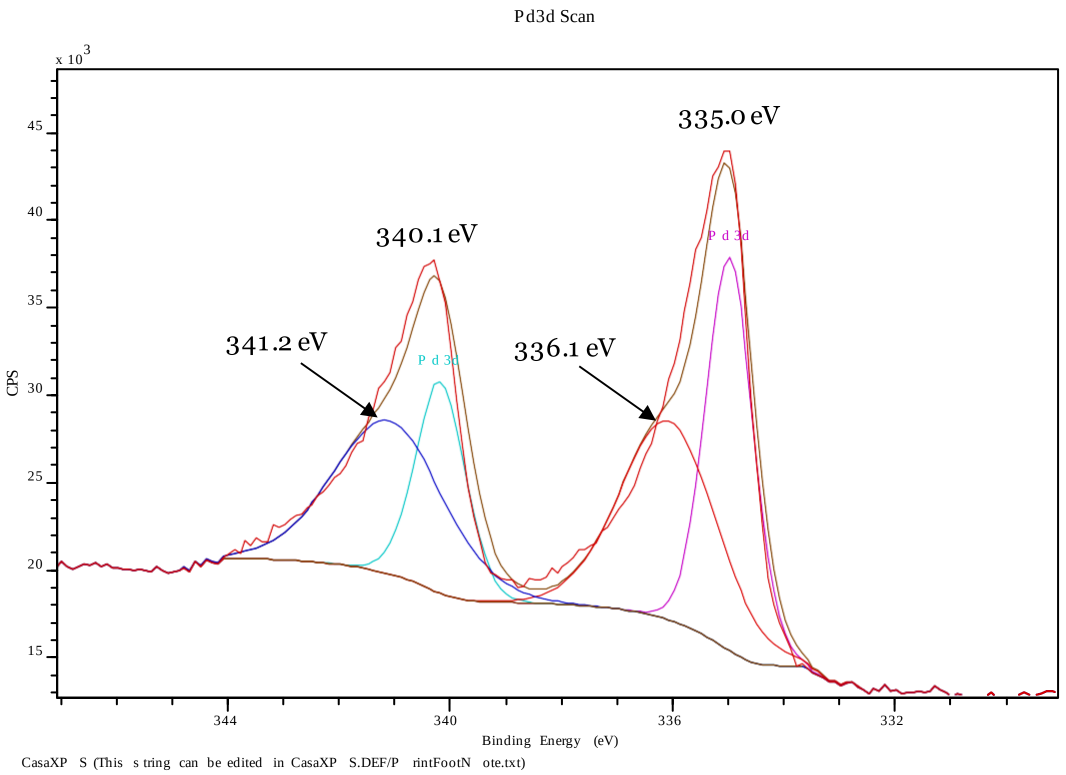


Figure S101 (a-d) TEM images of of PdNP@Styr-PIILP (8c) and e) histogram showing the distribution of particle sizes (average NP diameter = 3.01 ± 0.63 nm). Scale bars 25 nm (black) and 5 nm (white).

