Supporting Information for Manuscript

Highly efficient and selective aqueous phase hydrogenation of aryl ketones, aldehydes, furfural and levulinic acid and its ethyl ester catalyzed by phosphine oxide-decorated polymer immobilized ionic liquid-stabilized ruthenium nanoparticles

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Contents

Experimental

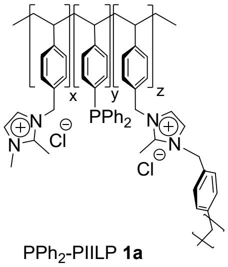
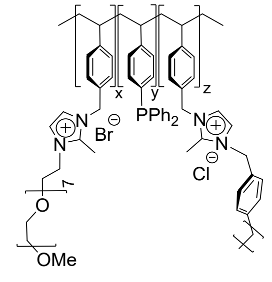
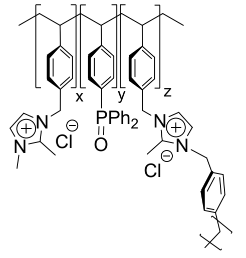
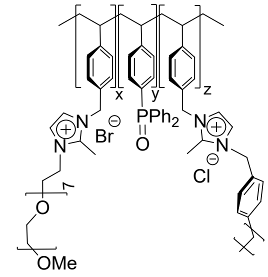
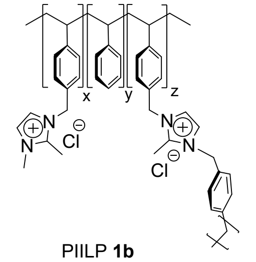
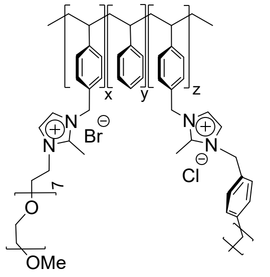
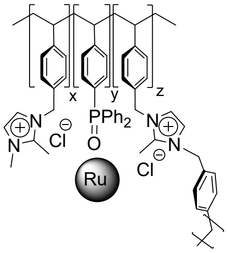
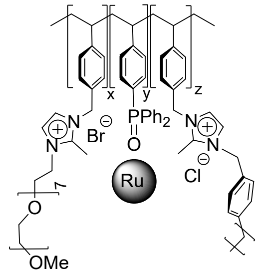
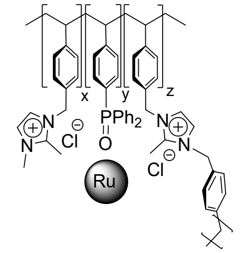
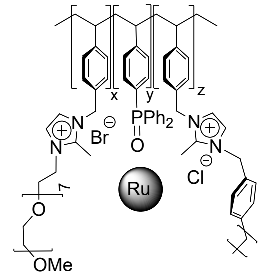
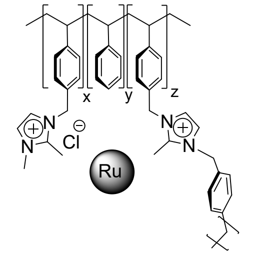
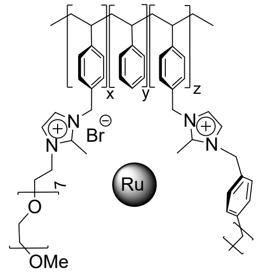
General Comments. All reagents were purchased from commercial suppliers and used without further purification. Monomers 1,2-dimethyl-3-(4-vinylbenzyl)-1H-imidazol-3-ium chloride and 2-methyl-1-(2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl)-3-(4-vinylbenzyl)-1H-3λ4-imidazolium chloride, polymers PPh_2-PIILP (**1a**), PPh_2-PEGPIILP (**1a.PEG**), PIILP (**1b**) and PEG-PIILP (**1b.PEG**) were prepared as previously described.[1] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on JEOL LAMBDA-500 or ECS-400 instruments. Solid-state ^{31}P spectra were recorded at 162.01 MHz using a Bruker Avance IIIHD 400 spectrometer and a 3.2 mm (rotor o.d.) magic-angle spinning probe. They were obtained using cross-polarization with a 2 s recycle delay, 2–3.5 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 10 kHz. Between 600 and 2000 repetitions were accumulated. Spectral referencing was with respect to an external sample of 85% phosphoric acid. Solid-state ^{13}C spectra were recorded at 100.64 MHz using a Bruker Avance IIIHD 400 spectrometer. They were obtained using cross-polarization with a 2.5 s recycle delay, 0.6-2 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 10 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). X-ray Photoelectron Spectroscopy (XPS) was performed with a Kratos AXIS Ultra DLD apparatus, with monochromated Al Kα radiation X-ray source, charge neutralizer and hemispherical electron energy analyser. During data acquisition, the analysis chamber pressure was kept below 10^{-9} mbar. The spectra were analysed in line with the Ru fitting parameters for RuO_2 as outlined by Morgan[1] using CasaXPS and corrected for charging using the C 1s feature at 284.8 eV. Peak fitting to a $Ru(OH)_3$ species was possible for all the catalysts but the fitting residuals improved when fitting a RuO_2 species. Fitting the data to a metallic Ru species in line with the parameters described by Morgan[1] did not give an appropriate fit. 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. Scanning transmission electron microscopy was performed on a FEI Titan3 Themis 300: X-FEG with an accelerating voltage of 300 KeV, fitted with a FEI Super-X-4-detector EDX system for elemental mapping. The ruthenium 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.) transmission with catalysts dispersed in KBr. ATR spectra were recorded using a PIKE ATR Max II accessory housed in a Bruker Tensor II spectrometer. The catalyst layers were prepared by depositing 1 ml of solution (ethanol or water) containing 10 mg of the respective catalyst (**2a**, **2a'**, **2b** or **2a.PEG**) onto a ZnSe crystal. The solution was left to dry in air overnight to form a catalyst film on the ZnSe crystal. The background spectrum was the respective dry catalyst layer which was recorded before introduction of ethanol (or water) to the catalyst. Once the solvent spectra were stable, the catalysts were exposed to $NaBH_4$/ethanol solution (15 min) before introduction of a flow of 10% CO/Ar to the cell to ensure the presence of metallic Ru nanoparticles. Spectra were recorded with 64 scans at a resolution of 4 cm^{-1}. Adsorption of CO over the RuNP@O=PPh_2-PEG-PIILP (**2a'.PEG**) catalyst was not possible as the catalyst layers deposited on the ATR crystal were unstable and removed under the solvent flow (before introduction of $NaBH_4$/ethanol). This was attributed to the increased hydrophilicity of this catalyst. All other catalyst layers were stable under the reaction conditions. CHN analysis was performed on a Carlo Erba 1108 Elemental Analyser and controlled with Carlo Erba Eager 200 software.

References

1. D. J. Morgan, *Surf. Interface Anal.*, 2015, **47**, 1072–1079.

Table S1 Structures of Polymers and PIILP-based Catalysts discussed in Table 1

 PPh$_2$-PIILP **1a**	 PPh$_2$-PEGPIILP **1a.PEG**	 O=PPh$_2$-PIILP **1a'**
 O=PPh$_2$-PEGPIILP **1a'.PEG**	 PIILP **1b**	 PEGPIILP **1b.PEG**
 RuNP@O=PPh$_2$-PIILP **2a**	 RuNP@O=PPh$_2$-PEGPIILP **2a.PEG**	 RuNP@O=PPh$_2$-PIILP **2a'**
 RuNP@O=PPh$_2$-PEGPIILP **2a'.PEG**	 RuNP@PIILP **2b**	 RuNP@PIILP **2b.PEG**

Synthesis of O=PPh$_2$-PIIL (1a`). An oven-dried Schlenk flask was charged with PPh$_2$-PIIL (5.0 g, 6.36 mmol) in dichloromethane (20 mL). To this, was added a solution of 35 wt% H_2O_2 (2 mL) in water (2 mL) and the resulting mixture stirred vigorously at room temperature overnight. After this, the reaction mixture was further diluted with dichloromethane (30 mL) and stirred with $MgSO_4$ (8 g) for 10 minutes. The reaction mixture was filtered, and the solvent was removed under reduced pressure to afford **1a`** as a white solid (5.03 g, 6.23 mmol, 98 % yield).

Synthesis of O=PPh$_2$-PEGPIIL (1a`.PEG). An oven-dried Schlenk flask was charged with PPh$_2$-PEGPIIL (5.0 g, 3.49 mmol) in dichloromethane (20 mL). To this, a solution of 35 wt% H_2O_2 (2 mL) in water (2 mL) was added and the resulting mixture stirred vigorously at room temperature overnight. After this, the reaction mixture was further diluted with dichloromethane (30 mL) and stirred with $MgSO_4$ (8 g) for 10 minutes. The reaction mixture was filtered with a funnel and the collected $MgSO_4$ filter was stirred with methanol (30 mL) for 10 minutes and filtered, the filtrate solvent was concentrated under reduced pressure to afford **1a`.PEG** as a white solid (4.54 g, 3.11 mmol, 89 % yield).

Synthesis of RuNP@O=PPh$_2$-PIILS (2a). A 100 mL round bottom flask was charged with **1a** (0.395 g, 0.5 mmol) suspended in ethanol (25 mL). To this, a solution of $RuCl_3{\cdot}3H_2O$ (0.13 g, 0.5 mmol) in ethanol (5 mL) was added in a single portion and the resulting mixture stirred vigorously at room temperature for 4 hours. After this time, the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.15 g, 4.0 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to green then black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was concentrated under reduced pressure to *ca*. 5 mL and added dropwise to cold acetone (300 mL). After stirring for 1 hour the solid was collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2a** as a black powder in 87%, yield (0.390 g). ICP-OES data: 2.88 wt% ruthenium and a ruthenium loading of 0.28 mmol g^{-1}.

Synthesis of RuNP@O=PPh$_2$-PEGPIILS (2a.PEG). A 100 mL round bottom flask was charged with **1a.PEG** (0.774 g, 0.5 mmol) suspended in ethanol (25 mL). To this, a solution of $RuCl_3{\cdot}3H_2O$ (0.13 g, 0.5 mmol) was added in a single portion and the mixture was stirred vigorously at room temperature for 4 hours. After this time, the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.15 g, 4 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to green then to black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was removed under reduced pressure, the resulting solid triturated with cold acetone collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2a.PEG** as a black powder in 79% yield (0.66 g). ICP-OES data: 4.48 wt% ruthenium and a ruthenium loading of 0.44 mmol g^{-1}.

Synthesis of RuNP@O=PPh$_2$-PIILS (2a`)**. A 100 mL round bottom flask was charged with **1a` (0.807 g, 1.0 mmol) suspended in ethanol (45 mL). To this, a solution of $RuCl_3{\cdot}3H_2O$ (0.26 g, 1.0 mmol) in ethanol (10 mL) was added in a single portion and the resulting mixture stirred vigorously at room temperature for 4 hours. After this time the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.30 g, 8.0 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to green then black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was concentrated under reduced pressure to *ca*. 5 mL and added dropwise to cold acetone (300 mL). After stirring for 1 hour the solid was collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2a`** as a black powder in 74%, yield (0.67 g). ICP-OES data: 3.61 wt% ruthenium and a ruthenium loading of 0.36 mmol g^{-1}.

Synthesis of RuNP@O=PPh$_2$-PEGPIILS (2a`.PEG)**. A 100 mL round bottom flask was charged with **1a`.PEG (1.17 g, 0.75 mmol) suspended in ethanol (35 mL). To this, a solution of $RuCl_3·3H_2O$ (0.195 g, 0.75 mmol) was added in a single portion and the mixture was stirred vigorously at room temperature for 4 hours. After this time, the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.23 g, 6.0 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to green then to black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was removed under reduced pressure to afford a black solid which was triturated with cold acetone collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2a`.PEG** as a black powder in 81% yield (1.01 g). ICP-OES data: 3.97 wt% ruthenium and a ruthenium loading of 0.39 mmol g^{-1}.

Synthesis of RuNP@PIILS (2b). A 100 mL round bottom flask was charged with **1b** (0.61g, 1.0 mmol) suspended in ethanol (20 mL). To this, a solution of $RuCl_3·3H_2O$ (0.260 g, 1.0 mmol) was added in a single portion and the mixture was stirred vigorously at room temperature for 4 hours. After this time, the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.30 g, 8.0 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was removed under reduced pressure to afford a black solid which was triturated with cold acetone, collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2b** as a black powder in 93% yield (0.66 g). ICP-OES data: 4.70 wt% ruthenium and a ruthenium loading of 0.47 mmol g^{-1}.

Synthesis of RuNP@PEGPIILS (2b.PEG). A 100 mL round bottom flask was charged with **1b.PEG** (1.36 g, 1.0 mmol) suspended in ethanol (20 mL). To this, a solution of $RuCl_3 \cdot 3H_2O$ (0.260 g, 1.0 mmol) was added in a single portion and the mixture was stirred vigorously at room temperature for 4 hours. After this time, the mixture was cooled to 0 °C and a solution of $NaBH_4$ (0.30 g, 8.0 mmol) in water (5 mL) was added dropwise. The mixture rapidly turned from dark brown to black and the resulting mixture was stirred vigorously overnight at room temperature under a nitrogen atmosphere. After this, the solvent was removed under reduced pressure to afford a black solid which was triturated with cold acetone, collected by filtration through a frit and washed with water (10 mL), ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL) to afford **2b.PEG** as a black powder in 78% yield 1.14 g). ICP-OES data: 1.41 wt% ruthenium and a ruthenium loading of 0.14 mmol g^{-1}.

General procedure for the selective hydrogenation of ketones and aldehydes to the corresponding aryl alcohol and characterisation data. All hydrogenations were conducted in a 50 mL temperature-controlled Parr benchtop reactor with a magnetically coupled stirrer and gas ballast. In a typical procedure, a 50 mL glass vessel was charged with substrate (1.0 mmol), the appropriate catalyst (0.1 mol % based on ruthenium content determined by ICP-OES) and 13 mL of the appropriate solvent. Reactions were conducted at 50 °C under 70 psi of hydrogen unless otherwise stated. Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds, before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 70 psi, heated to 50 °C and the solution stirred for the desired amount of time. For reactions conducted in ethanol, 2-methyl-THF, toluene, hexane or ethyl acetate, the mixture was passed through a silica plug and the solvent removed. If the reaction was conducted in aqueous medium, the mixture was transferred to a dropping funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was analysed by ^{1}H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and GC using n-decane as internal standard to quantify the composition of starting material and products and determine the selectivity. In all reactions mass balance was >99%. For each substrate, ^{1}H NMR spectra were recorded at relaxation times of 10, 20 and 30 seconds to ensure that peaks were integrated accurately.

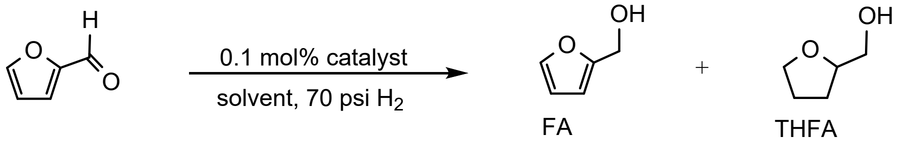
Hot Filtration Tests. Hot filtration studies were conducted in a 50 mL temperature-controlled Parr benchtop reactor with a magnetically coupled stirrer and gas ballast as described above. A 50 mL glass vessel was charged with acetophenone (0.117 mL, 1.0 mmol), 0.1 mol% catalyst **2a′.PEG** (1 μmol, 0.0026 g) and 13 mL of the water/ethanol (1:1, v/v). Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds, before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 70 psi, heated to 50 °C and the solution stirred. When the reaction had reached about 50% conversion, as judged by the conversion-time profile obtained under the same conditions (45 min), the reactor was vented to quench the reaction and the mixture filtered through a 0.45 μm syringe filter. The reactor was re-charged with the filtrate, pressurised to 70 psi as described above and heating continued for a further 3 h. After this time the mixture was transferred to a dropping funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue was analysed by ^1H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and GC using n-decane as internal standard to quantify the composition of starting material and products and determine the selectivity. In an alternative procedure, a hydrogenation of acetophenone (0.117 mL, 1.0 mmol) catalyzed by 0.1 mol% **2a′.PEG** (1 μmol, 0.0026 g) was allowed to reach completion after which time the reactor was vented, the reaction mixture filtered through a 0.45 μm syringe filter and a further portion of acetophenone added (0.117 mL, 1.0 mmol). The reactor was recharged with the resulting filtrate, pressurized to 70 psi and heating continued for an additional 4 h after which the reactor was vented, and the reaction mixture analyzed after an aqueous work-up as described above.

Scale-up hydrogenation of acetophenone. A scale up hydrogenation of acetophenone was conducted in a fully automated 75 mL temperature-controlled HEL DigiCAT benchtop reactor system with a magnetically coupled stirrer and gas ballast. The reactor was charged with acetophenone (1.17 mL, 10.0 mmol), 0.1 mol% catalyst **2a′.PEG** (10 μmol, 0.026 g) and 50 mL of the water/ethanol (1:1, v/v). Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds, before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 70 psi, heated to 50 °C and the solution stirred for 4 h. After this, the reactor was cooled to room temperature, the reaction mixture diluted with water and extracted with ethyl acetate (3 x 50 mL). The organic phases were combined, dried over $MgSO_4$, filtered, the solvent removed *in vacuo* and the residue analysed by ^1H NMR spectroscopy using 1,3-dinitrobenzene as internal standard.

Complete hydrogenation of substituted aryl ketones and benzaldehyde to the corresponding cyclohexylalcohol catalyzed by 2a.PEG. In a typical procedure, a 50 mL glass vessel was charged with acetophenone (0.12 g, 1 mmol), catalyst (0.1 mol % based on Ru content determined by ICP-OES) and the appropriate solvent (13 mL). Reactions were conducted at 110 °C under 400 psi of hydrogen unless otherwise stated. Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds, before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 400 psi, heated to 110 °C and the solution stirred for the desired amount of time. After this, the reactor was cooled to room temperature and the reaction mixture transferred to a dropping funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was analysed by ^1H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and GC using n-decane as internal standard to quantify the composition of starting material and products and determine the selectivity. In all reactions mass balance was >99%. For each substrate, ^1H NMR spectra were recorded at relaxation times of 10, 20 and 30 seconds to ensure that peaks were integrated accurately.

Selective hydrogenation of furfural to furfuryl alcohol catalyzed by 2a′.PEG. In a typical procedure, a 50 mL glass vessel was charged with furfural (0.98 g, 1 mmol), catalyst (0.1 mol % based on Ru content determined by ICP-OES) and solvent (13 mL). Reactions were conducted at 50 °C under 70 psi of hydrogen unless otherwise stated. Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 70 psi, heated to 50 °C and the solution stirred for the desired amount of time. After this, the reactor was cooled to room temperature and the reaction mixture was transferred to a separating funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was analysed by ^1H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and GC using n-decane as internal standard to quantify the composition of starting material and products and determine the selectivity. In all reactions mass balance was >99%. For each substrate, ^1H NMR spectra were recorded at relaxation times of 10, 20 and 30 seconds to ensure that peaks were integrated accurately.

