Active Palladium Colloids via Palladacycle Degradation as Efficient Catalysts for Oxidative Homocoupling and Cross-Coupling of Aryl Boronic Acids

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**General remarks:** Aldehydes and other commercially available chemicals were purchased locally and were used without further purification. All the solvents were dried by standard methods before use. Hermann-Beller complex (**palladacycle 1**) was synthesized by the literature procedure (Herrmann, W. A., Brossmer, C., Ofele, K., Reisinger, C. P., Piermeier, T., Beller, M., Fischer, H. *Angew. Chem. Int. Ed. Engl.* 1995, 34, 1844.) NMR data (**H**, **P** or **C**) were recorded locally on 500 spectrometers. ESI-MS analyses was performed locally. The ionization mechanism used was electrospray in positive and negative ion full scan mode using acetonitrile as solvent and nitrogen gas for desolvation. Transmission Electron Microscopic studies were carried out locally. X-ray Diffraction Powder analysis was done using in-house institutional facility. High-Resolution Transmission Electron Microscopic analyses and X-ray Photoelectron Spectroscopic studies were also performed on the samples, locally.

**EXAFS analysis:** The X-ray absorption experiments were performed at the beam line **BL-14B2** of SPring8, Japan. The samples for Extended X-ray Absorption Fine Structure (EXAFS) experiments were prepared by mixing BN with sample of interest and then homogenizing it in a mortar by a pestle. The samples were packed very tightly in aluminum cell of 10 mm diameter, taking care that no air is trapped. The sample was secured in the cell by applying scotch tape on both sides of cell. The ratio of sample to BN was chosen in such a way that the theoretical absorption jump (as calculated by software supplied by SPring-8) was about 1 unit at Pd K-edge. The energy calibration at the Pd-K edge was monitored by using a Pd foil as a reference material, and measured before and after the samples were done. Athena (Demeter) software was used for processing the raw data obtained above, which implement the FEFF6 and IFEFFIT codes. The AUTOBK method was used to isolate the $k$-space EXAFS data from the raw data. The energy calibration was done using reference Pd-foil collected simultaneously. The fitting was performed using Artemis software of Demeter 0.9.22, copyrights Bruce Ravel. The data were fit from 1.2 to 3.0 Å in R-space and 3.0 to 13.0 Å$^{-1}$ in $k$ weighing, with multiple $k$
weighing. The path degeneracy (N), energy correction ($\Delta E_0$), adjustment in half path length ($\Delta R$) and mean square displacement factor ($\sigma^2$), were used as variable parameters for fitting. For calibration purpose, energy of Pd-foil was used as reference.

For fitting purposes, Pd metal and Pd(OAc)$_2$ were used as theory. By fitting Pd-foil, the amplitude reduction factor calculated was 0.84 units, which was kept constant during the fitting. The SO$^2$ value was defined as amp*N where amp is set at 0.84 and N was kept variable (guess) for fitting. The rest of the values such as $\Delta E_0$, $\Delta R$ and $\sigma^2$ were also kept variable (guess) using Hanning’s window function.
Table S1: Screening studies for palladacycle 1 mediated diarylmethanol synthesis.

![Chemical structure](image)

| Entry | Catalyst (mol%) | Ligand (mol%) | Base       | Solvent      | %Yield |
|-------|-----------------|---------------|------------|--------------|--------|
| 1     | -               | -             | K₂CO₃      | PhMe         | 0      |
| 2     | Pd(OAc)₂ (5.0) | -             | K₂CO₃      | PhMe         | 7      |
| 3     | Pd(OAc)₂ (1.0) | -             | K₂CO₃      | PhMe         | 40     |
| 4     | Pd(OAc)₂ (1.0) | PPh₃ (1.0)    | K₂CO₃      | PhMe         | 55     |
| 5     | Pd(OAc)₂ (1.0) | P(o-Tol)₃ (1.0)| K₂CO₃      | PhMe         | 57     |
| 6     | Pd(OAc)₂ (1.0) | IPr.HCl (1.0) | K₂CO₃      | PhMe         | 55     |
| 7     | Pd(OAc)₂ (1.0) | IMes.HCl (1.0)| K₂CO₃      | PhMe         | 51     |
| 8     | Palladacycle 1 (1.0) | - | K₂CO₃ | PhMe | 80 |
| 9     | CombiPhos       | -             | K₂CO₃      | PhMe         | 61     |
| 10    | Palladacycle 1 (1.0) at r.t. | - | K₂CO₃ | PhMe | 0 |
| 11    | Palladacycle 1 (1.0) at 100 °C | - | K₂CO₃ | PhMe | 10 |
| 12    | Palladacycle 1 (1.0) at 80 °C | - | K₂CO₃ | PhMe | 80 |
| 13    | Palladacycle 1 (1.0) | - | Cs₂CO₃ | PhMe | 0 |
| 14    | Palladacycle 1 (1.0) | - | Et₃N | PhMe | 0 |
| 15    | Palladacycle 1 (1.0) | - | NaOAc | PhMe | 0 |
| 16    | Palladacycle 1 (1.0) | - | Na₂CO₃ | PhMe | 18 |
| 17    | Palladacycle 1 (1.0) | - | K₂CO₃ | PhMe | 80 |
| 18    | Palladacycle 1 (1.0) | - | Li₂CO₃ | PhMe | 0 |
| 19    | Palladacycle 1 (1.0) | - | K₂CO₃ | CHCl₃ | 81 |
| 20    | Palladacycle 1 (1.0) | - | K₂CO₃ | CH₂CN | 31 |
| 21    | Palladacycle 1 (1.0) | - | K₂CO₃ | CH₂Cl₂ | 0 |
| 22    | Palladacycle 1 (1.0) | - | K₂CO₃ | THF | 70 |
| 23    | Palladacycle 1 (1.0) | - | K₂CO₃ | Et₂O | 0 |
| 24    | Palladacycle 1 (1.0) | - | K₂CO₃ | H₂O | 0 |
| 25    | Palladacycle 1 (1.0) | - | K₂CO₃ | MeOH | 71 |
| 26    | Palladacycle 1 (1.0) | - | K₂CO₃ | CH₂CN/H₂O | 85 |

