Supporting Information for Manuscript Entitled

An Efficient Recyclable Peroxometalate-Based Polymer Immobilised Ionic Phase Catalyst for H_2O_2-Mediated Oxidations

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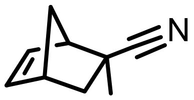
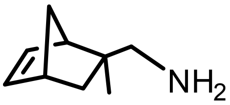
Contents

Experimental

General Comments. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware unless otherwise stated. Dichloromethane and chloroform were distilled from calcium hydride, THF from sodium and hexane and diethyl ether from Na/K alloy, under an atmosphere of nitrogen. Deuteriochloroform was pre-dried with calcium hydride, vacuum-transferred, and stored over 4 Å molecular sieves. All reagents were purchased from commercial suppliers and used without further purification. $[PO_4\{WO(O_2)\}_2][NEt_4]_3$ was prepared as previously described[1] and $H_3[PO_4\{WO(O_2)\}_4]$ was generated in situ immediately prior to use as previously described.[2] ^1H and $^{13}C\{^1H\}$ 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-polarisation 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 neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Thin-layer chromatography (TLC) was carried out on aluminium sheets pre-coated with silica gel 60F 254 and column chromatography was performed using Merck Kieselgel 60. Gas chromatography-mass spectrometry was performed on a Saturn 2220 GC-MS system using a factorFour VF-5ms capillary column, 30m, 0.25mm, 0.25µm and high resolution mass spectrometry was conducted on a Waters Micromass LCT Premier mass spectrometer. CHN analysis was undertaken using a Carlo-Erba 1100 elemental combustion analyser controlled with CE Eager 200 software and metal analysis was performed using a Perkin-Elmer Optima 4300 ICP-OES analyser. Thermogravimetric analysis (TGA) was performed using a TA TGA Q5000, at a heating rate of 5 °C min^{-1}. All samples were sealed in the glovebox into aluminium pans. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature. TEM images were acquired in bright field using a Tecnai 200 kV F20 Transmission Electron Microscope with a Field Emission Gun. A few drops of sample were pipetted onto an Agar holey carbon film copper TEM grids and the prepared grid was set aside for ca. 20 min prior to inserting it into the microscope, in order to allow the solvent to evaporate. Images were taken with a Gatan CCD digital camera attached to the microscope. Gel permeation chromatography (GPC) was conducted on a Varian ProStar instrument (Varian Inc.) equipped with a Varian 325 UV-vis dual wavelength detector (254 nm), a Dawn Heleos II multi-angle laser light scattering detector (Wyatt Technology Corp.), a Viscotek 3580 differential RI detector, and a pair of PL gel 5 μm Mixed D 300 × 7.5 mm columns with guard column (Polymer Laboratories Inc.) in series. Near monodisperse polystyrene standards (Agilent Technologies) were used for calibration. Data collection was performed with Galaxie software (Varian Inc.) and chromatograms analyzed with the Cirrus software (Varian Inc.) and Astra software (Wyatt Technology Corp.).

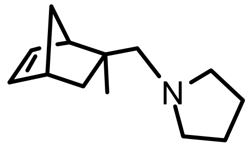


Synthesis of 2-methylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (1).[3] To a three-neck round bottomed flask charged with BCl_3 (1.0 M in hexane, 23.0 mL, 2.03 mmol) and cooled to 0 ˚C, was added methacrylonitrile (15.2 mL, 182 mmol) drop-wise with rapid stirring, resulting in precipitation of a white solid, which re-dissolved upon drop-wise addition of freshly cracked cyclopentadiene (10.0 mL, 151.0 mmol). The reaction was stirred overnight and allowed to warm to room temperature after which time the resulting pale yellow solution was poured on to an ice cold solution of saturated $NaHCO_3$ and extracted with diethyl ether (3 × 100 mL). The organic fractions were combined, dried $MgSO_4$, filtered, and the solvent removed under reduced pressure to give the desired product as a pale orange oil in 69% yield (13.90 g). *Exo*-diasteroisomer: ^{1}H NMR (500.16 MHz, $CDCl_3$, δ): 6.25 (dd, *J* = 5.4, 1.9 Hz, 1H, =C*H*), 5.96 (dd, *J* = 5.4, 2.1 Hz, 1H, =C*H*), 3.02 (br m, 1H, bridgehead), 2.93 (br m, 1H, bridgehead), 2.27 (dd, *J* = 13.7, 4.5 Hz, 1H, C*H*$_2$), 2.25 (dd, *J* = 13.7, 1.5 Hz, 1H, C*H*$_2$), 1.76 (dt, *J* = 14.3, 2.0 Hz, 1H, bridge C*H*), 1.53 (dt, *J* = 14.3, 2.8 Hz, 1H, bridge C*H*), 1.18 (s, 3H, C*H*$_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 138.9, 131.8, 127.3, 52.5, 49.6, 43.2, 40.7, 30.2, 23.9: LRMS (EI$^+$) *m/z* 134 $[M+H]^+$.

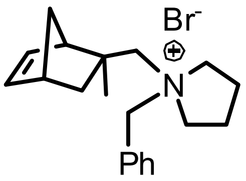


Synthesis of (2-methylbicyclo[2.2.1]hept-5-en-2-yl)methylamine (2). A flame-dried three-neck round bottomed flask charged with $LiAlH_4$ (7.7 g, 202 mmol) was suspended in freshly distilled diethyl ether (100 mL) and cooled to 0°C under a nitrogen atmosphere. A solution of **1** (13.48 g, 101 mmol) in diethylether (*ca.* 20 mL) was added drop-wise resulting in a vigorous and instantaneous exotherm. The reaction was then allowed to warm to room temperature, stirred for an additional 20 hr after which time NaOH solution (1.0 M, ~12 mL) was added drop wise with rapid stirring, followed by slow addition of water until no exotherm was observed. The resulting mixture was filtered through a celite pad which was washed through with diethyl ether (150 mL). The organic phase was extracted with water, separated and the solvent removed under reduced pressure. The crude product was purified by addition of HCl (1.0 M, 180 mL, 180 mmol) and extracted with diethyl ether (3 × 75 mL). The aqueous layer was treated with NaOH solution (1.0 M) to pH 12.0 and the product extracted with diethyl ether (3 × 100 mL), dried with anhydrous magnesium sulphate and the solvent removed under reduced pressure to afford **2** as a yellow-orange oil in 61% yield (8.5 g). *Exo*-diasteroisomer: ^{1}H NMR (300.13 MHz, CDCl$_3$, δ): 6.08 (dd, *J* = 5.4, 1.9 Hz, 1H, =C*H*), 6.04 (dd, *J* = 5.4, 1.9 Hz, 1H, =C*H*), 2.70 (m, 1H, bridgehead), 2.65 (br, 2H, CH_aH_b-NH$_2$), 2.26 (m, 1H, bridgehead), 1.53 (br d, *J* = 8.2 Hz, 1H, bridge C*H*), 1.42 (dd, *J* = 13.0, 4.5 Hz, 1H, CH_2), 1.33 (br d, *J* = 8.2 Hz, 1H, bridge C*H*), 1.15 (br, 2H, NH$_2$), 0.82 (s, 3H, CH_3), 0.73 (dd, *J* = 13.0, 2.5 Hz, 1H, CH_2); ^{13}C{^{1}H} NMR (100.52 MHz, CDCl$_3$, δ): 136.7, 135.5, 53.2, 48.7, 47.7, 43.3, 43.0, 38.3, 22.7; LRMS (EI$^+$) *m*/*z* 138 [M+H]$^+$.

Synthesis of 1-(-2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidine (3). A flask was charged with **2** (5.0 g, 37.0 mmol), 1,4-dibromobutane (4.42 mL, 37.0 mmol), potassium carbonate (10.23 g, 74 mmol) and acetonitrile (300 mL) and heated under nitrogen at reflux with rapid stirring for 20 h. The solvent was removed under reduced pressure and the resulting residue diluted with diethyl ether (*ca*. 50 mL) and HCl (1.0 M, 74 mL, 74 mmol) added. The aqueous layer was extracted with diethylether (2 × 70 mL), treated with NaOH solution (1.0 M) until the solution reached pH 12.0 and then extracted with diethyl ether (3 × 75 mL). The organic fractions were combined, dried with magnesium sulphate, filtered and the solvent removed in vacuo to give the product as an orange oil in 72% yield (5.09 g, 27.0 mmol). *Exo*-diastereoisomer: ^{1}H NMR (399.78 MHz, CDCl$_3$, δ): 6.06 (br m, 2H, =CH), 2.70 (br s, 1H, bridgehead C*H*), 2.58 (br m, 5H, pyrrolidine CH_2 + bridgehead C*H*), 2.42 (br s, 2H, CH_2), 1.70 (br m, 4H, pyrrolidine CH_2), 1.58 (br d, *J* = 8.3 Hz, 1H, bridge C*H*), 1.51 (dd, *J* = 11.4, 3.6 Hz, 1H, CH_2), 1.29 (br d, *J* = 8.3 Hz, 1H, bridge C*H*), 0.88 (s, 3H, CH_3), 0.78 (dd, *J* = 11.4, 1.9 Hz, 1H, bridge CH); ^{13}C{^{1}H} NMR (100.52 MHz, CDCl$_3$, δ): 136.6, 135.9, 68.5, 56.6, 50.8, 47.7, 43.5, 42.8, 39.7, 25.0, 23.7; LRMS (EI$^+$) *m*/*z* 192 [M+H]$^+$; HRMS (ESI$^+$) exact mass calcd for $C_{13}H_{22}N$ [M+H]$^+$ requires m/z 192.1752, found m/z 192.1749; Anal. Calc for $C_{13}H_{21}N$: C, 81.61; H, 11.06; N, 7.32. Found: C, 81.77; H, 11.34; N, 7.56.



Synthesis of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide (4). A flask was charged with **3** (5.09 g, 27 mmol), benzyl bromide (12.6 mL, 81 mmol) and acetone (30 mL) and the resulting



solution left to stir at ambient temperature for 19 h, during which time a white precipitate appeared. The solid was isolated by filtration, washed with hexane (20 mL), diethyl ether (2 × 40 mL) and acetone (20 mL) and dried under high vacuum to give the product as a spectroscopically pure white solid (7.09 g, 19.6 mmol). Crystals suitable for X-ray structure determination were grown by slow diffusion of a chloroform solution layered with hexane at room temperature. *Exo*-diastereoisomer: ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 7.63 (br d, *J* = 6.4, Hz, 2H, Ar-*H*), 7.37 (m, 3H, Ar-*H*), 6.13 (dd, *J* = 5.4, 2.0 Hz, 1H, =C*H*), 6.00 (dd, *J* = 5.4, 2.0 Hz, 1H, =C*H*), 5.14 (d, *J* = 12.1 Hz, 1H, N-CH_aH$_b$-Ph), 4.62 (d *J* = 12.1 Hz, 1H, N-CH$_a$$H_b$-Ph), 4.02 (d, *J* = 13.6 Hz, 1H, CMeCH_cH$_d$-N), 3.93 (m, 1H, pyrrolidine NCH_2CH$_2$) 3.79 (m, 1H, pyrrolidine NCH_2CH$_2$), 3.71 (d, *J* = 13.6 Hz, 1H, CMeCH$_c$$H_d$-N), 3.70 (m, 2H, pyrrolidine NCH_2CH$_2$), 2.44 (br s, 1H, bridgehead C*H*), 2.51 (br s, 1H, bridgehead C*H*), 2.06 (m, 1H, pyrrolidine NCH$_2$CH_2), 1.97 (dd, *J* = 11.4, 3.6 Hz, 1H, CH_eH$_f$), 1.90 (m, 1H, pyrrolidine NCH$_2$CH_2), 1.73 (m, 2H, pyrrolidine NCH$_2$CH_2), 1.66 (d, *J* = 9.2 Hz, 1H, bridge C*H*), 1.27 (br d, *J* = 9.2 Hz, 1H, bridge C*H*), 1.18 (2, 3H, CH_3), 0.87 (dd, *J* = 11.4, 2.3 Hz, 1H, CH$_e$$H_f$); ^{13}C{^{1}H} NMR (100.52 MHz, $CDCl_3$, δ): 138.8, 134.9, 133.2, 130.7, 129.3, 128.2, 72.9, 65.1, 62.8, 60.9, 53.2, 48.1, 44.5, 42.9, 40.5, 25.8, 22.8, 21.8; HRMS (ESI$^+$) exact mass calcd for $C_{20}H_{28}N$ [M]$^+$ requires m/z 282.2222, found m/z 282.2221; Anal. Calc for $C_{20}H_{28}BrN$: C, 66.29; H, 7.79; N, 3.87. Found: C, 66.54; H, 8.13; N, 4.09%.