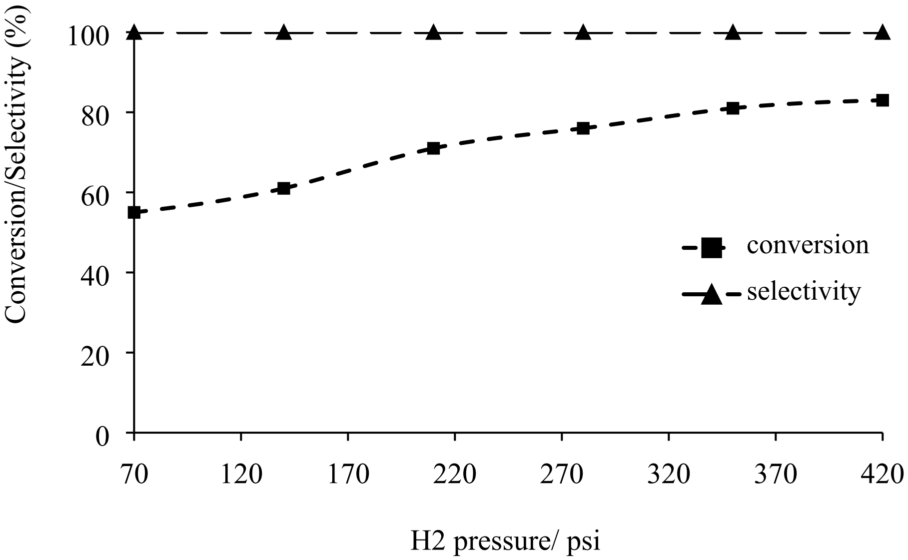
Table S2 Selective hydrogenation of furfural to furfuryl alcohol as a function of catalyst, solvent and base.[a]



Entry	Catalyst	Solvent	Base	Conv. (%)[c]	Selectivity (%)[d]
1	**2a′.PEG**	water	-	87	100
2	**2a′.PEG**	EtOH	-	71	100
3	**2a′.PEG**	water/EtOH	-	76	100
4	**2a′.PEG**	toluene	-	32	100
5	**2a′.PEG**	2-Me-THF	-	39	100
6[b]	**2a′.PEG**	water	K_2CO_3	84	100
7[b]	**2a′.PEG**	water	Na_2CO_3	87	100
8[b]	**2a′.PEG**	water	NaOAc	81	100
9[b]	**2a′.PEG**	water	K_3PO_4	83	100
10	**2a**	water	-	75	100
11	**a2.PEG**	water	-	80	100
12	**2a′**	water	-	77	100
13	**2b**	water	-	59	100
14	**b2.PEG**	water	-	61	100
16	**5% Ru/C**	water	-	21	100

[a] Reaction conditions: 1 mmol of furfural, 0.1 mol% Ru in **2a**, **2a.PEG**, **2a′**, **2a′.PEG**, **2b**, **2b.PEG** and 5 wt% Ru/C, 13 mL solvent, 3 h, 50 ºC, 70 psi H_2. [b] 10 mol% added base. [c] Conversions determined by ^1H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and gas chromatography using decane as internal standard. Average of at least three runs. [d] Selectivity for furfuryl alcohol = [% furfuryl alcohol/(% furfuryl alcohol) + (% tetrahydrofurfuryl alcohol)] x 100%.

Figure S1. Reaction profile and selectivity for furfuryl alcohol (FFA) as a function of pressure for the hydrogenation of furfural in a water after 45 min at 50 °C catalyzed by 0.1 mol% **2a`.PEG**.

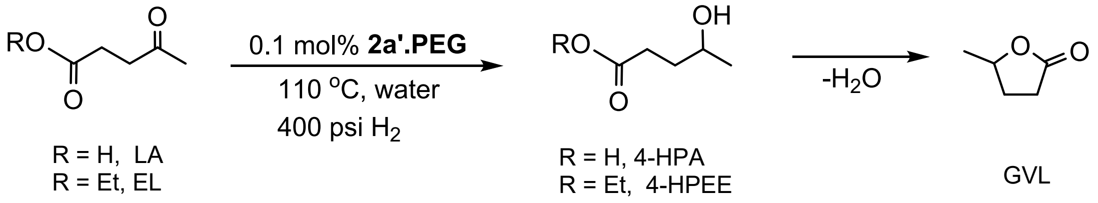


Reaction conditions: 1 mmol of furfural, 0.1 mol% Ru in **2a′.PEG**, 13 mL water, 45 min, 50 ºC.

General procedure for the selective hydrogenation of levulinic acid to γ-valerolactone catalyzed by 2a′.PEG. In a typical procedure, a 50 mL glass vessel was charged with levulinic acid (0.12 g, 1 mmol), catalyst (0.1 mol % based on Ru content determined by ICP-OES) and solvent (13 mL). Reactions were conducted at 110 °C under 400 psi of hydrogen unless otherwise stated. Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 400 psi, heated to 110 °C and the solution stirred for the desired amount of time. After this, the reactor was cooled to room temperature and the reaction mixture transferred to a dropping funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Conversion and selectivity were determined using ^{1}H NMR spectroscopy by quantifying the remaining starting material and products against 1,3-dinitrobenzene as the internal standard. In all reactions mass balance was >99%. Well-resolved resonances were used to calculate the composition of the mixture by normalising the relative integrations according to the number of protons associated with the chosen peaks. For each substrate, ^{1}H NMR spectra were recorded at relaxation times of 10, 20 and 30 seconds to ensure that peaks were integrated accurately.

General procedure for the selective hydrogenation of ethyl levulinate to γ-valerolactone catalyzed by 2a`.PEG. In a typical procedure, q 50 mL glass vessel was charged with ethyl levulinate (0.14 g, 1 mmol), potassium carbonate (0.013 g, 0.1 mmol), catalyst (0.1 mol % based on Ru content determined by ICP-OES) and solvent (13 mL). Reactions were conducted at 110 °C under 450 psi of hydrogen unless otherwise stated. Once assembled, the reactor was pressurised to 100 psi of hydrogen and left for 10 seconds before releasing the gas through the outlet valve. After repeating the sequence five times, the reactor was pressurised to 450 psi, heated to 110 °C and the solution was stirred for the desired amount of time. After this, the reactor was cooled to room temperature and the reaction mixture was transferred to a dropping funnel and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Conversion and selectivity were determined using ^{1}H NMR spectroscopy by quantifying the remaining starting material and products against 1,3-dinitrobenzene as internal standard. In all reactions mass balance was >99%. Well-resolved resonances were used to calculate the composition of the mixture by normalising the relative integrations according to the number of protons associated with the chosen peaks. For each substrate, ^{1}H NMR spectra were recorded at relaxation times of 10, 20 and 30 seconds to ensure that peaks were integrated accurately.

Table S3 Selective hydrogenation of levulinic acid to γ-valerolactone as a function of catalyst, solvent and base.[a]



Entry	Catalyst	Time (h)	Solvent	Base	Conv. (%)[c]	Selectivity (%)[d]
1	**2a′.PEG**	2	water	-	68	96
2	**2a′.PEG**	3	water	-	89	85
3	**2a′.PEG**	4	water	-	100	82
4	**2a′.PEG**	6	water	-	100	93
5	**2a′.PEG**	8	water	-	100	100
6[b]	**2a′.PEG**	8	water	K_2CO_3	57	74
7[b]	**2a′.PEG**	8	water	NaOAc	52	77
8[b]	**2a′.PEG**	8	water	K_3PO_4	49	79
9	**2a′.PEG**	2	water	Amberlyst	70	99
10	**2a′.PEG**	3	water	Amberlyst	89	100
11	**2a′.PEG**	4	water	Amberlyst	100	100
12	**a2**	8	water	-	63	94
13	**a.PEG2**	8	water	-	100	96
14	**2a`**	8	water	-	65	95
15	**b2**	8	water	-	68	91
16	**2b.PEG**	8	water	-	66	95
17	**5% Ru/C**	8	water	-	39	92

[a] Reaction conditions: 1 mmol of levulinic acid, 0.1 mol% Ru in **2a**, **2a.PEG**, **2a′**, **2a′.PEG**, **2b**, **2b.PEG** and 5 wt% Ru/C, 13 mL water, time (h), 110 ºC, 400 psi H_2. [b] 10 mol% added base. [c] Conversions determined by ^{1}H NMR spectroscopy using 1,3-dinitrobenzene as internal standard and gas chromatography using decane as internal standard. Average of at least three runs. [d] Selectivity for γ-valerolactone = [% γ-valerolactone /(% γ-valerolactone) + (% 4-hydroxypentanoic acid)] x 100%.

Figure S2 Solid state ^{13}C NMR spectrum of O=PPh$_2$-PIIL (**1a`**)

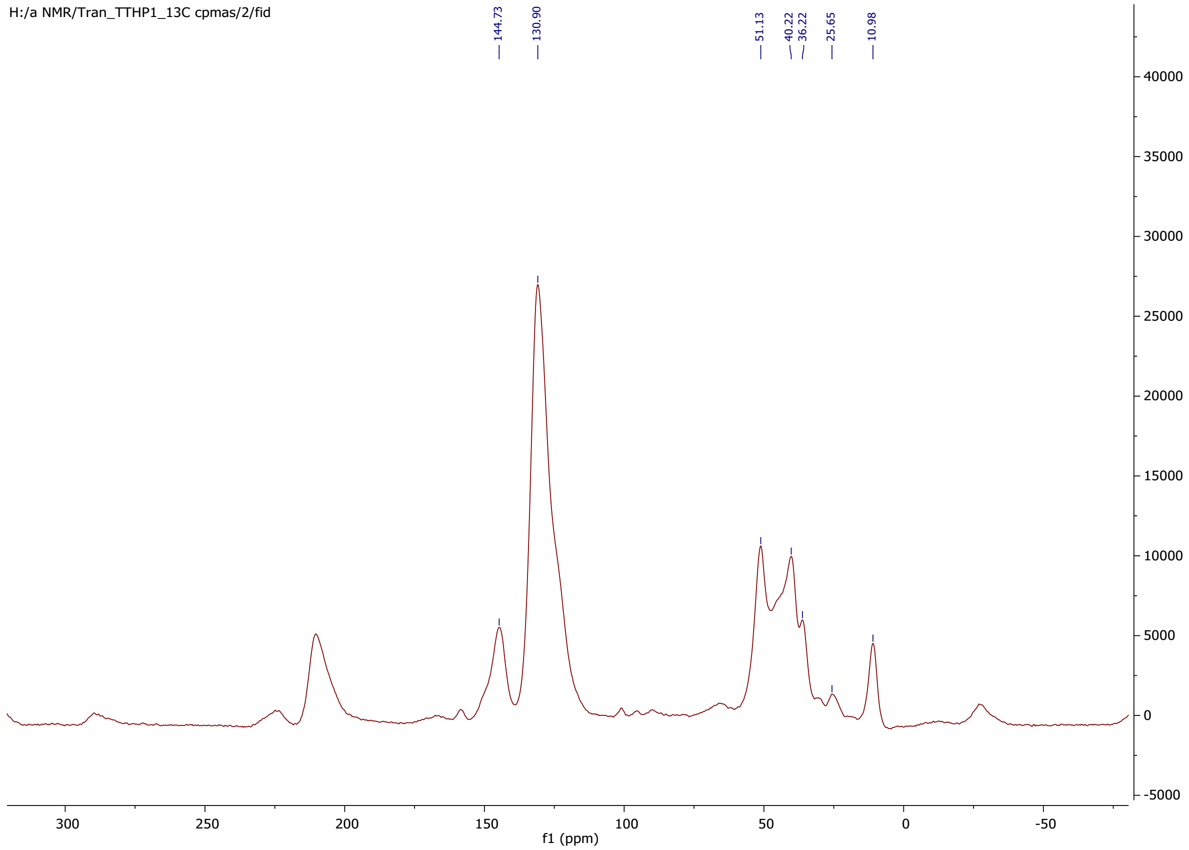


Figure S3 Solid state ^{31}P NMR spectrum of O=PPh$_2$-PIIL (**1a`**)

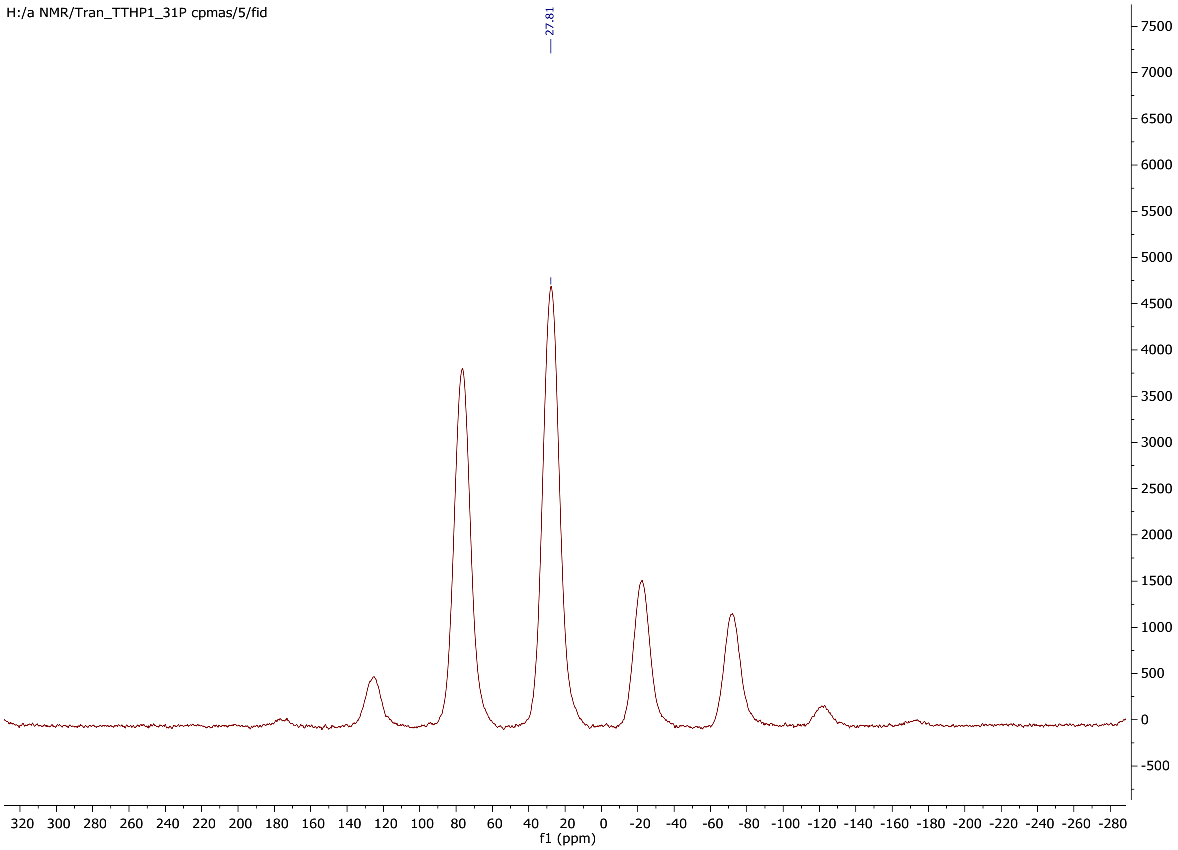


Figure S4 SEM image of freshly prepared O=PPh$_2$-PIIL (**1a`**)

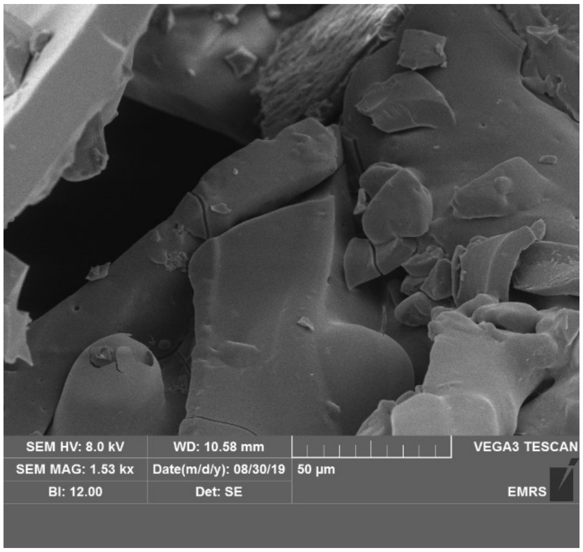


Figure S5 FT-IR spectrum of freshly prepared O=PPh_2-PIIL (**1a`**)

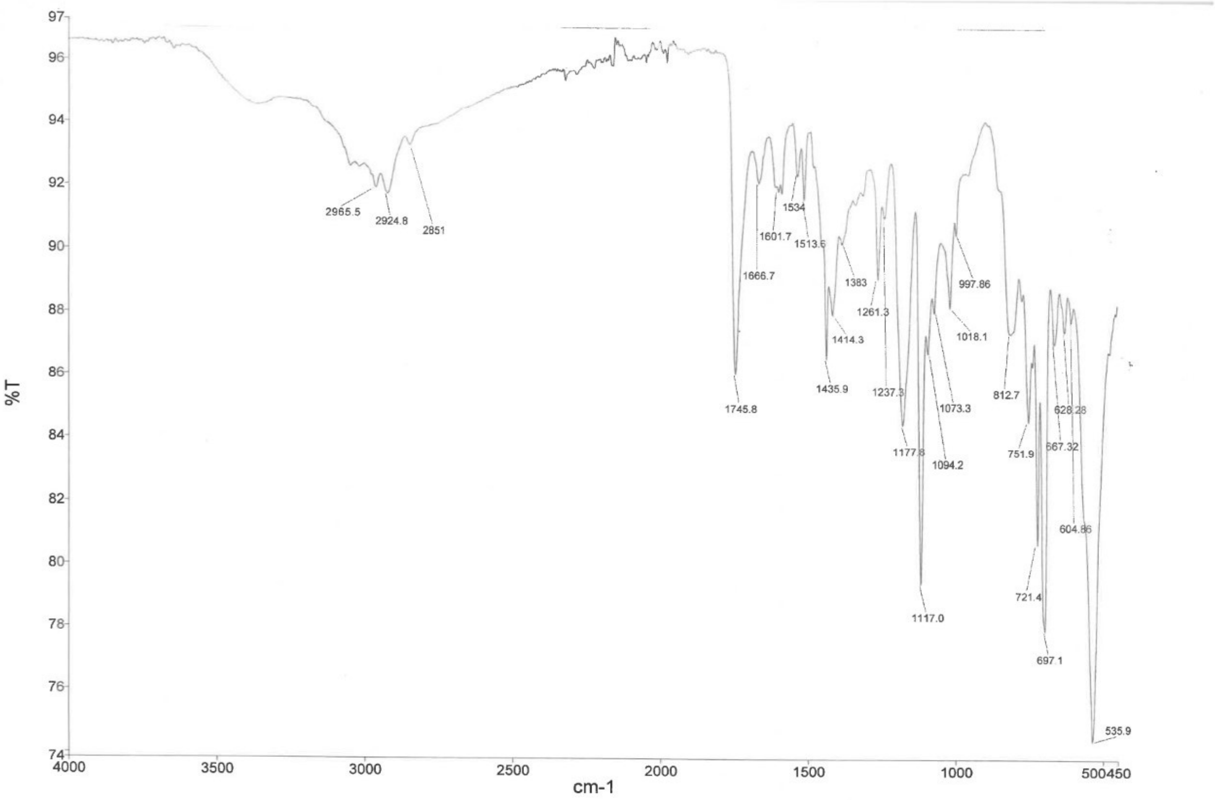


Figure S6 TGA curve for O=PPh$_2$-PIIL (**1a`**); wt% v temperature. Heating rate of 10 °C min^{-1} in air.