*a 1.0 mmol C₆H₅CHO, 2.0 mmol C₆H₅B(OH)₂, Catalyst (mol%), Solvent (2.0 mL), K₂CO₃ (2.0 Equiv.), CHCl₃ (0.1 mL) at 80 °C for 24 hrs.
Representative General Procedure for palladium-catalyzed synthesis of diarylmethanols:

In an oven dried schlenk tube, add palladacycle 1 (9.37 mg, 0.01 mmol, 1 mol%) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and CH$_3$CN/H$_2$O (1:1) (2 mL) under nitrogen followed by benzaldehyde (0.1 mL or 106 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C for 24 hrs. The reaction was then cooled and after addition of 1-2 gram silica was dried under vacuo. The crude product was then subjected to column chromatography on silica gel with pet ether/ethyl acetate (10/1) to give diphenylmethanol 4a as a white solid (184 mg, 0.82 mmol, 82%).

**Diphenylmethanol 4a:**

White Solid (82%). $^1$H NMR (500 MHz, CDCl$_3$): 7.42 – 7.22 (m, 10H), 5.78 (s, 1H), 2.69 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 143.8, 128.4, 127.5, 126.6, 76.1. GCMS (EI, m/z): 184.

(4-Chlorophenyl)(phenyl)methanol 4b:

White solid (85%). $^1$H NMR (500 MHz, CDCl$_3$): 7.27-7.23 (m, 4H), 7.22–7.16 (m, 5H), 5.71 (s, 1H; CH). $^{13}$C NMR (126 MHz, CDCl$_3$): 143.4, 142.2, 133.3, 128.6, 128.5, 127.8, 126.5, 75.6. GCMS (EI, m/z): 218.

(4-Nitrophenyl)(phenyl)methanol 4c:

White solid (60%). $^1$H NMR (500 MHz, CDCl$_3$): 8.09 (d, $J$ = 8.9 Hz, 2H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.37 – 7.15 (m, 5H), 5.82 (s, 1H), 2.42 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 150.7, 147.0, 142.7, 128.9, 128.2, 126.9, 126.5, 123.5, 77.5. GCMS (EI, m/z): 229.

(4-Cyanophenyl)(phenyl)methanol 4d:

White solid (62%). $^1$H NMR (500 MHz, CDCl$_3$): 7.54 (d, $J$ = 8.5 Hz, 2H), 7.43 (d, $J$ = 8.1 Hz, 2H), 7.32 – 7.20 (m, 5H), 5.79 (s, 1H), 2.08 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 148.7, 142.7, 132.1, 128.7, 128.3, 126.9, 126.5, 118.7, 111.1, 75.6. GCMS (EI, m/z): 209.

Naphthalen-2-yl(phenyl)methanol 4e:

White solid (73%). $^1$H NMR (500 MHz, CDCl$_3$): 7.88 (s, 1H), 7.85 – 7.76 (m, 3H), 7.51 – 7.44 (m, 2H), 7.41 (d, $J$ = 8.4 Hz, 3H), 7.33 (t, $J$ = 7.4 Hz, 2H), 7.26 (dd, $J$ = 12.5, 5.3 Hz, 1H), 5.98 (s, 1H), 2.44 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 143.6, 141.0, 133.2, 132.8, 128.5, 128.3, 128.0, 127.6, 126.6, 126.1, 125.9, 125.0, 124.7, 76.3.

