

## Supplementary Material

### Immobilisation of Homogeneous Pd Catalysts within a Type I Porous Liquid

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#### Experimental

##### *Materials*

All reagents were used as received unless otherwise stated. Butyl acrylate, (3-chloropropyl)trimethoxysilane, anhydrous *N,N*-dimethylformamide (DMF), iodobenzene, Pluronic F127, poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt (KPEGS), sodium carbonate anhydrous, tetramethoxysilane, tributylamine, toluene (all Sigma Aldrich), hydrochloric acid (32%), potassium sulfate anhydrous, mesitylene, silica gel (230–400 mesh), triethylamine (all Merck), acetone, ethanol (both UChem) Celite 545 (VWR), 1-chloro-4-iodobenzene (Combi-Blocks), hexadecane (Alfa Aesar), 4-iodoanisole (Fluka), *N,N*-didecyl-*N*-methyl-*N*-(3-triethoxysilylpropyl)ammonium chloride (organosilane, 40-42% in methanol, Gelest), palladium(II) acetate (Strem Chemicals). All water used was de-ionised using a MilliQ (Millipore) Ultra Pure Water System. Anhydrous toluene was obtained using a PureSolv MD 7 Solvent Purification System.

##### *Preparation of chloro-functionalised hollow silica spheres (Cl–SiO<sub>2</sub>)*

The following procedure was adapted from Zheng et al.<sup>1</sup> Pluronic F127 (1.4 g) and K<sub>2</sub>SO<sub>4</sub> (4.9 g) were dissolved in water (84 mL) and the resulting solution was cooled to 13.5 °C. A solution of (3-chloropropyl)trimethoxysilane (0.67 mL) in mesitylene (1.62 mL) was added

and the combined solutions stirred at 13.5 °C for 3 h. Tetramethoxysilane (4.11 mL) was added and the resulting mixture stirred at 13.5 °C for an additional 24 h. The mixture was aged at 100 °C for 24 h in a Teflon-lined stainless steel autoclave before filtering, washing the solid with excess water and drying at 60 °C to produce F127@Cl-SiO<sub>2</sub>.

To produce Cl-SiO<sub>2</sub>, F127@Cl-SiO<sub>2</sub> (2.5 g) was refluxed in a solution of hydrochloric acid (3.75 mL, 32%) in ethanol (500 mL) for 24 h. The mixture was filtered and the solid washed with water then ethanol before drying at 60 °C to produce a white powder.

#### *Preparation of imidazolium-functionalised hollow silica spheres (im-SiO<sub>2</sub>)*

A mixture of 1-methylimidazole (3.0 mL) and Cl-SiO<sub>2</sub> (3.0 g) in anhydrous toluene (150 mL) was refluxed under a nitrogen atmosphere for 24 h. The mixture was filtered and the solid washed with ethanol before drying at 60 °C to produce a white powder.

#### *Preparation of N-heterocyclic carbene palladium complex supported in hollow silica spheres (NHC-Pd@SiO<sub>2</sub>)*

The following procedure was adapted from Stevens *et al.*<sup>2</sup> Palladium(II) acetate (62.5 mg) dissolved in a mixture of DMF (62.5 mL) and an aqueous Na<sub>2</sub>CO<sub>3</sub> solution (1%, 62.5 mL) was stirred under a nitrogen atmosphere at room temperature for 30 min. Im-SiO<sub>2</sub> (2.5 g) was added and the resulting mixture was stirred under a nitrogen atmosphere at 50 °C for 16 h. The mixture was filtered and the solid washed with acetone before drying at 60 °C to produce an off-white powder.