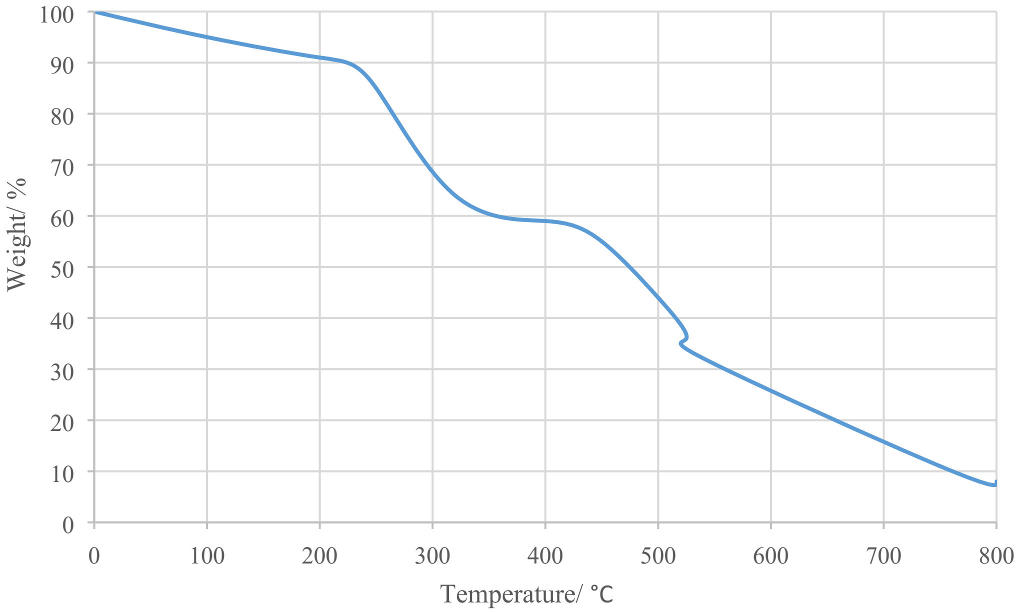


Figure S7 Solid state ^{13}C NMR spectrum of O=PPh$_2$-PEGPIIL (**1a`.PEG**)

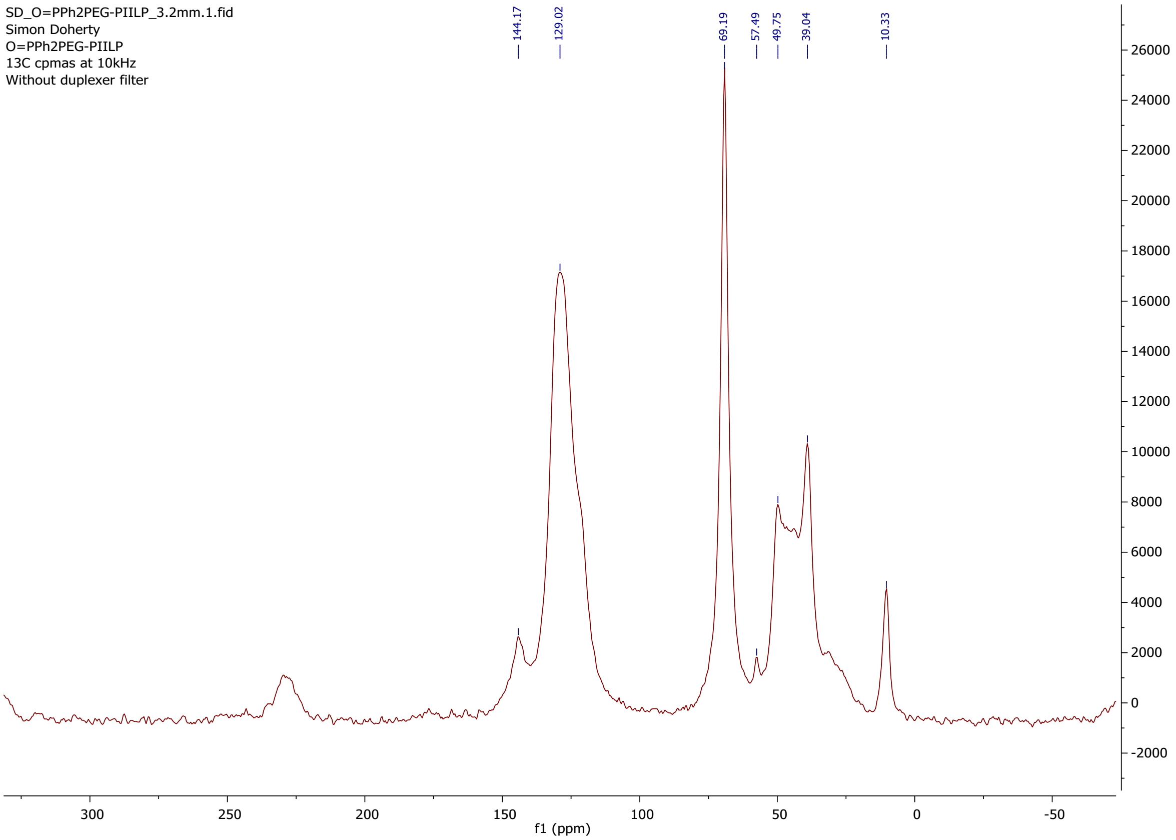


Figure S8 Solid state ^{31}P NMR spectrum of O=PPh$_2$-PEGPIIL (**1a`.PEG**)

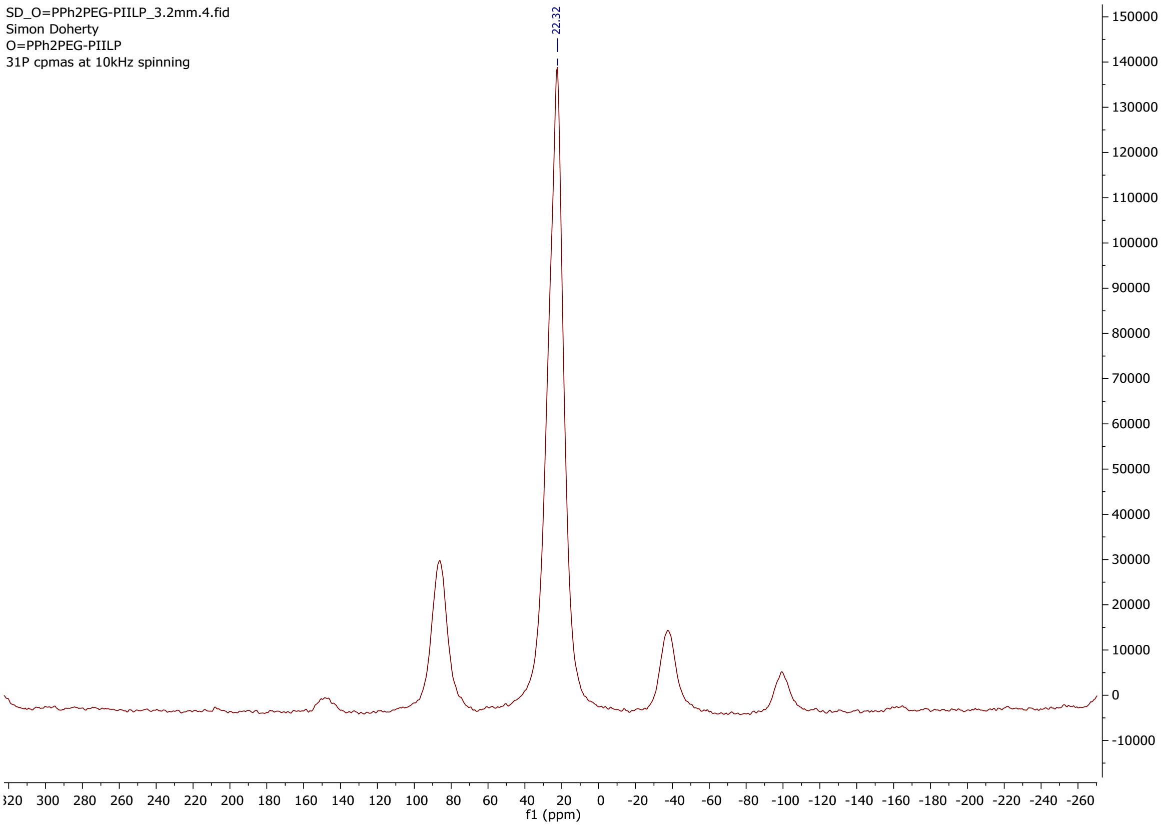


Figure S9 SEM image of freshly prepared O=PPh$_2$-PEGPIIL (**1a`.PEG**)

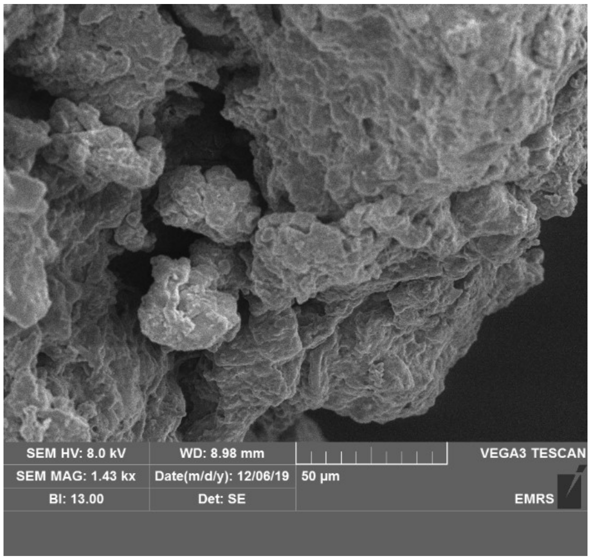


Figure S10 FT-IR spectrum of freshly prepared O=PPh$_2$-PEGPIIL (**1a`.PEG**)

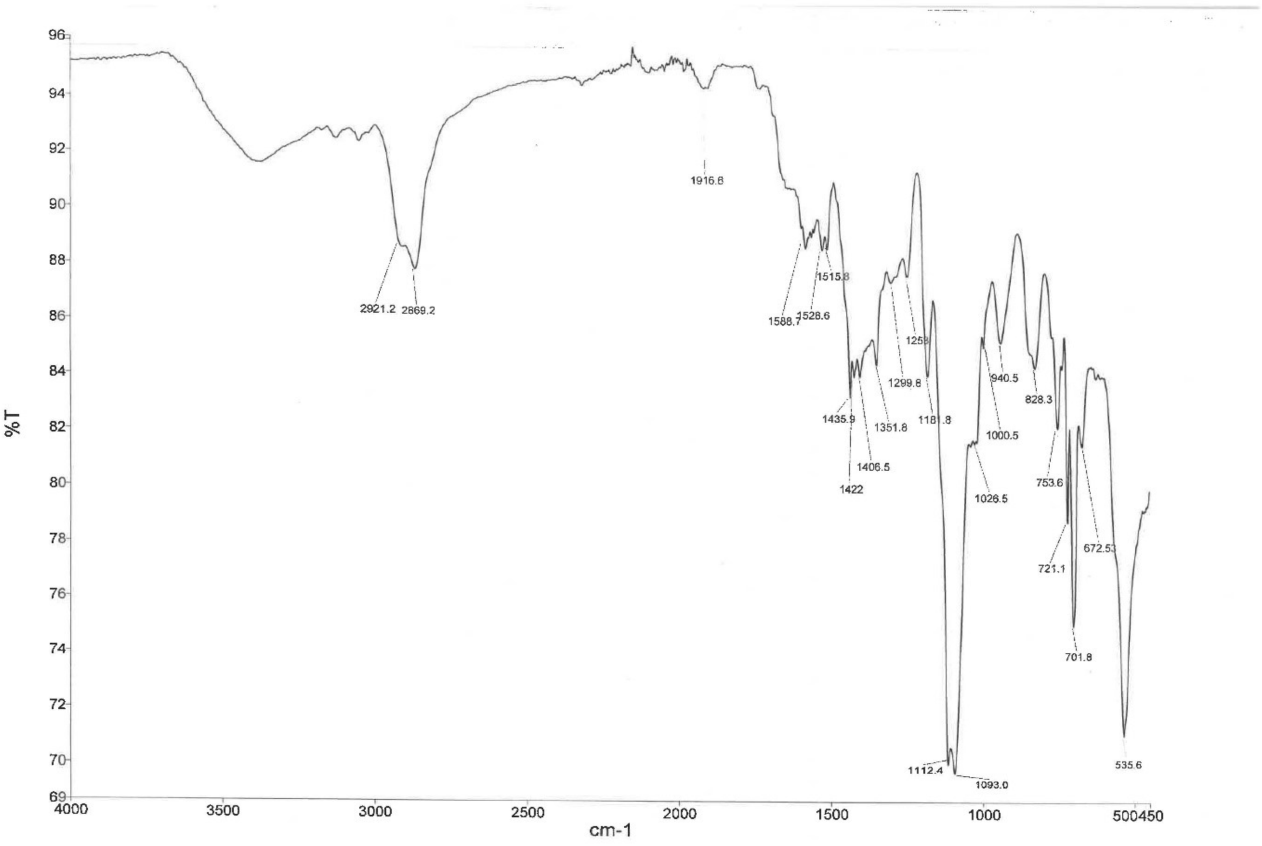


Figure S11 TGA curve for O=PPh$_2$-PEGPIIL (**1a`.PEG**); wt% v temperature. Heating rate of 10 °C min^{-1} in air.

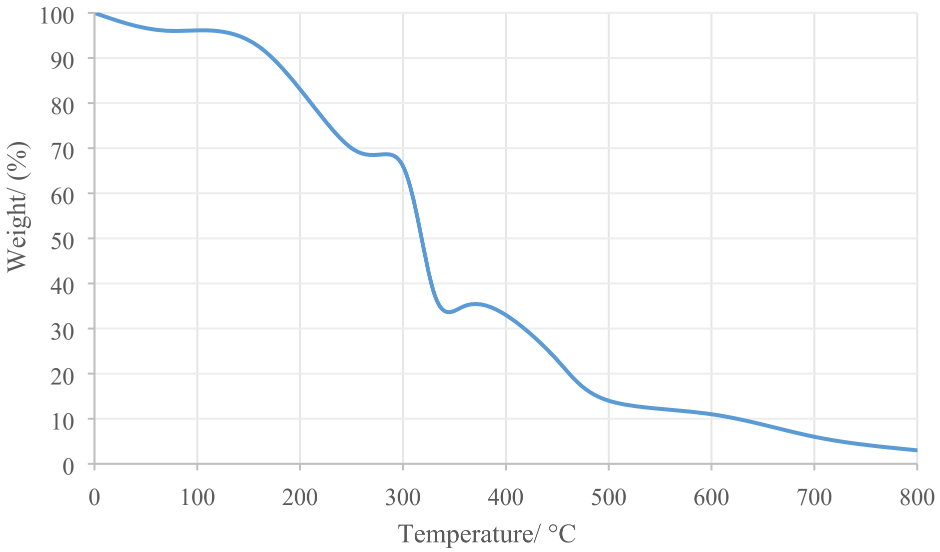


Figure S12 Solid state ^{13}C NMR spectrum of RuNP@O=PPh$_2$-PIILS (**2a**)

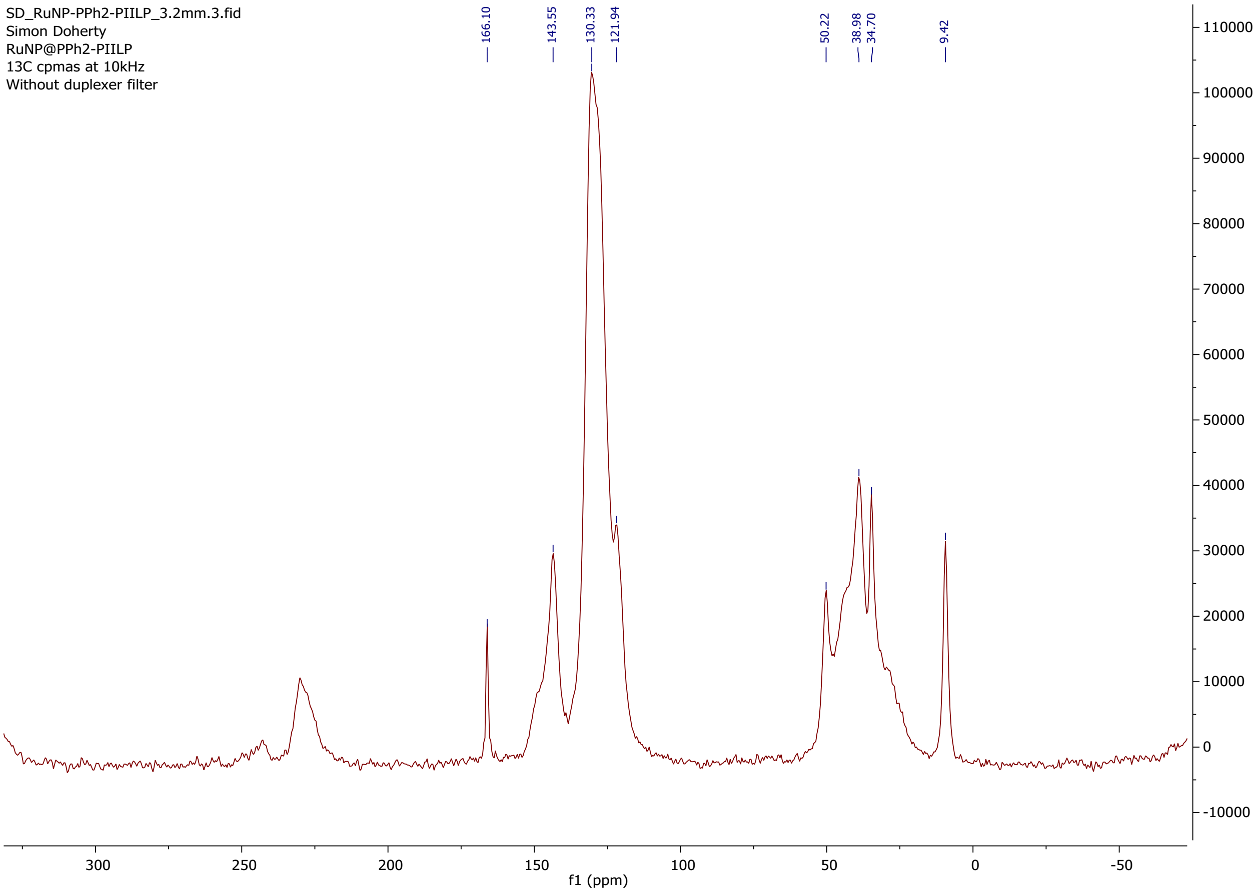


Figure S13 Solid state ^{31}P NMR spectrum of RuNP@O=PPh$_2$-PIILS (**2a**)

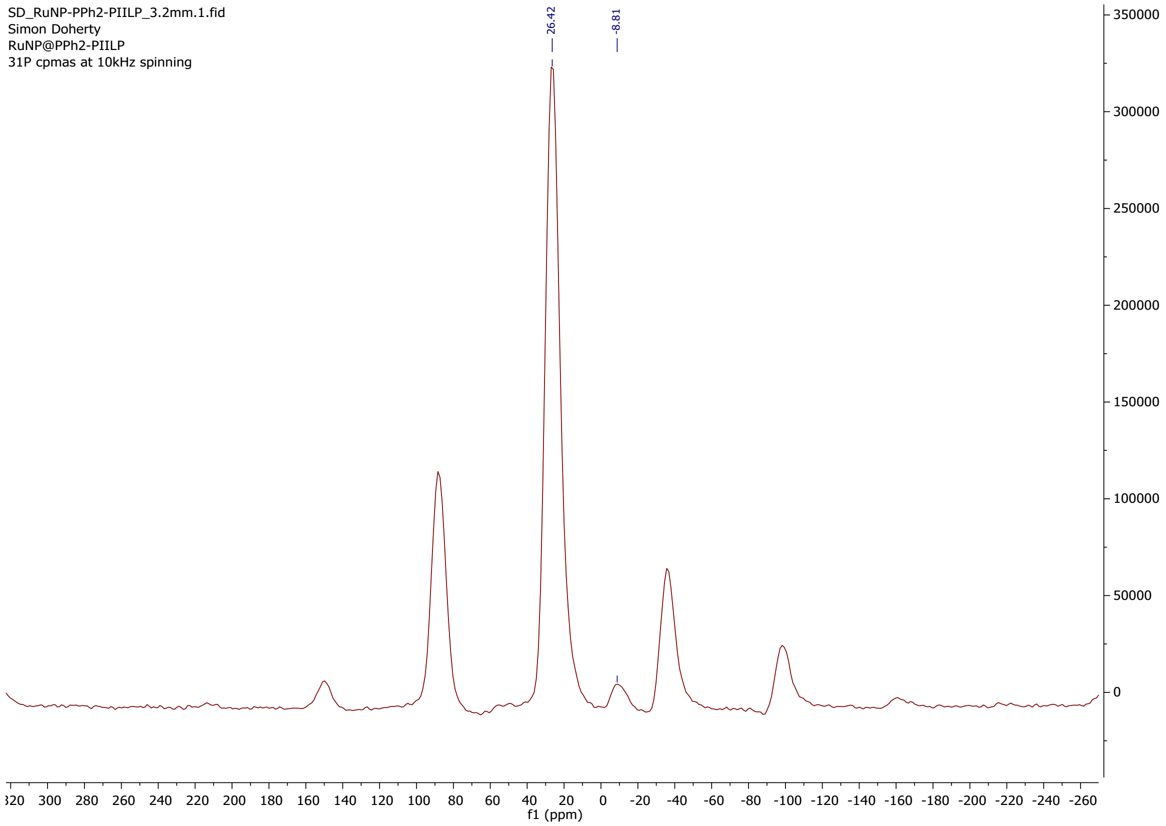


Figure S14 SEM image of freshly prepared RuNP@O=PPh$_2$-PIILS (**2a**)

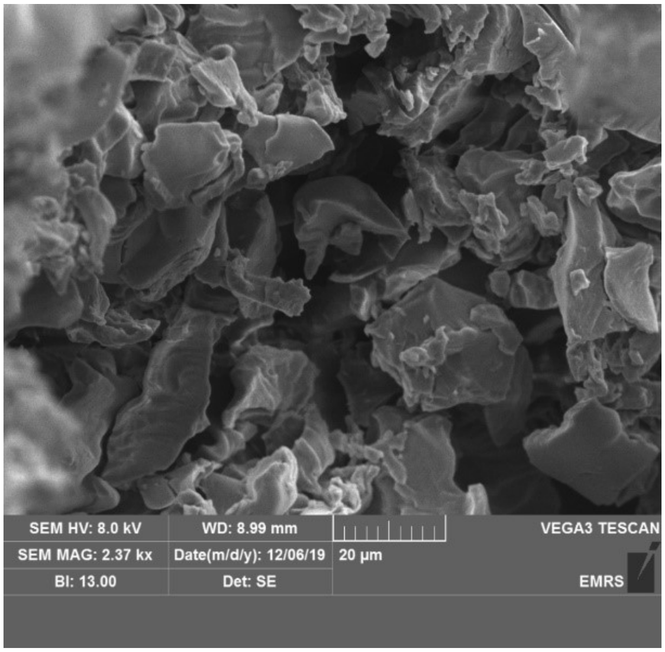


Figure S15 FT-IR spectrum of freshly prepared RuNP@O=PPh_2-PIILS (**2a**)