(4-Fluorophenyl)(phenyl)methanol 4f:

Semi Solid (68%). $^1$H NMR (500 MHz, CDCl$_3$): 7.27–7.12 (m, 7H), 6.93–6.83 (m, 2H), 5.68 (s, 1H), 2.41 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 162.2 ($^3$J$_{CF}$ = 251.0 Hz), 143.6, 139.5, 128.5, 128.2 ($^3$J$_{CF}$ = 8.2 Hz), 127.7, 126.4, 115.2 ($^3$J$_{CF}$ = 21.9 Hz), 75.5. $^{19}$F NMR (470 MHz): -115.07. GCMS (EI, m/z): 202.
[1,1'-Biphenyl]-4-yl(phenyl)methanol 4g: White Solid (64%). $^1$H NMR (500 MHz, DMSO-d$_6$): 7.62 – 7.56 (m, 4H), 7.46 – 7.38 (m, 6H), 7.34 – 7.28 (m, 3H), 7.20 (dd, $J = 10.4, 4.2$ Hz, 1H), 5.91 (d, $J = 4.0$ Hz, 1H), 5.74 (d, $J = 3.9$ Hz, 1H). $^{13}$C NMR (126 MHz, DMSO-d$_6$): 146.0, 145.38, 140.48, 139.1, 129.3, 128.5, 127.7, 127.2, 127.1, 127.0, 126.8, 126.6, 74.4. GCMS (EI, m/z): 260.

(4-Methylphenyl)(phenyl)methanol 4h: White Solid (66%). $^1$H NMR (500 MHz, CDCl$_3$): 7.34 (dt, $J = 15.0, 7.4$ Hz, 4H), 7.29 – 7.21 (m, 3H), 7.14 (d, $J = 7.8$ Hz, 2H), 5.78 (s, 1H), 2.34 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): 143.9, 140.9, 137.2, 129.1, 128.4, 127.4, 126.5, 126.4, 76.0, 21.1. GCMS (EI, m/z): 198.

Naphthalen-1-yl(phenyl)methanol 4i: White Solid (60%). $^1$H NMR (500 MHz, CDCl$_3$): 7.90 – 7.75 (m, 4H), 7.52 – 7.37 (m, 5H), 7.33 (t, $J = 7.3$ Hz, 2H), 7.27–7.17 (m, 1H), 5.98 (s, 1H), 2.36 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 143.6, 141.0, 133.2, 132.8, 128.5, 128.3, 128.0, 127.6, 126.7, 126.1, 125.9, 124.9, 124.7, 76.3. GCMS (EI, m/z): 234.

(4-Methoxyphenyl)(phenyl)methanol 4j: White Solid (70%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.32 (m, 4H), 7.28 (dd, $J = 13.4, 5.4$ Hz, 3H), 6.86 (d, $J = 8.6$ Hz, 2H), 5.71 (s, 1H), 3.76 (s, 3H), 3.02 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 158.9, 144.1, 136.3, 128.4, 127.9, 127.3, 126.5, 113.8, 75.6, 55.2. GCMS (EI, m/z): 214.
General procedure for the synthesis of Pd colloids.
In an oven dried schlenk tube, add palladacycle 1 (9.37 mg, 1.0 mmol, 1 mol%) under a continuous flow of nitrogen followed by K$_2$CO$_3$ (276 mg, 2.0 mmol) and 4-chlorobenzaldehyde (0.140 mg, 1.0 mmol) via syringe. Chloroform (2.0 mL) was then added under nitrogen and the reaction mass was stirred and refluxed in an oil bath at 80°C for 24 hrs. The reaction mass was then cooled and transferred to a conical flask containing ethanol (4.0 mL) and stirred for 30 min at room temperature. The suspension thus obtained was centrifuged at 10,000 RPM for 15 min. and the supernatant was discarded, while the obtained precipitate was washed with water (4.0 mL) and again centrifuged at 10,000 RPM for 15 min. This procedure was repeated 3 times to get a black residue, which was then vacuum dried for 1 hr and subjected to all the characterization techniques.

General procedure for Mercury(Hg) poisoning study
In an oven dried schlenk tube, add palladacycle 1 (9.37 mg, 0.01 mmol, 1 mol%) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and CH$_3$CN/H$_2$O (1:1) (2 mL) under nitrogen followed by 4-chlorobenzaldehyde (0.140 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C. After 2h, Hg (0.3 mmol, 60 mg) was added and the reaction was continued at 80°C for a further 22 h. On completion of the stipulated time, TLC analysis of the reaction mixture revealed no progress in the reaction, thus suggesting complete inhibition of the catalytic reaction. This was also confirmed by injecting an aliquot into GC.

General procedure for carbon disulphide poisoning study
In an oven dried schlenk tube, add palladacycle 1 (9.37 mg, 0.01 mmol, 1 mol%) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and CH$_3$CN/H$_2$O (1:1) (2 mL) under nitrogen followed by 4-chlorobenzaldehyde (0.1405 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C. After 2h, Carbon disulfide (CS$_2$) (0.5 mL, 10 mmol) was added and the reaction was continued at 80°C for a further 22 h. On completion of the stipulated time, TLC analysis
of the reaction mixture revealed no progress in the reaction, thus suggesting complete inhibition of the catalytic reaction. This was also confirmed by injecting an aliquot into GC.

