

Electronic Supplementary Information

**Synthesis of colloidal Pd nanoparticles immobilised on poly(*N*-vinylacetamide): characterisation and application in catalysis**

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## 1. General information

Unless otherwise noted, we purchased commercially available chemicals from common sources (Tokyo Chemical Industry Co., Ltd.; Sigma-Aldrich; and FUJIFILM Wako Pure Chemical Corp.). Gas chromatography (GC) analyses were performed on a Shimadzu GC-2025 with a BP-5 column (25 m × 0.22 mm) and a flame ionization detector. All nuclear magnetic resonance (NMR) spectra were recorded on JEOL ECS-400 and ECZ-400 spectrometers. Spectra were referenced using either CDCl<sub>3</sub> with the residual solvent peak or tetramethylsilane as the internal standard (<sup>1</sup>H NMR: δ 7.26 ppm, <sup>13</sup>C NMR: δ 77.0 ppm for CDCl<sub>3</sub>; <sup>1</sup>H NMR: δ 0.00 ppm, <sup>13</sup>C NMR: δ 0.0 ppm for tetramethylsilane). GC–mass Spectrometry (GC–MS) was performed on a Shimadzu GCMS-QP2010 SE mass spectrometer using electron impact (EI) ionization.

## 2. Experimental procedures

### 2.1 Preparation of the Pd NPs-PNVA

#### 2.1.1 Preparation of the DMF-stabilised Pd NPs (1 mM)

DMF (50 mL) was added to a 300-mL three-necked round-bottom flask. The solution was then preheated to 140 °C and stirred at 1500 rpm for 5 min. A solution of PdCl<sub>2</sub> (0.1 M, 500 μL) dissolved in a mixture of water:conc. HCl(aq) = 9:1 (v/v) was added to the hot DMF solution. The resulting mixture was stirred at 140 °C and 1500 rpm for 10 h under reflux. The resulting clear orange solution is denoted as 1 mM DMF-stabilised Pd NP solution in DMF.

#### 2.1.2 Preparation of PNVA

To a 300-mL three-necked round-bottom flask, recrystallised *N*-vinylacetamide (NVA, 5 g) from toluene and cyclohexane DMF (50 mL) was dissolved in DMF (50 mL). A solution of azobisisobutyronitrile (AIBN, 1 mol%) was then dissolved in DMF (1 mL) and added to the mixture. The mixture was stirred at 60 °C for 24 h. After the reaction, the solvents were removed by evaporation and the polymer mixture precipitated. The polymer mixture was poured into diethyl ether (300 mL) to separate the monomers. The polymer product was then obtained by centrifugation (AS ONE CN-2060, 3000 g). The obtained polymers were dissolved in methanol (5 mL) and the resulting mixture was added dropwise to diethyl ether (300 mL). The resulting polymer was reprecipitated according to the above procedure. After drying under reduced pressure, PNVA (2.7 g) was obtained.

#### 2.1.3 Preparation of Pd NPs-PNVA

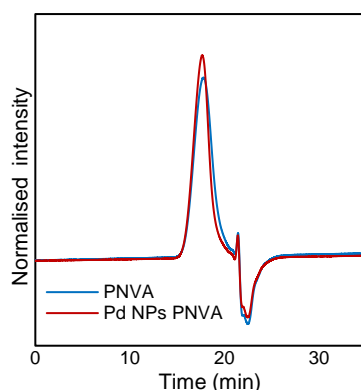
A portion of the DMF-stabilised Pd NPs (1 mM, 35 mL) was added to a 50-mL round-bottom flask and the solvent was removed by evaporation. Ethanol (10 mL) and PNVA (0.3 g) were added to the residue and the mixture was stirred at 70 °C for 90 min. The solvents were removed by evaporation and the polymer was dissolved in methanol (2 mL). The resulting solution was added dropwise to an

excess amount of diethyl ether (30 mL). The polymer was then obtained by centrifugation. This purification process was repeated once more. The purified polymer was dried under reduced pressure overnight and Pd NPs-PNVA (0.12 g) was obtained.

## 2.2 Characterisation of the Pd NPs-PNVA

### Size exclusion chromatography measurements

Number-average molecular weight ( $M_n$ ) and dispersity ( $D$ ) values of polymers were determined by a size exclusion chromatography (SEC) system consisting of JASCO CO-965 column oven, UV-2075 Plus UV detector, RI-930 refractive index detector, PU-980 pump, and DG-980-50 degasser equipped with Shodex GPC KD-G and TSK gel  $\alpha$ -gel C0053 columns eluted with LiBr solution (10 mM) in *N,N*-dimethylformamide (DMF) at 40 °C calibrated with polystyrene standards.



**Fig. S1** SEC chart of PNVA ( $M_n = 12000$ ,  $D = 3.2$ ) and the Pd NPs-PNVA ( $M_n = 19000$ ,  $D = 2.4$ ).

### TEM measurements

The Pd NPs-PNVA (20 mg) was dissolved in ethanol (2 mL) and the solution was dropped directly onto copper TEM grids. Electron microscope images were obtained using a JEOL JEM-ARM200F microscope operating at an accelerating voltage of 200 kV and equipped with an energy-dispersive X-ray analyser.

### DLS measurements

The Pd NPs-PNVA (20 mg) was dissolved in ethanol (1 mL) and the solution was filtered with a filter (pore size: 0.02  $\mu\text{m}$ ). DLS measurements performed using a Malvern Zetasizer Nano ZSP at 25 °C.