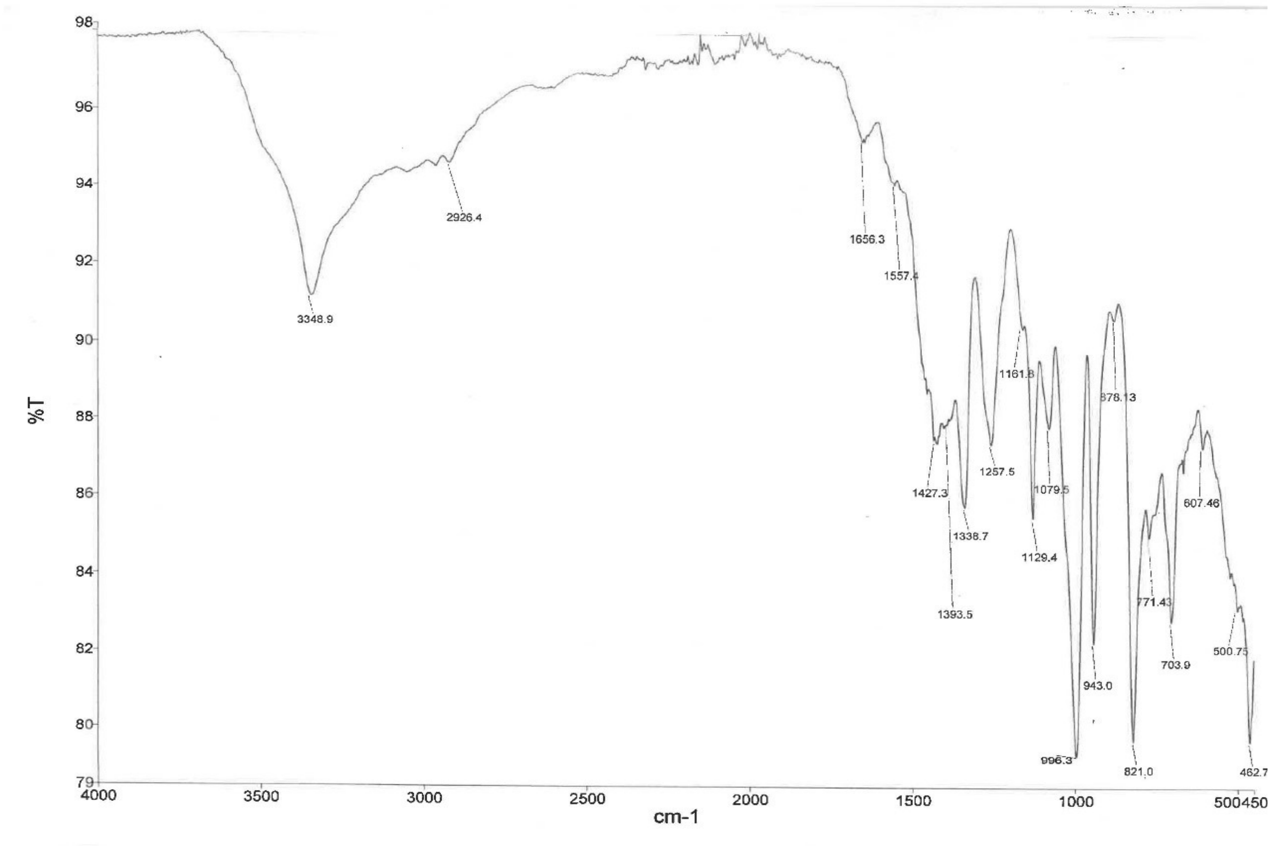


Figure S16 XPS spectrum of the P 2p region for RuNP@O=PPh_2-PIILS (**2a**)

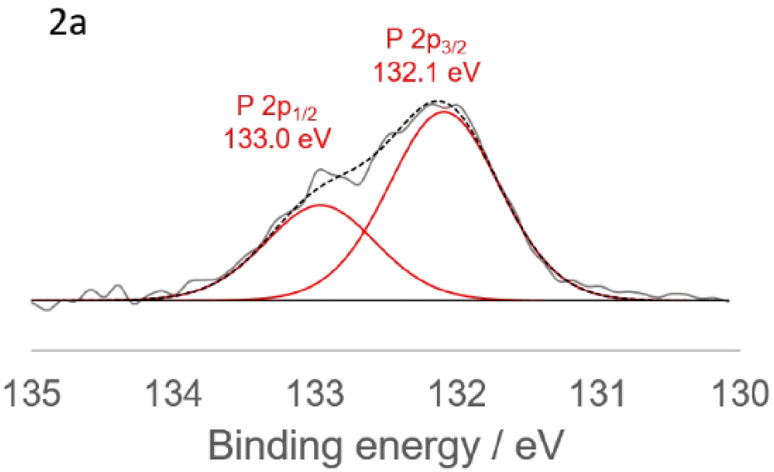


Figure S17 Ru 3p core level XPS spectra for RuNP@O=PPh$_2$-PIILS (**2a**) referenced to the C 1s alkyl peak at 284.8 eV.

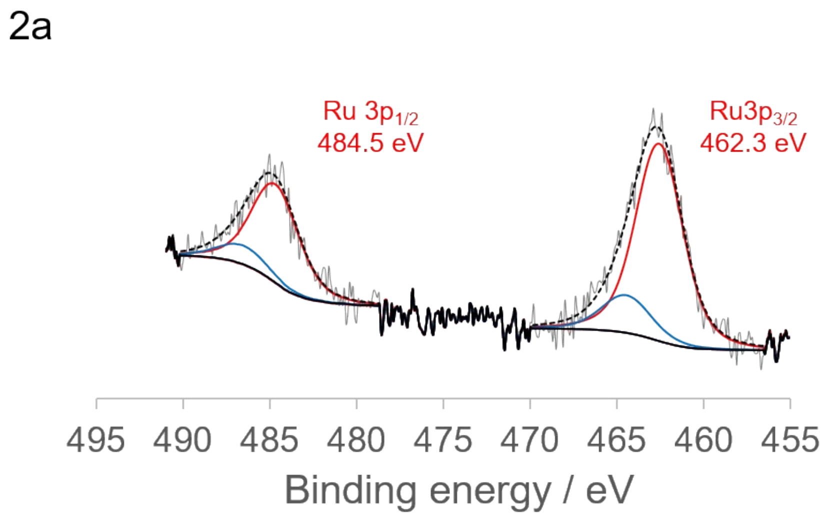


Figure S18 (a-d) TEM images of RuNP@O=PPh$_2$-PIILS (**2a**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 20 nm (black).

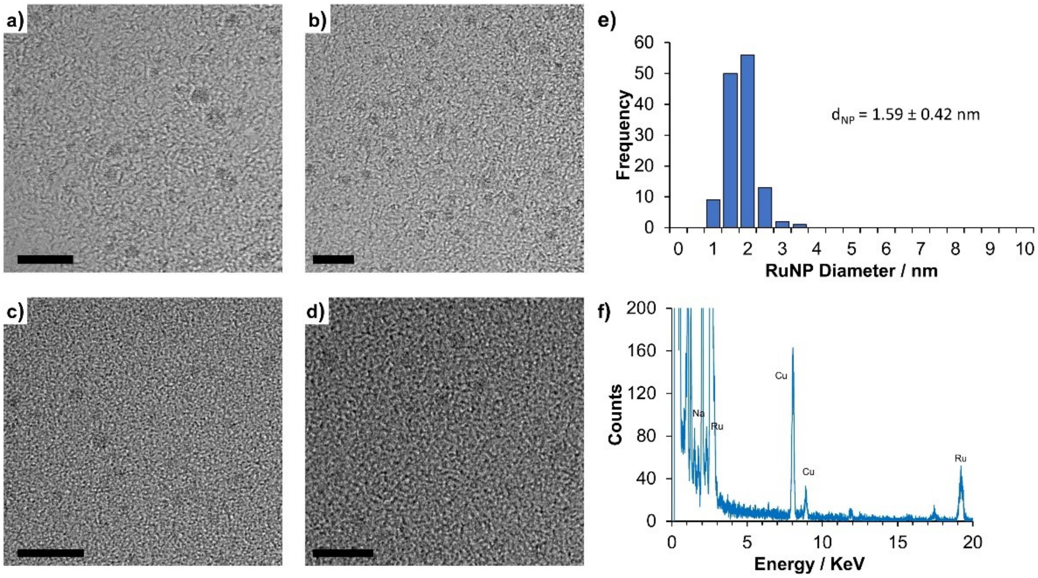


Figure S19 a) HRTEM micrograph of **2a** and enlarged views of a single RuNPs, b) 1 and c) 2. Scale bars are 10 nm (white) and 0.5 nm (black).

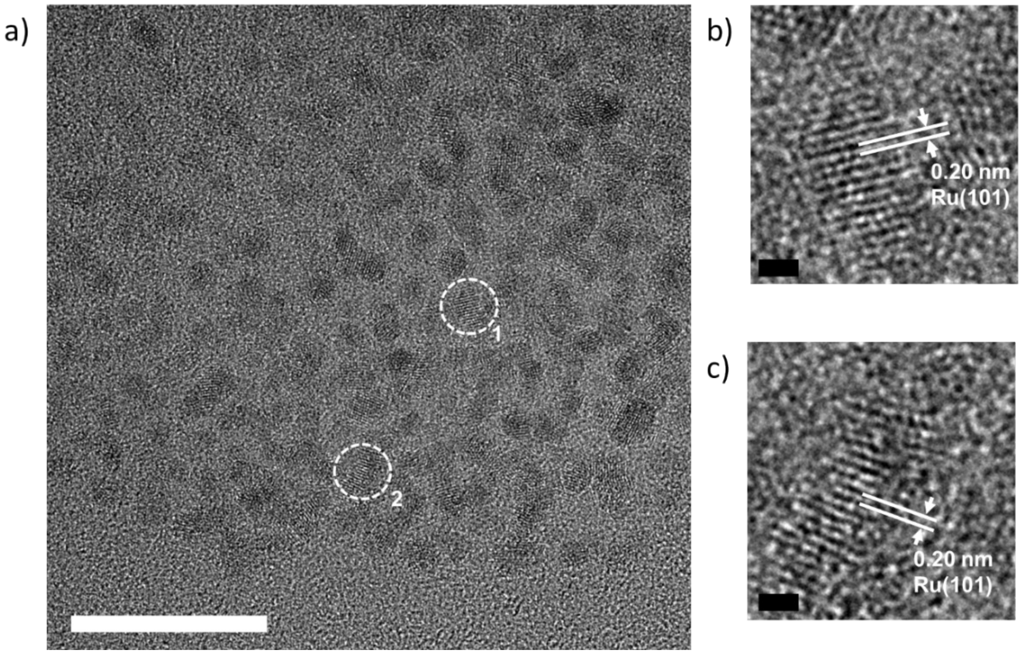


Figure S20 a) HRTEM micrograph of **2a** and b) an enlarged view of a single RuNPs. Scale bars are 10 nm (white) and 0.5 nm (black).

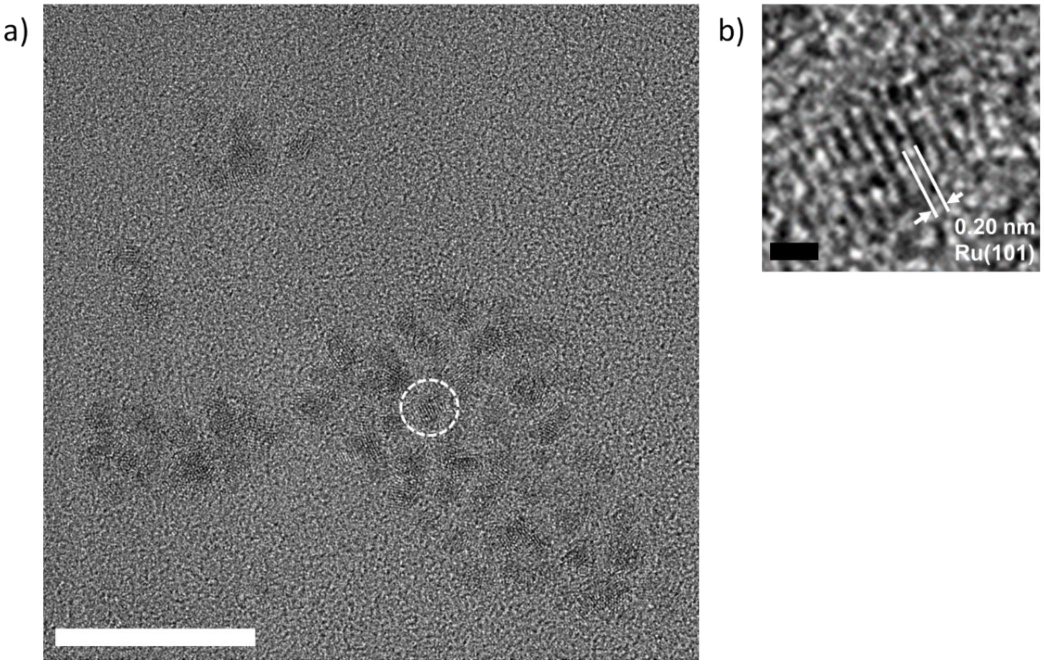


Figure S21 HAADF STEM micrographs of **2a**.

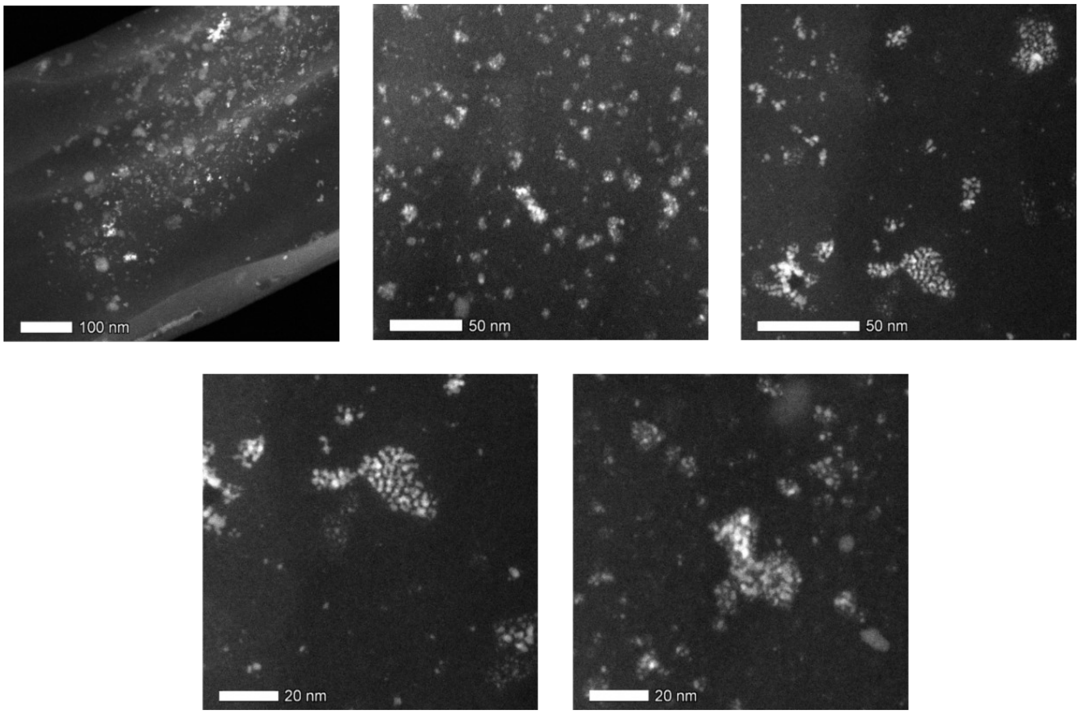


Figure S22 HAADF STEM micrograph and STEM-EDX map showing the composition of **2a**.

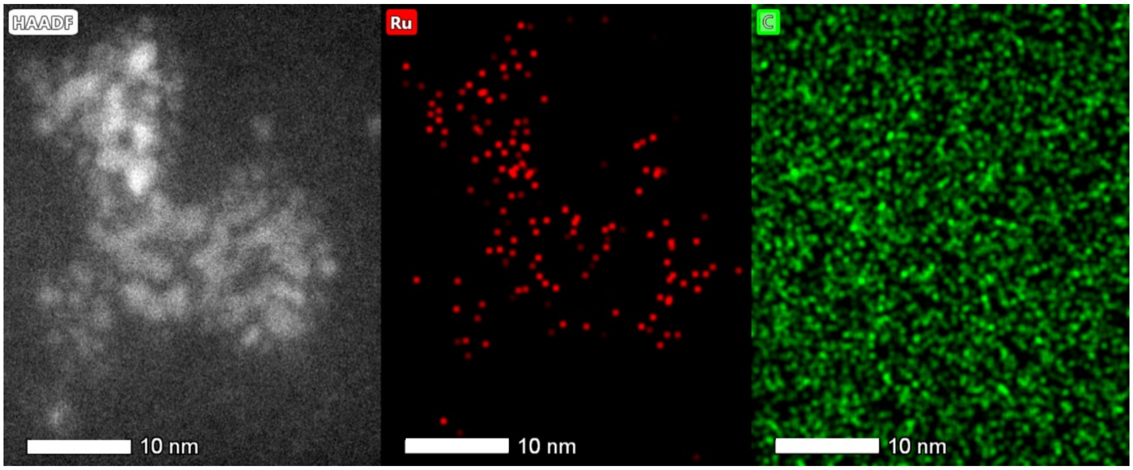


Figure S23 HAADF STEM micrograph and STEM-EDX map showing the composition of **2a**.