#### *Synthesis of porous liquid*

The porous liquids were synthesised following a procedure by Zhang *et al.*<sup>3</sup> The functionalised silica spheres (2.0 g) were sonicated in an aqueous alkaline solution (40 mL, pH ~9-10, NH<sub>4</sub>OH) for 30 min. The organosilane (4.0 mL) was added and the mixture was stirred at room temperature for 24 h. The mixture was filtered and the solid was washed with water then ethanol before drying at 60 °C. The organosilane-functionalised silica (1.8 g) was treated with an aqueous KPEGS solution (12.5 %, 54 mL) at 70 °C for 24 h. The excess KPEGS was extracted with warm toluene three times and the aqueous phase was dried using a rotary evaporator. The remaining material was dispersed in acetone and centrifuged at 16000 rpm for 20 min and the supernatant was separated. The residual solid was washed once by being

re-suspended in acetone before centrifuging at 16000 rpm for 20 min. The combined supernatants were dried overnight at 40 °C under reduced pressure to produce a viscous liquid.

For the synthesis of NHC–Pd@SiO<sub>2</sub> PL, all synthetic steps were completed under an atmosphere of nitrogen.

#### *General procedure for the catalytic Mizoroki–Heck reaction*

Tributylamine (240 μL), butyl acrylate (110 μL) and the aryl iodide (0.5 mmol) were added to a solution of NHC–Pd@SiO<sub>2</sub> PL (0.1 g) in DMF (1 mL). The resulting mixture was stirred at 130 °C under a nitrogen atmosphere for 5 h. Hexadecane (20 μL) was added as an external standard and a sample (~20 μL) was passed through a plug of Celite and diluted with ethanol. The diluted reaction mixtures were analysed by Gas Chromatography-Mass Spectrometry (GC-MS, Shimadzu GCMS-QP2010 Gas Chromatograph).

#### *General procedure for the synthesis of substituted butyl cinnamate*

Triethylamine (1.4 mL), butyl acrylate (1.1 mL) and the desired aryl iodide (5.0 mmol) were added to a solution of palladium acetate (5.0 mg) in DMF (10 mL), and stirred at 90 °C for 3 h. The mixture was filtered and the solvent removed under reduced pressure at 40 °C. The crude product was purified by flash chromatography using hexanes/ethyl acetate as the eluent to produce the desired substituted butyl cinnamate.

**Butyl cinnamate:** Obtained as a yellow liquid (0.88 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 0.96 (3H, t, *J* = 7.3 Hz, –CH<sub>3</sub>), 1.30–1.56 (2H, m, –CH<sub>2</sub>CH<sub>3</sub>), 1.61–1.82 (2H, m, –CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.21 (2H, t, *J* = 6.7 Hz, –OCH<sub>2</sub>), 6.44 (1H, d, *J* = 16.0 Hz, =CHCOOBu), 7.35–7.40 (3H, m, ArH), 7.45–7.57 (2H, m, ArH), 7.68 (1H, d, *J* = 16.0 Hz, =CHAr). **Selected GC-MS data** (*m/z*, %): 204 (12, [M]<sup>+</sup>), 148 (65), 131 (100), 103 (66), 77 (51).