Ring opening metathesis polymerisation of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide with cis-cyclooctene. A flame-dried three-neck round bottom flask under a nitrogen atmosphere was charged with chloroform (80 mL), cis-cyclooctene (3.0 mL, 23.0 mmol) and **4** (4.23 g 11.7 mmol). To this was added a solution of $[RuCl_2(PCy_3)_2(=CHPh)]$ (0.571 g, 0.694 mmol) in chloroform (*ca.*10 mL) and the resulting mixture was heated at 40°C and left to stir for 19 h. Upon completion the reaction was allowed to cool to room temperature, ethyl vinyl ether (0.69 mL, 7.0 mmol) added and the solution stirred for an additional hour. The polymer was precipitated by slowly adding the reaction mixture portion wise to diethyl ether (*ca.* 600 mL) with vigorous stirring; after stirring for a further 60 minutes the polymer was isolated by filtration, using a sintered glass frit, washed with diethyl ether and dried to yield 5.2 g of a pale green solid. A solution of tris-(hydroxymethyl)-phosphine was prepared by degassing 2-propanol (90 mL) with nitrogen for 30 min prior to adding tetrakis(hydroxymethyl)phosphonium chloride (2.6 mL, 18 mmol). Potassium hydroxide (1.0 g, 18.0 mmol) was added slowly over 15 minutes to the vigorously stirred solution during which time a white precipitate formed. The mixture was allowed to stir for an additional 10 min and then added to a solution of the polymer in chloroform (*ca*. 100-150 mL). After heating at 60 °C for 19 h, NaBr (18.52 g, 180 mmol) was added and the mixture stirred for an additional 3 h at 60 ˚C. The mixture was then filtered, washed rigorously with distilled water (3 × 50 mL) and the resultant organic layer added dropwise to diethyl ether (*ca*. 500 mL) with vigorous stirring. After stirring for a minimum of 60 min the polymer was allowed to settle, isolated by filtration through a frit, washed with diethyl ether (2 × 50 mL) and dried under high vacuum to afford **5** as a buff brown solid in 61% yield (4.1 g). Anal. Calc for $C_{36}H_{56}NBr$: C, 74.20, H, 9.69, N, 2.40. Found: C, 73.82, H, 10.01, N, 2.35 (corresponding to a pyrrolidinium monomer content of 62.5 mol%, 1.72 mmol g^{-1}); GPC (average over 3 runs): M_w = 9100, M_n = 8600, PDI = 1.06 (Figure S1).

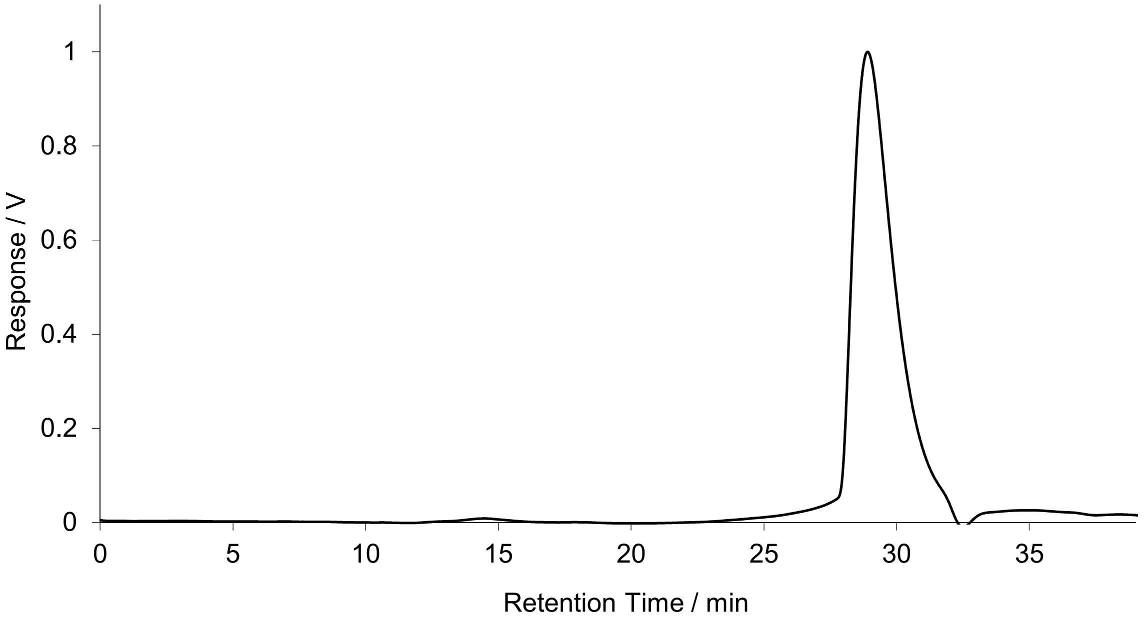


Figure S1 Differential refractive index (dRI) GPC trace of polymer **4** in DMF (0.6 mL/ min).

Synthesis of polymer supported peroxophosphotungstate 6: A hydrogen peroxide solution (35% w/w, 9.7 mL, 100 mmol) was added to phosphotungstic acid (1.73 g, 0.6 mmol) dissolved in a minimum volume of water and stirred at room temperature for 30 min. After this time, pyridine (0.145 mL, 1.8 mmol) was added followed by a solution of **5** (0.877 g, 1.8 mmol) in the minimum volume of ethanol, which resulted in the immediate precipitation of an amorphous white solid. The mixture was cooled to 0 ˚C, filtered through a sintered glass frit and the precipitate washed with water (2 × 10 mL) and diethyl ether (3 × 75 mL) and dried under vacuum to afford **6** in 84% yield. FT-IR (KBr plates): $\tilde{\nu}$ = 1086, 1058, 1035 (P-O), 957 (W=O), 837 (O-O), 563, 535 $W(O_2)_{s,as}$: Anal. Calc for $C_{108}H_{168}N_3O_{24}PW_4$: N, 1.58; W, 27.66. Found: N, 1.46; W, 26.00.

X-Ray Crystallography. Data were measured on an Agilent Gemini A Ultra diffractometer at 150 K, with Mo K_α (λ = 0.71073Å) radiation. Semiempirical absorption corrections were applied, based on symmetry-equivalent and repeated reflections. Structures were solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained riding isotropic H atoms for carbon atoms ; U(H) was set at 1.2 (1.5 for methyl groups) times Ueq of the parent atom. Hydrogen atoms for the water molecule were constrained to a distance of 0.94 Å and U(H) set at 1.2 times Ueq of the parent atom. There is evidence that there is some positional disorder within the molecules but this could not be modelled satisfactorily, and restraints were employed to improve the model. Programs were CrysAlisPro[10] for data collection, integration, and absorption corrections and SHELXTL[11] for structure solution, refinement, and graphics. A perspective view of the molecular structure of one of the crystallographically independent molecules is shown in Figure S2, confirming that the major adduct is the *exo*-diastereoisomer.

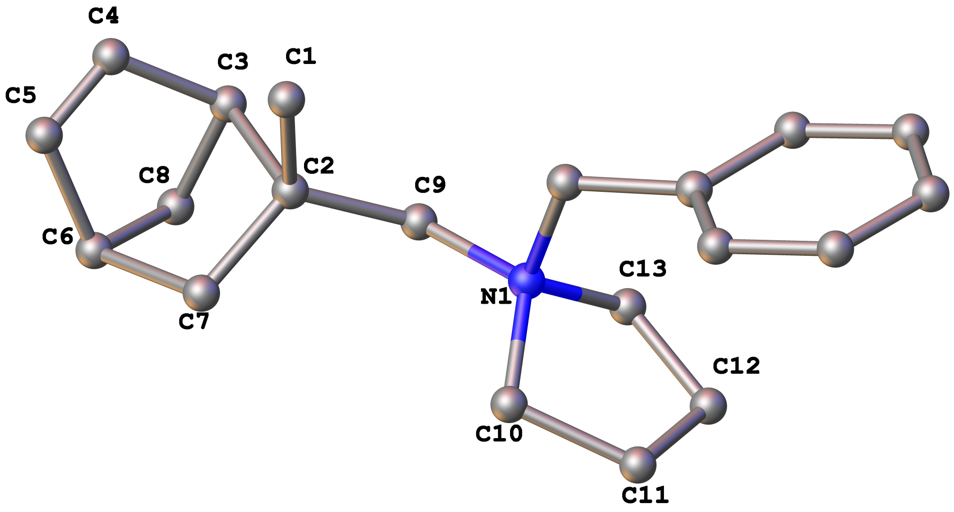
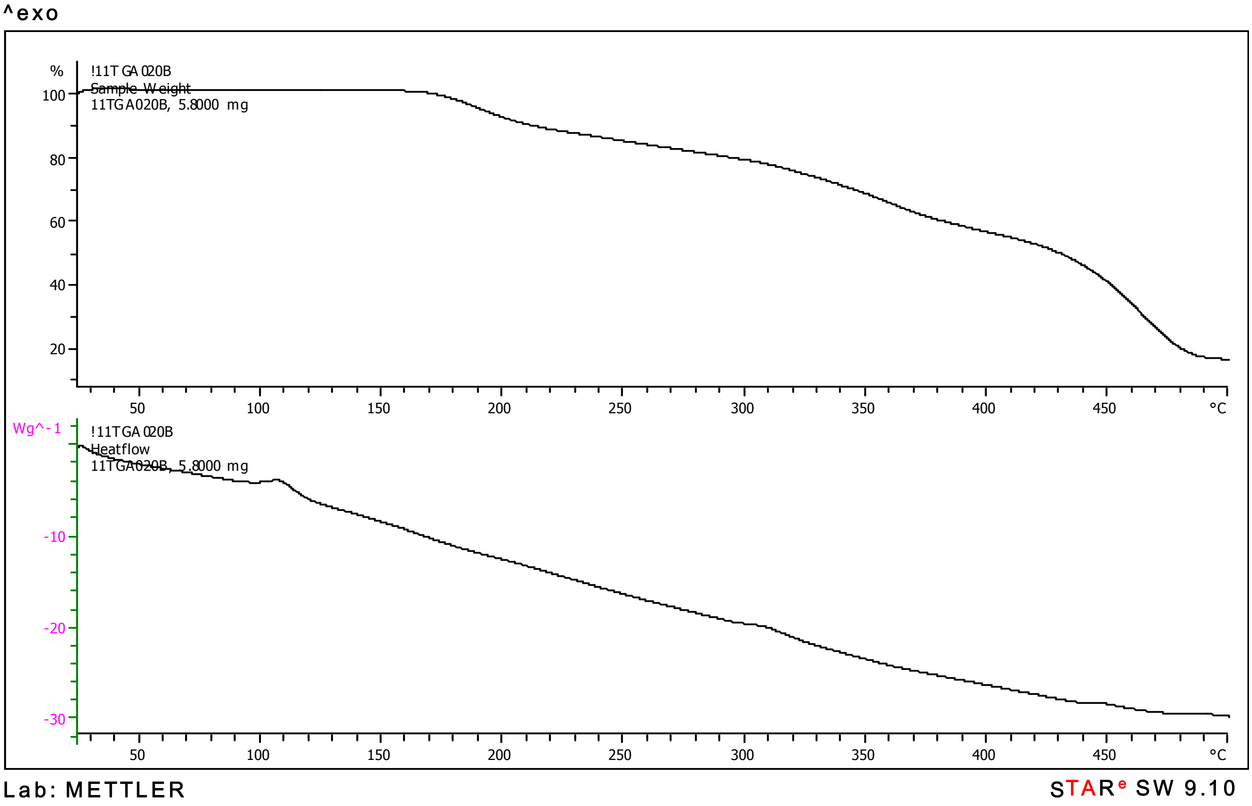