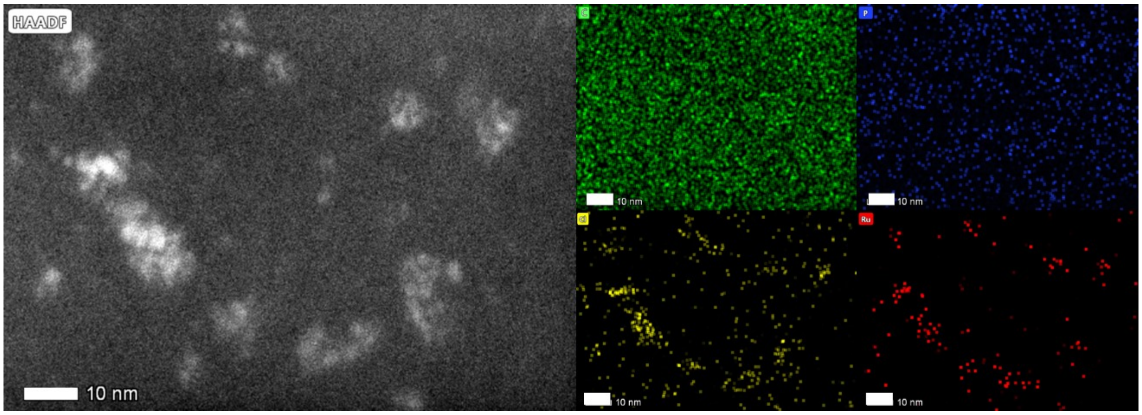


Figure S24 HAADF STEM micrograph and STEM-EDX map showing the composition of **2a.**

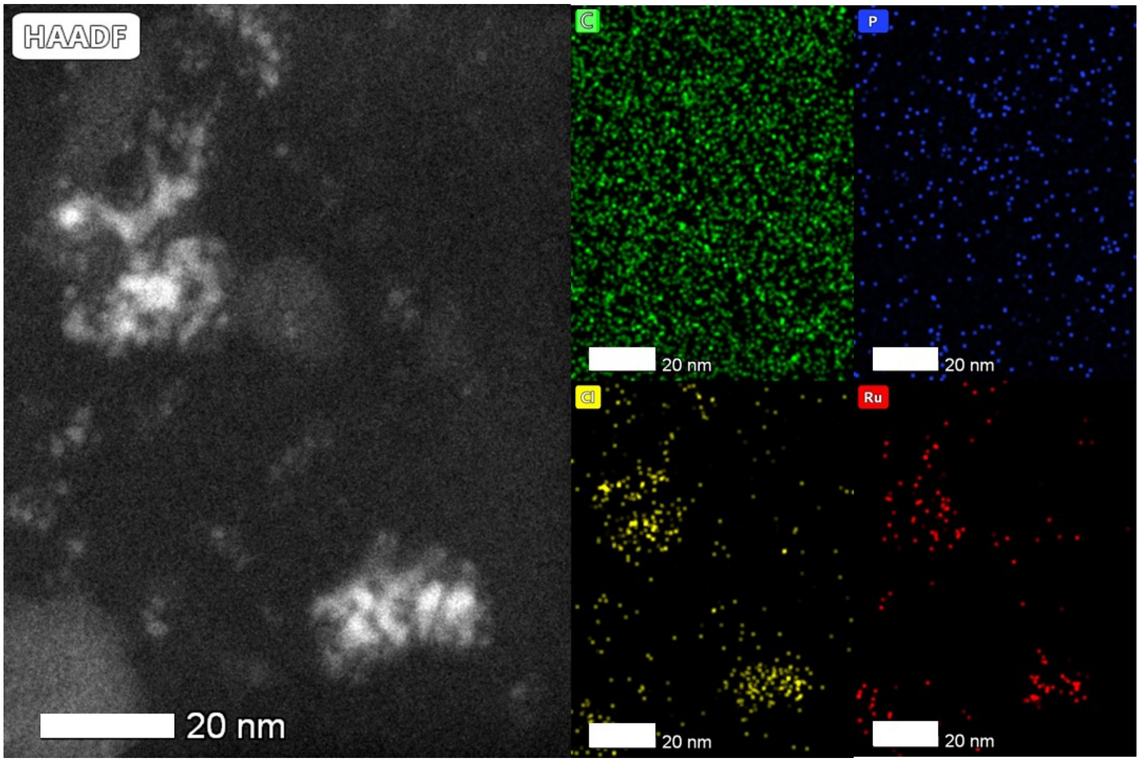


Figure S25 Solid state ^{13}C NMR spectrum of RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**)

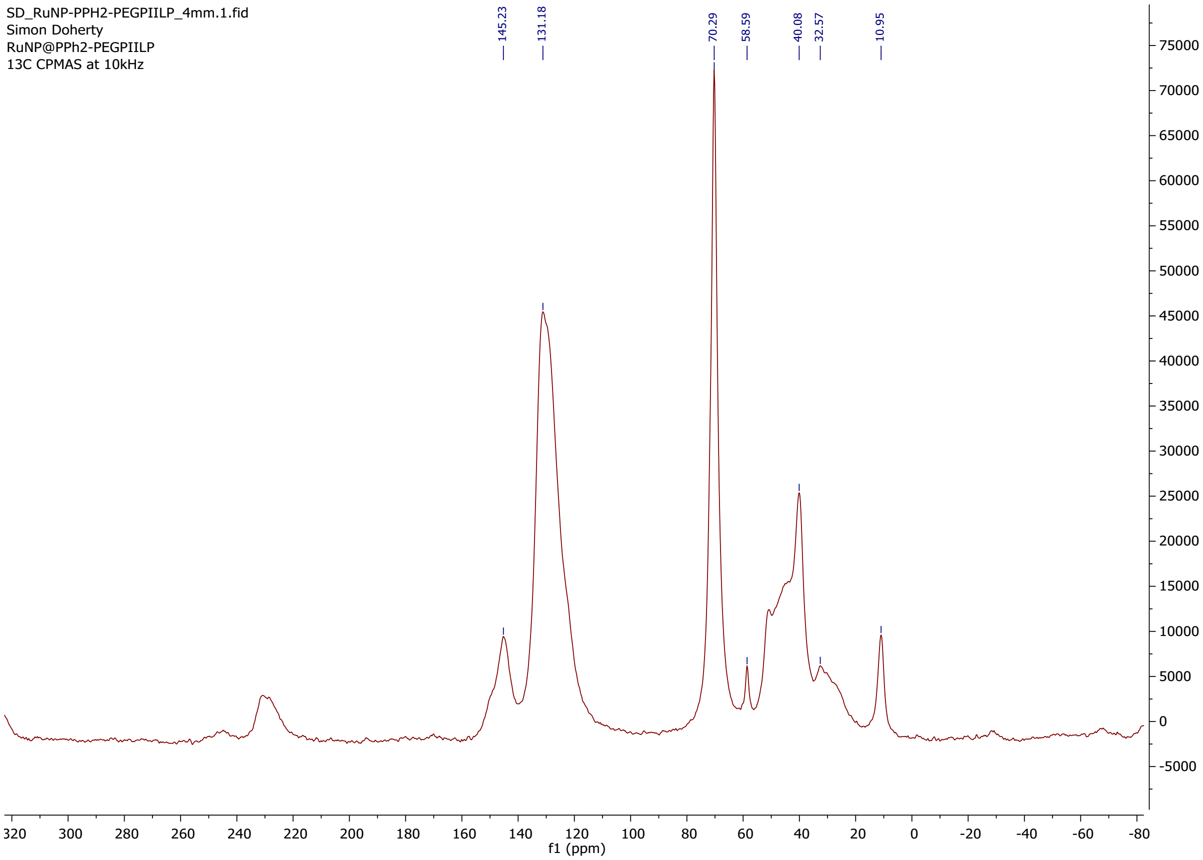


Figure S26 Solid state ^{31}P NMR spectrum of RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**)

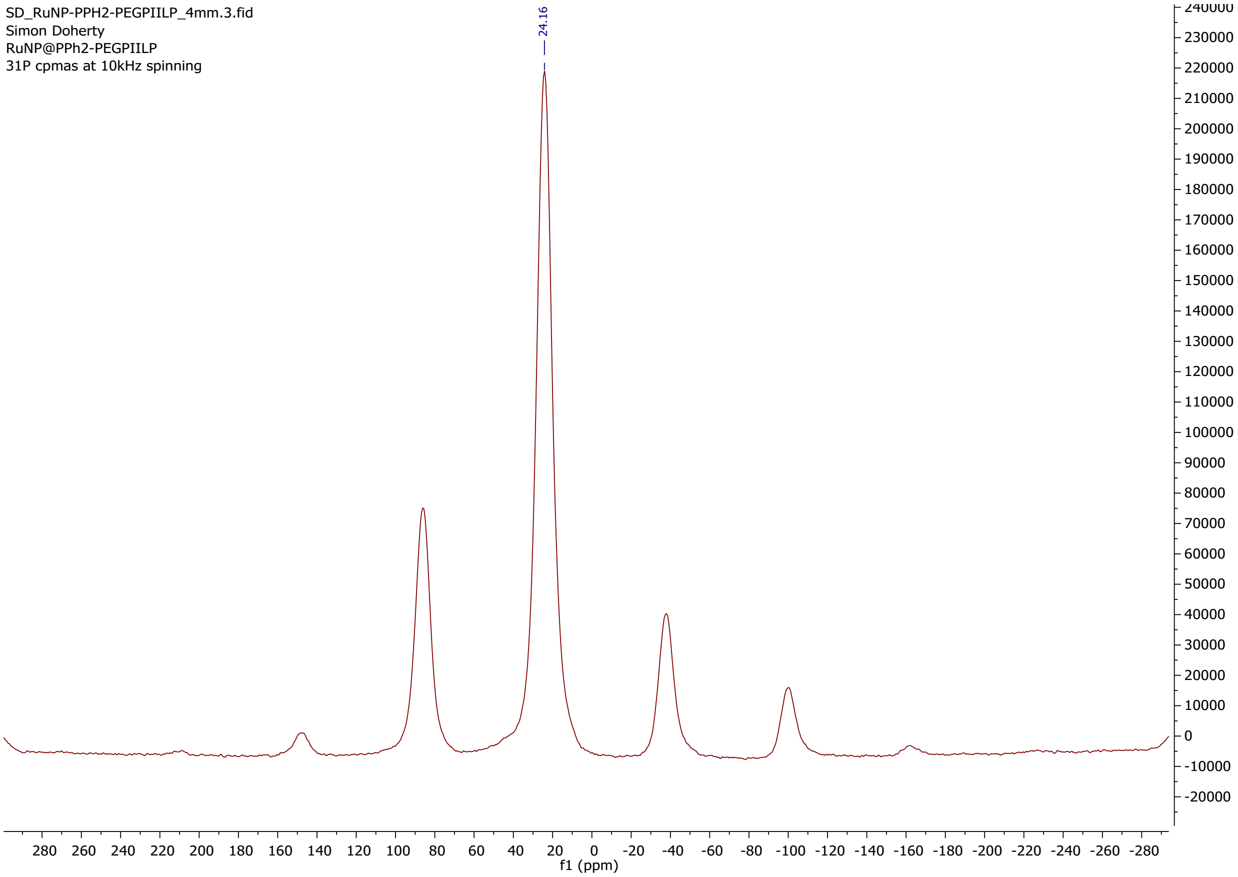


Figure S27 SEM image of freshly prepared RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**)

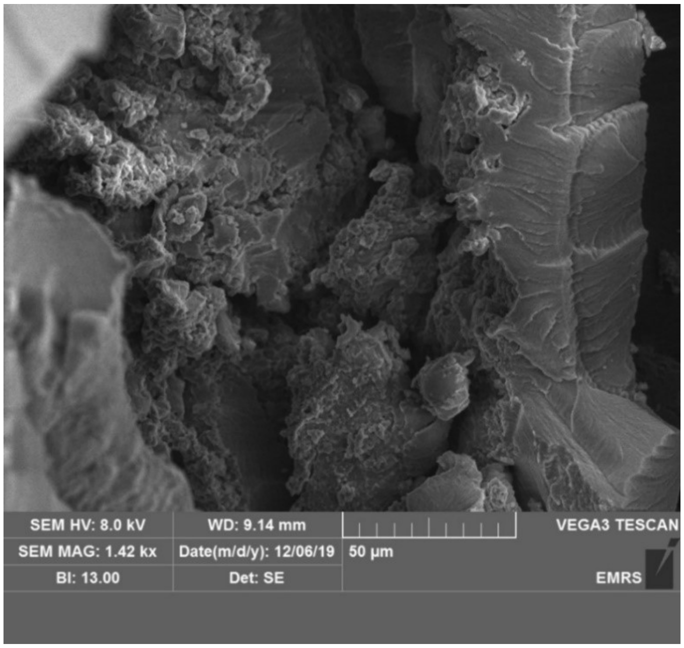


Figure S28 FT-IR spectrum of freshly prepared RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**)

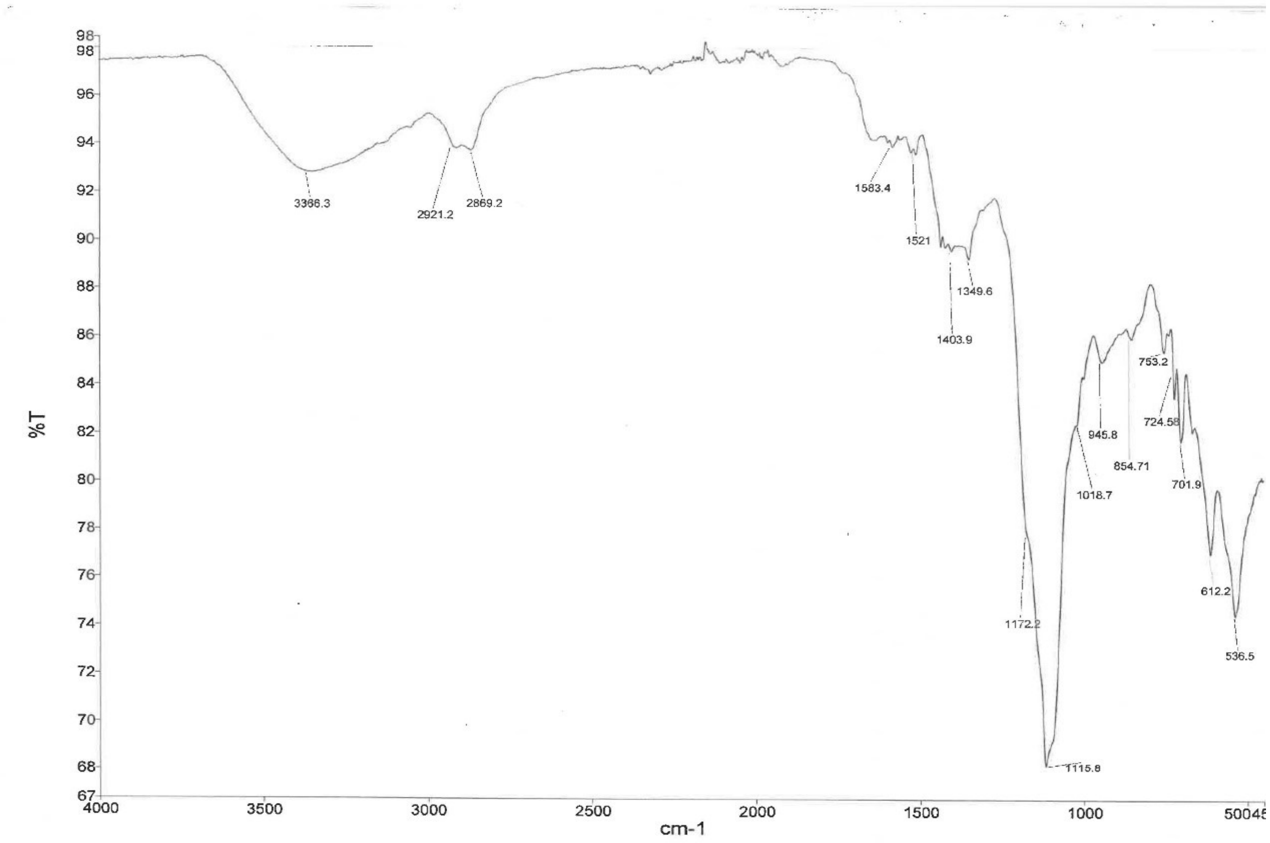


Figure S29 XPS spectrum of the P 2p region for RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**)

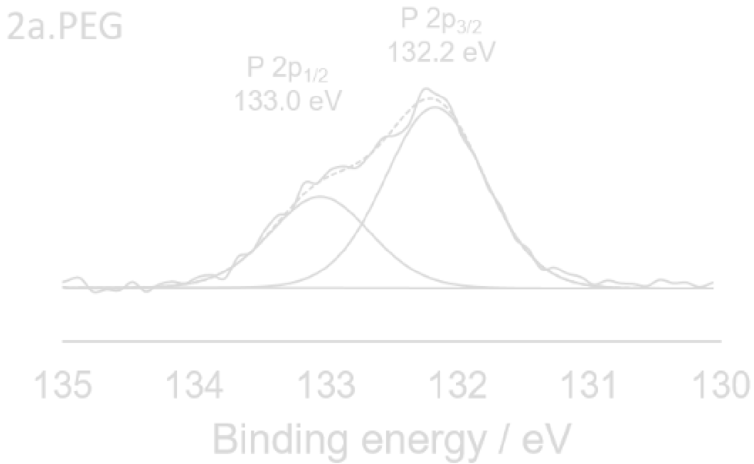


Figure S30 Ru 3p core level XPS spectra for RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**) referenced to the C 1s alkyl peak at 284.8 eV.

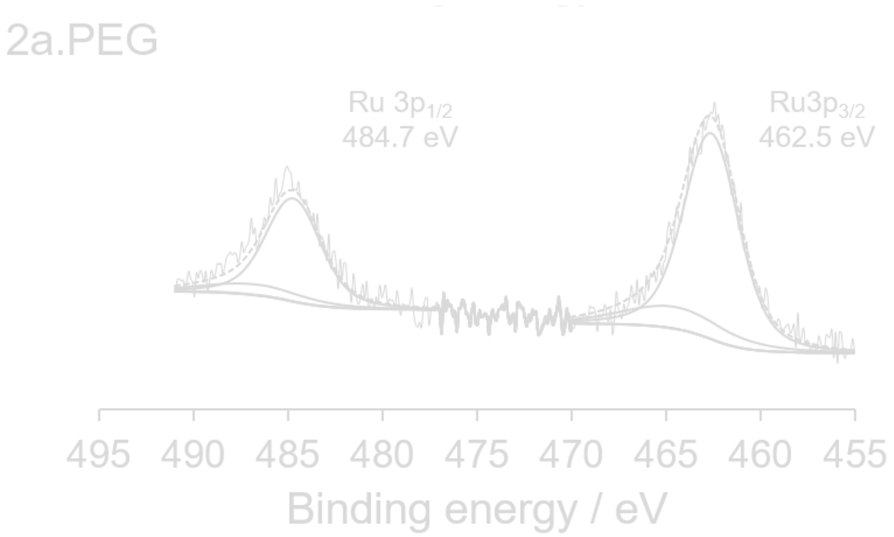


Figure S31 (a-d) TEM images of RuNP@O=PPh$_2$-PEGPIILS (**2a.PEG**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 20 nm (black) and 5 nm (white).

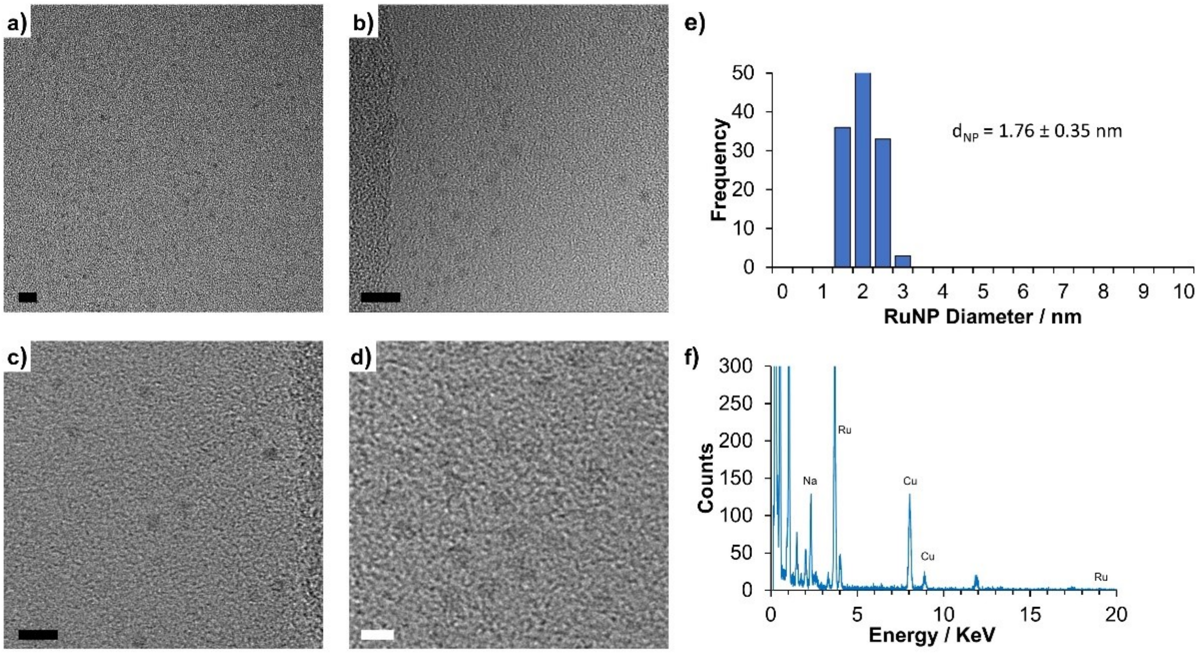


Figure S32 Solid state ^{13}C NMR spectrum of RuNP@O=PPh$_2$-PIILS (**2a`**)