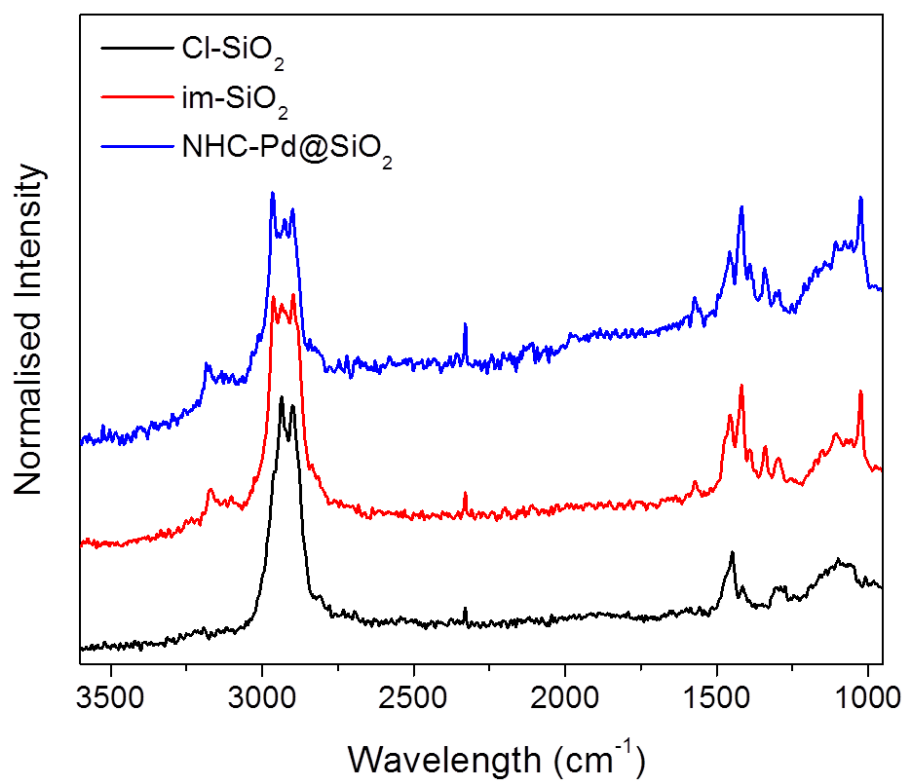
**Butyl 4-methoxycinnamate:** Obtained as a yellow liquid (0.70 g, 59%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 0.96 (3H, t, *J* = 7.3 Hz, –CH<sub>3</sub>), 1.35–1.50 (2H, m, –CH<sub>2</sub>CH<sub>3</sub>), 1.60–1.75 (2H, m, –CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.83 (3H, s, –OCH<sub>3</sub>), 4.20 (2H, t, *J* = 6.6 Hz, –OCH<sub>2</sub>), 6.31 (1H, d, *J* = 15.9 Hz, =CHCOOBu), 6.90 (2H, d, *J* = 8.6 Hz, ArH), 7.47 (2H, d, *J* = 8.5 Hz, ArH), 7.63 (1H, d, *J* = 16.0 Hz, =CHAr). **Selected GC-MS data** (*m/z*, %): 234 (50, [M]<sup>+</sup>), 178 (96), 161 (100), 134 (44), 103 (9), 90 (15), 77 (16).

**Butyl 4-chlorocinnamate:** Obtained as a yellow crystals (0.89 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 0.96 (3H, t, *J* = 7.3 Hz, –CH<sub>3</sub>), 1.35–1.52 (2H, m, –CH<sub>2</sub>CH<sub>3</sub>), 1.63–1.75 (2H, m,

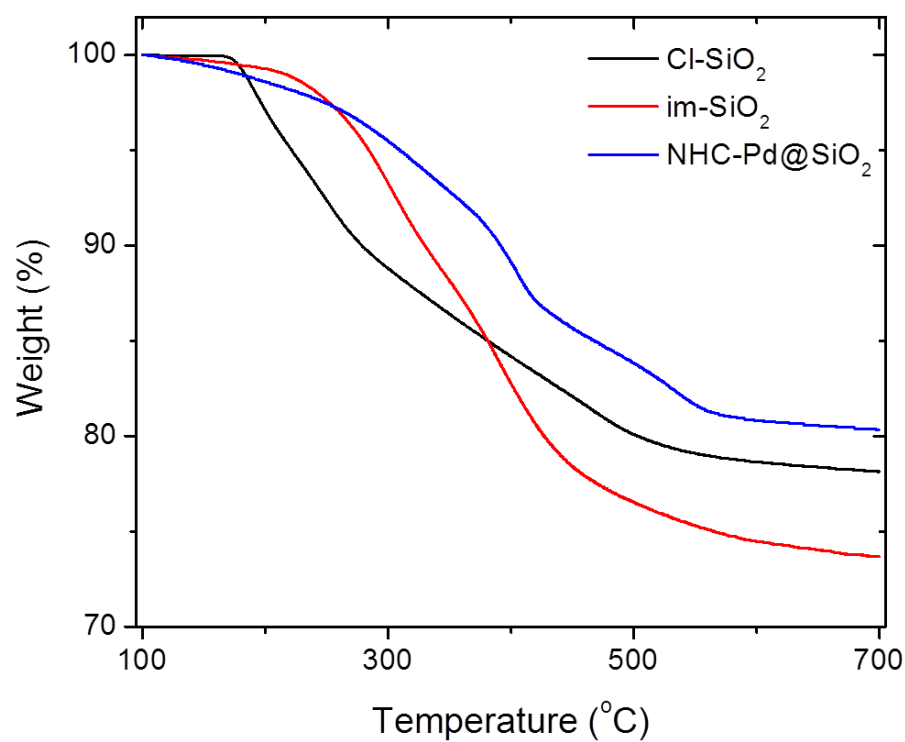
–CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.21 (2H, t,  $J = 6.7$  Hz, –OCH<sub>2</sub>), 6.41 (1H, d,  $J = 16.0$  Hz, =CHCOOBu), 7.30–7.40 (2H, m, ArH), 7.42–7.48 (2H, m, ArH), 7.62 (1H, d,  $J = 16.0$  Hz, =CHAr). **Selected GC-MS data** ( $m/z$ , %): 238 (26, [M]<sup>+</sup>), 182 (100), 165 (91), 137 (37), 102 (53), 75 (24).