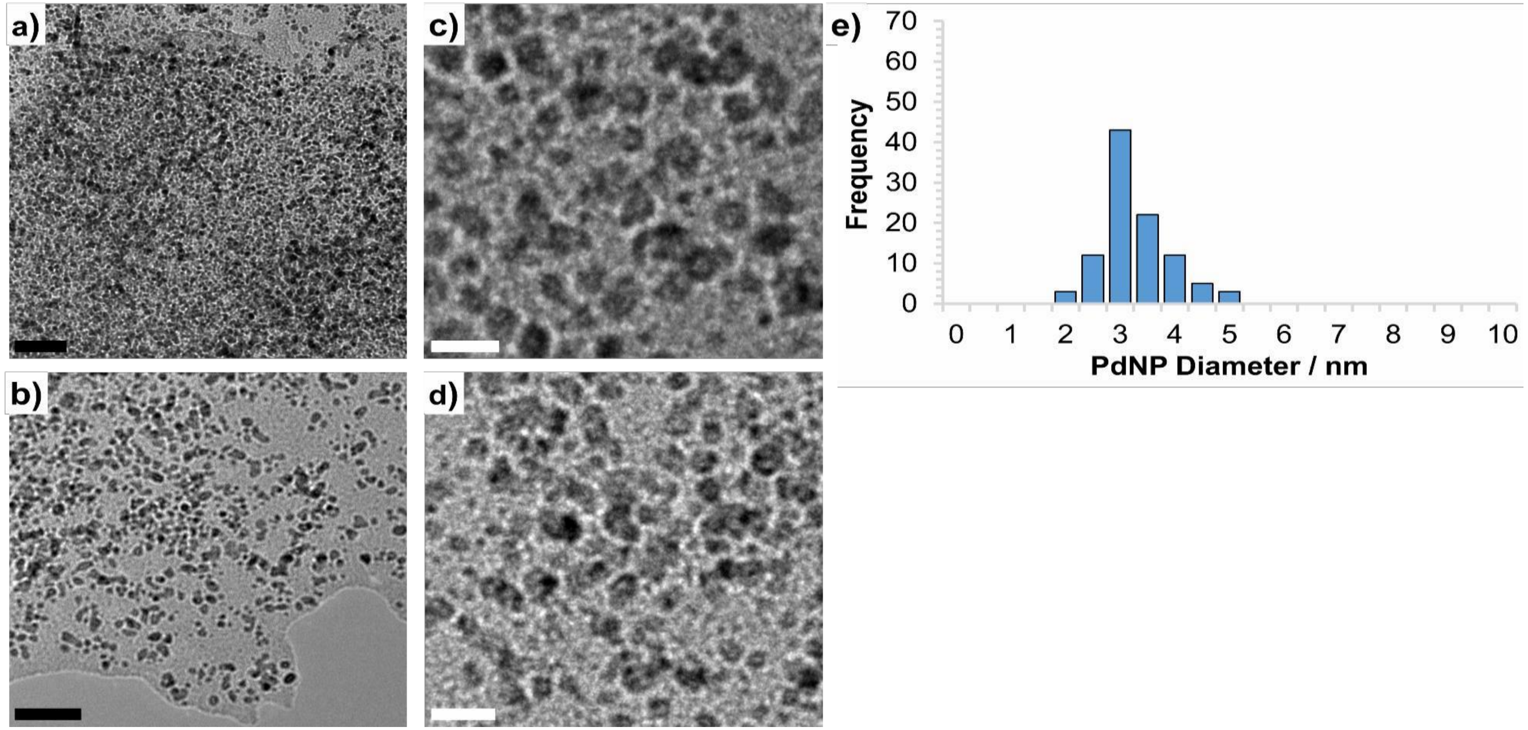


Figure S102 Powder X-ray Diffraction Pattern of PdNP@Styr-PIILP (8c)

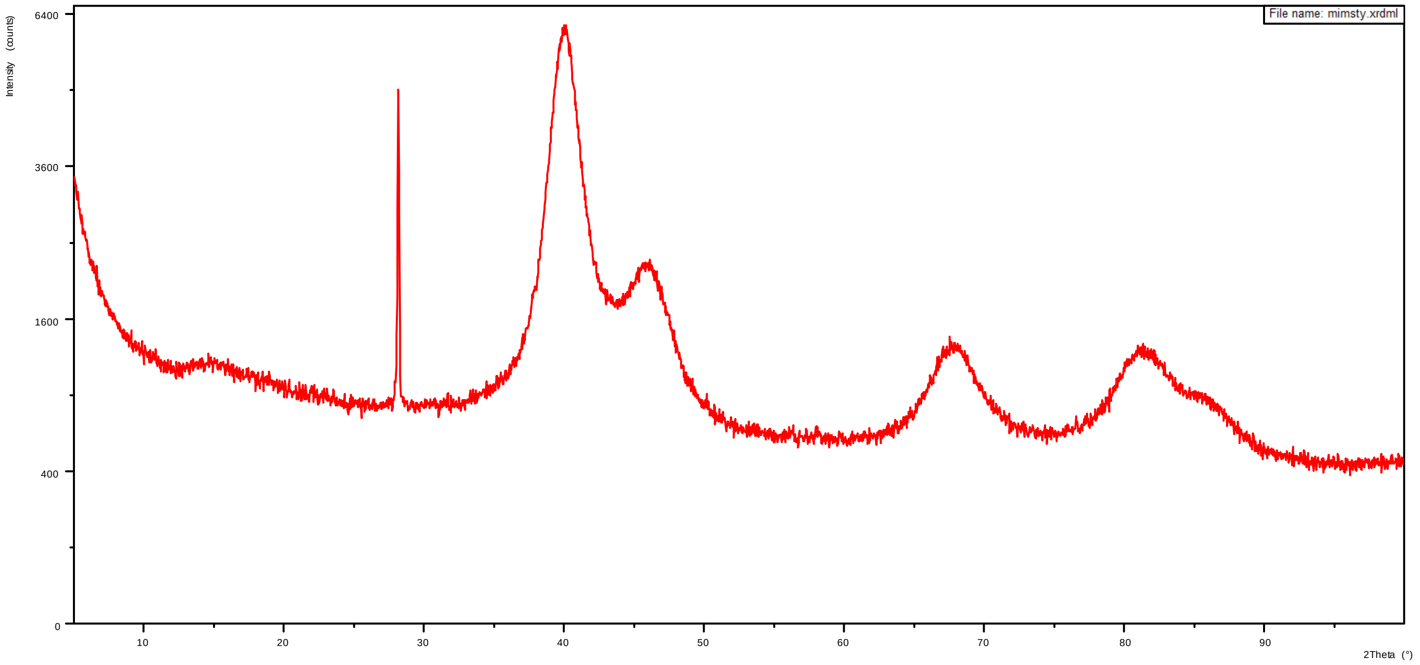


Figure S103 FD-XAS spectra showing the Pd L_{III} edges of **1a** (red), **1b** (green) and **1c** (blue). The raw data (black) has been overlaid on the smoothed versions.