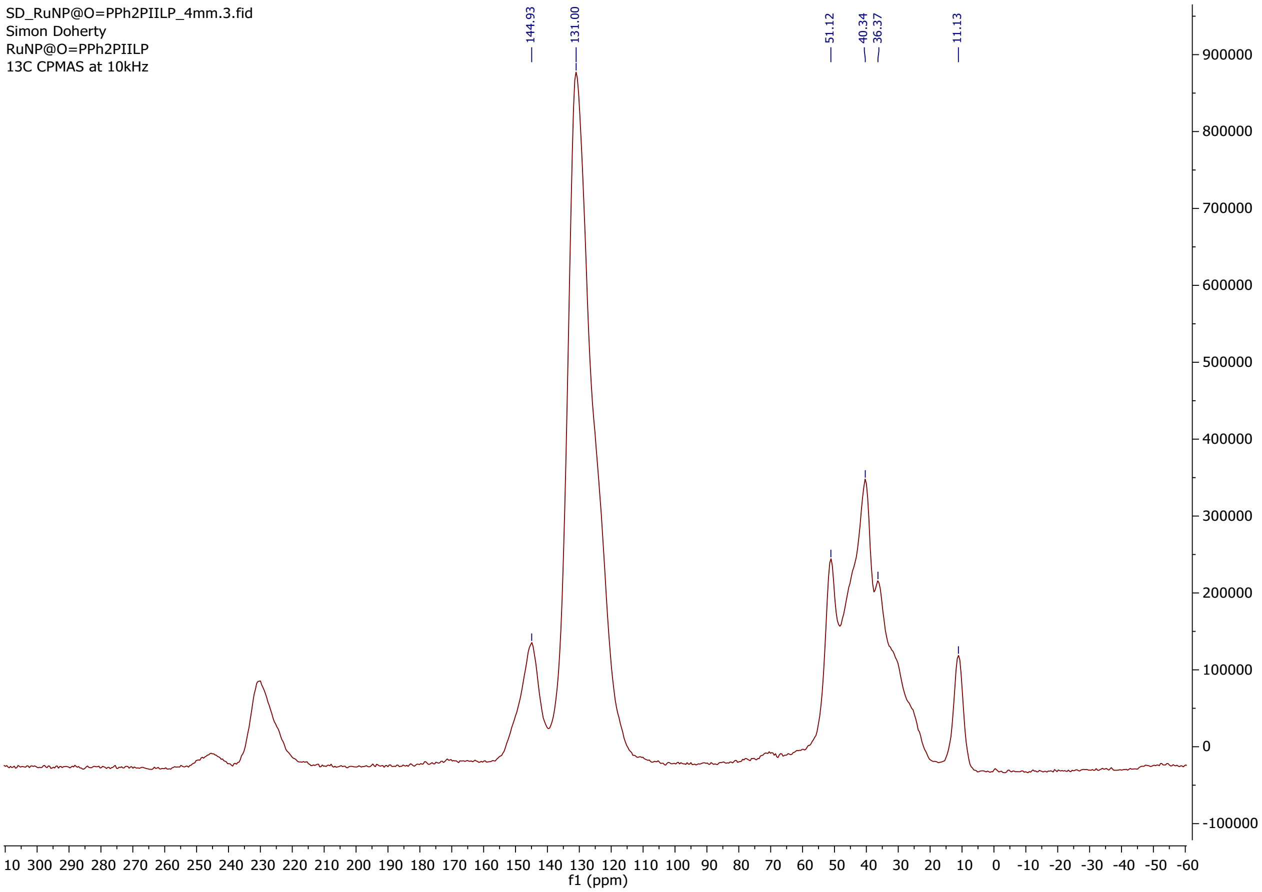


Figure S33 Solid state ^{31}P NMR spectrum of RuNP@O=PPh$_2$-PIILS (**2a`**)

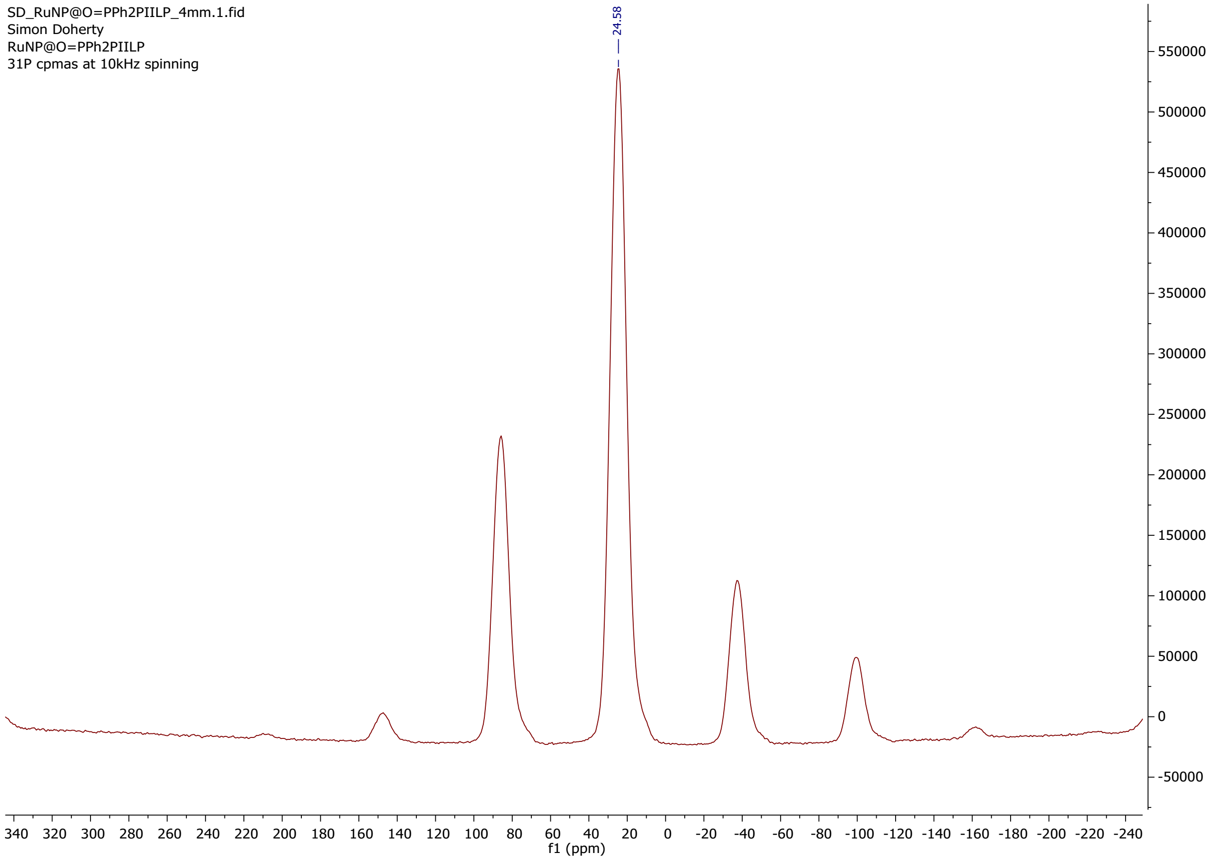


Figure S34 SEM image of freshly prepared RuNP@O=PPh$_2$-PIILS (**2a`**)

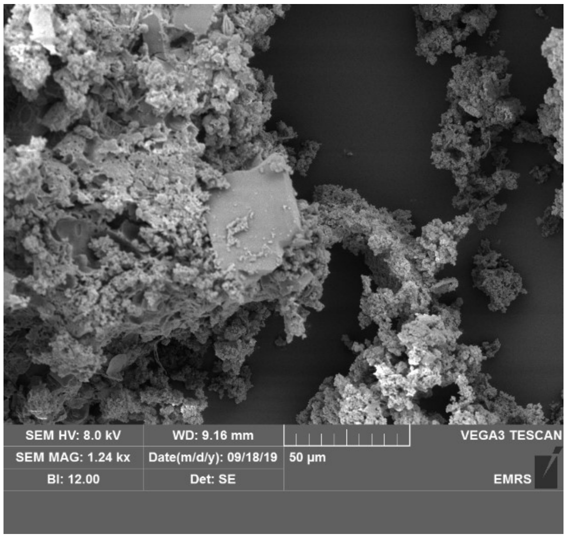


Figure S35 FT-IR spectrum of freshly prepared RuNP@O=PPh$_2$-PIILS (**2a`**)

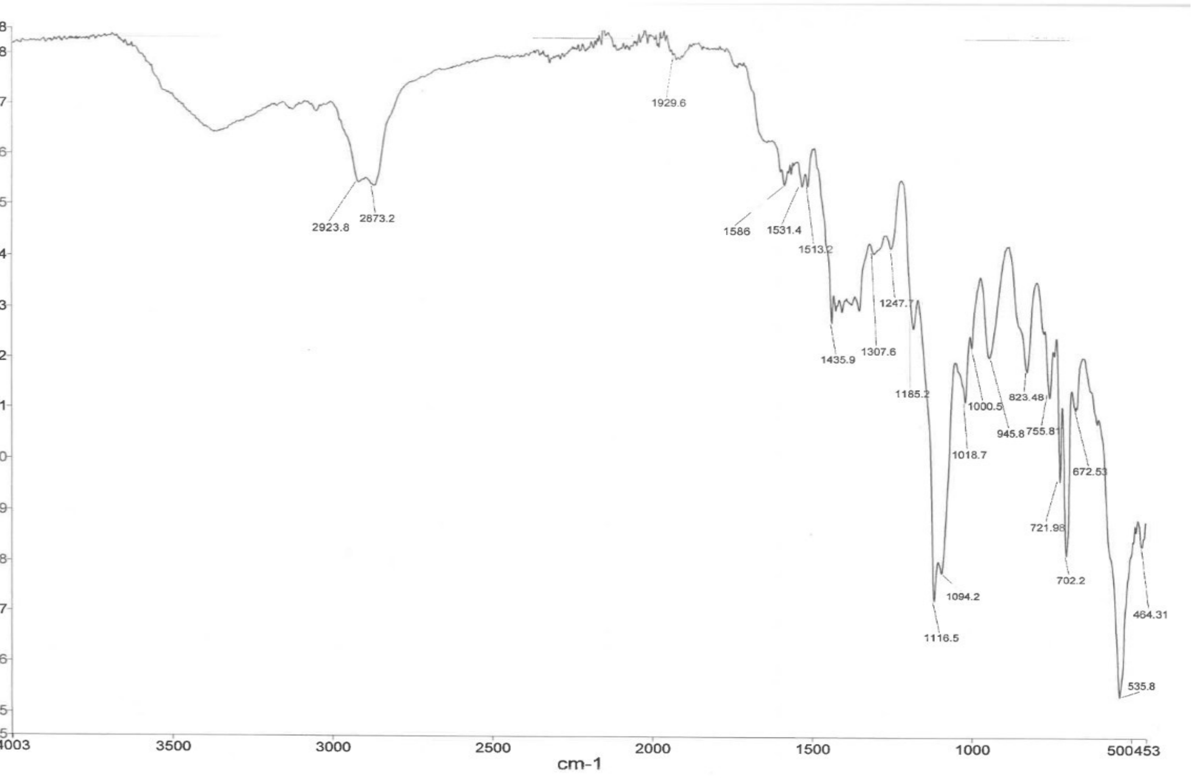


Figure S36 XPS spectrum of the P 2p region for RuNP@O=PPh_2-PIILS (**2a'**)

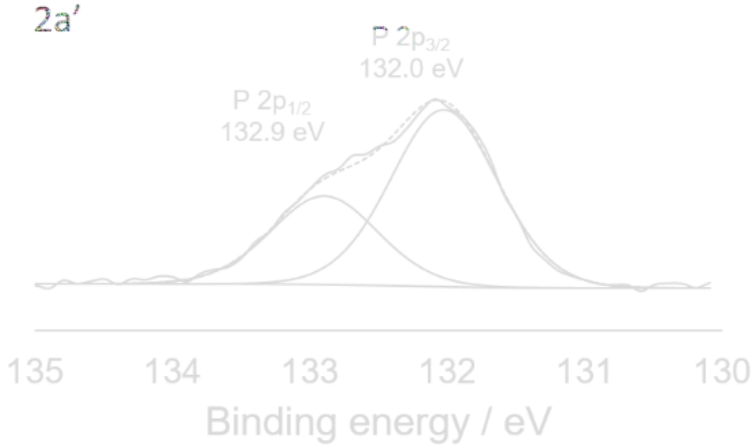


Figure S37 Ru 3p core level XPS spectra for RuNP@O=PPh_2-PIILS (**2a`**) referenced to the C 1s alkyl peak at 284.8 eV.

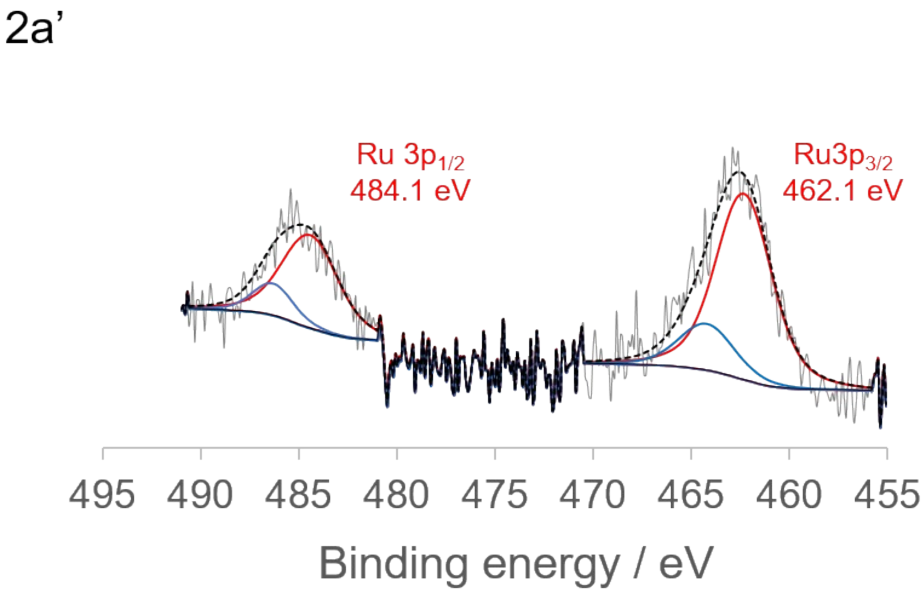


Figure S38 (a-d) TEM images of RuNP@O=PPh$_2$-PIILS (**2a`**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 20 nm (black) and 5 nm (white).

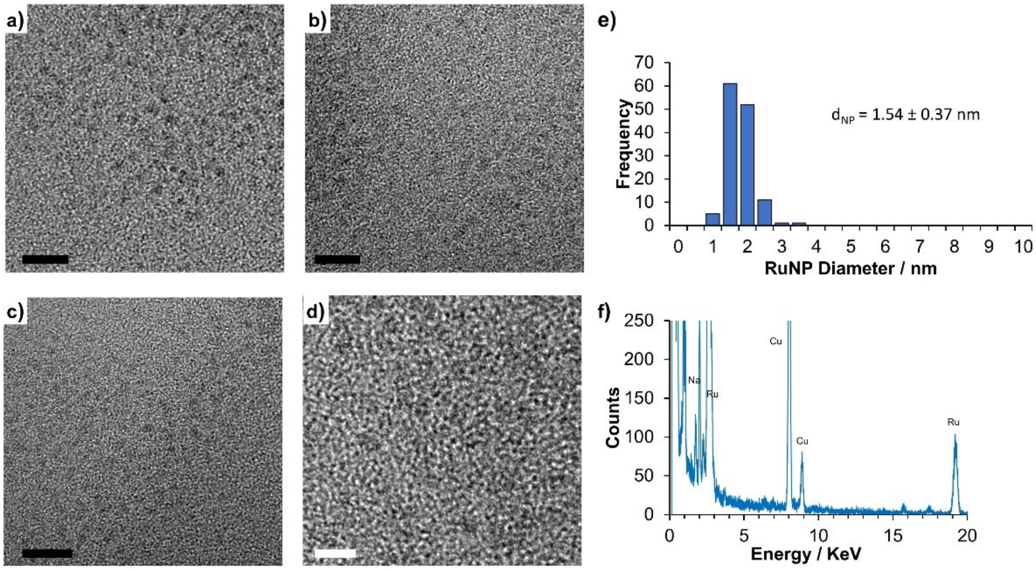


Figure S39 Solid state ^{13}C NMR spectrum of RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**)

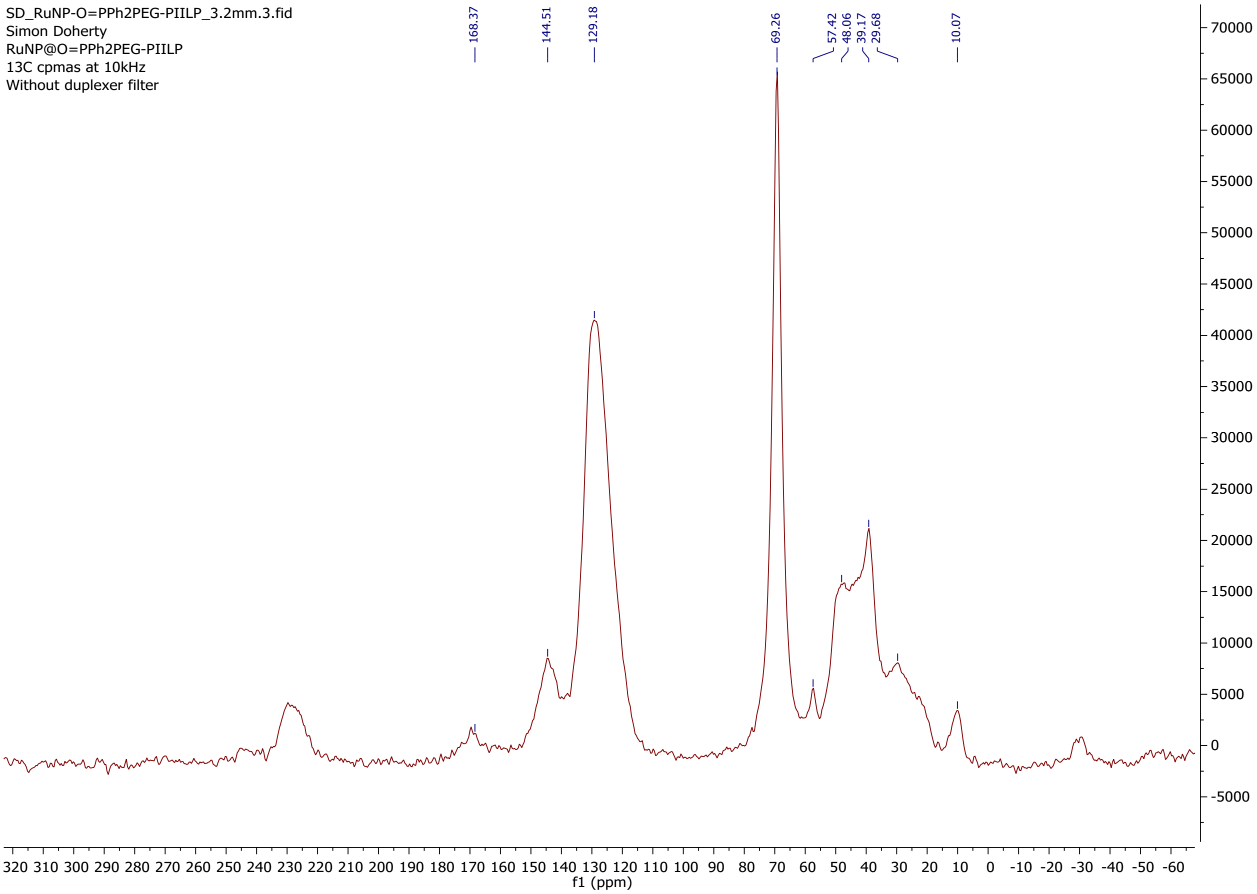


Figure S40 Solid state ^{31}P NMR spectrum of RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**)

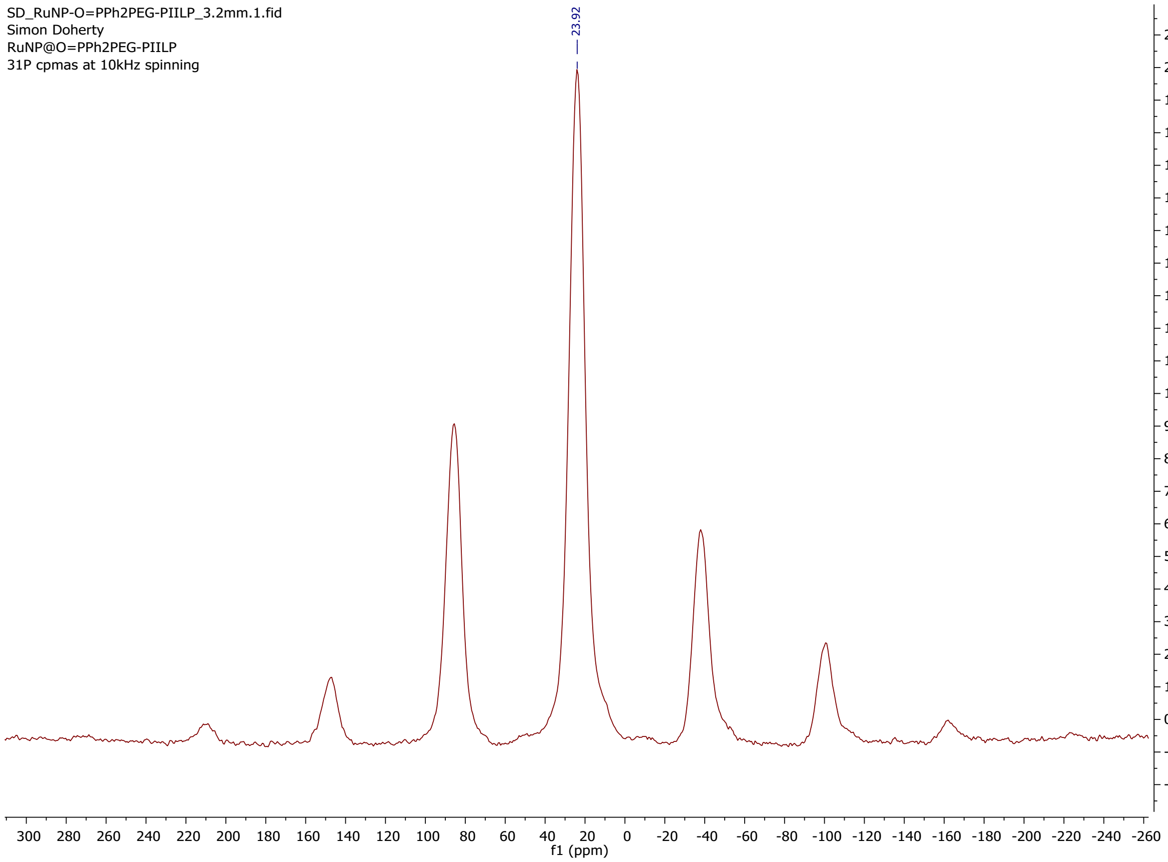


Figure S41 SEM image of freshly prepared RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**)