**General procedure for tetra-n-butylammonium bromide (TBAB) study**

In an oven dried schlenk tube, add **palladacycle 1** (9.37 mg, 0.01 mmol, 1 mol%) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and CH$_3$CN/H$_2$O (1:1) (2 mL) under nitrogen followed by 4-chlorobenzaldehyde (0.1405 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C. After 2h, TBAB (0.322 g, 1.0 mmol, 1.0 equiv.) was added and the reaction was continued at 80°C for a further 22 h. On completion of the stipulated time, TLC analysis of the reaction mixture revealed similar conversion pattern to the general catalytic reaction. The reaction was then cooled and after addition of 1-2 gram silica was dried under vacuo. The crude product was then subjected to column chromatography on silica gel with pet ether/ethyl acetate (10/1) to give (**4-Chlorophenyl**(phenyl)methanol 4b as a white solid (85%).

**Crabtree Test:**

In an oven dried schlenk tube, add **palladacycle 1** (9.37 mg, 0.01 mmol, 1 mol%) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and CH$_3$CN/H$_2$O (1:1) (2 mL) under nitrogen followed by 4-chlorobenzaldehyde (0.1405 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C. After 15 min, DCT (0.004 g, 2 x 10$^{-2}$ mmol) was added and the reaction was continued at 80°C for 24 h. On completion of the stipulated time, TLC analysis of the reaction mixture revealed some amount of conversion. The reaction was then cooled and after addition of 1-2 gram silica was dried under vacuo. The crude product was then subjected to column chromatography on silica gel with pet ether/ethyl acetate (10/1) to give (**4-Chlorophenyl**)(phenyl)methanol 4b as a white solid (39%).
Representative General Procedure for palladium-catalyzed synthesis of diarylmethanols using palladium colloids:

In an oven dried schlenk tube, add **palladium colloids** (10 mg) under a continuous flow of nitrogen, followed by K$_2$CO$_3$ (276 mg, 2.0 mmol). To this was added CHCl$_3$ (0.1 mL) and H$_2$O/CH$_3$CN (1:1) (2 mL) under nitrogen followed by 4-chlorobenzaldehyde (0.1405 mg, 1.0 mmol) via syringe. The reaction mass was then refluxed in an oil bath at 80°C for 15 min for activation. After cooling the reaction mass to room temperature, PhB(OH)$_2$ (244 mg, 2 mmol) was then added and the mixture was stirred at 80°C for 24 hrs. The reaction was then cooled and after addition of 1-2 gram silica was dried under vacuo. The crude product was then subjected to column chromatography on silica gel with pet ether/ethyl acetate (10/1) to give **(4-Chlorophenyl)(phenyl)methanol 4b** as a white solid (90%).
Figure S1: 1H and 13C NMR for 4a

4a
(500 MHz, CDCl₃)

1H NMR

13C NMR

4a
(126 MHz, CDCl₃)
Figure S2: 1H and 13C NMR for 4b
Figure S3: 1H and 13C NMR for 4c
**Figure S4:** 1H and 13C NMR for 4d

![NMR spectra](image)

**Chemical Shift (ppm):**

1H NMR (500 MHz, CDCl₃)

13C NMR (126 MHz, CDCl₃)

VSA-87, processed file C13.esp
Figure S5: 1H and 13C NMR for 4e

4e (500 MHz, CDCl₃)

4e (126 MHz, CDCl₃)
Figure S6: 1H and 13C and 19F NMR for 4f
4f
(470 MHz, CDCl$_3$)
Figure S7: 1H and 13C NMR for 4g

Chemical Shift (ppm)

2642_rsekar_ARK_VSA_96_CARBON_01
Figure S8: 1H and 13C NMR for 4h
Figure S9: 1H and 13C NMR for 4i

4i
(500 MHz, CDCl₃)

4i
(126 MHz, CDCl₃)
Figure S10: 1H and 13C NMR for 4j

(500 MHz, CDCl₃)

(126 MHz, CDCl₃)
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d) A. Yu, B. Cheng, Y. Wu, J. Li, W. A. Kun, *Tetrahedron Lett.* 2008, 49, 5405.

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General procedure for oxidative homocoupling of aryl boronic acids.

In a 30 mL Schlenck tube, Pd colloids (10 mg), K$_2$CO$_3$ (1.0 Equiv., 1 mmol, 0.138 g) and CH$_3$CN/H$_2$O (1 mL) were added. The reaction mixture was refluxed at 80 °C for 15 minutes. The reaction mixture was cooled down to room temperature for the addition of aryl boronic acid (1.0 Equiv., 1 mmol) and CH$_3$CN/H$_2$O (1 mL) the reaction mixture was refluxed in air at 80 °C for 24 hours. The reaction was quenched by the addition of 1-2 g silica and solvent was removed under vacuo. The product was then isolated by column chromatography on silica gel using Pet Ether/Ethyl Acetate (99:1) to give a white solid.