### TG measurements

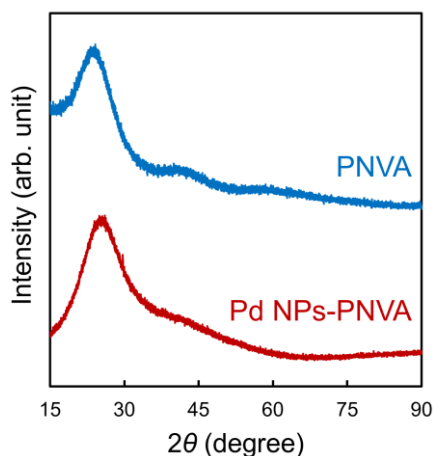
Thermogravimetric analysis was performed using a PerkinElmer TGA 4000 with a heating rate of 5 °C/min from 50 to 500 °C under  $\text{N}_2$  at a flow rate of 50 mL/min.

### FT-IR measurements

FT-IR absorption spectra were measured on an IRAffinity-1 spectrophotometer by the KBr pellet method.

### XRD measurements

XRD profiles were measured on a Rigaku Miniflex using Cu K $\alpha$  radiation (X-ray voltage 40 kV, current 15 mA). Samples were placed on a silicon crystal sample holder.



**Fig S2.** XRD profiles of PNVA and the Pd NPs-PNVA.

### XAS measurements

X-ray absorption spectroscopy (XAS) was recorded at the BL14B2 beamline of SPring-8. The incident X-rays were monochromated by a Si (311) double crystal monochromator. Double Rh-coated mirrors were used to remove the higher harmonics of the incident X-rays. The cross section of the beam was collimated into a width of 5.0 mm and height of 1.0 mm by a divergence slit. Incident and fluorescence X-ray were monitored by an ionization chamber filled with Ar 100% gas and a 19-element Ge solid state detector, respectively. X-ray absorption near edge structure (XANES) analyses were conducted using the Athena software package.<sup>1</sup>

The XAS sample was prepared by dissolving the Pd NPs-PNVA (60 mg) in DMF (0.2 mL) and transferring the mixture to a polytetrafluoroethylene cell.

## XPS measurements

XPS analysis was performed with a ULVAC-PHI PHI5000 VersaProbe with Al K $\alpha$  radiation. The measured spectra were calibrated against the C 1 s electron peak (284.6 eV).

**Table S1** XPS peak positions of the Pd NPs-PNVA

Element	Binding Energy (eV) [FWHM]				
	Pd 3d <sub>5/2</sub>	Pd 3d <sub>3/2</sub>	C 1s	N 1s	O 1s
	335.8 [1.4]	341.5 [1.4]	284.2 [1.4]	399.1 [2.0]	530.1 [1.0]
	337.3 [1.5]	342.5 [1.5]	285.2 [1.4]		530.9 [1.8]
	338.3 [2.0]	343.2 [2.0]	287.1 [2.1]		

## 2.3 Pd NPs-PNVA-catalysed Suzuki–Miyaura cross-coupling reaction

### 2.3.1 Typical procedure for the catalytic reaction

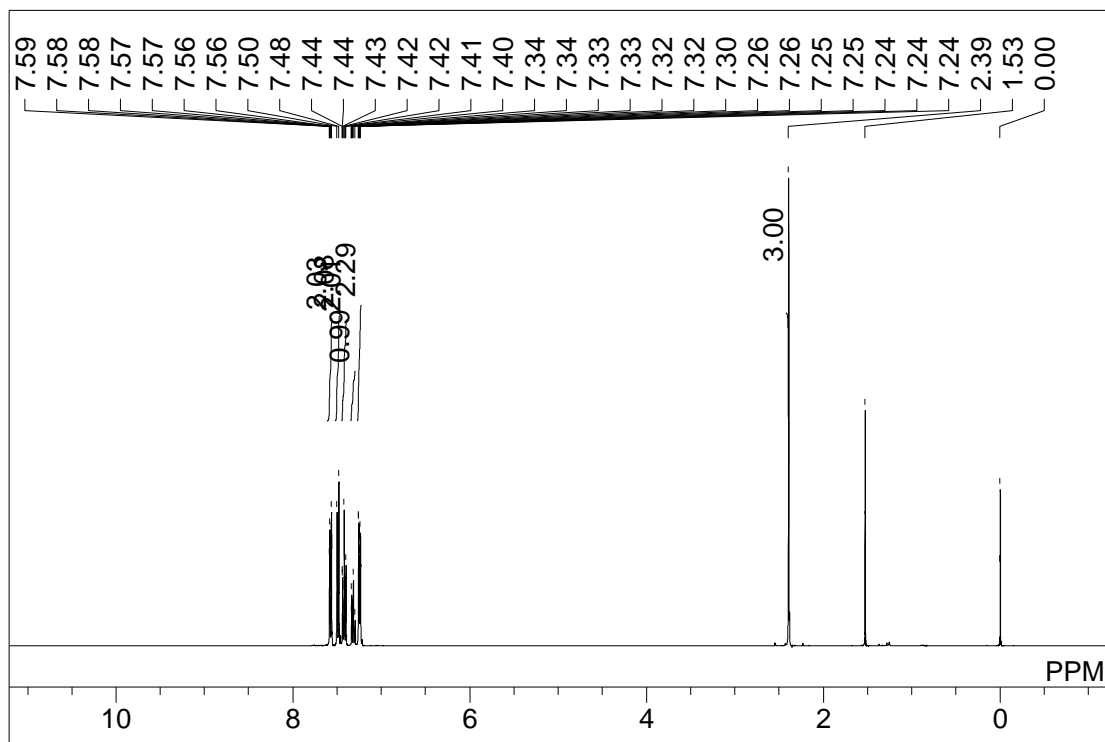
The Pd NPs-PNVA (20 mg, Pd content 0.55wt%), 4-methylphenylboronic acid (**2a**, 102 mg, 0.75 mmol), and base (0.5 mmol) were added to a 20-mL Schlenk tube. Then, air was replaced with Ar. Aryl halide (**1**, 0.5 mmol) and solvent (2 mL) were added to the mixture. The reaction was run at 100 °C for 24 h. Conversions and yields were determined by GC with tridecane as an internal standard.