### *Characterisation*

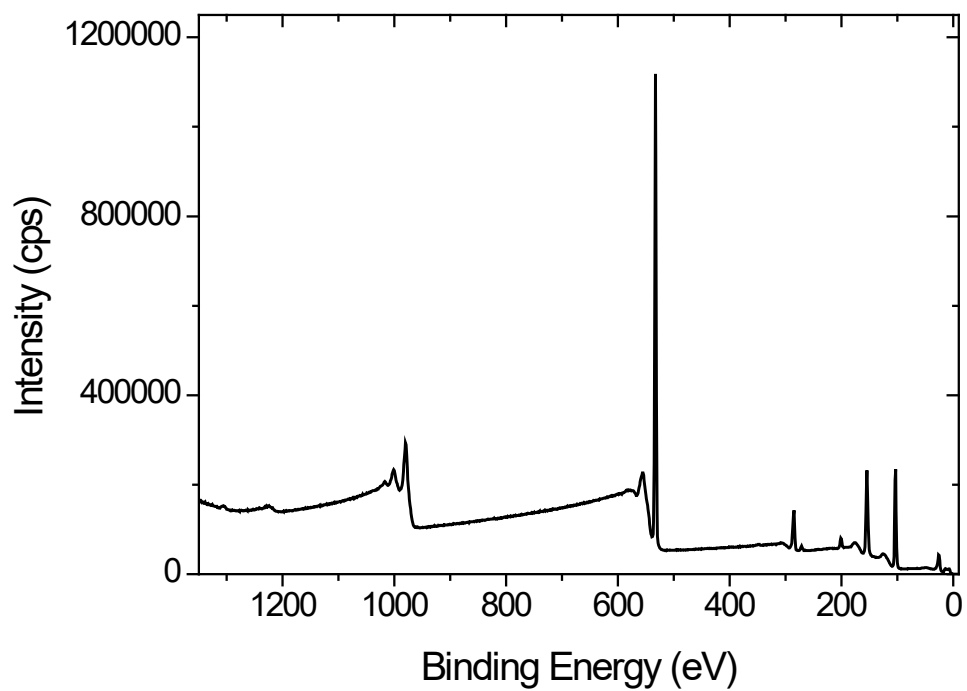
X-ray photoelectron spectroscopy (XPS) data were collected with a Thermo Fisher Scientific K-Alpha+ X-ray Photoelectron Spectrometer. The binding energies were referenced to the C 1s peak at 284.8 eV from adventitious carbon. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 operating at 200 kV. Thermogravimetric analysis (TGA) was performed using a TA Instruments Discovery TGA and was completed under air. The TGA traces were normalised to the sample weight at 100 °C to remove any disparity in the amounts of adsorbed water. Raman spectra were recorded using a Bruker MultiRAM FT-Raman Spectrometer. Spectra were recorded using a 1064 nm laser operating at 500 mW. Inductively coupled plasma – mass spectroscopy (ICP–MS) was completed using a Perkin Elmer Nexion 350X Inductively Coupled Mass Spectrometer. Samples were prepared by first drying under vacuum at 50 °C overnight before stirring in concentrated nitric acid at 70 °C overnight, diluting and then analysing. The N<sub>2</sub> adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity analyser at –196 °C. The samples were degassed at 100 °C before analysis. The specific surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively. <sup>1</sup>H NMR spectra were recorded at 25 °C on a Bruker AVANCE DPX300 spectrometer operating at 300.13 MHz, and were referenced internally to tetramethylsilane (TMS).