Figure S2 Molecular structure of *Exo*-2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidine (**3**), confirming the stereochemistry of cycloaddition. Hydrogen atoms, the water molecule of crystallisation and the bromide anion have been omitted for clarity.

Figure S3 TGA and DSC curves for benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide-cis-cyclooctene copolymer **5.** The heating rate was 5 ºC min^{-1}.



The heat flow plot (lower trace) of co-polymer **5** clearly shows an exotherm at 100 ^{o}C which could correspond to Hoffmann elimination with no loss in mass.

TEM Studies

Figure S4 TEM image of freshly prepared polymer supported peroxophosphotungstate **6**

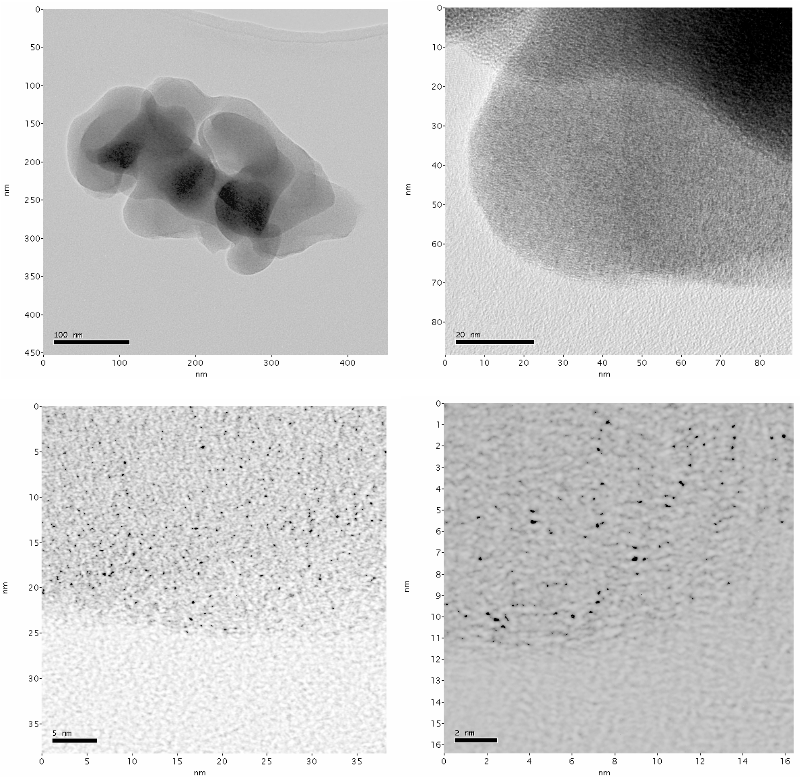
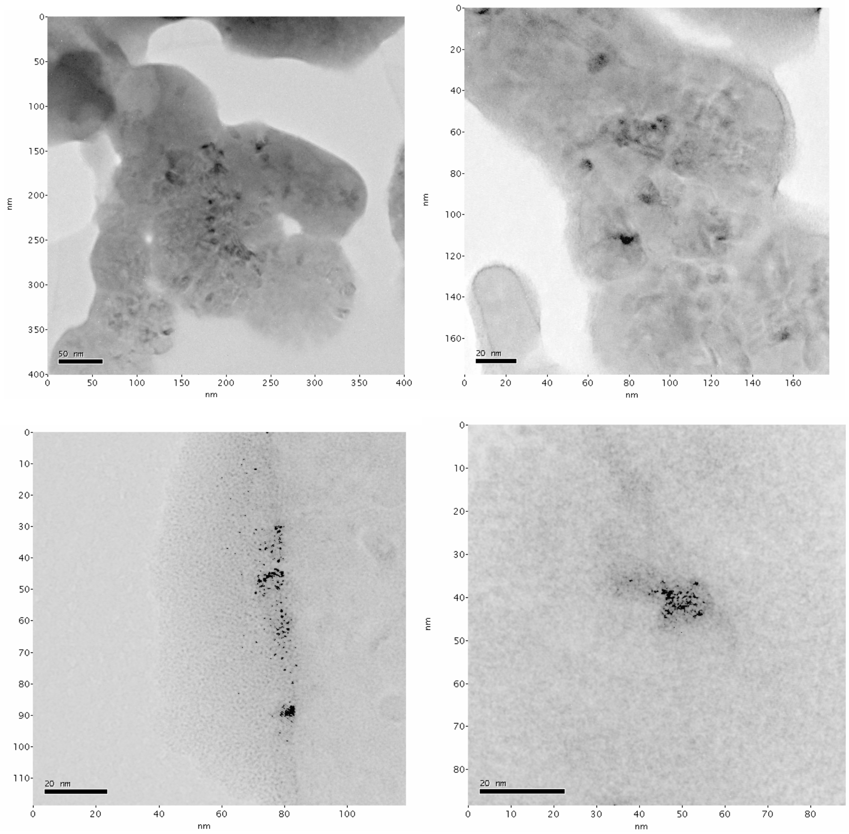


Figure S5 TEM image of polymer supported peroxophosphotungstate **6** recovered after use in catalysis



General Procedure for Catalytic Epoxidations

A Schlenk flask was charged with substrate (1.0 mmol), catalyst (2 mol% based on W) and acetonitrile (3 mL) and the resulting mixture heated at 50 ºC with rapid stirring. The reaction was initiated by the addition of hydrogen peroxide (35% solution, 0.18 mL, 2 mmol) and stirred for the allocated time. After the reaction mixture had cooled to room temperature decane (0.195 mL, 1.0 mmol) was added as internal standard and the resulting mixture diluted with diethyl ether (25 mL) and washed with water. The organic layer was separated, dried over magnesium sulphate, concentrated under reduced pressure and analyzed by GC-MS to determine the conversion before being purified by column chromatography.

General procedure for Recycle Experiments

An oven dried Schlenk flask charged with polymer supported catalyst (0.0405 g, 1.5 mol %) and acetonitrile (12 mL) was heated to 60 °C. Cyclooctene (0.40 mL, 3.0 mmol) was added, the reaction initiated by the addition of hydrogen peroxide (35% solution, 0.75 mL, 6.0 mmol) and the resulting mixture left to stir at 60 ºC for 3 hours. After this time, decane (0.195 mL, 1.0 mmol) was added as internal standard, the solution centrifuged (10 min, 12000 rpm), decanted and the remaining catalyst washed with water and diethyl ether and dried prior to reuse under the same conditions.

Trans-2,3-epoxyhexan-1-ol.[3] ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 3.91 (m, 1H), 3.60 (m, 1H), 2.92 (m, 2H), 1.77 (t, *J* = 6.2 Hz, 1H), 1.44 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 61.6, 58.2, 55.7, 33.5, 19.2, 13.8; GC-MS (EI), m/z = 99 [M^+-17].

Cis-2,3-epoxyhexen-1-ol.[4] ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 3.81 (dd, *J* = 12.2, 3.9 Hz, 1H), 3.60 (dd, *J* = 12.2, 7.0 Hz, 1H), 3.20-3.13 (m, 1H), 3.07-3.00 (m 1H), 2.14-2.03 (m 1H), 1.61-1.39 (m 4H), 1.05-0.99 (m, 3H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 61.1, 57.4, 56.8, 30.1, 19.9, 14.2; GC-MS (EI), m/z = 99 [M^+-17].

3-Methyl-2,3-epoxybutan-1-ol.[5] ^{1}H NMR (399.78 MHz, $CDCl_3$, δ): 3.83 (m, 1H), 3.65 (m, 1H), 2.95 dd, *J* = 6.5, 2.5 Hz, 1H), 1.78 (m, 1H), 1.31 (s, 3H), 1.29 (s, 3H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 63.8, 61.2, 58.7, 24.5, 18.6; GC-MS (EI), m/z = 101 [M^+-1].

2,3-epoxy-3,7-dimethyl-6-octene-1-ol.[6] ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 5.11 (br t, *J* = 7.1 Hz, 1H), 3.72 (dd, J = 12.2, 4.2 Hz, 1H), 3.60, dd, *J* = 12.2, 6.8 Hz, 1H), 2.99 (dd, *J* = 6.6, 4.2

Hz, 1H), 2.04 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H). 1.31 (s, 3H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 132.1, 123.2, 63.1, 61.4. 61.0, 33.1, 25.4, 24.2, 17.7, 16.5; GC-MS (EI), m/z = 149 [M^+-21].

Trans-3,4-epxoyhexan-1-ol.[3,4] ^1H NMR (399.78 MHz, $CDCl_3$, δ): 3.71 (d, *J* = 6.1 Hz, 2H), 2.79 (ddd, *J* = 7.6, 4.4, 2.2 Hz, 1H), 2.71 (dt, *J* = 5.4, 2.3 Hz, 1H), 2.15 (s, 1H), 1.91-1.80 (m, 1H), 1.66-1.54 (m, 1H), 1.58-1.43 (m, 2H), 0.91 (t, *J* = 7.7 Hz, 3H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 62.4, 50.0, 56.2, 33.9, 19.7, 14.1.

Cis-cycloctene epoxide.[7] ^1H NMR (399.78 MHz, $CDCl_3$, δ): 2.88 (m, 2H), 2.12 (m, 2H), 1.65-1.42 (m, 8H), 1.22 (m, 2H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 55.6, 26.5, 26.2, 25.7. GC-MS (EI), m/z = 126 [M^+].

Cyclohexene epoxide.[8] ^1H NMR (399.78 MHz, $CDCl_3$, δ): 3.11 (s, 2H), 1.95-1.72 (m, 4H), 1.44-1.12 (m, 4H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 52.2, 24.7, 19.6; GC-MS (EI), m/z = 98 [M^+].