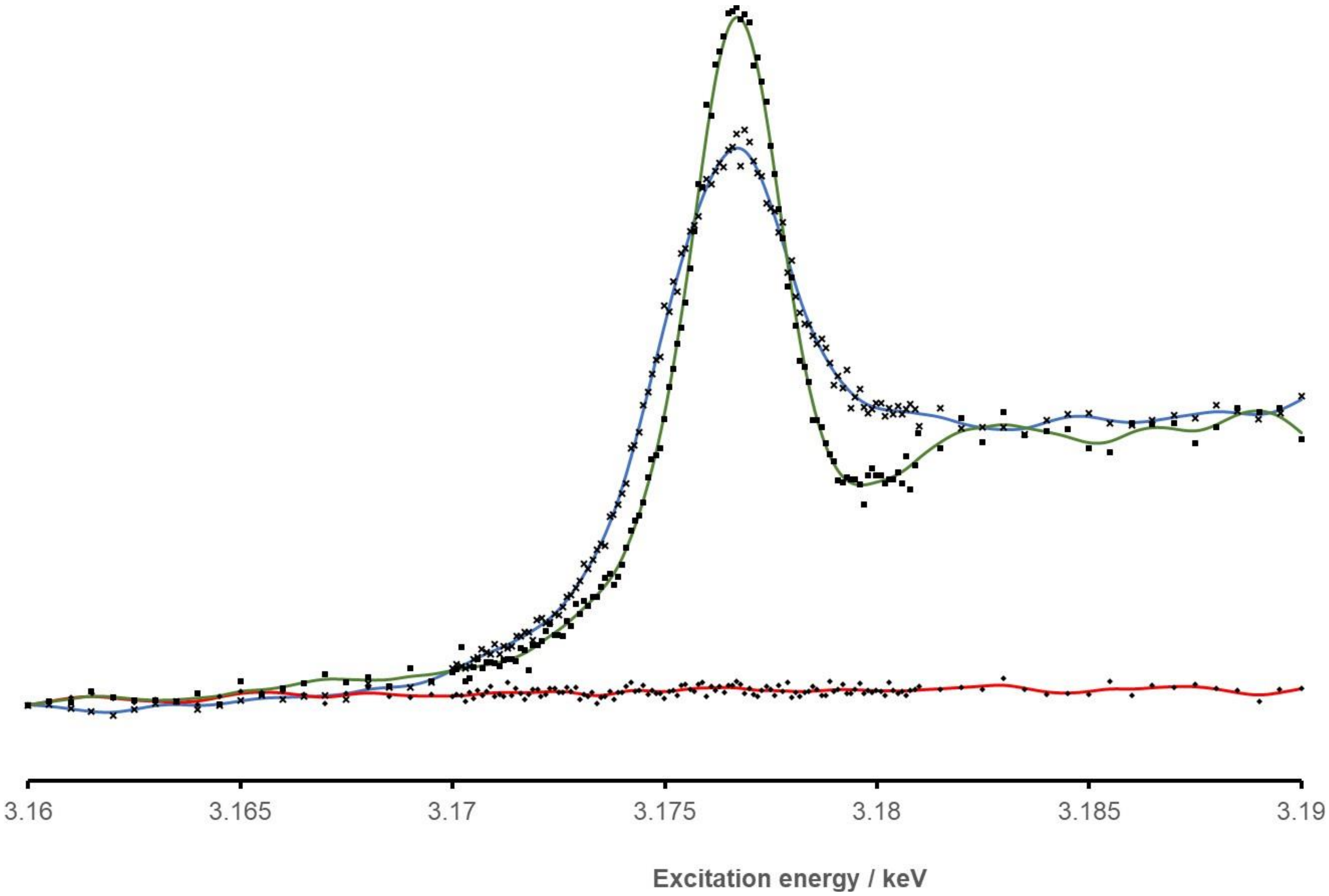


Figure S104 FD-XAS spectra showing the Pd L_{III} edges of **2a** (red), **2b** (green) and **2c** (blue). The raw data (black) has been overlaid on the smoothed versions.