3,3'-Dinitrobiphenyl (5a): \(^1H\) NMR (500 MHz, CDCl$_3$): 8.48 (s, 2H), 8.28 (d, $J = 8.2$ Hz, 2H), 7.95 (d, $J = 7.7$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H). \(^{13}C\) NMR (126 MHz, CDCl$_3$): 148.86, 140.30, 133.02, 130.26, 123.27, 122.07. GCMS (EI, m/z): 244.

4,4'-Difluorobiphenyl (5b): \(^1H\) NMR (500 MHz, CDCl$_3$): 7.63-7.57 (m, 4H), 7.51-7.46 (m, 4H); \(^{13}C\) NMR (126 MHz, CDCl$_3$): 149.8, 138.2, 126.6, 125.6; \(^{19}F\) NMR (470 MHz, CDCl$_3$): -62.3; GCMS (EI, m/z): 190 (100).

4,4'-Dinitrobiphenyl (5c): \(^1H\) NMR (500 MHz, CDCl$_3$): 8.34 (d, $J = 8.8$ Hz, 4H), 7.77 (d, $J = 8.8$ Hz, 4H). \(^{13}C\) NMR (126 MHz, CDCl$_3$): 147.9, 144.9, 128.3, 124.3. GCMS (EI, m/z): 244.

4,4'-Dimethylbiphenyl (5d): \(^1H\) NMR (500 MHz, CDCl$_3$): 7.50 (d, $J = 7.8$ Hz, 4H), 7.24 (d, $J = 7.8$ Hz, 4H), 2.40 (s, 6H); \(^{13}C\) NMR (126 MHz, CDCl$_3$): 138.2, 136.6, 129.4, 126.8, 21.0; GCMS (EI, m/z): 182 (100).

4,4'-Dimethoxybiphenyl (5e): \(^1H\) NMR (500 MHz, CDCl$_3$): 7.49 (d, $J = 8.1$ Hz, 4H), 7.01 (d, $J = 8.0$ Hz, 4H), 3.83 (s, 6H); \(^{13}C\) NMR (126 MHz, CDCl$_3$): 158.6, 133.4, 127.7, 114.1, 55.3; GCMS (EI, m/z): 214 (100).

Biphenyl-4,4'-dicarbaldehyde (5f): \(^1H\) NMR (500 MHz, CDCl$_3$): 10.07 (s, 2H), 7.98 (d, $J = 8.4$ Hz, 4H), 7.78 (d, $J = 8.2$ Hz, 4H). \(^{13}C\) NMR (126 MHz, CDCl$_3$): 191.6, 145.6, 135.7, 130.2, 128.1. GCMS (EI, m/z): 306.

3,3'-Dimethylbiphenyl (5g): \(^1H\) NMR (500 MHz, CDCl$_3$): 7.44-7.39 (m, 4H), 7.35-7.31 (m, 2H), 7.17-7.15 (m, 2H), 2.42 (s, 6H). \(^{13}C\) NMR (126 MHz, CDCl$_3$): 141.3, 138.3, 128.6, 128.0, 127.9, 124.3, 21.4; GCMS (EI, m/z): 182 (100).

3,3'-Dimethoxybiphenyl (5h): \(^1H\) NMR (500 MHz, CDCl$_3$): 7.36-7.34 (m, 2H), 7.20-7.17 (m, 2H), 7.14-7.12 (m, 2H), 6.91-6.89 (m, 2H), 3.86 (s, 6H); \(^{13}C\) NMR (126 MHz, CDCl$_3$): 159.9, 142.6, 129.7, 119.6, 112.7, 55.2; GCMS (EI, m/z): 214 (100).
Dimethyl [1,1'-biphenyl]-3,3'-dicarboxylate (5i): $^1$H NMR (500 MHz, CDCl$_3$): 8.27 (s, 2H), 8.01 (d, $J$ = 7.7 Hz, 2H), 7.77 (d, $J$ = 7.7 Hz, 2H), 7.50 (t, $J$ = 7.7 Hz, 2H), 3.92 (s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): 166.8, 140.3, 131.4, 130.8, 128.9, 128.7, 128.2, 52.2. GCMS (EI, m/z): 270. Elemental analysis for C$_{16}$H$_{14}$O$_4$; Calculated: C, 71.10; H, 5.22. Observed: C, 70.98; H, 5.17.

4,4'-Di(naphthalen-1-yl)-1,1'-biphenyl (5j): $^1$H NMR (500 MHz, CDCl$_3$): 7.94 (d, $J$ = 8.2 Hz, 2H), 7.83 (dd, $J$ = 17.1, 7.9 Hz, 4H), 7.74 (d, $J$ = 7.8 Hz, 4H), 7.55 (d, $J$ = 7.8 Hz, 4H), 7.51 – 7.37 (m, 8H). $^{13}$C NMR (126 MHz, CDCl$_3$): 139.8, 139.8, 139.6, 133.8, 131.6, 130.5, 128.3, 127.7, 126.9, 126.1, 126.0, 125.8, 125.4. Elemental analysis for C$_{32}$H$_{22}$; Calculated: C, 94.55; H, 5.45. Observed: C, 94.47; H, 5.38.