2,3-Epoxybicyclo[2.2.1]heptanes[8] ^1H NMR (399.78 00 MHz, $CDCl_3$, δ): 3.01 (s, 2H), 2.38 (br s, 2H), 1.45.-1.40 (m, 2H), 1.30-1.25 (m, 1H), 1.18-1.12 (m, 2H), 0.64 (d, *J* = 9.8 Hz, 1H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 51.2, 36.5, 26.1, 24.9; GC-MS (EI), m/z = 110 [M^+].

Styrene epoxide.[9] ^1H NMR (399.78 MHz, $CDCl_3$, δ):7.30 (m, 5H), 3.82 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.11 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.77 (dd, *J* = 5.2, 2.5 Hz, 1H); $^{13}C\{^1H\}$ (100.52 MHz, $CDCl_3$, δ): 137.4, 128.2, 128.0, 125.4, 52.2, 51.3; GC-MS (EI), m/z = 120 [M^+].

Figure S6 ^{1}H NMR spectrum of 2-methylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (**1**) (a mixture of diasterisomers)

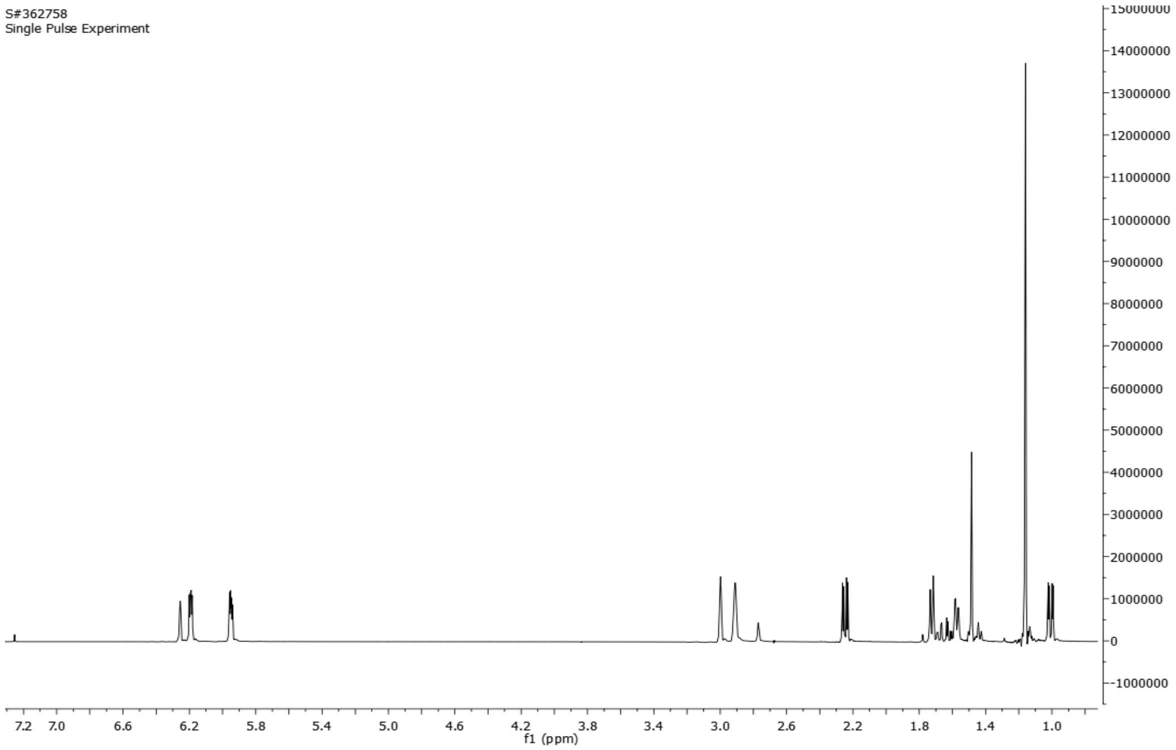


Figure S7 ^{13}C{^{1}H} NMR spectrum of 2-methylbicyclo[2.2.1]hept-5-ene-2-carbonitrile (**1**) (a mixture of diasterisomers)

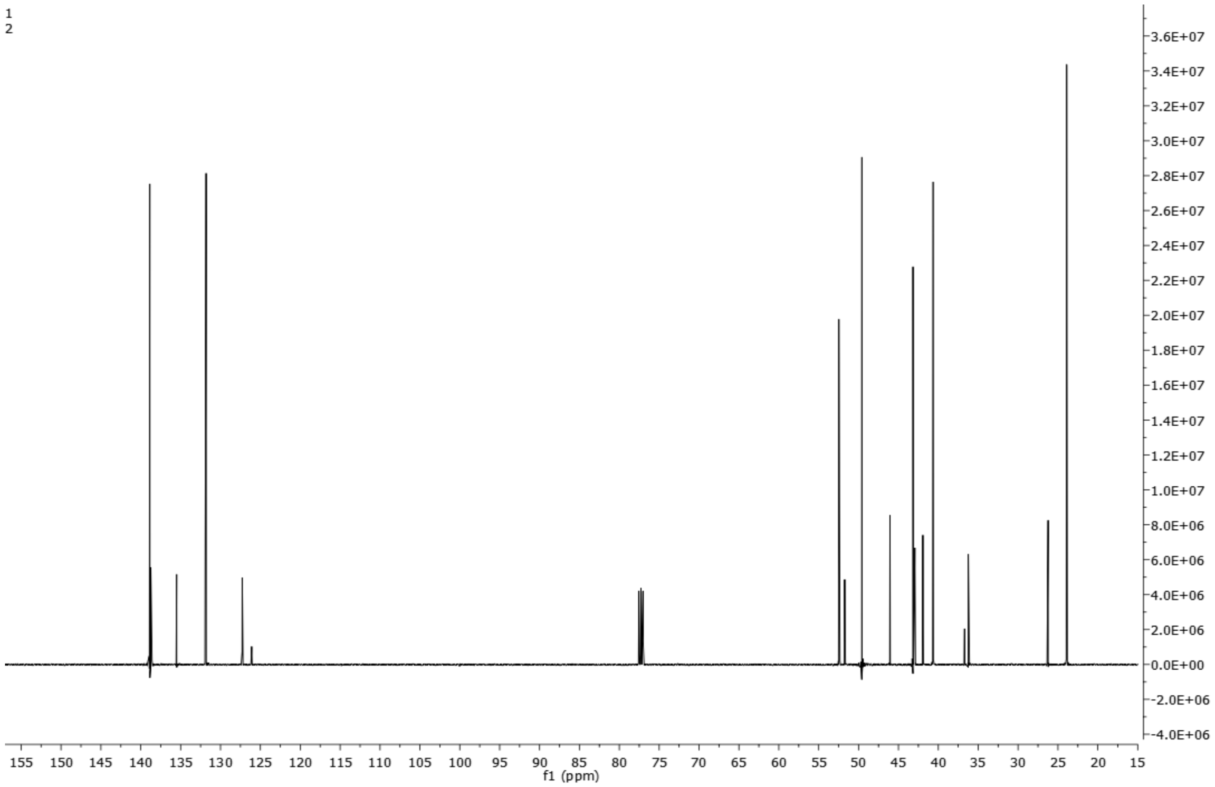


Figure S8 ^{1}H NMR spectrum of (2-methylbicyclo[2.2.1]hept-5-en-2-yl)methylamine (**2**)

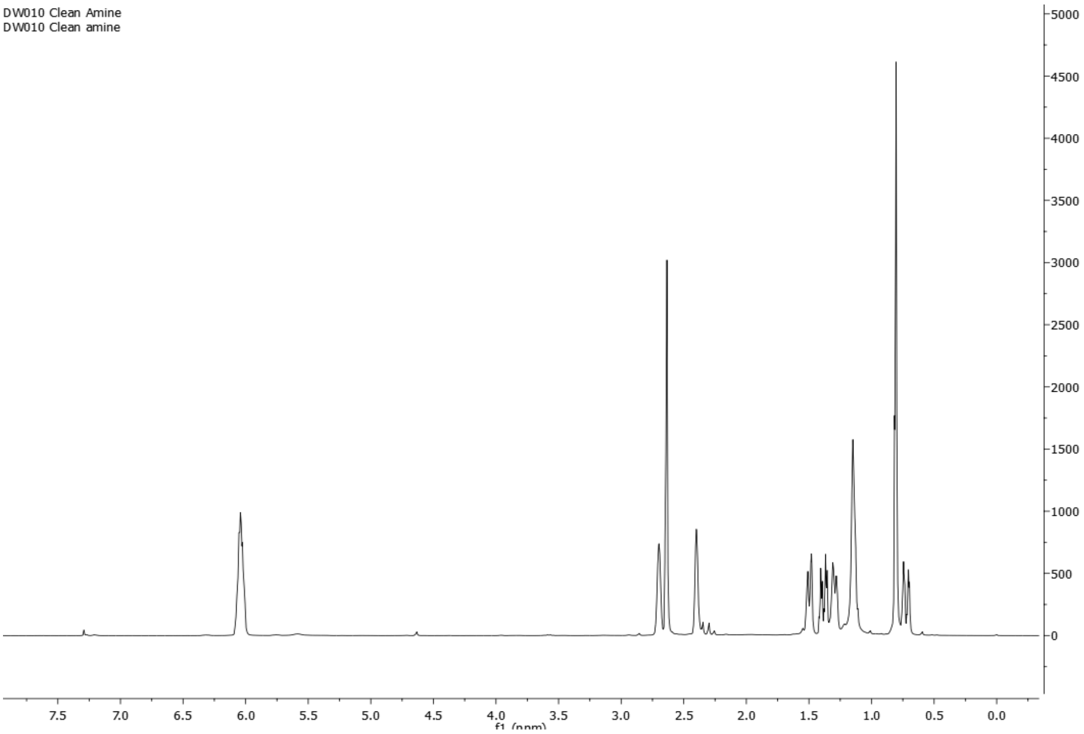


Figure S9 ^{13}C{^{1}H} NMR spectrum of (2-methylbicyclo[2.2.1]hept-5-en-2-yl)methylamine (**2**)

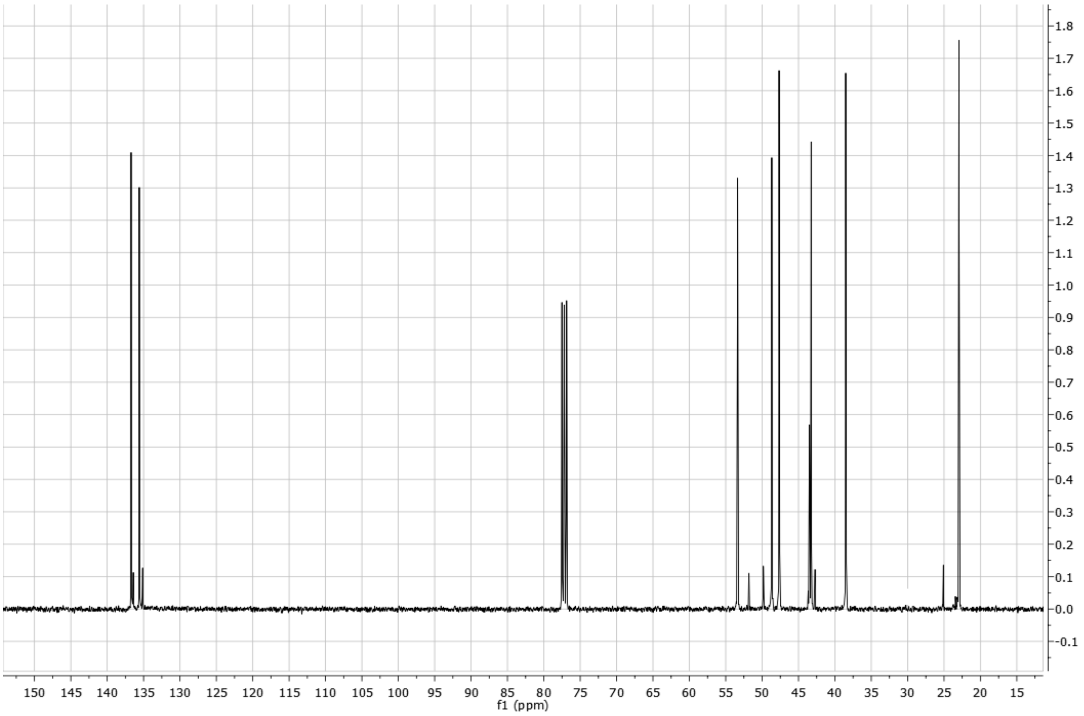


Figure S10 ^{1}H NMR spectrum of 1-(-2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidine (**3**).

