Practical Preparation Method of Polymer Incarcerated Palladium Catalysts Using Pd (II) Salts

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SUPPORTING INFORMATION

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Experimental Details and Physical Data

General Methods: ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300 or JNM-ECX400 spectrometer in CDCl_3 unless otherwise noted. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^1H NMR and CDCl_3 was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. GC yield was determined with SHIMADZU GC-17A using naphthalene as an internal standard. Fluorocene X-ray analysis (XRF) was measured with SHIMADZU EDX-800. Dry solvents (hexane, THF, and toluene) were purchased from Wako Pure Chemical Industry.

N-Methyl-2-pyrrolidone was purchased from Kanto Chemical Industry.

TEM Analysis: TEM images were obtained using JEOL JEM-1200EX II instrument operated at 80 kv. For the TEM specimens, a drop of suspension of a catalyst in MeOH, which was ground in a mortar with pestle after free-drying with benzene, was placed on a Cu grid.

Chemicals:

Palladium acetate was obtained from Wako Pure Chemical Industry. Palladium nitrate was purchased from Kanto Chemical Industry. Alkali metal salts (NaOAc, NaNO₃, NaCl, NaOAc, KOAc and LiOAc) were supplied from Wako Pure Chemical Industry. Iodobenzene and ethyl acrylate were obtained from Kanto Chemical. Other aryl halides were purchased from Tokyo Kasei Kogyo Co., Ltd. These reagents were purified prior to use. All other chemicals were obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification.

A typical procedure for the preparation of PI Pd.

Preparation of Copolymer 2:

Copolymer **2** was prepared according to the literature.¹⁾

The molar ratio of the components were determined by ¹H NMR analysis (x/y/z = 91/5/4). *M_w*: 32180, *M_n*: 19120, *M_w*/*M_n* = 1.68 (gel permeation chromatography analysis).

Preparation of polymer incarcerated palladium (PI Pd B): Copolymer (**2**, 200 mg) and sodium acetate (21.7 mg, 0.26 mmol), and palladium nitrate (Pd(NO₃)₂, 30.4 mg, 0.13 mmol) were dissolved in tetrahydrofuran (3 mL) at room temperature. The mixture was stirred for 1 h at that temperature and heated at 66°C for 3 h. After being cooled to room temperature, hexane (20 mL) was slowly added to the mixture. The mixture was left to stand at room temperature for 12 h, and the catalyst capsules were then washed with hexane several times and dried at room temperature for 1 h.

The catalyst capsules were then heated with stirring at 120 °C for 2 h to cross-link the polymer chain. The cross-linked catalyst was then washed with tetrahydrofuran, water and DCM several times and dried under vacuum at room temperature for 24 h to give polymer incarcerated palladium (PI Pd **B**, 169 mg, 0.44 mmol/g of palladium metal was loaded).

Determination of loading of the palladium: PI Pd **B** (20.0 mg) was placed in 50 mL-test tube, and concentrated sulfuric acid (1.0 mL) was added. The mixture was heated at 180 °C for 30 min, and concentrated nitric acid (1.0 mL) was added. The mixture was further stirred at the same temperature for 3 h to give a clear solution. The solution was diluted with water, and the amount of palladium was measured by fluorescence X-ray analysis (XRF).

TEM Images of PI Pd A, B, and H: The dotted square boxes highlights viewpoints of palladium particles.

PI Pd **A**: (80 kv, scale bar = 10 nm) (Table 1, entry 2)

PI Pd **B**: (80 kv, scale bar = 10 nm) (Table 1, entry 3)

PI Pd **B**: after the 1st use (80 kv, scale bar = 25 nm) (Table 2, entry 3)

PI Pd **B**: after the 2nd use (80 kv, scale bar = 25 nm) (Table 2, entry 3)

PI Pd **B**: after the 3rd use (80 kv, scale bar = 25 nm) (Table 2, entry 3)

PI Pd **H**: (80 kv, scale bar = 25 nm) (Table 1, entry 9)

PI Pd **H**: after the 1st use (80 kv, scale bar = 25 nm) (Table 2, entry 9)

PI Pd **H**: after the 2nd use (80 kv, scale bar = 25 nm) (Table 2, entry 9)