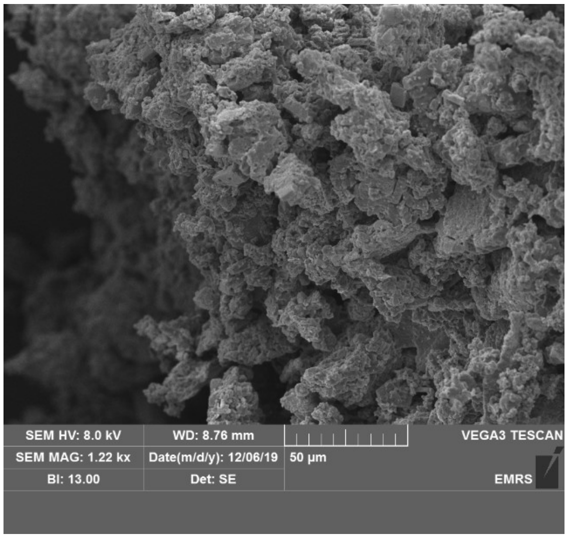


Figure S42 FT-IR spectrum of freshly prepared RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**)

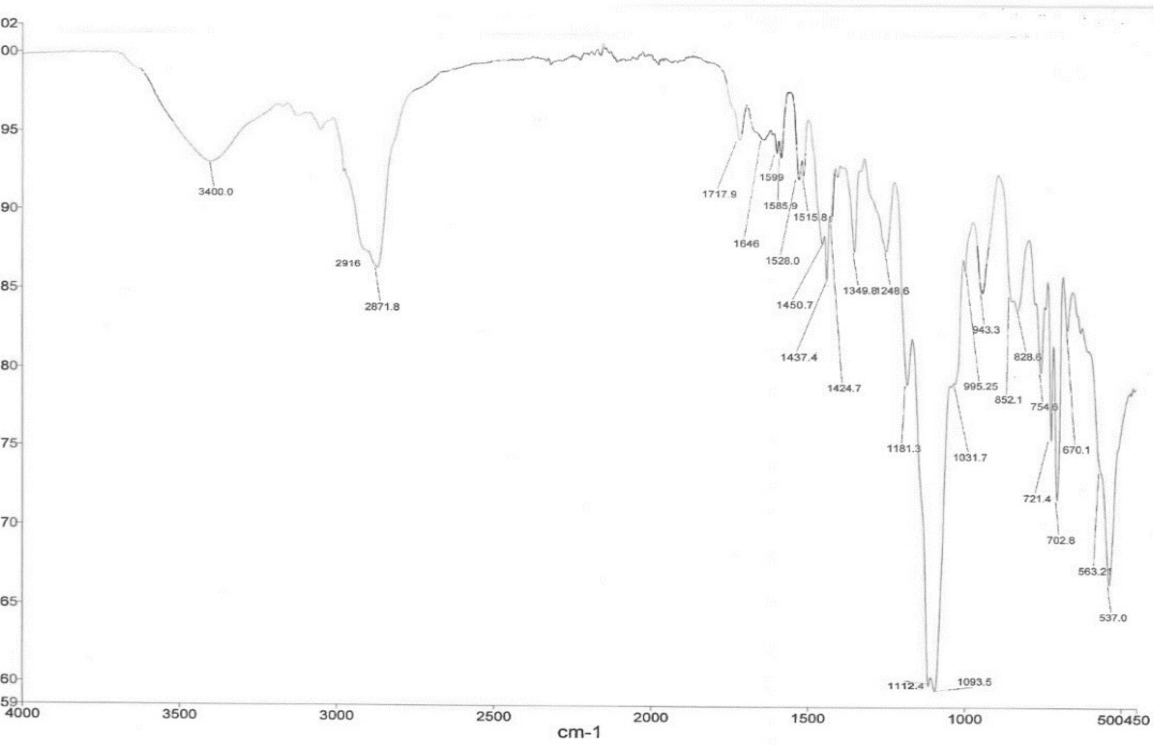


Figure S43 XPS spectrum of the P 2p region for RuNP@O=PPh$_2$-PEGPIILS (**2a'.PEG**)

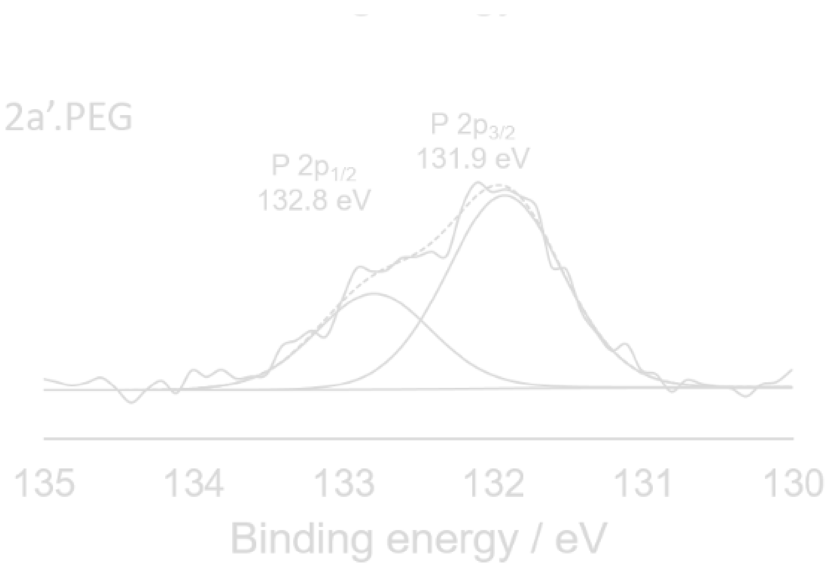


Figure S44 Ru 3p core level XPS spectra for RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**) referenced to the C 1s alkyl peak at 284.8 eV.

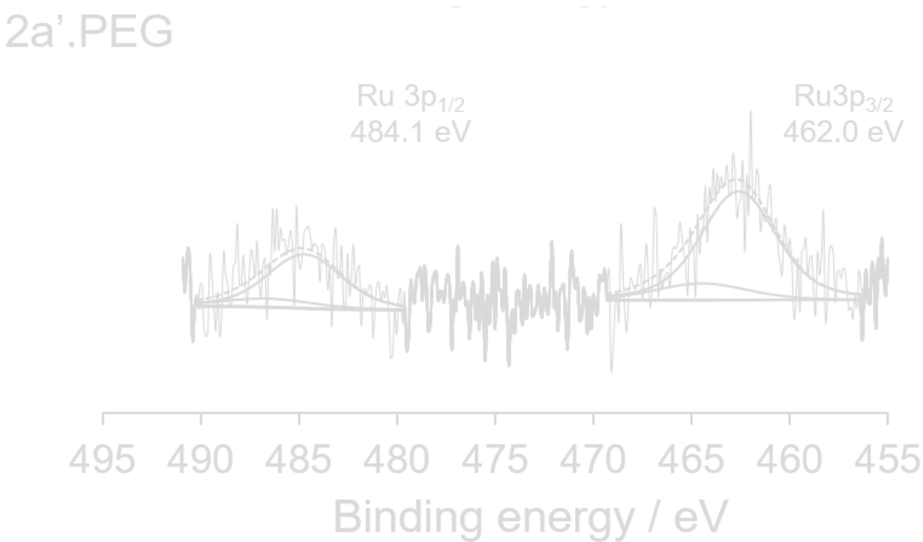


Figure S45 (a-d) TEM images of RuNP@O=PPh$_2$-PEGPIILS (**2a`.PEG**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 20 nm (black) and 5 nm (white).

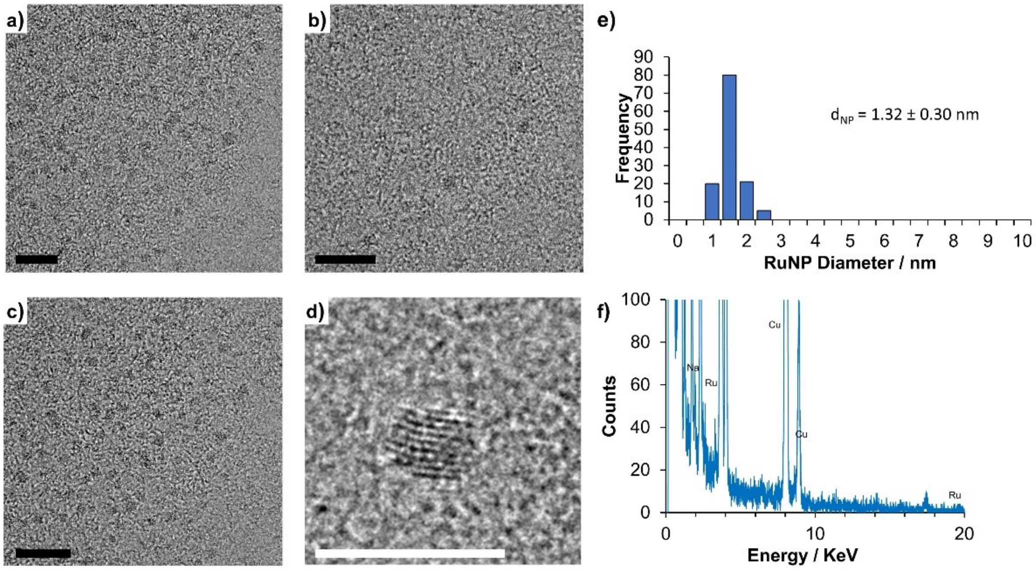


Figure S46 Solid state ^{13}C NMR spectrum of RuNP@PIILS (**2b**)

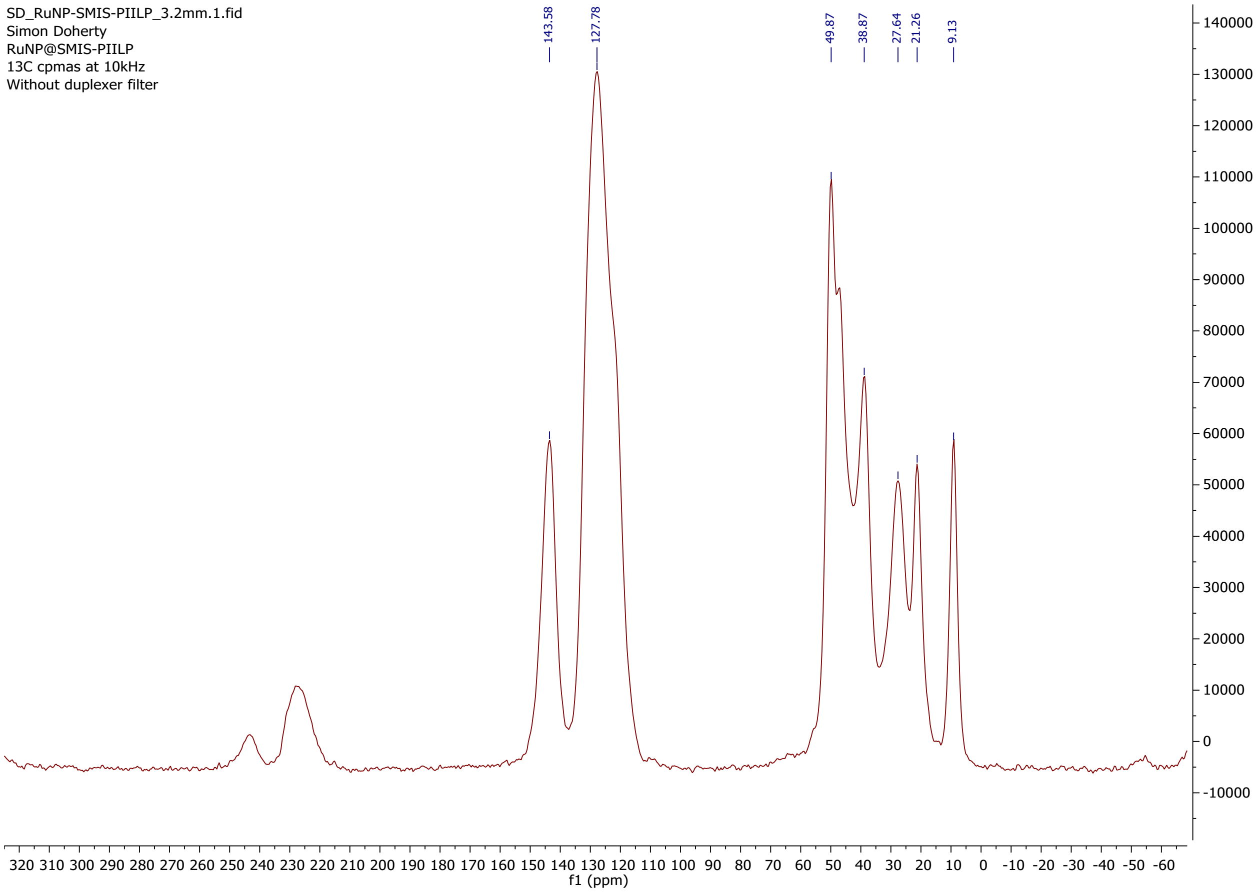


Figure S47 SEM image of freshly prepared RuNP@PIILS (**2b**)

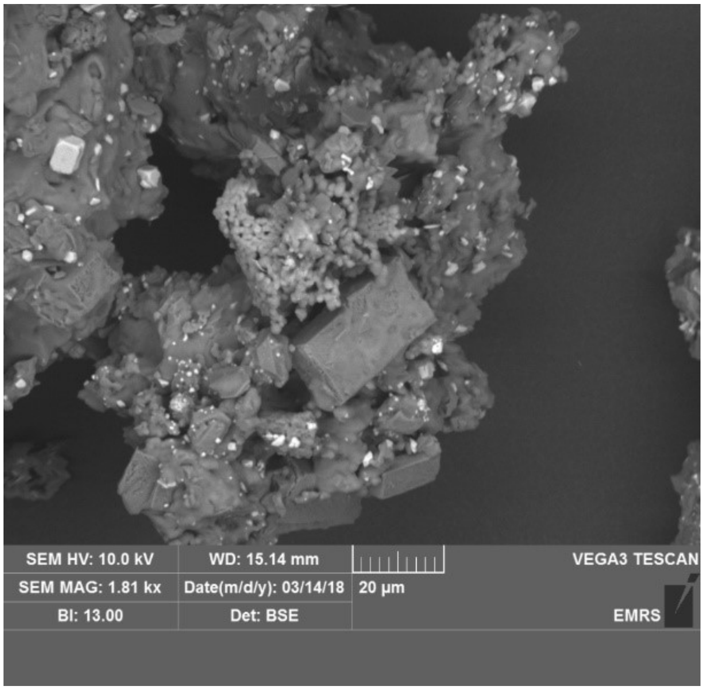


Figure S48 FT-IR spectrum of freshly prepared RuNP@PIILS (**2b**)

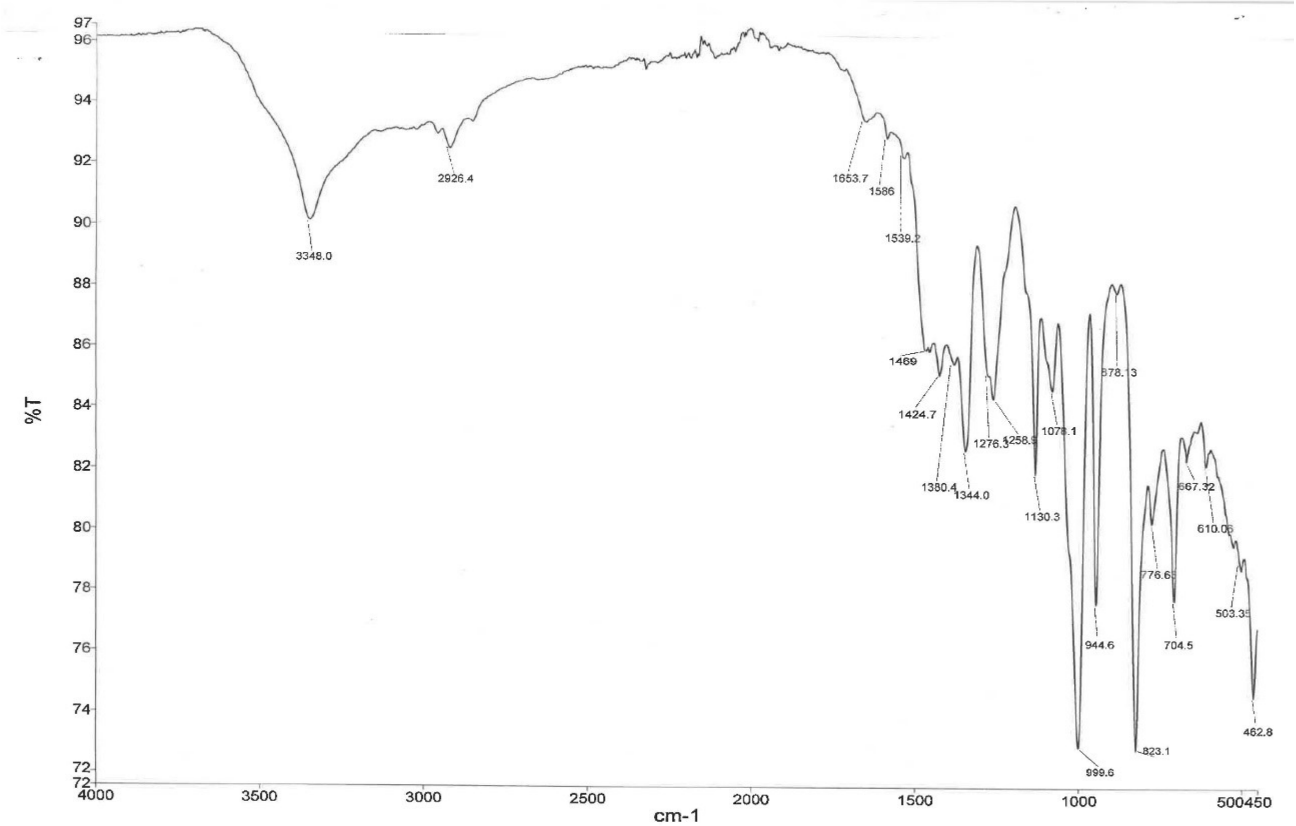


Figure S49 Ru 3p core level XPS spectrum of RuNP@PIILS (**2b**) referenced to the C 1s alkyl peak at 284.8 eV.