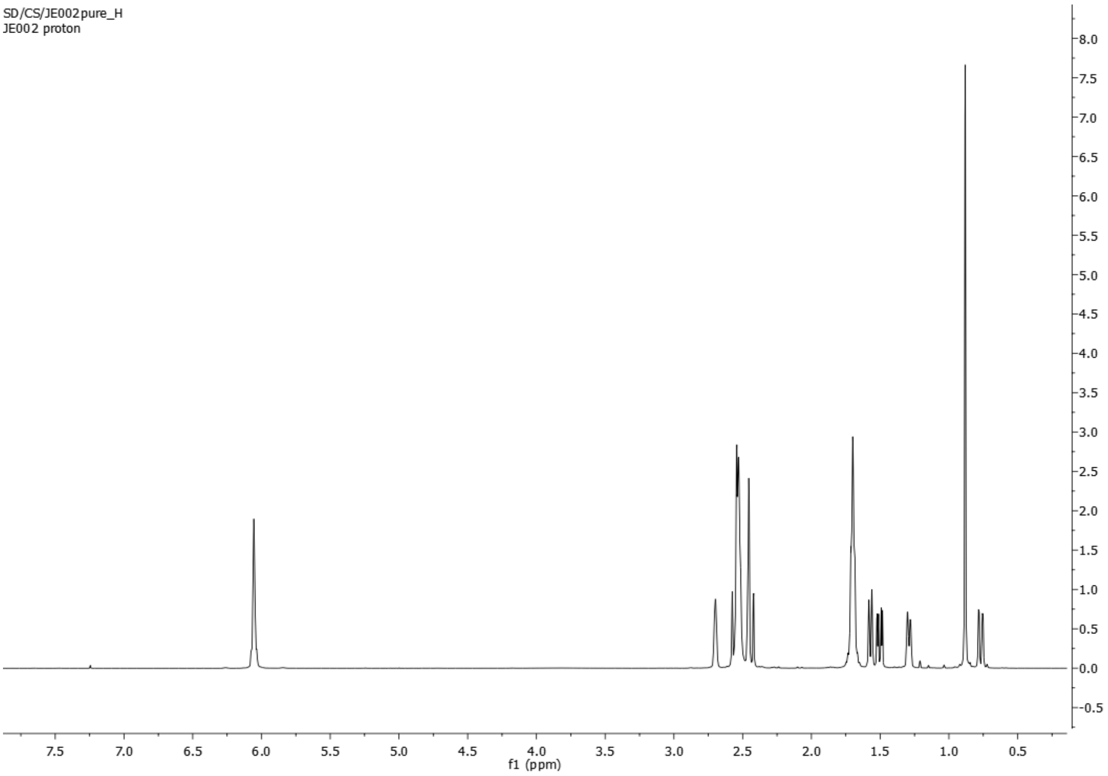


Figure S11 $^{13}C\{^1H\}$ NMR spectrum of 1-(-2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidine (**3**).

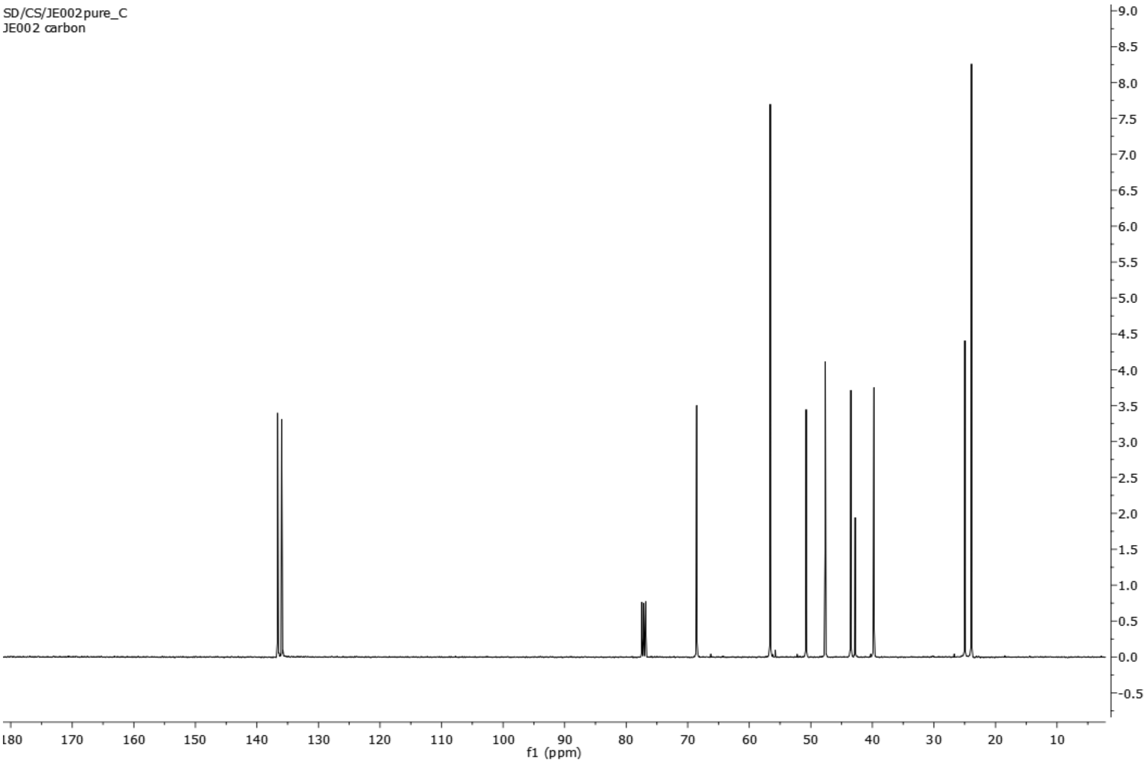


Figure S12 ^{1}H NMR spectrum of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide (**4**).

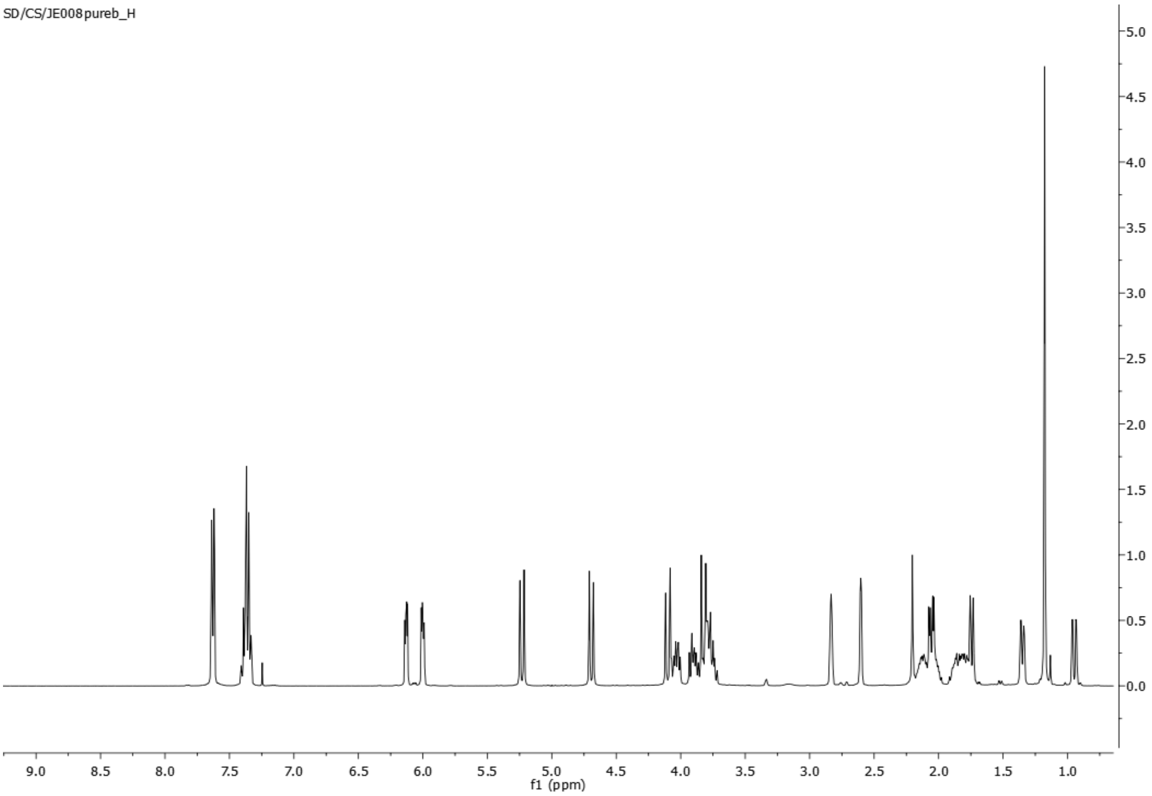


Figure S13 $^{13}C\{^{1}H\}$ NMR spectrum of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide (**4**).