4,4'-Di(naphthalen-2-yl)-1,1'-biphenyl (5k): $^1$H NMR (500 MHz, CDCl$_3$): 7.97 (s, 2H), 7.86 (dd, $J$ = 15.8, 8.4 Hz, 6H), 7.69 (d, $J$ = 8.4 Hz, 2H), 7.60 (d, $J$ = 8.3 Hz, 4H), 7.51 – 7.42 (m, 4H), 6.94 (d, $J$ = 8.3 Hz, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 155.1, 138.0, 133.8, 133.6, 132.2, 131.1, 128.6, 128.3, 128.0, 127.5, 126.2, 125.6, 125.3, 125.0, 115.7. Elemental analysis for C$_{32}$H$_{22}$; Calculated: C, 94.55; H, 5.45. Observed: C, 94.50; H, 5.39.

4,4'-(B)idibenzo[b,d]furan (5l): $^1$H NMR (500 MHz, CDCl$_3$): 8.09 – 7.93 (m, 6H), 7.53 (dd, $J$ = 17.6, 7.3 Hz, 2H), 7.45 (t, $J$ = 7.3 Hz, 2H), 7.36 (t, $J$ = 7.3 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 156.2, 153.6, 128.5, 127.2, 124.9, 124.2, 122.9, 122.7, 120.9, 120.6, 120.2, 111.8. GCMS (EI, m/z): 334. Elemental analysis for C$_{24}$H$_{14}$O$_2$; Calculated: C, 86.21; H, 4.22. Observed: C, 86.16; H, 4.15.

2,2'-Dibenzofuran (5m): $^1$H NMR (500 MHz, CDCl$_3$): 7.53 (d, $J$ = 7.5 Hz, 2H), 7.45 (d, $J$ = 8.1 Hz, 2H), 7.23 (t, $J$ = 7.7 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.06 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): 155.1, 147.6, 128.5, 125.0, 123.3, 121.3, 111.2, 103.6. GCMS (EI, m/z): 234.

2,2'-Biphenyl (5n): $^1$H NMR (500 MHz, CDCl$_3$): 7.47–7.57 (m, 4 H), 7.87–7.94 (m, 4 H), 7.95 (t, $J$ = 8.7 Hz, 4 H), 8.18 (s, 2 H); $^{13}$C NMR (126 MHz, CDCl$_3$): 125.7, 126.0, 126.1, 126.3, 127.7, 128.2, 128.5, 132.7, 133.8, 138.4; GCMS (EI, m/z): 254 (100).

9,9'-Biphenanthrene (5o): $^1$H NMR (500 MHz, CDCl$_3$) δ 8.81 (d, $J$ = 8.3 Hz, 4H), 7.93 (d, $J$ = 7.8 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.77 – 7.59 (m, 6H), 7.51 (d, $J$ = 8.3 Hz, 2H), 7.41 – 7.34 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): 137.1, 132.1, 131.6, 130.3, 130.2, 128.7, 128.4, 127.5, 126.9, 126.7, 126.6, 126.5, 122.7, 122.6. GCMS (EI, m/z): 354.

2,2'-Dimethylbiphenyl (5p): $^1$H NMR (500 MHz, CDCl$_3$): 7.31–7.27 (m, 4H), 7.24–7.19 (m, 2H), 7.13 (d, $J$ = 7.9 Hz, 2H), 2.12 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): 141.5, 135.8, 129.7, 129.2, 127.1, 125.5, 20.2; GCMS (EI, m/z): 182 (100).
Figure S11: 1H and 13C NMR for 5a

(CDC6, 500 MHz)

122.073
123.266
130.261
133.018
140.305
148.864

(CDC6, 126 MHz)
Figure S12: 1H and 13C and 19F NMR for 5b
Figure S13: 1H and 13C NMR for 5c

\[
\text{O}_2\text{N}-\begin{array}{c}
\text{H} \\
\text{H}
\end{array}-\text{H} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array}-\text{NO}_2
\]

5c

(CDC\textsubscript{6}, 500 MHz)

\[
\text{O}_2\text{N}-\begin{array}{c}
\text{H} \\
\text{H}
\end{array}-\text{H} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array}-\text{NO}_2
\]

5c

(CDC\textsubscript{6}, 126 MHz)
Figure S14: 1H and 13C NMR for 5d

NMR FILES FOR 4,4DIMETHYL BIPHENYL.010.esp

NMR FILES FOR 4,4DIMETHYL BIPHENYL.011.esp
Figure S15: 1H and 13C NMR for 5e
Figure S16: 1H and 13C NMR for 5f
Figure S17: 1H and 13C NMR for 5g
Figure S18: 1H and 13C NMR for 5h
Figure S19: 1H and 13C NMR for 5i
Figure S20: 1H and 13C NMR for 5j