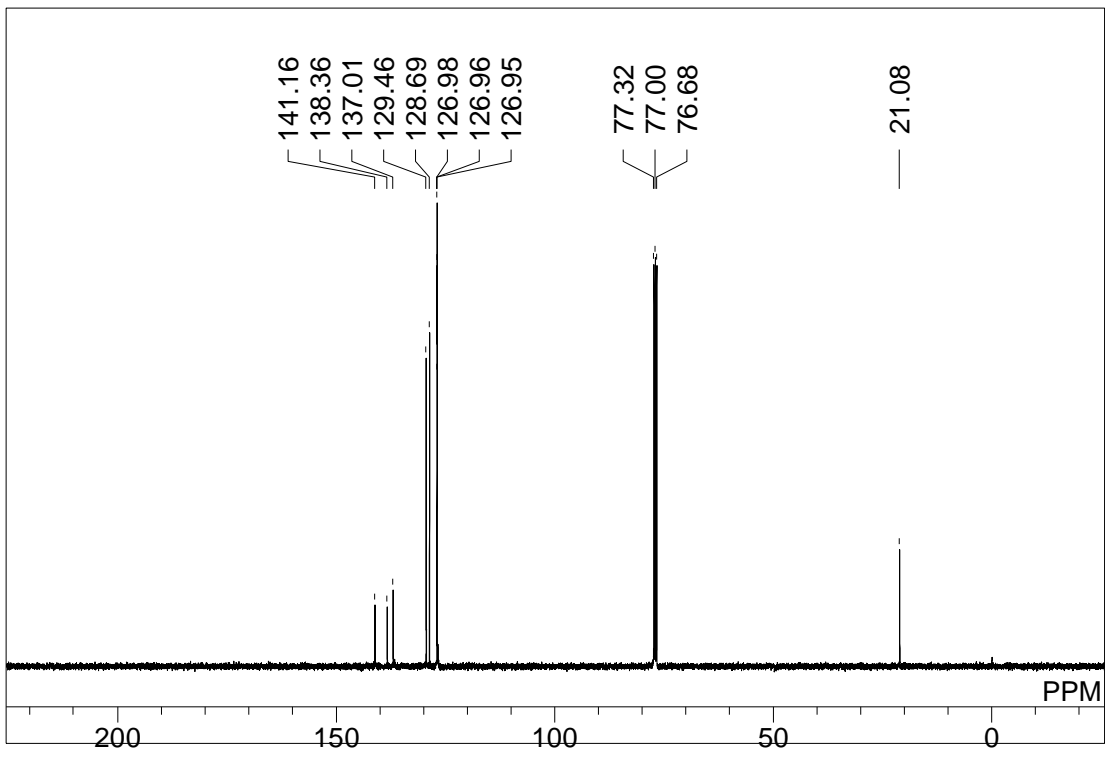
### 2.3.2 Substrate scope

The Pd NPs-PNVA (20 mg, Pd content 0.55wt%), arylboronic acid (**2**, 0.75 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.5 mmol, 69 mg) were added to a 20-mL Schlenk tube. Then, air was replaced with Ar. Aryl halide (**1**, 0.5 mmol) and H<sub>2</sub>O/NMP (v/v) (2 mL) were added to the mixture. The reaction was run at 100 °C for 24 h. After the reaction, the resulting solution was extracted with toluene (4 mL  $\times$  5). The combined organic layer was washed by water (10 mL  $\times$  2), and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvents were removed by evaporation. Products were purified by a silica-gel flush column chromatography (eluent: hexane : ethyl acetate = 95 : 5).

**4-methylbiphenyl (3a)**<sup>2</sup>

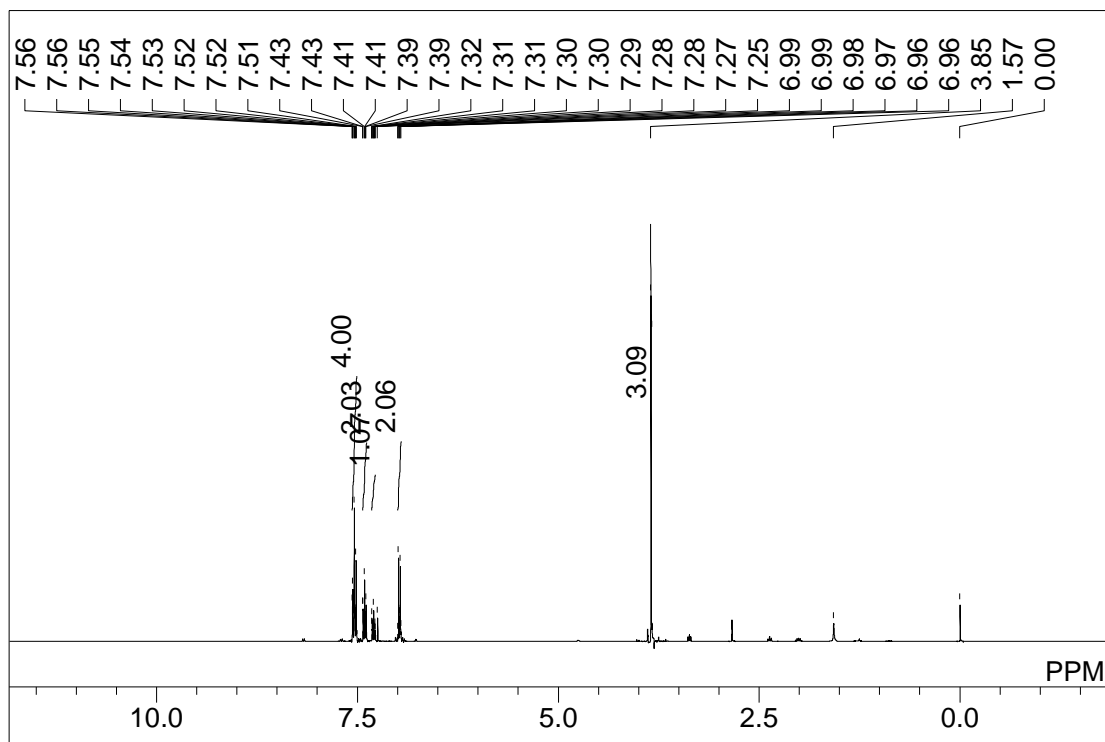
<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 7.59-7.56 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.44-7.40 (m, 2H), 7.34-7.30 (m, 1H), 7.26-7.24 (m, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ: 141.2, 138.4, 137.0, 129.5, 128.7, 126.98, 126.96, 126.95, 21.1.