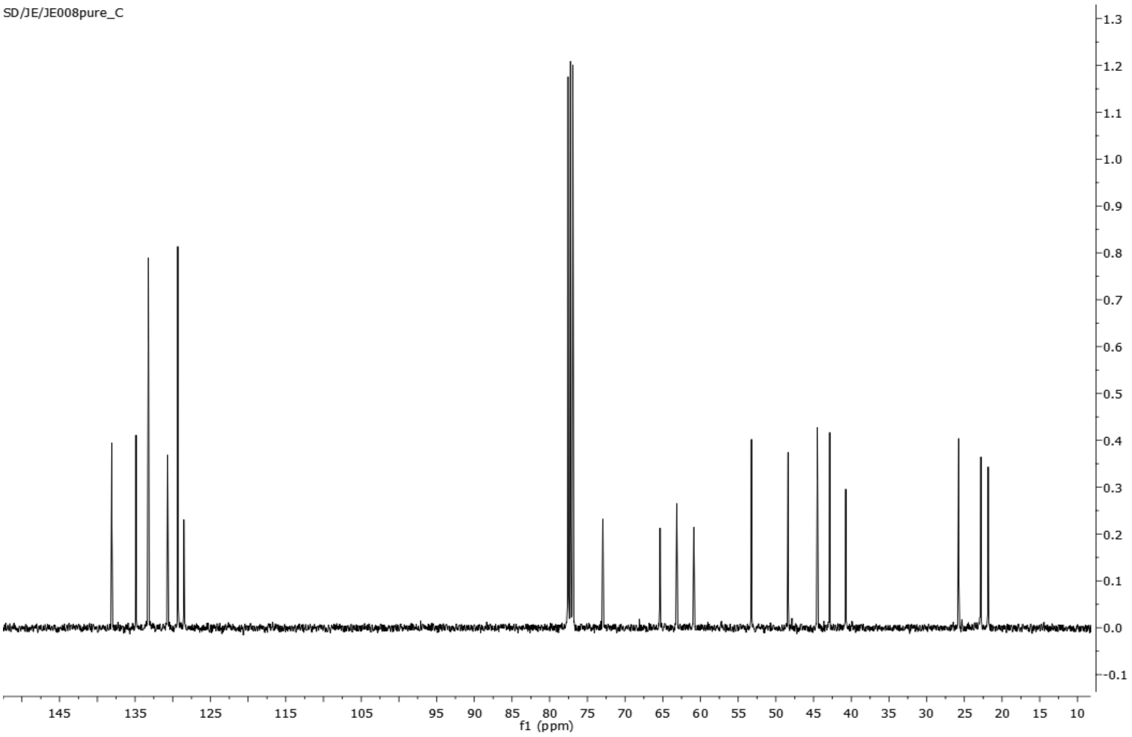


Figure S14 ^{1}H NMR spectrum of polymer **5**

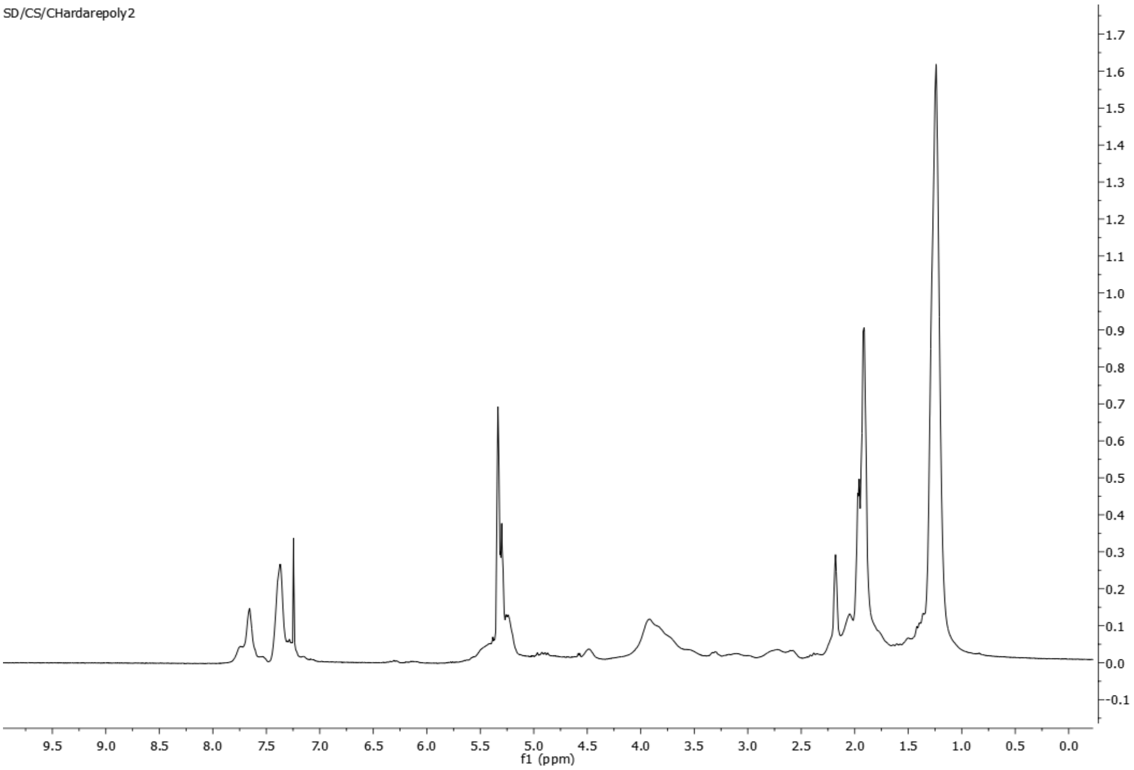


Figure S15 ^{13}C{^{1}H} NMR spectrum of polymer **5** .

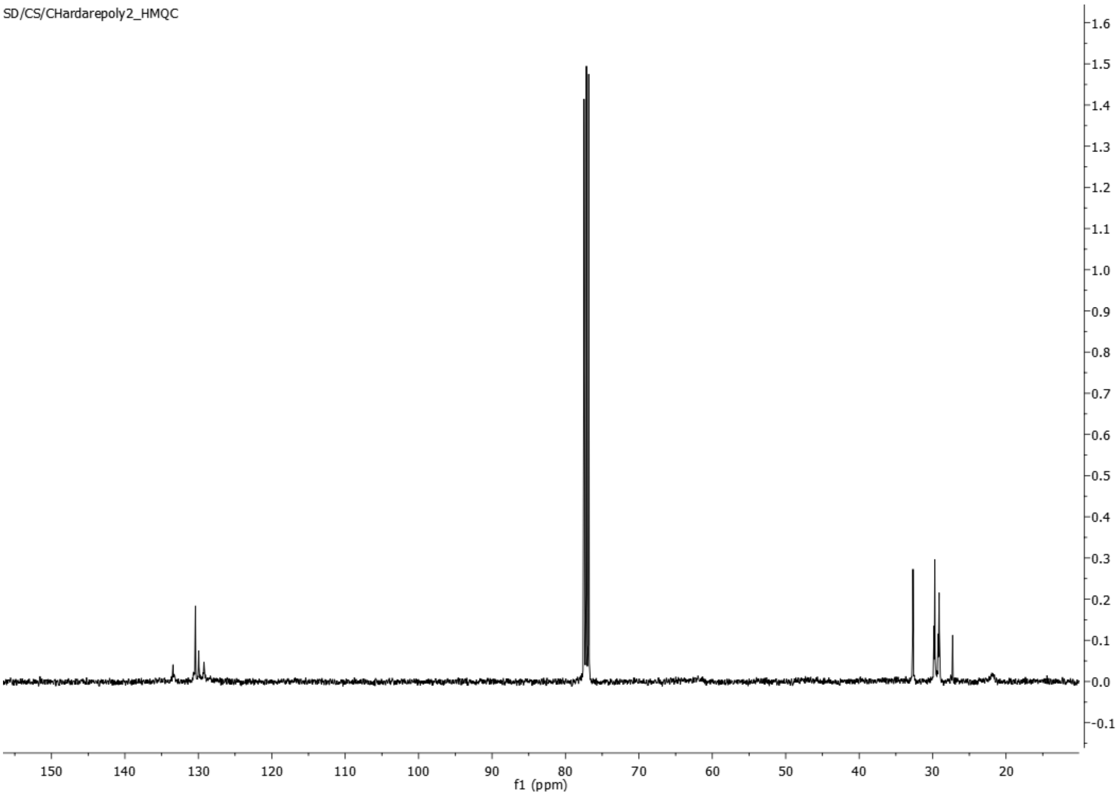


Figure S16 Nitrogen adsorption-desorption of copolymer **6**

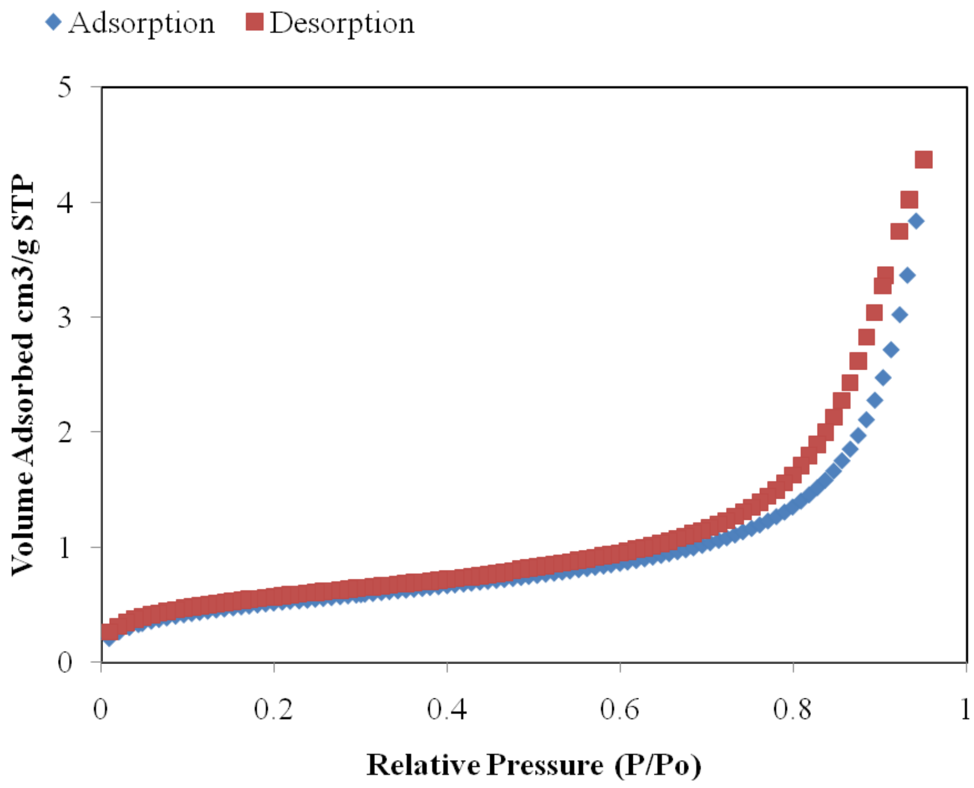
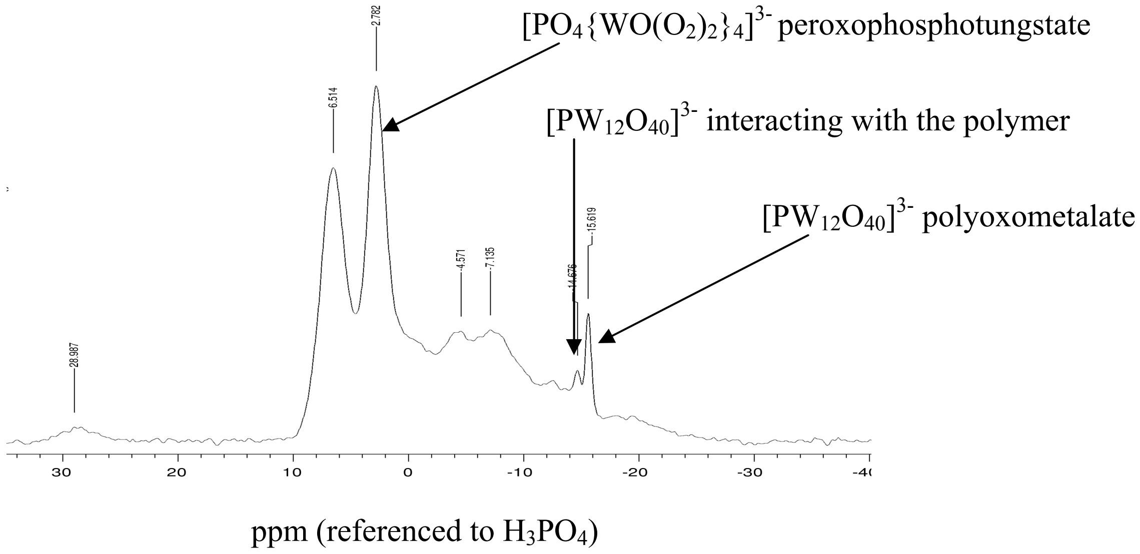