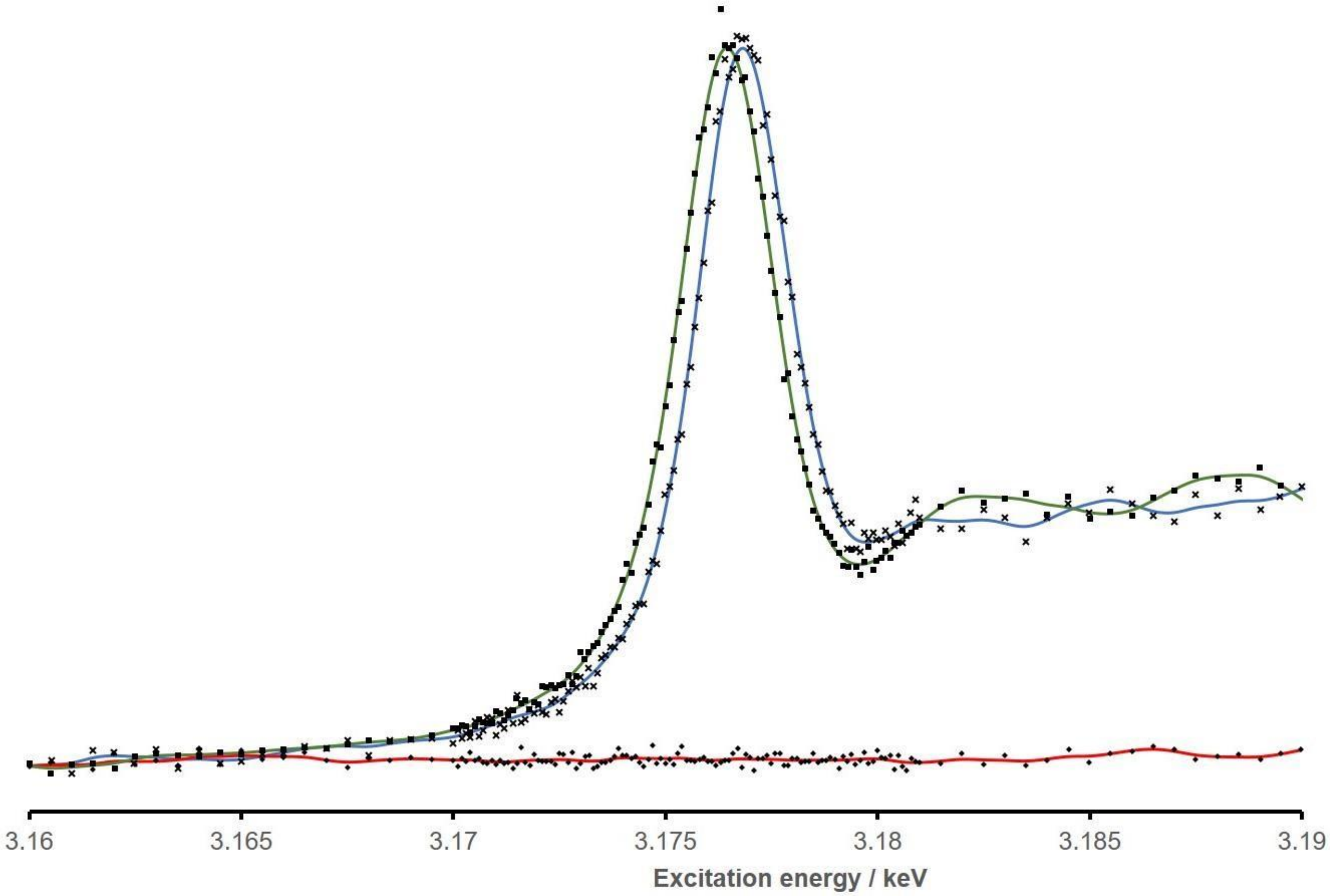


Figure S105 FD-XAS spectra showing the Pd L_{III} edges of **3a** (red), **3b** (green) and **3c** (blue). The raw data (black) has been overlaid on the smoothed versions. The raw data (black) has been overlaid on the smoothed versions.

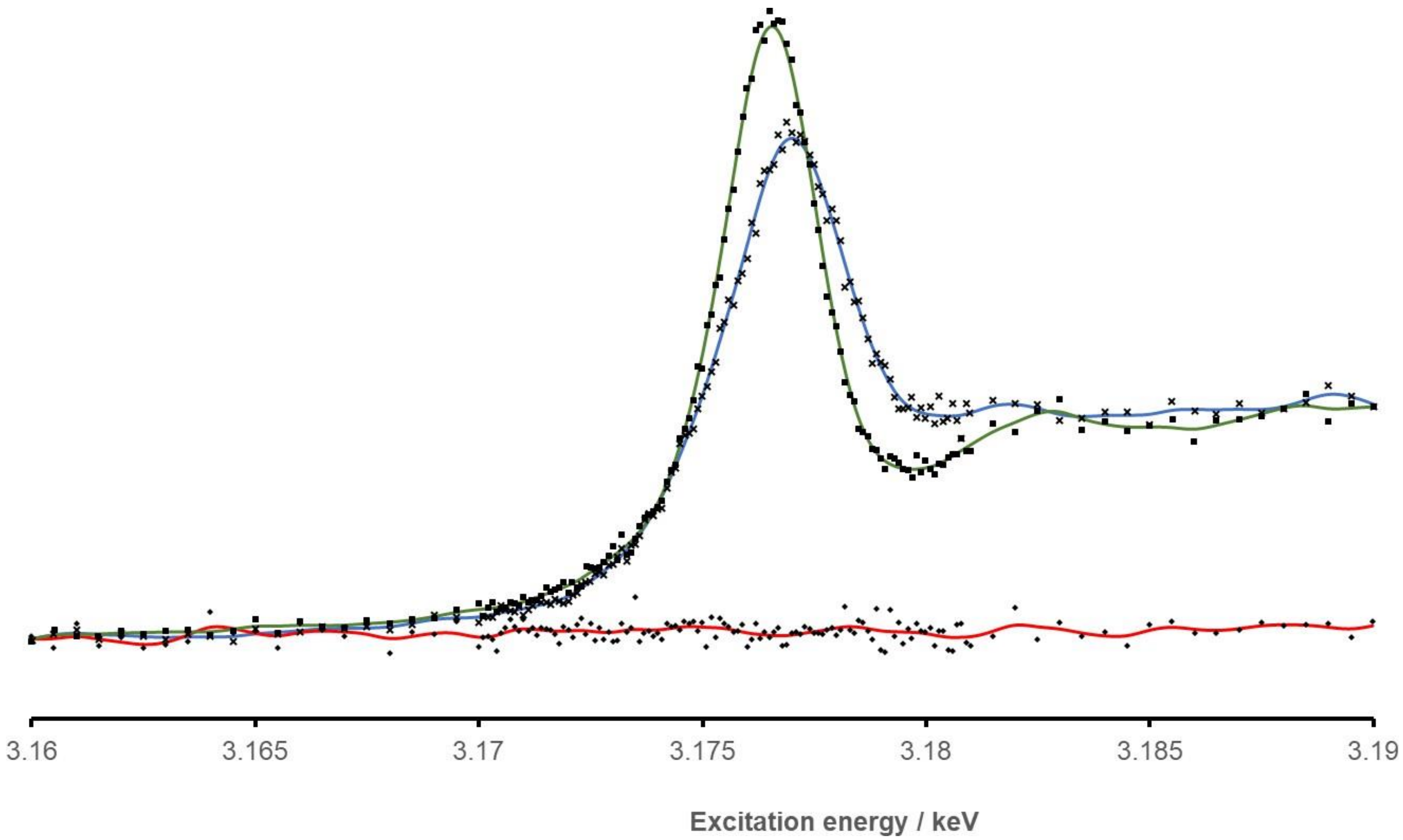


Figure S106 FD-XAS spectra showing the Pd L_{III} edges of **4a** (red), **4b** (green) and **4c** (blue). The raw data (black) has been overlaid on the smoothed versions.