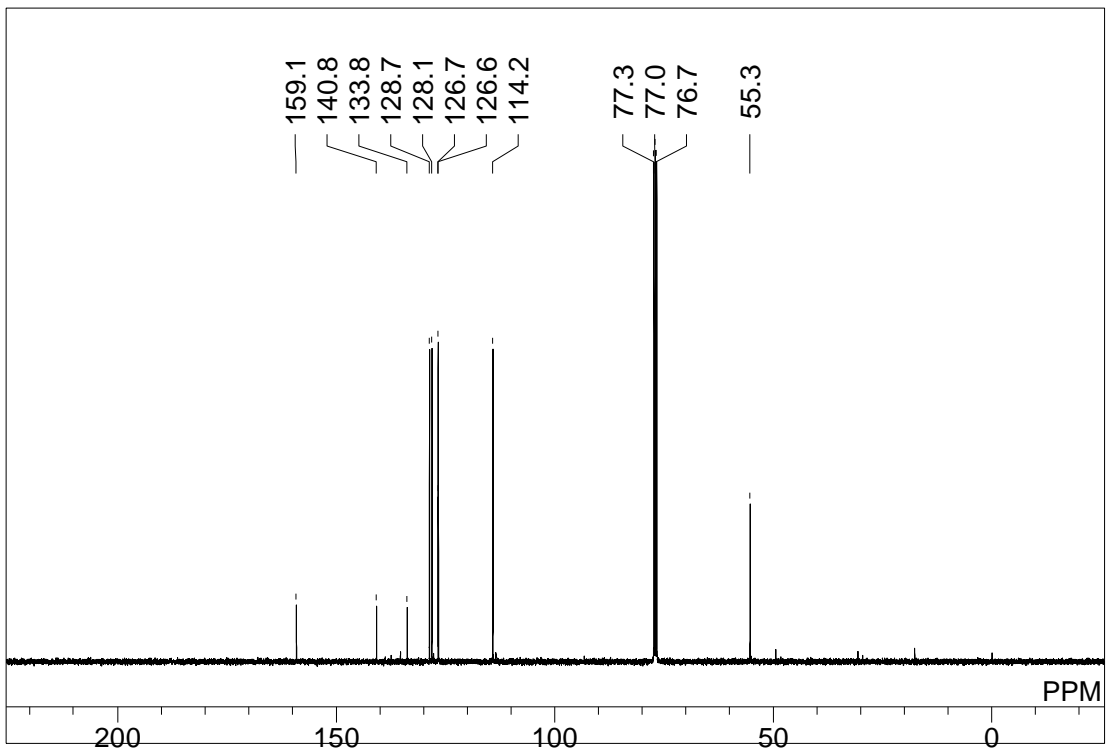


**4-methoxybiphenyl (3b)** <sup>2</sup>

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 7.55-7.52 (m, 4H), 7.42-7.40 (m, 2H), 7.30 (tt, *J* = 7.4, 1.4 Hz, 1H), 6.98 (dt, *J* = 9.4, 2.6 Hz, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ: 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.