(CDCl$_3$, 500 MHz)

(CDCl$_3$, 126 MHz)
Figure S21: 1H and 13C NMR for 5k
Figure S22: 1H and 13C NMR for 5I

5I (CDCl₃, 500 MHz)

5I (CDCl₃, 126 MHz)
Figure S23: 1H and 13C NMR for 5m

(CDCl₃, 500 MHz)

(CDCl₃, 126 MHz)
Figure S24: 1H and 13C NMR for 5n

5n
(CDCl₃, 500 MHz)

5n
(CDCl₃, 126 MHz)
Figure S25: 1H and 13C NMR for 5o

(Chemical structures and NMR spectra are shown, with peaks and chemical shifts indicated. The spectra are labeled with chemical environments and frequencies.)
Figure S26: 1H and 13C NMR for 5p

(CDCl₃, 500 MHz)

(CDCl₃, 126 MHz)
General procedure for cross-coupling of aryl boronic acids.

In a 30 mL Schlenck tube, Pd colloids (10 mg), K$_2$CO$_3$ (1.0 Equiv., 1 mmol, 0.138 g), less reactive aryl boronic acid (1.0 Equiv., 1 mmol) and CH$_3$CN/H$_2$O (1 mL) were added. The reaction mixture was refluxed in pure O$_2$ at 80 °C for 5 mins. To this was added via syringe slowly over a period of 20 mins, the second aryl boronic acid (1.3 Equiv., 1.3 mmol) in CH$_3$CN/H$_2$O (1 mL) and the resultant reaction mixture was refluxed for 24 hr at 80 °C. On completion, the reaction was quenched by the addition of 1-2 g silica and solvent was removed under vacuo. The product was then isolated by column chromatography on silica gel using Pet Ether/Ethyl Acetate (99:1) to give a white solid.

4'-Methoxy-3-nitro-1,1'-biphenyl (7a): $^1$H NMR (500 MHz, CDCl$_3$): 8.33 – 8.22 (m, 1H), 8.01 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.44 (dd, $J = 8.3$, 5.5 Hz, 3H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.74 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): 160.0, 148.7, 142.4, 132.5, 131.0, 131.0, 129.6, 128.2, 126.4, 126.4, 121.3, 114.5, 55.4. GCMS (EI, m/z): 229 (100). Elemental analysis for C$_{13}$H$_{11}$NO$_3$; Calculated: C, 68.11; H, 4.84; N, 6.11. Observed: C, 68.09; H, 4.79; N, 6.02.

2-(3-Nitrophenyl)benzofuran (7b): $^1$H NMR (500 MHz, CDCl$_3$): 8.65 – 8.61 (m, 1H), 8.10 (td, $J = 8.6$, 1.2 Hz, 2H), 7.55 (t, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 1H), 7.31 – 7.26 (m, 1H), 7.21 (dd, $J = 9.6$, 2.8 Hz, 1H), 7.12 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 155.0, 153.1, 148.7, 132.1, 130.3, 129.8, 128.6, 125.3, 123.4, 122.8, 121.4, 119.6, 117.0, 111.4, 103.5. GCMS (EI, m/z): 239 (100). Elemental analysis for C$_{14}$H$_9$NO$_3$; Calculated: C, 70.29; H, 3.79; N, 5.86. Observed: C, 70.23; H, 3.74; N, 5.81.

4'-Fluoro-4'-nitrobiphenyl (7c): $^1$H NMR (500 MHz, CDCl$_3$): 8.29 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.59 (dd, $J = 7.7$, 5.4 Hz, 1H), 7.18 (t, $J = 8.4$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): 163.3 ($^1$J$_{C-F} = 251.0$ Hz), 146.5, 134.9, 134.8, 129.1 ($^3$J$_{C-F} = 8.6$ Hz), 127.6, 124.1, 116.2 ($^2$J$_{C-F} = 22.0$ Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): –112.7. GCMS (EI, m/z): 217 (100).

4'-Fluoro-4'-methoxybiphenyl (7d): $^1$H NMR (500 MHz, CDCl$_3$): 7.59–7.36 (m, 4H), 7.16–7.04 (m, 2H), 7.00–6.92 (m, 2H), 3.84 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): 162.0 ($^1$J$_{C-F} = 245.0$ Hz), 159.1, 136.9, 132.8, 128.2 ($^3$J$_{C-F} = 7.9$ Hz), 128.0, 115.5 ($^2$J$_{C-F} = 21.5$ Hz), 114.2, 55.3; $^{19}$F NMR (470 MHz, CDCl$_3$): –116.7; GCMS (EI, m/z): 202 (100).