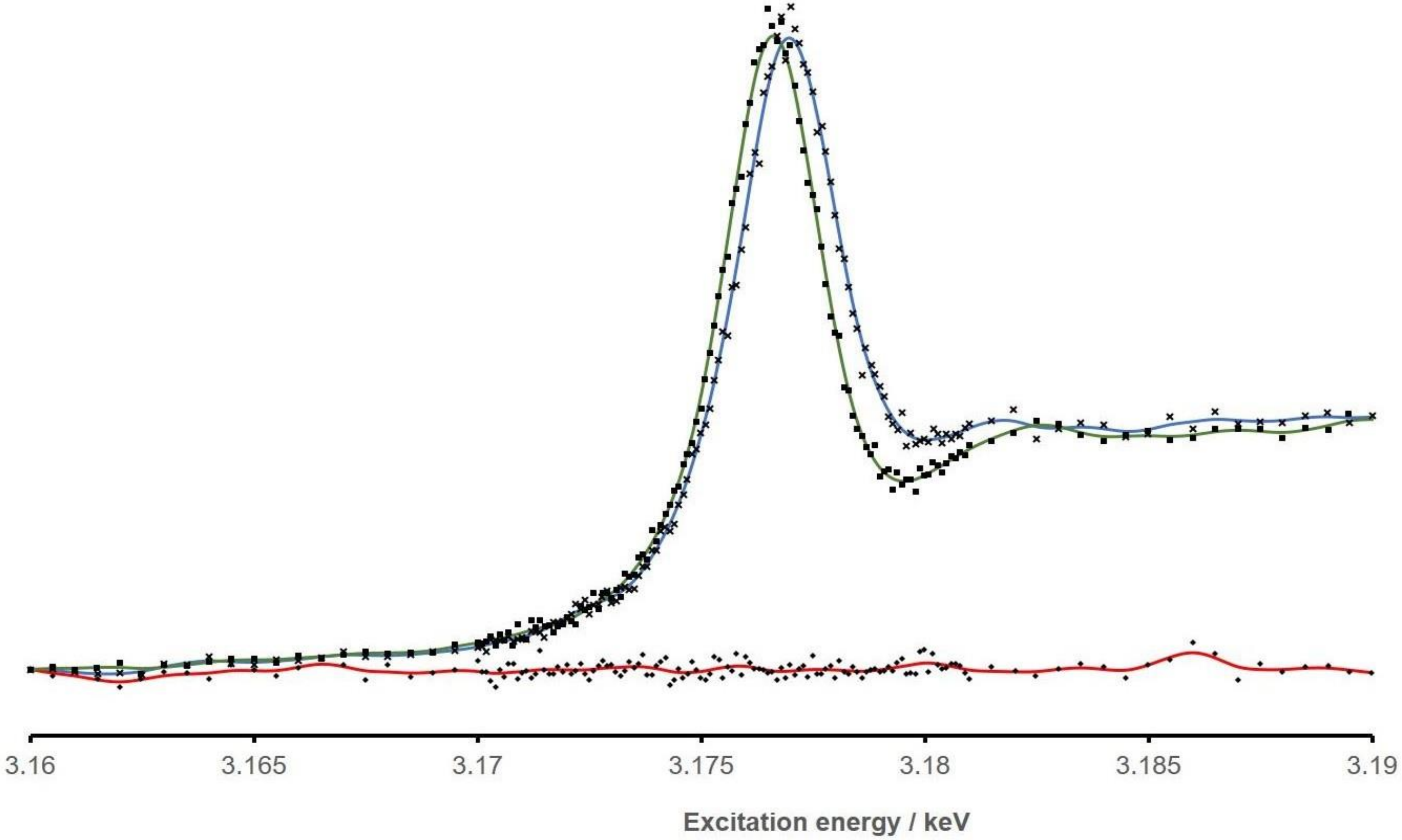


Figure S107 FD-XAS data for **1b-4b** and **1c-4c** showing the Pd L_{III} edge and white line energies.

Sample	Edge energy / KeV	White line energy / KeV	Shift from $Na_2[PdCl_4]$ / eV	Sample	Edge energy / KeV	White line energy / KeV	Shift from Pd/C / eV
1b	3.175706	3.176722	+0.51	**1c**	3.174740	3.176730	+0.12
2b	3.175440	3.176433	+0.22	**2c**	3.175874	3.176880	+0.27
3b	3.175624	3.176591	+0.38	**3c**	3.175883	3.177000	+0.39
4b	3.175646	3.176590	+0.38	**4c**	3.176035	3.176982	+0.37
$Na_2[PdCl_4]$	3.175202	3.176215	-	**Pd/C**	3.175485	3.176614	-

Figure S108 FD-XAS spectra showing the Pd L_{III} edges for **1b** (red), **2b** (blue), **3b** (green), **4b** (yellow) and $Na_2[PdCl_4]$ (purple). The raw data (black) has been overlaid on the smoothed versions.