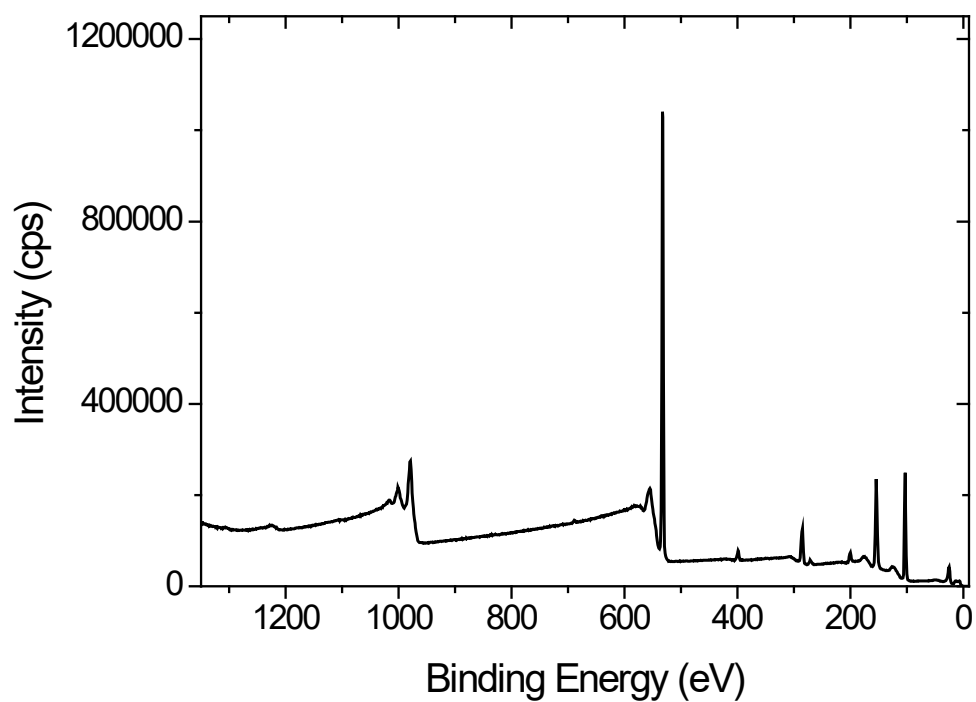
**Figure S1.** Normalised Raman spectra of Cl-SiO<sub>2</sub> (black), im-SiO<sub>2</sub> (red) and NHC-Pd@SiO<sub>2</sub> (blue).



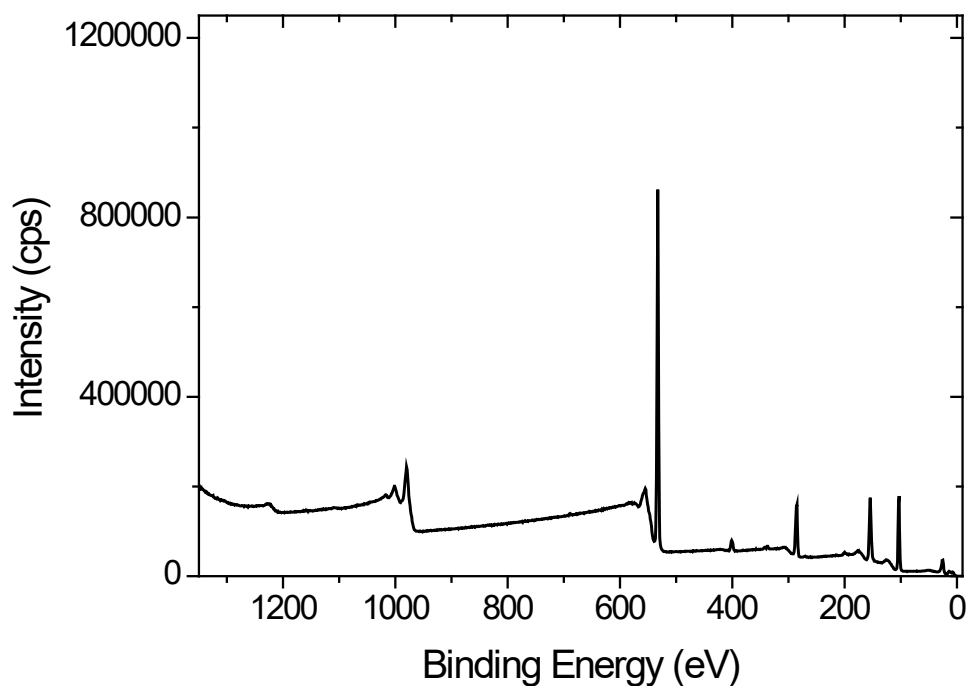
**Figure S2.** TGA traces of Cl-SiO<sub>2</sub> (black), im-SiO<sub>2</sub> (red) and NHC-Pd@SiO<sub>2</sub> (blue).