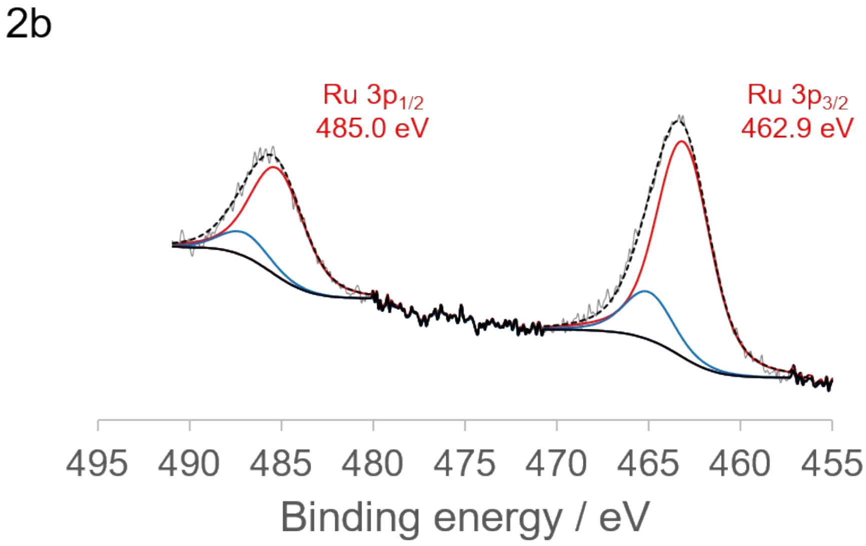
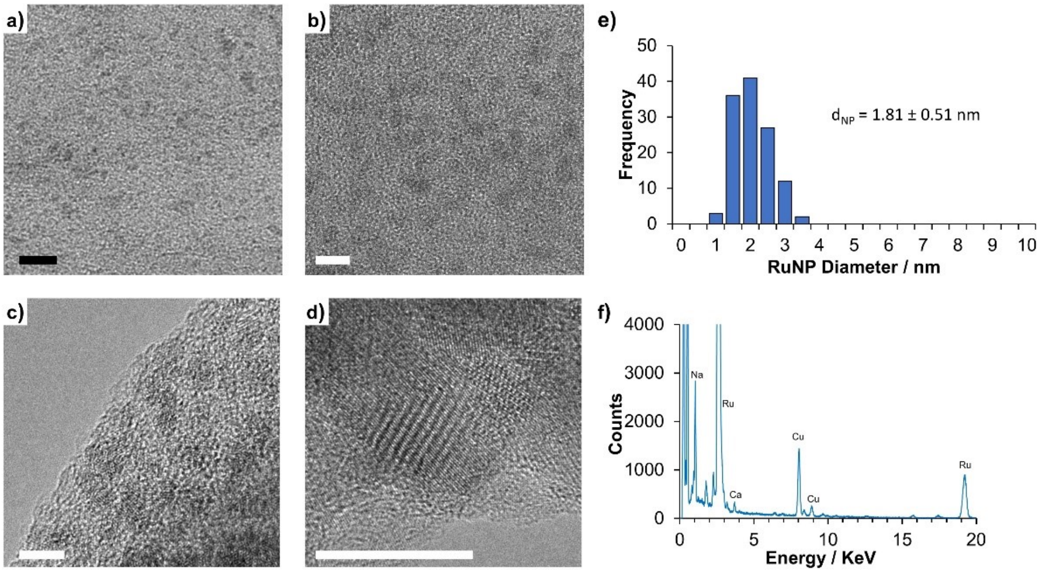


Figure S50 (a-d) TEM images of RuNP@PIILS (**2b**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 10 nm (black) and 5 nm (white).



RuNPs@PILP_Sept 19

Black scale bar = 10 nm
White scale bar 5 nm

Figure S51 Solid state ^{13}C NMR spectrum of RuNP@PEGPIILS (**2b.PEG**)

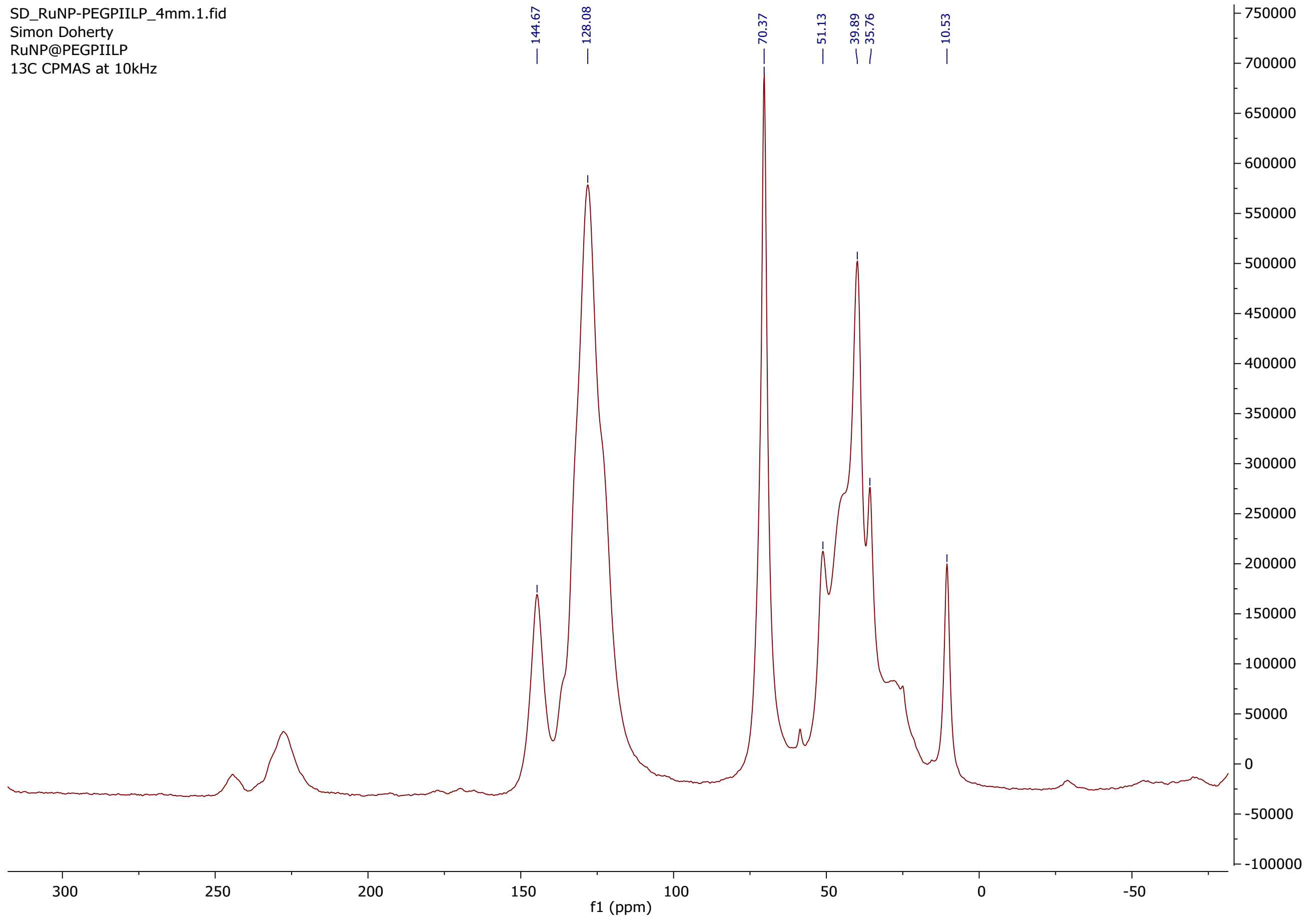


Figure S52 SEM image of freshly prepared RuNP@PEGPIILS (**2b.PEG**)

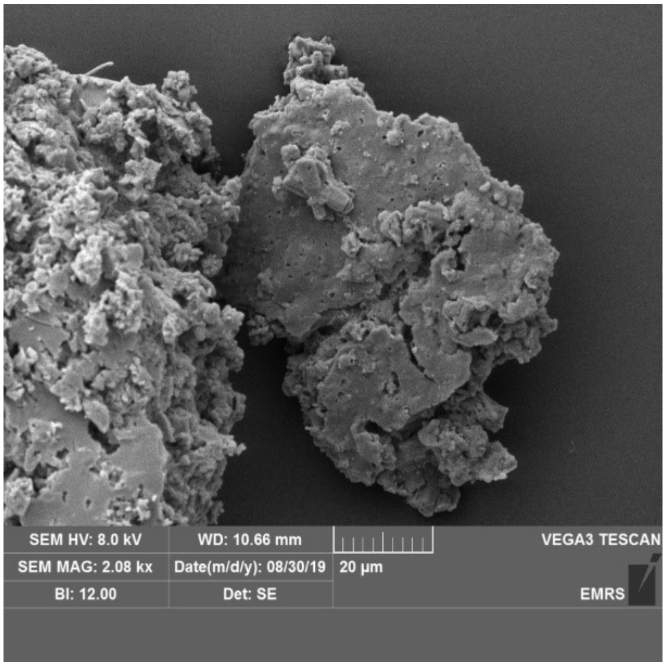


Figure S53 FT-IR spectrum of freshly prepared RuNP@PEGPIILS (**2b.PEG**)

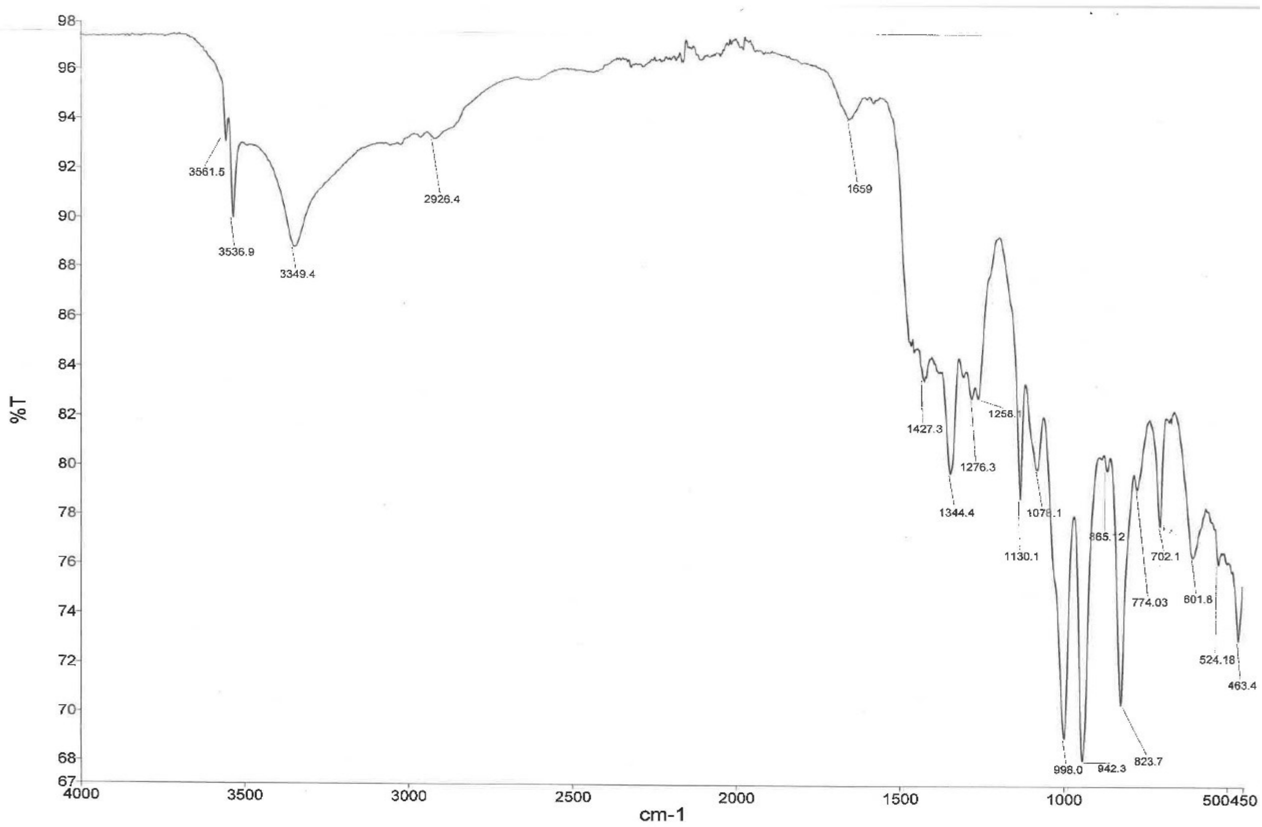


Figure S54 Ru 3p core level XPS spectrum of RuNP@PEGPIILS (**2b.PEG**) referenced to the C 1s alkyl peak at 284.8 eV.

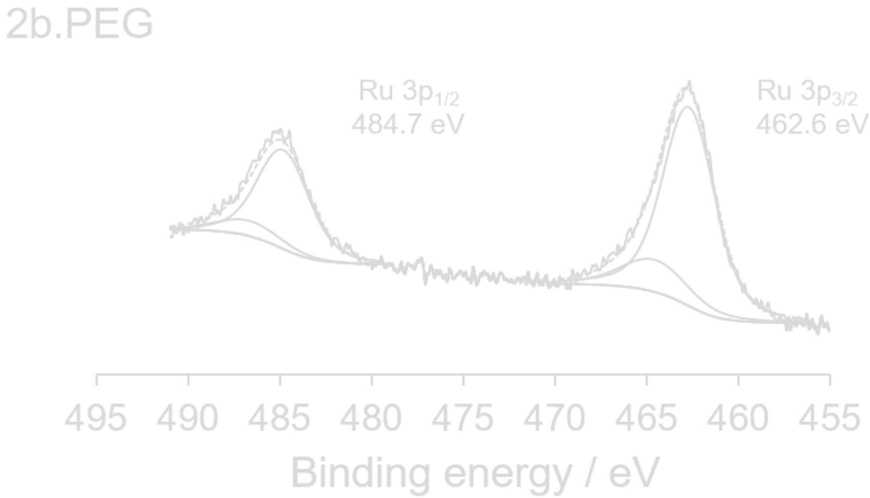


Figure S55 (a-d) TEM images of RuNP@PEGPIILS (**2b.PEG**), (e) histogram of particle size (diameter, nm) and f) EDX spectra (N.B. Cu signals are from the TEM grid). Scale bars are 20 nm (black) and 5 nm (white).

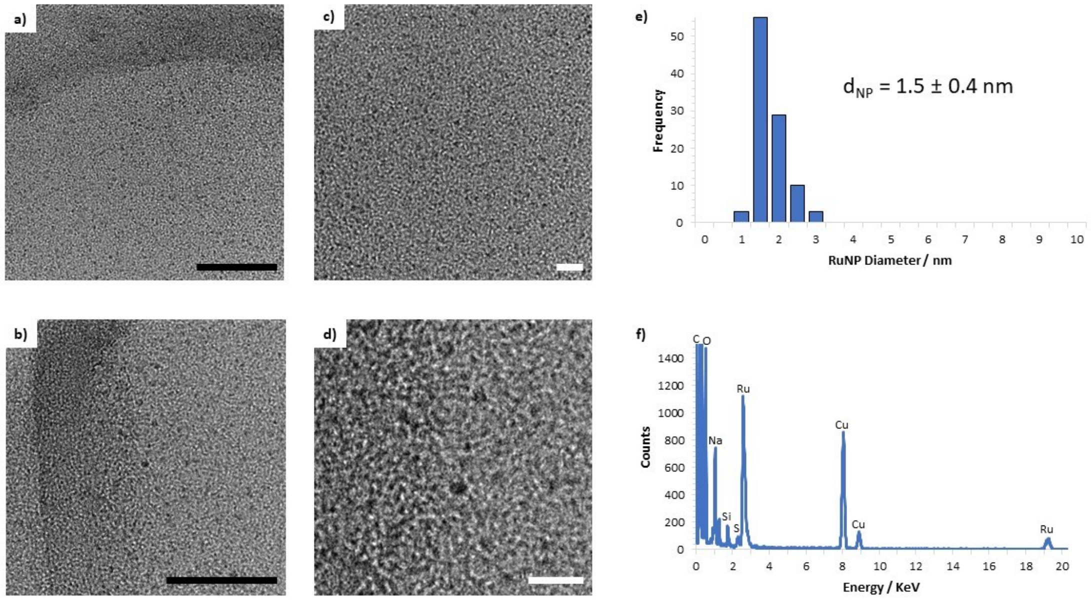


Table S4: Peak positions of Ru $3p_{3/2}$ (position of satellite peak) and P $2p_{3/2}$.

Catalyst	**Binding energy / eV** **Ru $3p_{3/2}$**	**Binding energy / eV** **$P2p_{3/2}$**
2b	462.9 (464.8)	/
2a	462.3 (464.2)	132.1
2a’	462.1 (464.0)	132.0
2b.PEG	462.6 (464.5)	/
2a.PEG	462.5 (464.7)	132.2
2a’.PEG	462.0 (463.9)	131.9

ATR Spectroscopy

Figure S56 ATR spectra of CO adsorption (10% CO in Ar) at RT over catalyst **2a'** (RuNP@O=PPh$_2$-PIILP).

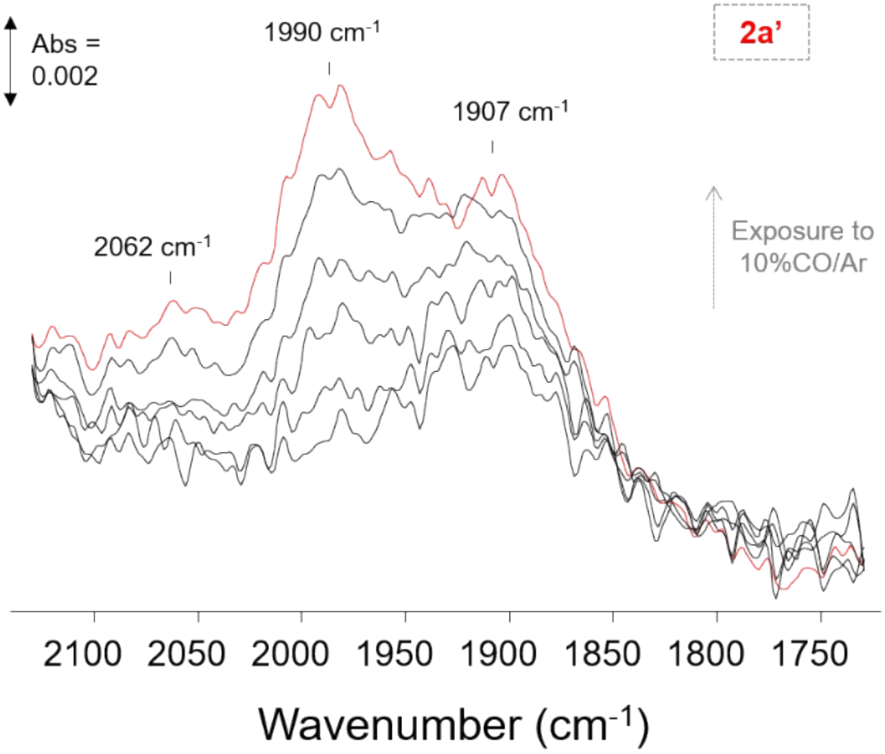


Figure S57 ATR spectra of CO adsorption (10% CO in Ar) at RT over catalyst **2a** (RuNP@PPh$_2$-PIILP), **2a'** (RuNP@O=PPh$_2$-PIILP) and **2a.PEG** (RuNP@PPh$_2$-PEG-PIILP).

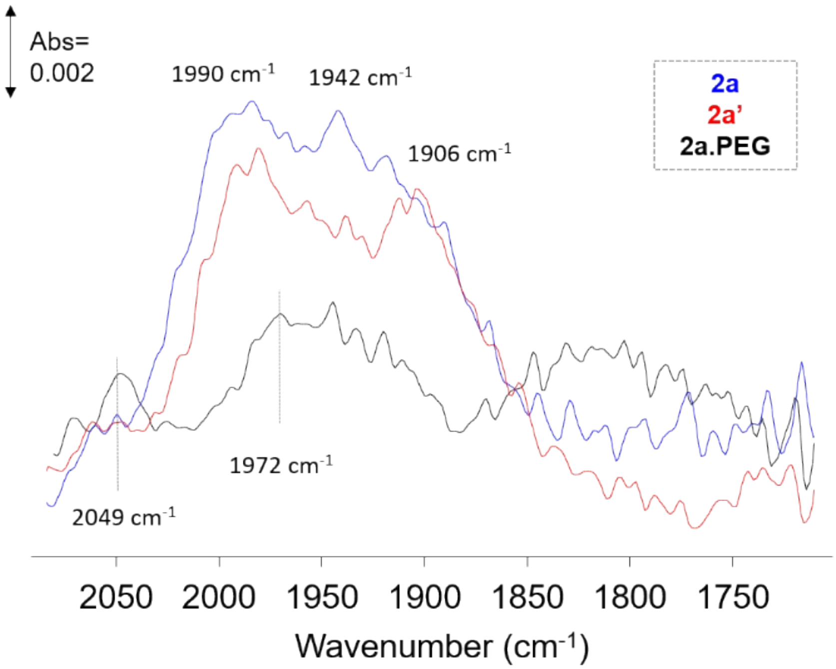


Figure S58 ATR spectra of CO adsorption (10% CO in Ar) at RT over catalyst **2a.PEG** (RuNP@PPh$_2$-PEG-PIILP) (a) after reduction by NaBH$_4$/ethanol at RT and (b) H$_2$/water at 50 °C.