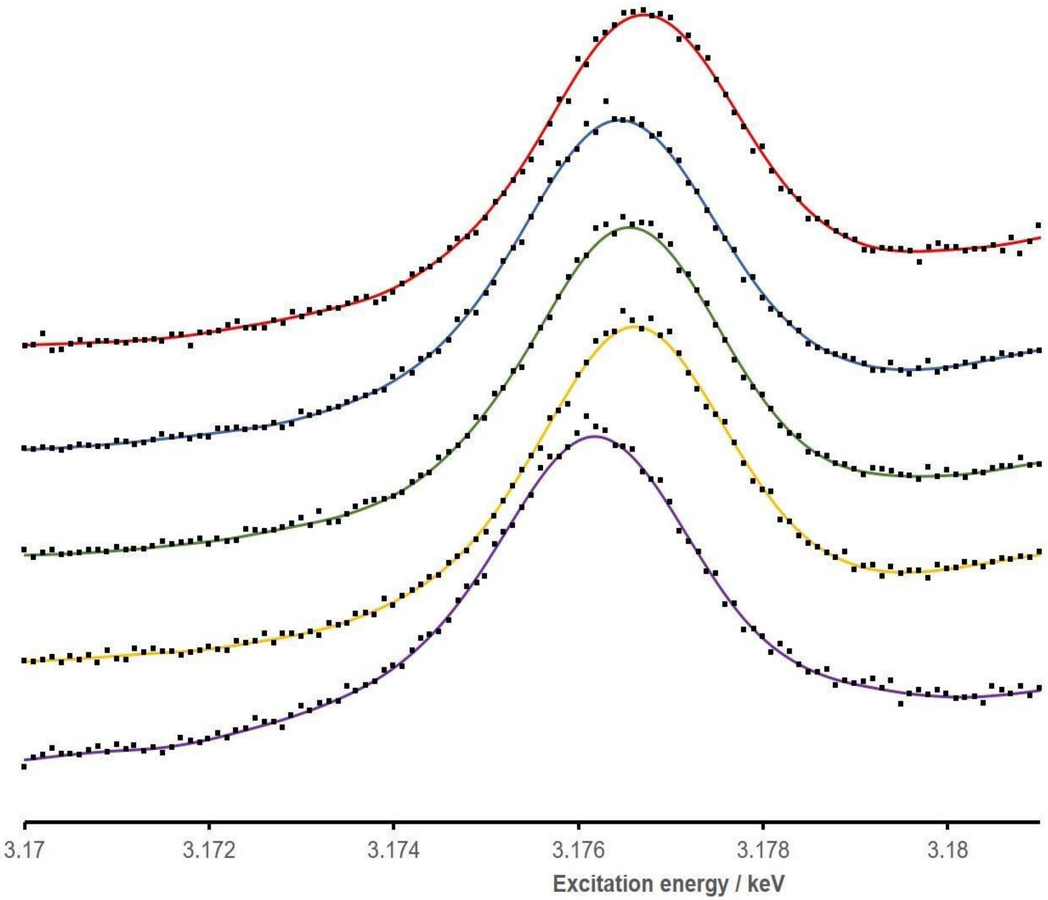


Figure S109 FD-XAS spectra showing the Pt L_{III} edges for **1c** (red), **2c** (blue), **3c** (green), **4c** (yellow) and Pd/C (purple). The raw data (black) has been overlaid on the smoothed versions.

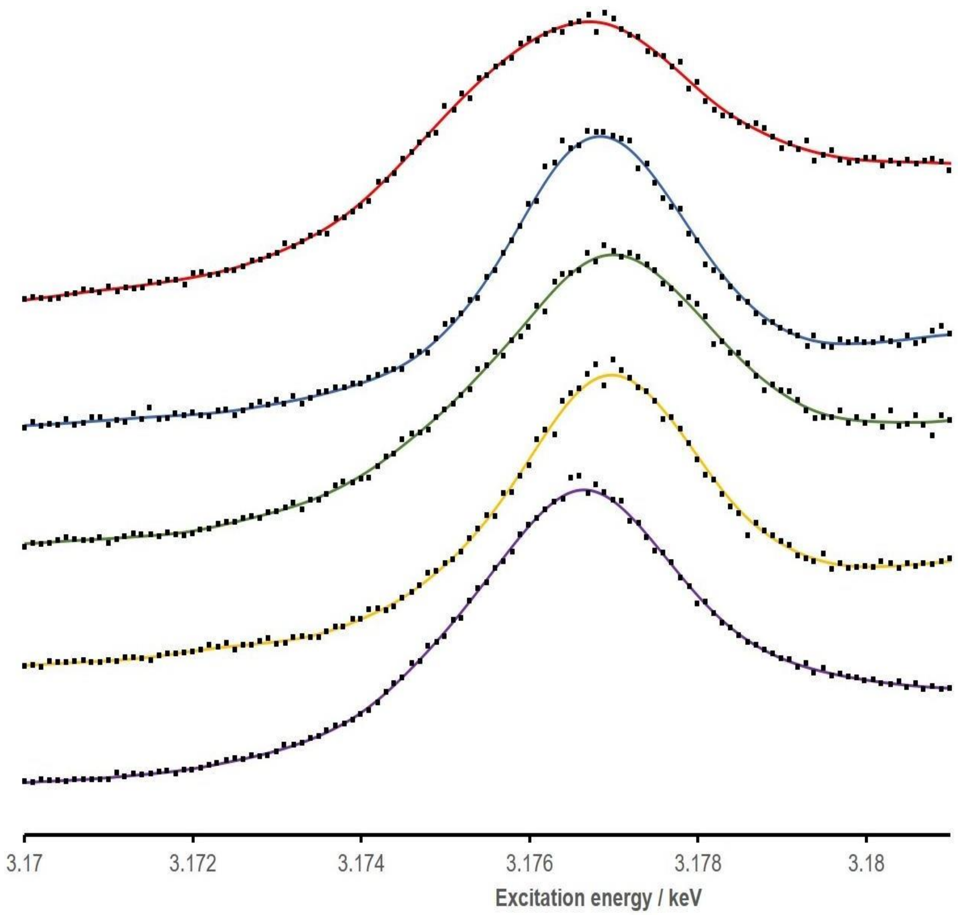


Figure S110 (a-d) TEM images of **2c** formed in situ and e) histogram showing the distribution of particle sizes (average NP diameter = 3.36 ± 0.61 nm). Scale bars 25 nm (black) and 5 nm (white).