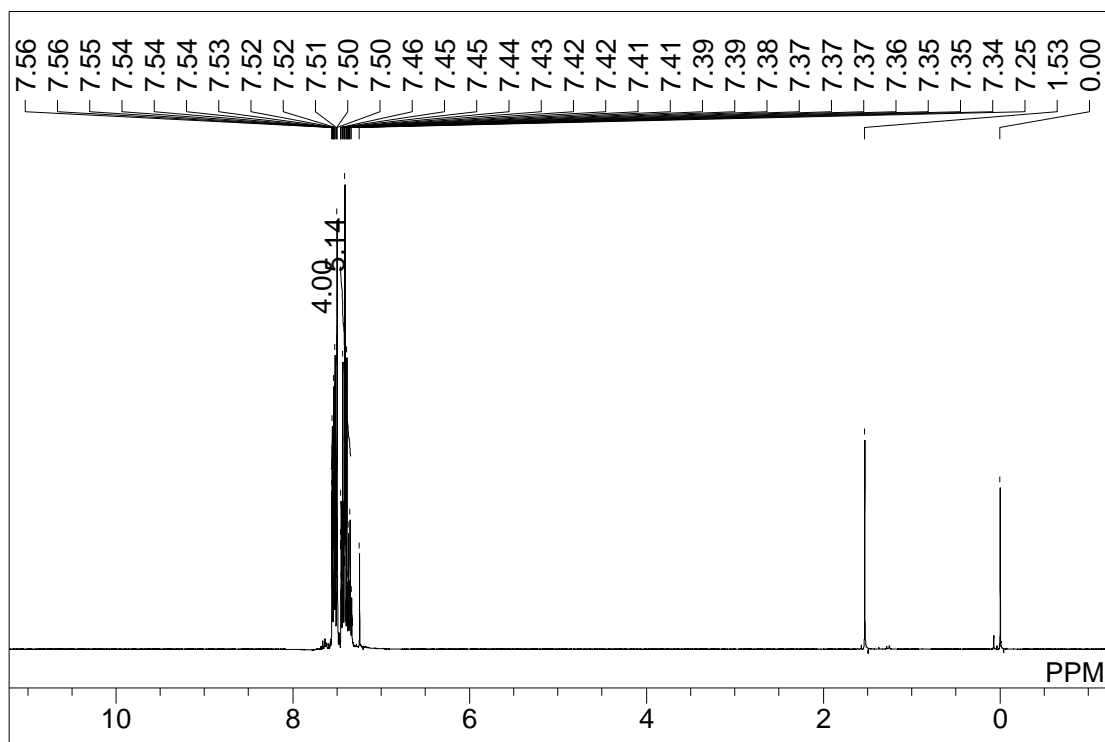


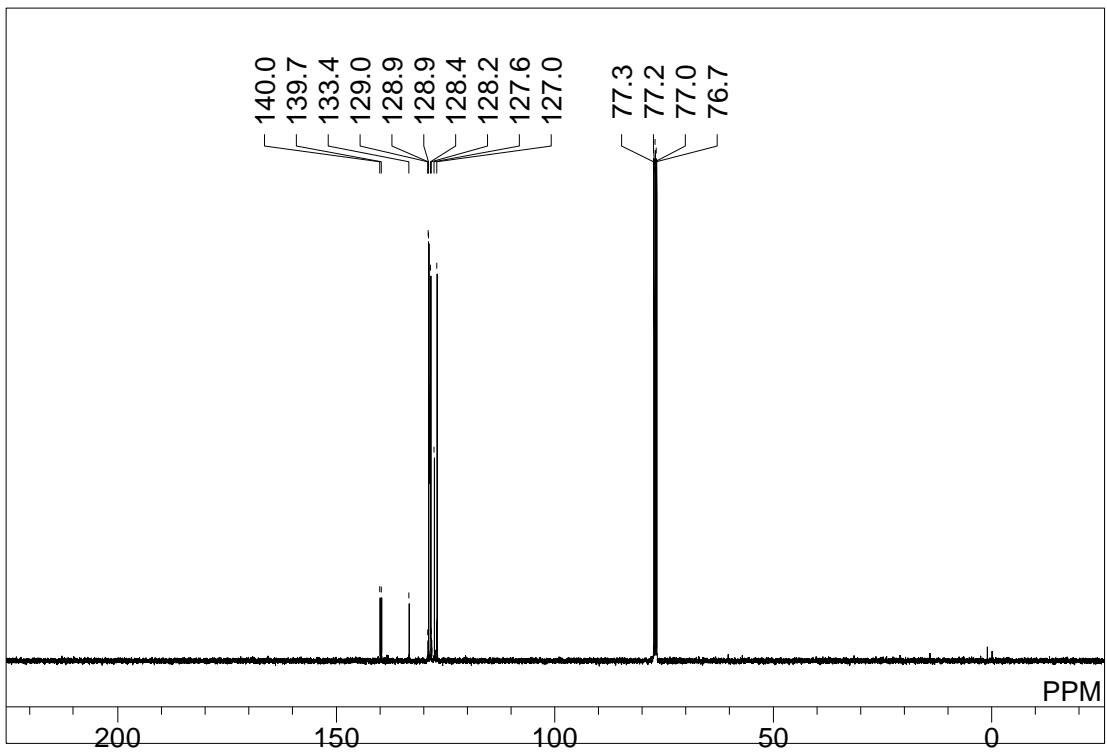


**4-chlorobiphenyl (3c) <sup>2</sup>**

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 7.54-7.51 (m, 4H), 7.43-7.37 (m, 5H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>)

δ: 140.0, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.0.