Figure S17 ^{31}P Solid state NMR spectra of fresh and used catalyst **6**

a) Freshly prepared PIILP catalyst **6**



b) Copolymer **6** isolated after use in catalysis

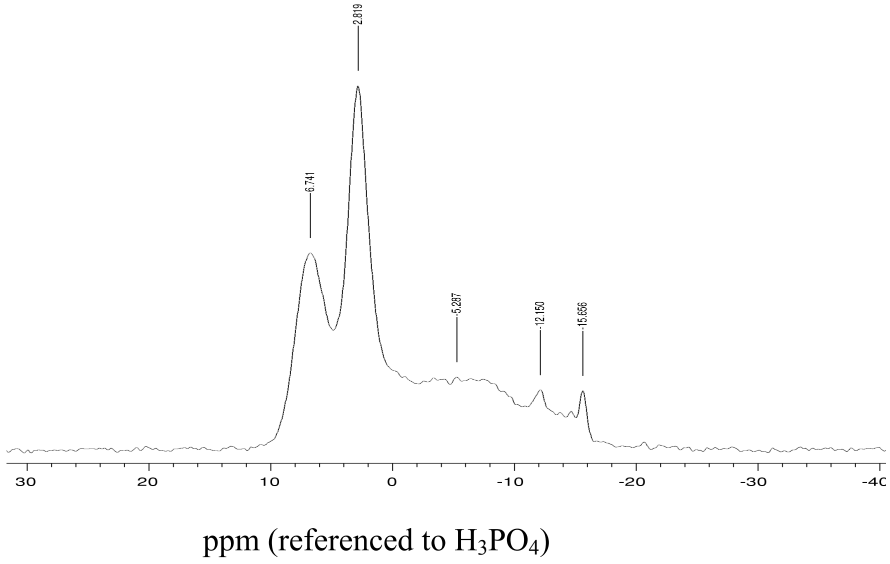


Table S1 Crystal data and structure refinement for **3**.

Identification code	sd304_compound 3	
Chemical formula (moiety)	$2C_{20}H_{28}N^{+}\cdot 2Br^{-}\cdot H_2O$	
Chemical formula (total)	$C_{40}H_{58}Br_2N_2O$	
Formula weight	742.70	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P12_1/c1$	
Unit cell parameters	a = 11.8140(5) Å	α = 90°
	b = 21.2181(11) Å	β = 95.337(4)°
	c = 14.6684(6) Å	γ = 90°
Cell volume	3661.0(3) $Å^3$	
Z	4	
Calculated density	1.347 g/cm^3	
Absorption coefficient μ	2.247 mm^{-1}	
F(000)	1560	
Crystal colour and size	colourless, 0.30 × 0.10 × 0.02 mm^3	
Reflections for cell refinement	5693 (θ range 2.8 to 26.8°)	
Data collection method	Xcalibur, Atlas, Gemini ultra thick-slice ω scans	
θ range for data collection	2.8 to 26.0°	
Index ranges	h −14 to 14, k −25 to 26, l −17 to 17	
Completeness to θ = 25.0°	99.9 %	
Reflections collected	22964	
Independent reflections	7010 (R_{int} = 0.0636)	
Reflections with $F^2>2\sigma$	4646	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.5521 and 0.9564	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0624, 11.2873	
Data / restraints / parameters	7010 / 85 / 415	
Final R indices [$F^2>2\sigma$]	R1 = 0.0619, wR2 = 0.1392	
R indices (all data)	R1 = 0.1057, wR2 = 0.1671	
Goodness-of-fit on F^2	1.025	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	1.13 and −0.75 e $Å^{-3}$	

Table S2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	0.93100(5)	0.17478(3)	0.56105(4)	0.03769(18)
Br(2)	0.38999(5)	0.24152(3)	0.21446(4)	0.0427(2)
N(1)	0.0564(4)	0.2100(2)	0.2897(3)	0.0438(13)
N(2)	0.5437(3)	0.1900(2)	0.4725(3)	0.0249(9)
C(1)	0.1588(7)	0.3057(4)	0.4570(5)	0.064(2)
C(2)	0.0923(7)	0.3248(3)	0.3712(5)	0.070(2)
C(3)	0.1702(10)	0.3848(4)	0.3452(6)	0.106(3)
C(4)	0.1811(13)	0.4233(8)	0.4307(10)	0.179(6)
C(5)	0.0946(13)	0.4397(6)	0.4523(10)	0.143(5)
C(6)	0.0110(14)	0.4271(7)	0.3704(10)	0.151(4)
C(7)	–0.0185(10)	0.3514(6)	0.3895(8)	0.124(3)
C(8)	0.0786(11)	0.4201(6)	0.2928(9)	0.125(3)
C(9)	0.0976(7)	0.2815(4)	0.2878(5)	0.067(2)
C(10)	–0.0632(7)	0.1954(6)	0.3014(6)	0.107(4)
C(11)	–0.0912(7)	0.1354(6)	0.2467(7)	0.104(4)
C(12)	–0.0122(6)	0.1347(4)	0.1747(5)	0.067(2)
C(13)	0.0659(6)	0.1890(3)	0.1925(4)	0.0497(17)
C(14)	0.1390(5)	0.1753(3)	0.3579(4)	0.0319(12)
C(15)	0.1522(4)	0.1058(3)	0.3462(3)	0.0291(12)
C(16)	0.0919(5)	0.0639(3)	0.3955(4)	0.0410(14)
C(17)	0.1068(6)	–0.0009(3)	0.3866(5)	0.0525(17)
C(18)	0.1825(6)	–0.0229(3)	0.3305(5)	0.0574(19)
C(19)	0.2470(5)	0.0181(3)	0.2832(5)	0.0546(18)
C(20)	0.2315(5)	0.0822(3)	0.2909(4)	0.0404(14)
C(21)	0.6894(6)	0.3008(3)	0.5644(6)	0.067(2)
C(22)	0.5993(6)	0.3122(3)	0.4860(4)	0.0439(15)
C(23)	0.6475(7)	0.3301(3)	0.3921(6)	0.073(2)
C(24)	0.6000(11)	0.3952(4)	0.3671(6)	0.100(3)
C(25)	0.6657(11)	0.4361(5)	0.4407(6)	0.112(4)
C(26)	0.6243(9)	0.4266(4)	0.5143(7)	0.093(3)
C(27)	0.5310(7)	0.3742(3)	0.5024(5)	0.063(2)
C(28)	0.4924(8)	0.3933(5)	0.4026(7)	0.100(3)
C(29)	0.5097(5)	0.2599(2)	0.4769(4)	0.0306(12)
C(30)	0.4337(4)	0.1535(3)	0.4501(4)	0.0300(12)
C(31)	0.4517(5)	0.0889(3)	0.4913(4)	0.0355(13)
C(32)	0.5324(5)	0.1008(3)	0.5776(4)	0.0487(17)
C(33)	0.5906(4)	0.1634(3)	0.5651(3)	0.0277(12)
C(34)	0.6239(4)	0.1815(3)	0.3985(3)	0.0292(12)
C(35)	0.6413(4)	0.1147(3)	0.3673(4)	0.0302(12)
C(36)	0.5761(5)	0.0932(3)	0.2893(4)	0.0346(13)
C(37)	0.5880(5)	0.0315(3)	0.2600(4)	0.0441(15)
C(38)	0.6663(6)	–0.0077(3)	0.3061(4)	0.0470(16)
C(39)	0.7332(5)	0.0138(3)	0.3822(4)	0.0400(14)
C(40)	0.7215(4)	0.0753(3)	0.4125(4)	0.0325(13)
O(1)	0.2240(4)	0.1516(2)	0.5882(3)	0.0524(12)

Table S3 Bond lengths [Å] and angles [°] for **3**.

N(1)–C(9)	1.596(9)	N(1)–C(10)	1.472(10)
N(1)–C(13)	1.508(8)	N(1)–C(14)	1.520(7)
N(2)–C(29)	1.539(6)	N(2)–C(30)	1.521(6)
N(2)–C(33)	1.527(6)	N(2)–C(34)	1.516(6)
C(1)–C(2)	1.476(11)	C(2)–C(3)	1.637(8)
C(2)–C(7)	1.472(12)	C(2)–C(9)	1.536(10)
C(3)–C(4)	1.492(14)	C(3)–C(8)	1.472(14)
C(4)–C(5)	1.152(16)	C(5)–C(6)	1.507(19)
C(6)–C(7)	1.671(18)	C(6)–C(8)	1.457(15)
C(10)–C(11)	1.524(15)	C(11)–C(12)	1.473(12)
C(12)–C(13)	1.483(9)	C(14)–C(15)	1.495(8)
C(15)–C(16)	1.384(8)	C(15)–C(20)	1.389(8)
C(16)–C(17)	1.394(9)	C(17)–C(18)	1.354(10)
C(18)–C(19)	1.384(10)	C(19)–C(20)	1.379(9)
C(21)–C(22)	1.512(9)	C(22)–C(23)	1.585(10)
C(22)–C(27)	1.573(9)	C(22)–C(29)	1.530(8)
C(23)–C(24)	1.524(12)	C(24)–C(25)	1.537(13)
C(24)–C(28)	1.418(13)	C(25)–C(26)	1.242(12)
C(26)–C(27)	1.565(12)	C(27)–C(28)	1.547(11)
C(30)–C(31)	1.506(7)	C(31)–C(32)	1.534(8)
C(32)–C(33)	1.514(8)	C(34)–C(35)	1.509(7)
C(35)–C(36)	1.395(7)	C(35)–C(40)	1.386(8)
C(36)–C(37)	1.388(8)	C(37)–C(38)	1.375(9)
C(38)–C(39)	1.383(9)	C(39)–C(40)	1.390(8)

C(9)–N(1)–C(10)	120.0(7)	C(9)–N(1)–C(13)	102.4(5)
C(9)–N(1)–C(14)	107.1(5)	C(10)–N(1)–C(13)	101.8(6)
C(10)–N(1)–C(14)	112.7(6)	C(13)–N(1)–C(14)	112.3(5)
C(29)–N(2)–C(30)	106.2(4)	C(29)–N(2)–C(33)	113.2(4)
C(29)–N(2)–C(34)	109.1(4)	C(30)–N(2)–C(33)	103.7(4)
C(30)–N(2)–C(34)	111.3(4)	C(33)–N(2)–C(34)	113.2(4)
C(1)–C(2)–C(3)	98.4(7)	C(1)–C(2)–C(7)	111.3(7)
C(1)–C(2)–C(9)	117.1(6)	C(3)–C(2)–C(7)	105.9(8)
C(3)–C(2)–C(9)	102.3(6)	C(7)–C(2)–C(9)	118.5(9)
C(2)–C(3)–C(4)	103.7(8)	C(2)–C(3)–C(8)	96.6(9)
C(4)–C(3)–C(8)	99.3(11)	C(3)–C(4)–C(5)	112.8(14)
C(4)–C(5)–C(6)	105.1(13)	C(5)–C(6)–C(7)	99.7(11)
C(5)–C(6)–C(8)	105.9(13)	C(7)–C(6)–C(8)	99.8(10)
C(2)–C(7)–C(6)	97.8(9)	C(3)–C(8)–C(6)	94.3(10)
N(1)–C(9)–C(2)	121.3(5)	N(1)–C(10)–C(11)	106.1(6)
C(10)–C(11)–C(12)	105.3(7)	C(11)–C(12)–C(13)	107.0(7)
N(1)–C(13)–C(12)	107.2(5)	N(1)–C(14)–C(15)	118.0(4)
C(14)–C(15)–C(16)	120.6(5)	C(14)–C(15)–C(20)	120.4(5)
C(16)–C(15)–C(20)	118.8(5)	C(15)–C(16)–C(17)	120.6(6)
C(16)–C(17)–C(18)	119.6(6)	C(17)–C(18)–C(19)	120.9(6)
C(18)–C(19)–C(20)	119.7(6)	C(15)–C(20)–C(19)	120.3(6)
C(21)–C(22)–C(23)	114.5(6)	C(21)–C(22)–C(27)	110.6(5)
C(21)–C(22)–C(29)	112.5(5)	C(23)–C(22)–C(27)	99.4(5)
C(23)–C(22)–C(29)	113.6(5)	C(27)–C(22)–C(29)	105.0(5)
C(22)–C(23)–C(24)	105.8(6)	C(23)–C(24)–C(25)	101.1(9)
C(23)–C(24)–C(28)	102.0(7)	C(25)–C(24)–C(28)	99.8(8)
C(24)–C(25)–C(26)	107.8(9)	C(25)–C(26)–C(27)	110.4(8)
C(22)–C(27)–C(26)	104.2(6)	C(22)–C(27)–C(28)	100.6(6)
C(26)–C(27)–C(28)	93.5(7)	C(24)–C(28)–C(27)	99.2(7)