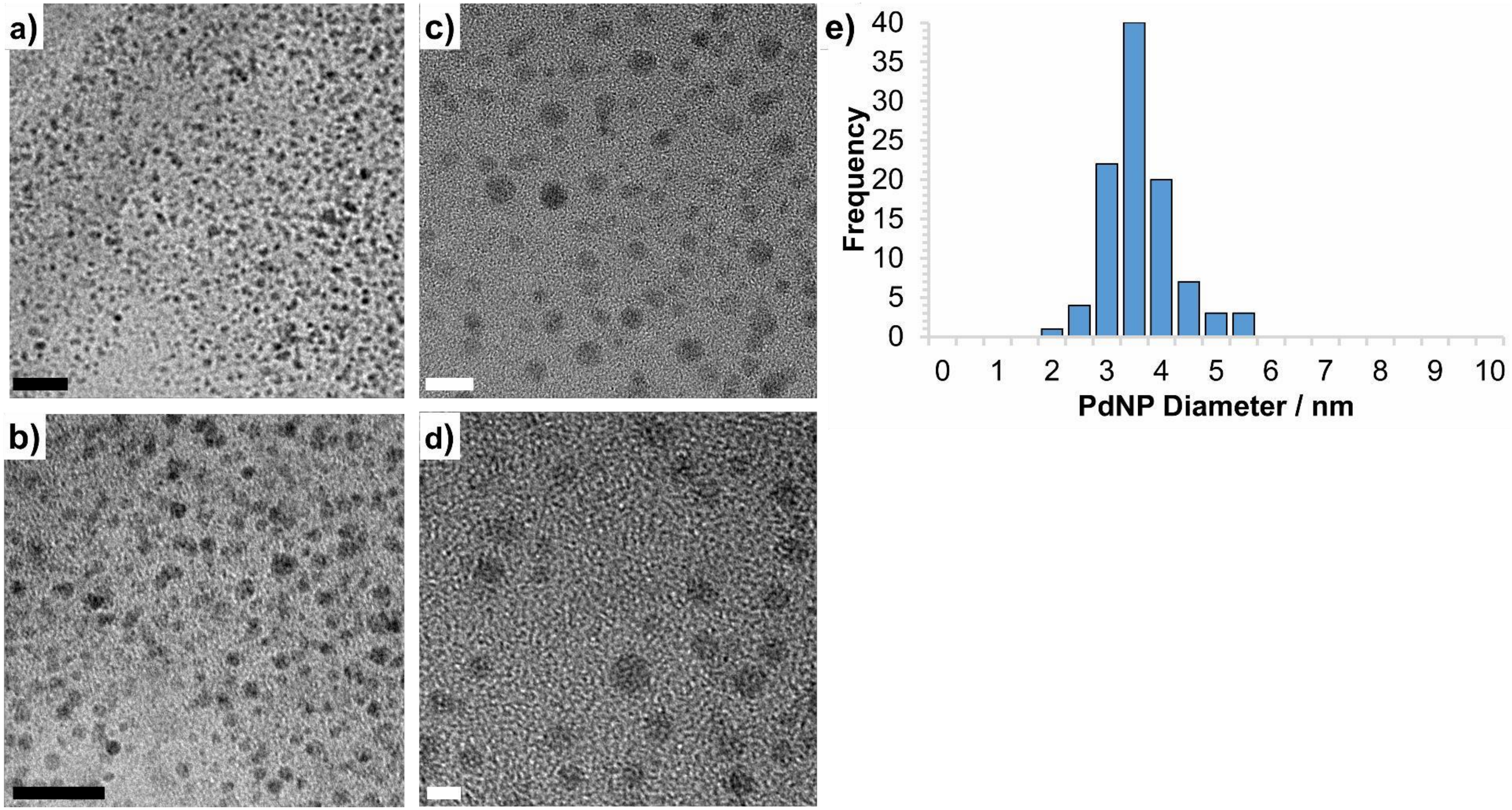


Figure S111 (a-d) TEM images of **4c** formed in situ and e) histogram showing the distribution of particle sizes (average NP diameter = 2.55 ± 0.97 nm). Scale bars 25 nm (black) and 5 nm (white).