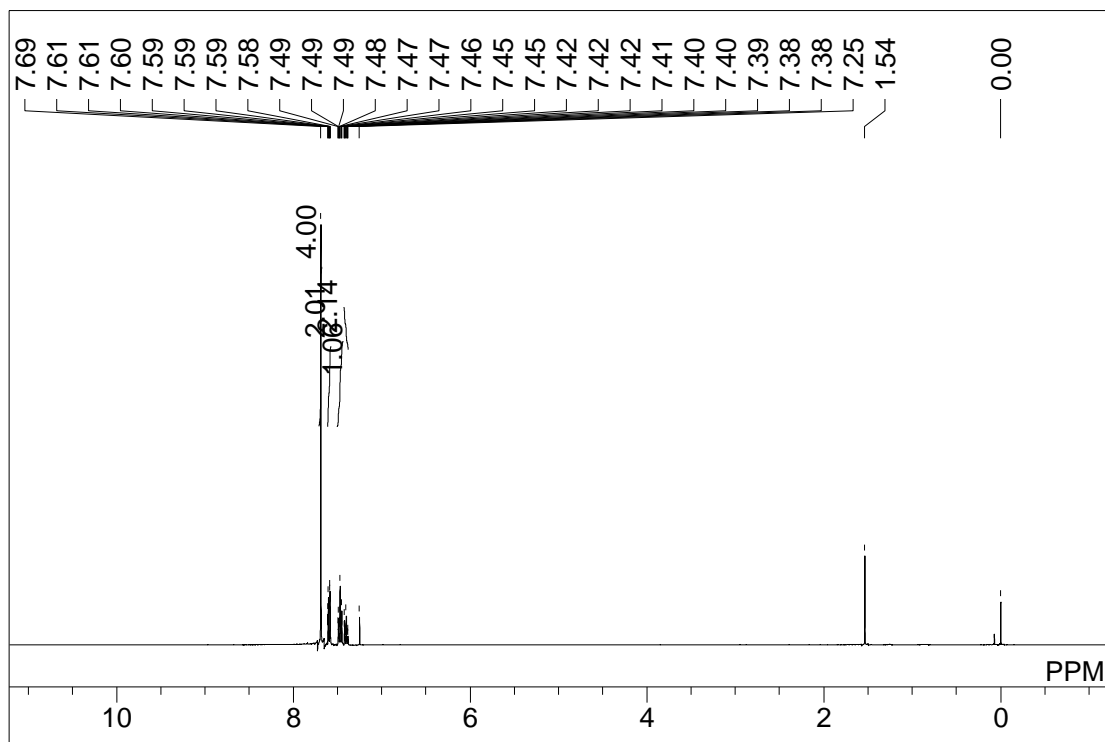


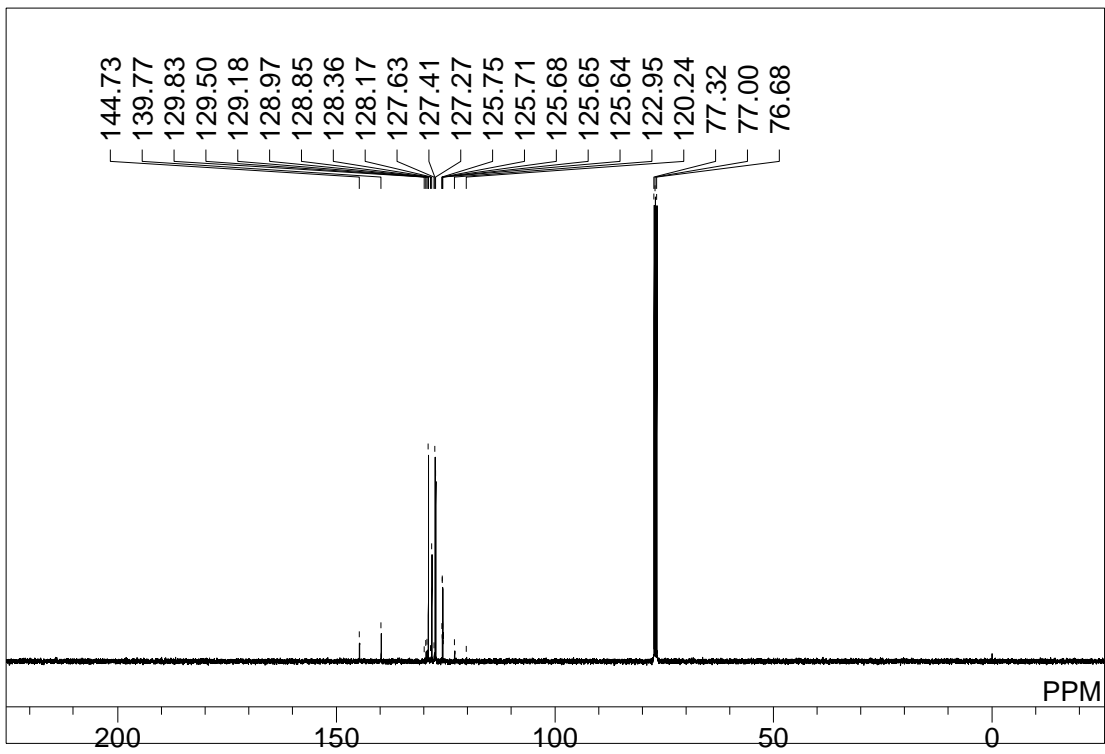


**4-(trifluoromethyl)biphenyl (3d)**<sup>3</sup>

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 7.69 (s, 4H), 7.61-7.58 (m, 2H), 7.48-7.46 (m, 2H), 7.41-7.39 (m, 1H).

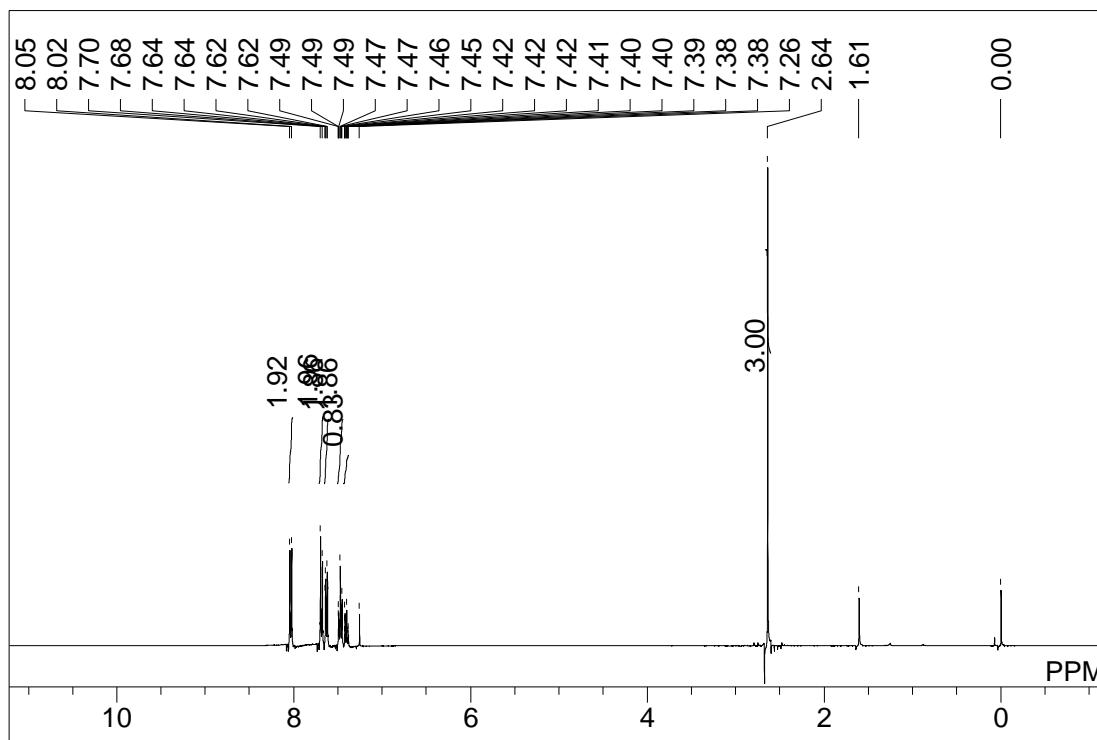
<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ: 144.7, 139.8, 129.4 (<sup>2</sup>J<sub>C-F</sub> = 32.2 Hz), 129.0, 128.2, 127.4, 127.3, 125.7 (<sup>3</sup>J<sub>C-F</sub> = 3.8 Hz), 124.3 (<sup>1</sup>J<sub>C-F</sub> = 270.6 Hz).