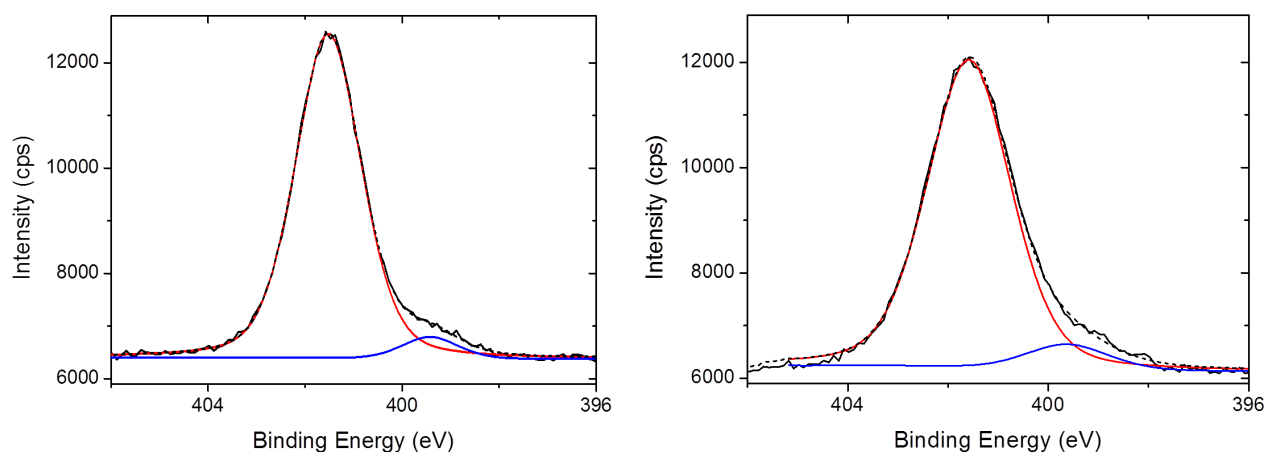
**Figure S3.** XPS survey spectrum of Cl-SiO<sub>2</sub>.



**Figure S4.** XPS survey spectrum of im-SiO<sub>2</sub>.



**Figure S5.** XPS survey spectrum of NHC-Pd@SiO<sub>2</sub>.



**Figure S6.** XPS spectra of the N 1s region for im-SiO<sub>2</sub> (left) and NHC-Pd@SiO<sub>2</sub> (right).

## References

1. Y. Zheng, X. Zhang, Y. Yao, X. Chen and Q. Yang, *Rsc Advances*, 2015, **5**, 105747-105752.
2. P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen and Y. Gao, *Organic Letters*, 2005, **7**, 2085-2088.
3. J. S. Zhang, S. H. Chai, Z. A. Qiao, S. M. Mahurin, J. H. Chen, Y. X. Fang, S. Wan, K. Nelson, P. F. Zhang and S. Dai, *Angewandte Chemie-International Edition*, 2015, **54**, 932-936.