N(2)–C(29)–C(22)	121.4(4)	N(2)–C(30)–C(31)	106.9(4)
C(30)–C(31)–C(32)	103.6(5)	C(31)–C(32)–C(33)	107.4(5)
N(2)–C(33)–C(32)	107.5(4)	N(2)–C(34)–C(35)	116.2(4)
C(34)–C(35)–C(36)	118.4(5)	C(34)–C(35)–C(40)	121.9(5)
C(36)–C(35)–C(40)	119.6(5)	C(35)–C(36)–C(37)	119.9(6)
C(36)–C(37)–C(38)	120.1(6)	C(37)–C(38)–C(39)	120.3(6)
C(38)–C(39)–C(40)	120.1(6)	C(35)–C(40)–C(39)	119.9(5)

Table S4 Anisotropic displacement parameters (Å^2) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	0.0346(3)	0.0369(4)	0.0411(3)	−0.0050(3)	0.0012(2)	−0.0048(2)
Br(2)	0.0397(3)	0.0515(4)	0.0371(3)	0.0147(3)	0.0046(3)	−0.0005(3)
N(1)	0.051(3)	0.035(3)	0.043(3)	0.003(2)	−0.006(2)	0.018(2)
N(2)	0.026(2)	0.026(2)	0.023(2)	0.0009(18)	0.0029(17)	−0.0001(18)
C(1)	0.086(5)	0.059(5)	0.049(4)	−0.017(3)	0.011(4)	−0.022(4)
C(2)	0.117(6)	0.051(4)	0.048(4)	0.002(3)	0.037(4)	0.027(4)
C(3)	0.201(8)	0.054(5)	0.070(5)	0.014(4)	0.057(6)	0.025(5)
C(4)	0.147(9)	0.236(14)	0.161(10)	−0.128(10)	0.055(7)	−0.080(10)
C(5)	0.164(11)	0.128(10)	0.153(9)	−0.061(8)	0.100(8)	−0.014(8)
C(6)	0.198(10)	0.117(7)	0.147(10)	0.021(8)	0.063(7)	0.079(8)
C(7)	0.123(7)	0.141(8)	0.109(8)	−0.001(6)	0.021(6)	0.064(6)
C(8)	0.147(10)	0.096(8)	0.137(7)	−0.001(6)	0.033(6)	0.032(7)
C(9)	0.096(6)	0.057(5)	0.050(4)	0.016(4)	0.019(4)	0.013(4)
C(10)	0.045(5)	0.226(14)	0.054(5)	0.021(7)	0.021(4)	0.056(7)
C(11)	0.048(5)	0.153(10)	0.103(7)	0.082(7)	−0.031(5)	−0.040(6)
C(12)	0.061(5)	0.083(6)	0.052(4)	0.001(4)	−0.023(4)	−0.009(4)
C(13)	0.054(4)	0.065(5)	0.028(3)	0.019(3)	−0.009(3)	−0.013(3)
C(14)	0.037(3)	0.030(3)	0.027(3)	0.006(2)	−0.004(2)	0.001(2)
C(15)	0.031(3)	0.028(3)	0.026(3)	0.006(2)	−0.009(2)	0.006(2)
C(16)	0.049(4)	0.040(4)	0.034(3)	0.009(3)	0.003(3)	0.000(3)
C(17)	0.061(4)	0.039(4)	0.057(4)	0.012(3)	0.002(3)	−0.004(3)
C(18)	0.058(4)	0.030(4)	0.082(5)	0.006(4)	−0.005(4)	0.005(3)
C(19)	0.044(4)	0.047(4)	0.073(5)	−0.014(4)	0.006(3)	0.010(3)
C(20)	0.037(3)	0.040(4)	0.043(3)	0.001(3)	0.002(3)	−0.002(3)
C(21)	0.068(5)	0.035(4)	0.091(6)	0.000(4)	−0.027(4)	−0.010(3)
C(22)	0.059(4)	0.024(3)	0.047(4)	−0.004(3)	−0.006(3)	−0.002(3)
C(23)	0.097(6)	0.038(4)	0.089(6)	0.005(4)	0.035(5)	−0.030(4)
C(24)	0.186(11)	0.060(6)	0.059(6)	0.005(5)	0.034(6)	−0.005(7)
C(25)	0.186(11)	0.100(8)	0.051(5)	−0.009(5)	0.012(6)	−0.091(8)
C(26)	0.137(9)	0.041(5)	0.099(8)	−0.027(5)	0.008(7)	0.005(5)
C(27)	0.101(6)	0.030(4)	0.055(4)	−0.007(3)	−0.008(4)	0.011(4)
C(28)	0.092(7)	0.074(7)	0.130(9)	0.065(6)	−0.012(6)	0.004(5)
C(29)	0.037(3)	0.028(3)	0.028(3)	0.002(2)	0.004(2)	0.010(2)
C(30)	0.023(3)	0.040(3)	0.028(3)	0.005(2)	0.002(2)	−0.004(2)
C(31)	0.034(3)	0.030(3)	0.043(3)	0.011(3)	0.010(3)	−0.004(2)
C(32)	0.051(4)	0.049(4)	0.045(4)	0.020(3)	−0.005(3)	−0.011(3)
C(33)	0.030(3)	0.033(3)	0.020(3)	0.002(2)	0.002(2)	0.004(2)
C(34)	0.028(3)	0.034(3)	0.028(3)	−0.003(2)	0.010(2)	−0.003(2)
C(35)	0.031(3)	0.030(3)	0.031(3)	−0.005(2)	0.015(2)	−0.008(2)
C(36)	0.036(3)	0.041(4)	0.028(3)	−0.005(3)	0.008(2)	−0.004(3)
C(37)	0.056(4)	0.044(4)	0.033(3)	−0.013(3)	0.009(3)	−0.011(3)
C(38)	0.061(4)	0.030(3)	0.054(4)	−0.012(3)	0.029(3)	−0.005(3)
C(39)	0.041(3)	0.037(4)	0.044(4)	0.000(3)	0.014(3)	0.003(3)
C(40)	0.029(3)	0.038(3)	0.032(3)	0.000(3)	0.008(2)	−0.002(2)
O(1)	0.043(3)	0.055(3)	0.060(3)	−0.017(2)	0.009(2)	0.001(2)

Table S5 Hydrogen coordinates and isotropic displacement parameters (Å^2) for **3**.

	x	y	z	U
H(1C)	0.1107	0.2808	0.4943	0.097
H(1D)	0.1859	0.3433	0.4911	0.097
H(1E)	0.2240	0.2803	0.4424	0.097
H(3A)	0.2409	0.3759	0.3149	0.127
H(4A)	0.2519	0.4332	0.4638	0.214
H(5A)	0.0792	0.4574	0.5093	0.172
H(6A)	−0.0556	0.4562	0.3615	0.181
H(7A)	−0.0360	0.3439	0.4533	0.148
H(7B)	−0.0813	0.3354	0.3463	0.148
H(8A)	0.1045	0.4609	0.2696	0.150
H(8B)	0.0396	0.3951	0.2422	0.150
H(9A)	0.1776	0.2810	0.2730	0.080
H(9B)	0.0528	0.3021	0.2357	0.080
H(10A)	−0.1132	0.2303	0.2780	0.129
H(10B)	−0.0736	0.1887	0.3669	0.129
H(11A)	−0.0798	0.0977	0.2864	0.124
H(11B)	−0.1711	0.1360	0.2194	0.124
H(12A)	−0.0547	0.1387	0.1136	0.080
H(12B)	0.0312	0.0948	0.1768	0.080
H(13A)	0.0443	0.2237	0.1494	0.060
H(13B)	0.1450	0.1763	0.1845	0.060
H(14A)	0.2148	0.1949	0.3559	0.038
H(14B)	0.1150	0.1828	0.4199	0.038
H(16A)	0.0399	0.0795	0.4358	0.049
H(17A)	0.0641	−0.0294	0.4197	0.063
H(18A)	0.1915	−0.0671	0.3234	0.069
H(19A)	0.3017	0.0021	0.2456	0.065
H(20A)	0.2753	0.1104	0.2581	0.048
H(21A)	0.6534	0.2971	0.6217	0.100
H(21B)	0.7431	0.3361	0.5688	0.100
H(21C)	0.7302	0.2617	0.5534	0.100
H(23A)	0.7317	0.3310	0.3993	0.088
H(23B)	0.6223	0.2991	0.3440	0.088
H(24A)	0.6015	0.4089	0.3020	0.120
H(25A)	0.7270	0.4637	0.4316	0.135
H(26A)	0.6463	0.4481	0.5700	0.111
H(27A)	0.4725	0.3727	0.5474	0.076
H(28A)	0.4417	0.3613	0.3711	0.120
H(28B)	0.4544	0.4349	0.3992	0.120
H(29A)	0.4590	0.2689	0.4209	0.037
H(29B)	0.4632	0.2644	0.5293	0.037
H(30A)	0.3699	0.1750	0.4764	0.036
H(30B)	0.4159	0.1504	0.3830	0.036
H(31A)	0.4866	0.0602	0.4487	0.043
H(31B)	0.3789	0.0705	0.5070	0.043
H(32A)	0.4892	0.1023	0.6323	0.058
H(32B)	0.5895	0.0667	0.5860	0.058
H(33A)	0.6738	0.1574	0.5666	0.033
H(33B)	0.5750	0.1928	0.6148	0.033
H(34A)	0.5947	0.2067	0.3446	0.035

H(34B)	0.6988	0.1991	0.4213	0.035
H(36A)	0.5237	0.1206	0.2563	0.042
H(37A)	0.5421	0.0164	0.2080	0.053
H(38A)	0.6745	–0.0498	0.2857	0.056
H(39A)	0.7873	–0.0135	0.4137	0.048
H(40A)	0.7684	0.0903	0.4640	0.039
H(1B)	0.146(2)	0.156(3)	0.595(5)	0.063
H(1A)	0.263(5)	0.186(2)	0.616(4)	0.063

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