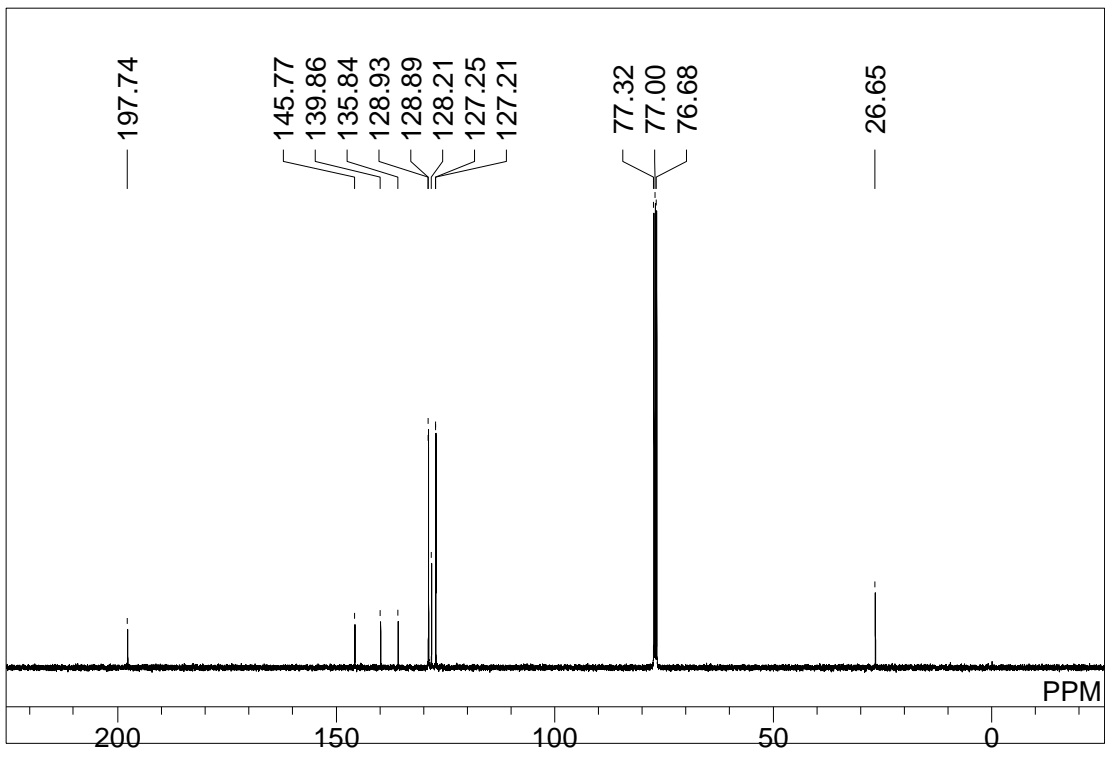




**4-acetylbiphenyl (3e)**<sup>2</sup>

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 8.03 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.64-7.62 (m, 2H), 7.49-7.45 (m, 2H), 7.41-7.39 (m, 1H), 2.64 (s, 3H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ: 197.7, 145.8, 139.9, 135.8, 128.93, 128.89, 128.2, 127.25, 127.21, 26.7.