Typical Experimental procedure for Heck reaction (Table 2, entry 3). PI Pd **B** (0.025 mmol), iodobenzene (**1a**) (56 μ L, 0.50 mmol), ethyl acrylate (**2a**) (81 μ L, 0.75 mmol), and potassium carbonate (196 μ L, 1.0 mmol) were combined in NMP (3 mL) under argon atmosphere. The mixture was stirred at 120 $^{\circ}$ C for 2 h and cooled. After hexane was added to quench the reaction, the catalyst was collected by filtration and washed with THF, water, and DCM, and dried before reuse. The solvents of the filtrate were then removed under reduced pressure, and the volume of the residue was

adjusted to 5 mL using MeCN to prepare a sample for XRF analysis (measurement of leaching of palladium). The sample solution after measurement of leaching was evaporated. Yield of ethyl *trans*-cinnamate (**3a**) was determined by GC analysis using naphthalene as an internal standard.

Ethyl *trans*-cinnamate (3a**):**

¹H NMR (400 MHz, CDCl₃) δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.53-7.51 (m, 2H), 7.42-7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 166.9, 144.5, 134.4, 130.2, 128.3, 128.0, 118.2, 60.4, 14.3.

Typical Experimental procedure for Suzuki-Miyaura coupling (Table 3, entry 1).

PI Pd **B** (0.025 mmol), 2-bromotoluene (**4a**) (60 μL, 0.50 mmol), phenylboronic acid (**5a**) (91.4 mg, 0.75 mmol), P(*o*-MeOC₆H₄)₃ (8.8 mg, 0.025 mmol) and potassium phosphate (106 mg, 0.5 mmol) were combined in toluene-H₂O (4/1) (5 mL) under argon atmosphere. The mixture was stirred for 4 h under refluxing. After hexane was added to quench the reaction, the catalyst was collected by filtration and washed with THF, water, and DCM, and dried before reuse. The solvent of the filtrate was removed under reduced pressure and the volume of the residue was adjusted to 5 mL using MeCN to prepare a sample for XRF analysis (measurement of leaching of palladium). The sample solution after measurement of leaching was evaporated and the residual of the crude product was purified by preparative thin-layer chromatography (PTLC) to afford 2-methylbiphenyl (90.4 mg, 95%).

2-methylbiphenyl²

¹H NMR (300 MHz, CDCl₃) δ = 7.42-7.21 (m, 9H), 2.26 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 141.9, 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.

4-Acetylbiphenyl³ (Table 4, entries 1 and 7): ¹H NMR (300 MHz, CDCl₃) δ = 8.00 (d, *J* = 8.6 Hz, 2H), 7.66-7.58 (m, 4H), 7.46-7.35 (m, 3H), 2.60 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 197.6, 145.6, 139.7, 135.7, 128.8, 128.8, 128.1, 127.1, 127.1, 26.5.

4-Methoxybiphenyl² (Table 4, entry 2): ¹H NMR (400 MHz, CDCl₃) δ = 7.54 (t, *J* = 8.0 Hz, 4H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

2-Methyl-4'-*tert*-butylbiphenyl³ (Table 4, entry 3): ¹H NMR (400 MHz, CDCl₃) δ = 7.42 (d, *J* = 8.3 Hz, 2H), 7.30-7.20 (m, 6H), 2.29 (s, 3H), 1.36 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ = 149.5, 141.9, 139.0, 135.4, 130.3, 129.9, 128.8, 127.0, 125.7, 124.9, 34.5, 31.4, 20.5.

4-Acetyl-2'-methylbiphenyl⁴ (Table 4, entry 4): ¹H NMR (400 MHz, CDCl₃) δ = 8.00 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30-7.20 (m, 4H), 2.65 (s, 3H), 2.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 197.7, 146.9, 140.6, 135.5, 135.0, 130.4, 129.4, 129.4, 128.1, 127.8, 125.8, 26.5, 20.3.

4-*o*-Tolylpyridine⁵ (Table 4, entry 5): ¹H NMR (300 MHz, CDCl₃) δ = 8.65 (d, *J* = 6.1 Hz, 2H), 7.33-7.19 (m, 6H), 2.27 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 149.9, 149.3, 138.9, 134.9, 130.6, 129.2, 128.3, 126.0, 124.2, 20.2.

4-Methoxy-2'-methylbiphenyl⁴ (Table 4, entry 6): ¹H NMR (300 MHz, CDCl₃) δ = 7.25-7.19 (m, 6H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.26 (s, 3H).
¹³C NMR (75 MHz, CDCl₃) δ = 158.5, 141.5, 135.5, 134.3, 130.3, 130.2, 129.9, 126.9, 125.7, 113.5, 55.3, 20.5.

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