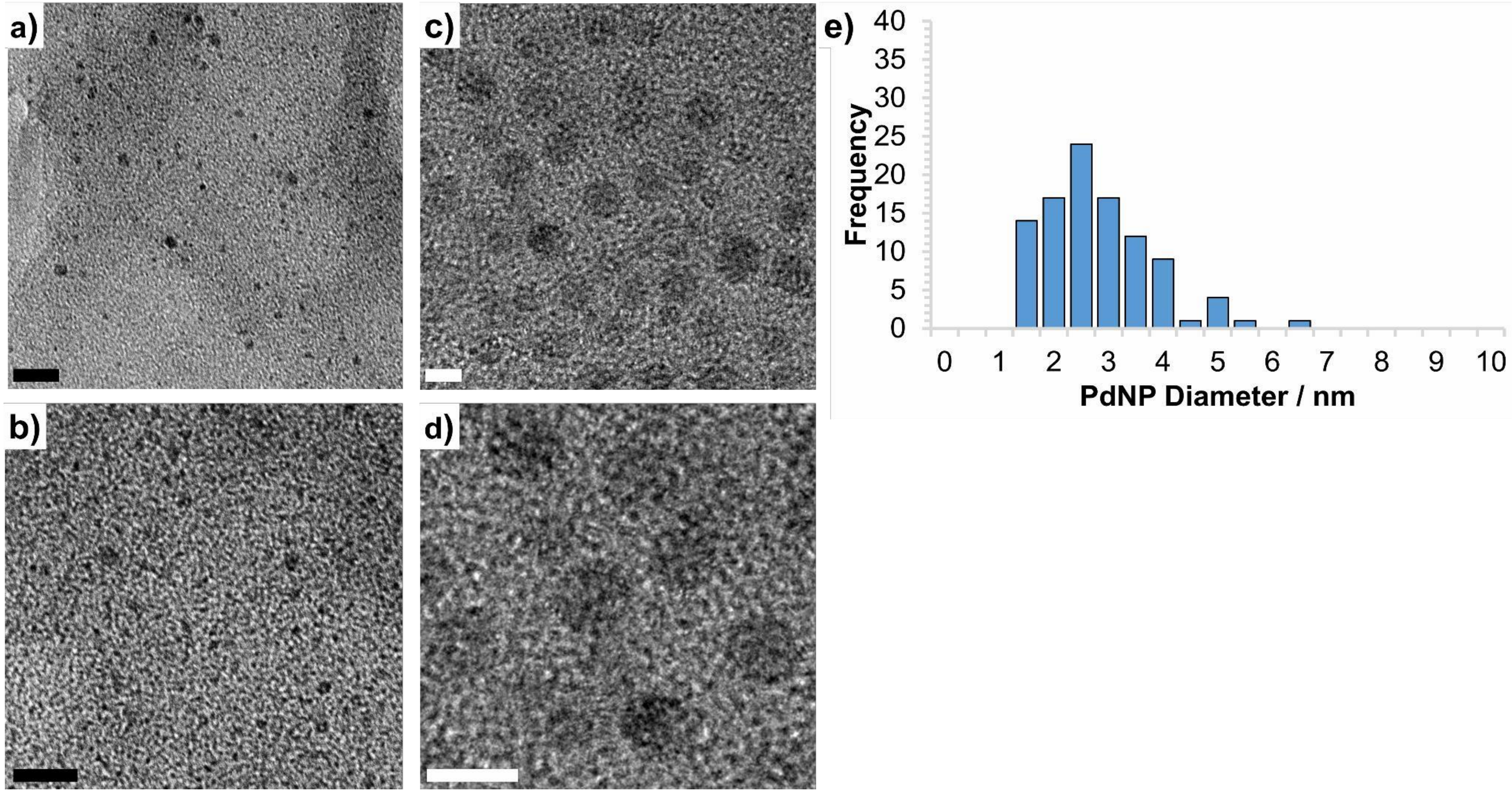
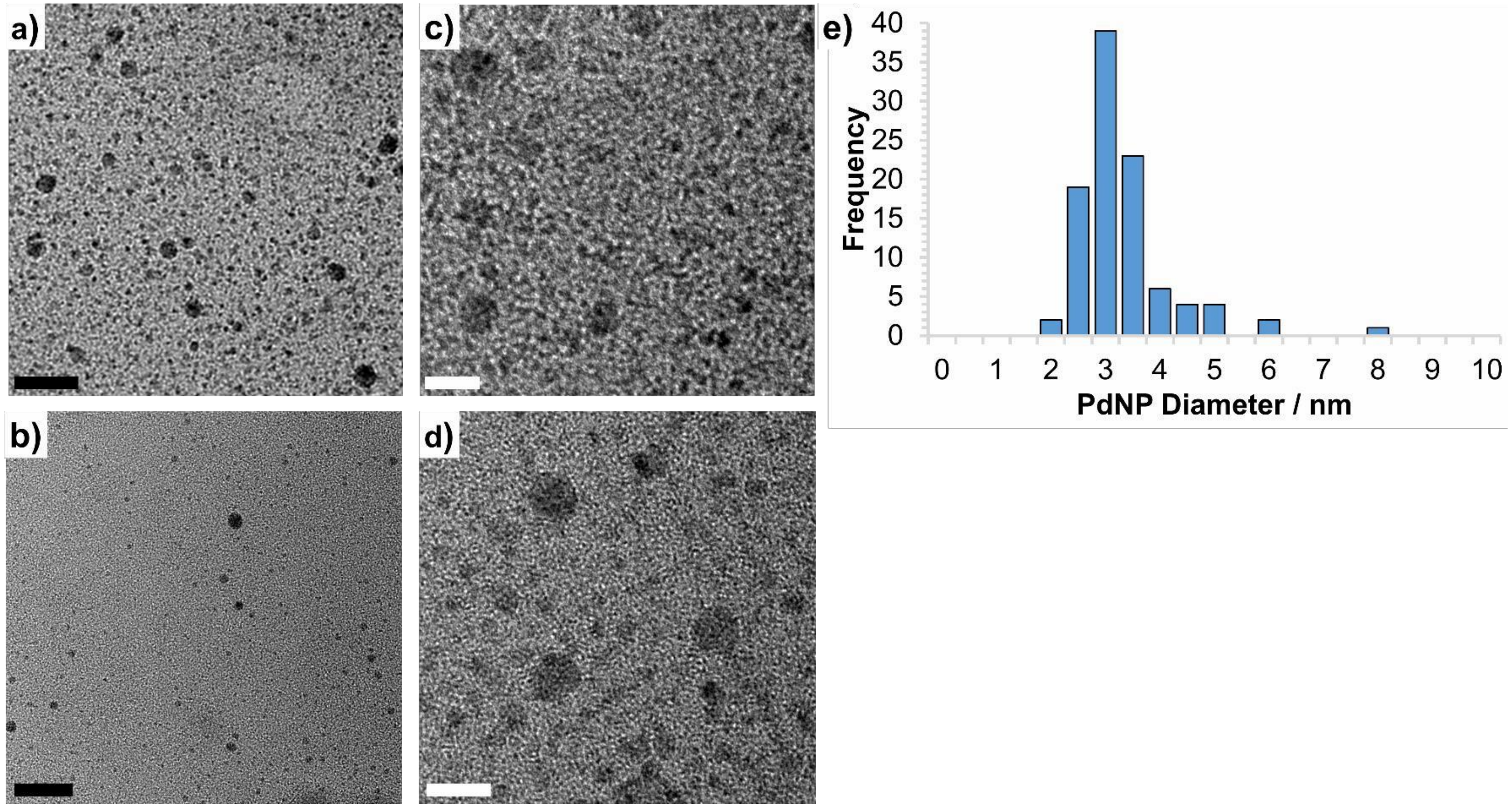


Figure S112 (a-d) TEM images of **2c** after recycling and e) histogram showing the distribution of particle sizes (average NP diameter = 3.05 ± 0.86 nm). Scale bars 25 nm (black) and 5 nm (white).



References

1 S. Doherty, J. G. Knight, T. Backhouse, E. Abood, H. Alshaikh, I. J. S. Fairlamb, R. A. Bourne, T. W. Chamberlain and R. Stones, *Green Chem.*, 2017, **19**, 1635-1641.