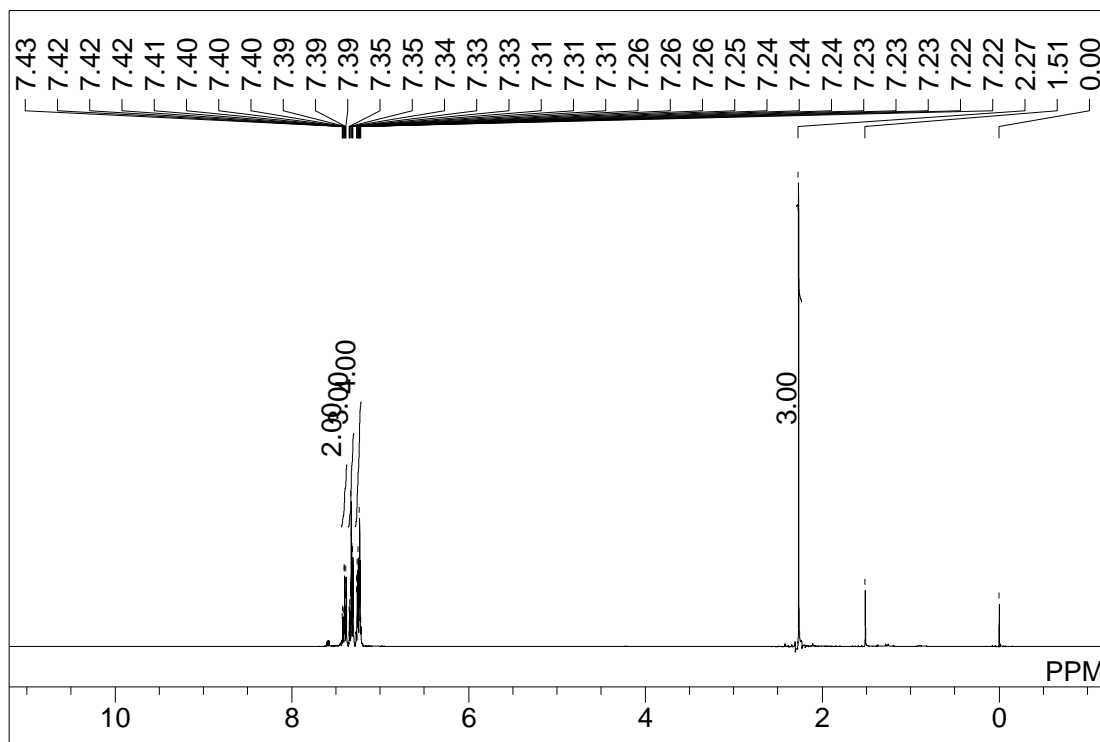




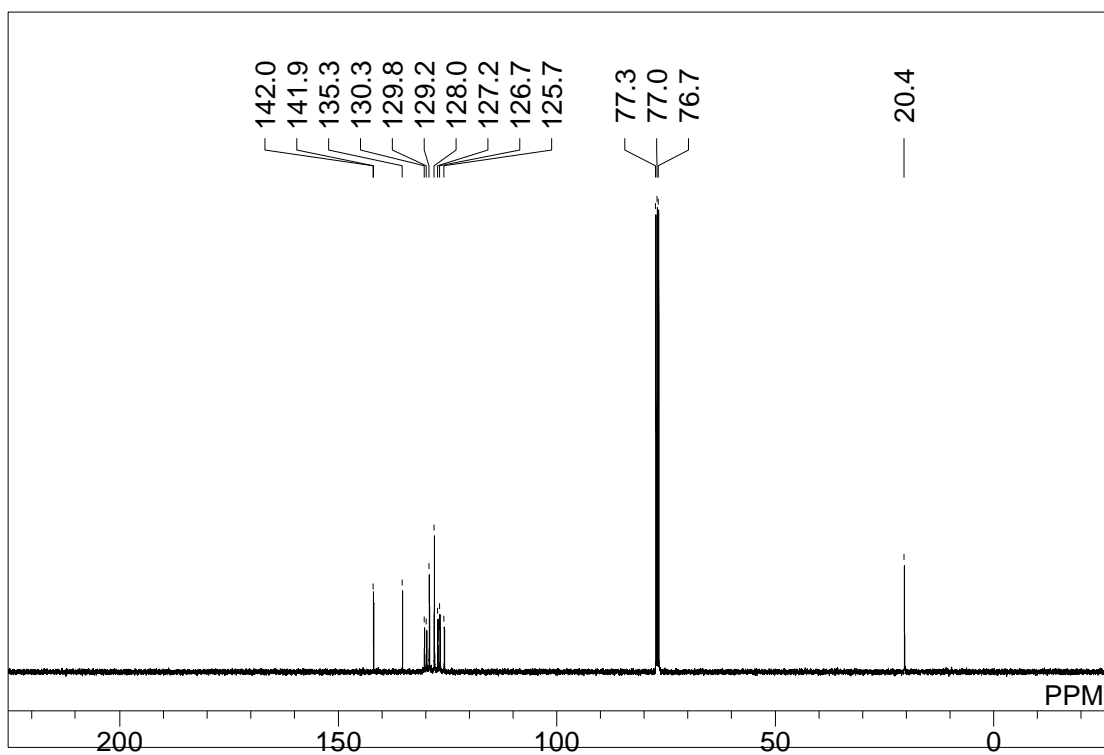
**2-methylbiphenyl (3f)** <sup>2</sup>

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 7.43-7.39 (m, 2H), 7.35-7.31 (m, 3H), 7.27-7.22 (m, 4H), 2.27 (s, 3H).

<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ: 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.



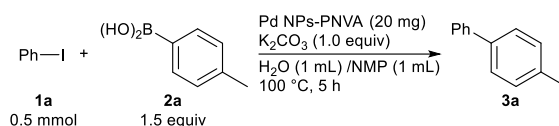




### 2.3.3 Recycling experiments

The Pd NPs-PNVA (20 mg, Pd content 0.55wt%), 4-methylphenylboronic acid (**2a**, 102 mg, 0.75 mmol), and K<sub>2</sub>CO<sub>3</sub> (69 mg, 0.5 mmol) were added to a 20-mL Schlenk tube. Then, air was replaced with Ar. Iodobenzene (**1a**, 102 mg, 0.5 mmol), H<sub>2</sub>O (1 mL), and NMP (1 mL) were added to the mixture. The reaction (run 1) was carried out at 100 °C for 5 h. After the reaction, the reaction mixture was extracted with hexane to separate small molecules from the polymer. Then, **2a** (102 mg, 0.75 mmol), and K<sub>2</sub>CO<sub>3</sub> (69 mg, 0.5 mmol), **1a** (102 mg, 0.5 mmol) were added to the residual polymer under Ar. The next reaction was also run at 100 °C for 5 h and following recycling experiments were performed according to the procedures mentioned above. Conversions and yields were determined by GC with the use of an internal standard. Catalyst leaching was confirmed by ICP-AES (Shimadzu, ICPS-8100). Samples were prepared with concentrated hydrochloric acid and pure water after removal of solvents from the combined organic layers in the recycling experiment.

**Scheme S1.** The Pd NPs-PNVA-catalysed Suzuki–Miyaura cross-coupling reaction of **1a** with **2a**



Run	Conversion of <b>1a</b> (%)	Yield of <b>3a</b> (%)	Pd leaching (ppm) <sup>a</sup>
1	99	92	0.106
2	95	90	0.101
3	98	98	0.103
4	91	88	0.091

<sup>a</sup> Detection limit: 0.032ppm

### 3. References

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