2-(4'-Methoxyphenyl)naphthalene (7e): $^1$H NMR (500 MHz, CDCl$_3$): 8.00 (s, 1H), 7.93–7. 83 (m, 3H), 7.74 (dd, $J = 8.5$, 1.9 Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.54–7.42 (m, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 3.87 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.3. GCMS (EI, m/z): 234 [100].
Figure S27: $^1$H and $^{13}$C NMR for 7a
Figure S28: 1H and 13C NMR for 7b
Figure S29: 1H and 13C NMR for 7c
Figure S30: $^1$H, $^{13}$C and $^{19}$F NMR for 7d
Figure S31: 1H and 13C NMR for 7e

7e
(CDCl₃, 500 MHz)

7e
(CDCl₃, 126 MHz)
Figure S32: TEM characterization of catalytic solution
Figure S33: TEM for PEGylated colloids from catalytic solution
Figure S34: HRTEM for isolated Mercury Engulfed Palladium Colloids and EDAX Spectra
Figure S35: TEM for isolated Palladium colloids
Figure S36: High Resolution TEM for isolated Pd colloids
Table S2: XPS data for isolated palladium colloids

| C1s | O1s  | Pd3d |
|-----|------|------|
| 298 | 6067.5 | 12640 | 350 | 10510.83 |
| 297.8 | 5995 | 542.8 | 12924.17 | 349.8 | 10505.83 |
| 297.6 | 5970 | 542.6 | 12752.5 | 349.6 | 10538.33 |
| 297.4 | 5925 | 542.4 | 12835 | 349.4 | 10578.33 |
| 297.2 | 5802.5 | 542.2 | 12760 | 349.2 | 10719.17 |
| 297 | 5885 | 542 | 12813.33 | 349 | 10317.5 |
| 296.8 | 5878.334 | 541.8 | 12810.83 | 348.8 | 10361.67 |
| 296.6 | 5758.334 | 541.6 | 12875.83 | 348.6 | 10417.5 |
| 296.4 | 5728.334 | 541.4 | 12558.33 | 348.4 | 10324.17 |
| 296.2 | 5695 | 541.2 | 12870.83 | 348.2 | 10410 |
| 296 | 5620.834 | 541 | 12675 | 348 | 10456.67 |
| 295.8 | 5434.167 | 540.8 | 12710 | 347.8 | 10395.83 |
| 295.6 | 5636.666 | 540.6 | 12600.83 | 347.6 | 10371.67 |
| 295.4 | 5727.5 | 540.4 | 12705.83 | 347.4 | 10385.83 |
| 295.2 | 5550.834 | 540.2 | 12707.5 | 347.2 | 10493.33 |
| 295 | 5566.667 | 540 | 12581.67 | 347 | 10440.83 |
| 294.8 | 5630.834 | 539.8 | 12720 | 346.8 | 10329.17 |
| 294.6 | 5493.334 | 539.6 | 12615 | 346.6 | 10287.5 |
| 294.4 | 5522.5 | 539.4 | 12765 | 346.4 | 10460 |
| 294.2 | 5461.667 | 539.2 | 12548.33 | 346.2 | 10396.67 |
| 294 | 5455.834 | 539 | 12749.17 | 346 | 10326.67 |
| 293.8 | 5555.834 | 538.8 | 12809.17 | 345.8 | 10383.33 |
| 293.6 | 5499.167 | 538.6 | 12768.33 | 345.6 | 10433.33 |
| 293.4 | 5419.167 | 538.4 | 12821.67 | 345.4 | 10385.83 |
| 293.2 | 5460 | 538.2 | 12643.33 | 345.2 | 10160 |
| 293 | 5435.834 | 538 | 12650 | 345 | 10346.67 |
| 292.8 | 5495.834 | 537.8 | 12757.5 | 344.8 | 10347.5 |
| 292.6 | 5474.167 | 537.6 | 12733.33 | 344.6 | 10575 |
| 292.4 | 5544.167 | 537.4 | 12663.33 | 344.4 | 10394.17 |
| 292.2 | 5400 | 537.2 | 12901.67 | 344.2 | 10326.67 |
| 292 | 5550.834 | 537 | 12885 | 344 | 10345 |
| 291.8 | 5624.167 | 536.8 | 12658.33 | 343.8 | 10348.33 |
| 291.6 | 5569.167 | 536.6 | 12899.17 | 343.6 | 10432.5 |
| 291.4 | 5635 | 536.4 | 12855.83 | 343.4 | 10626.67 |
| 291.2 | 5758.334 | 536.2 | 13082.5 | 343.2 | 10693.33 |
| 291 | 5729.167 | 536 | 13028.33 | 343 | 10972.5 |
| 290.8 | 5832.5 | 535.8 | 13036.67 | 342.8 | 10962.5 |
| 290.6 | 5755.834 | 535.6 | 12971.67 | 342.6 | 11003.33 |
| 290.4 | 6007.5 | 535.4 | 13192.5 | 342.4 | 11360 |
| 290.2 | 5925 | 535.2 | 13099.17 | 342.2 | 11764.17 |
| 290 | 5967.5 | 535 | 13180 | 342 | 11837.5 |
| 289.8 | 6018.334 | 534.8 | 13340.83 | 341.8 | 12301.67 |
| 289.6 | 5910 | 534.6 | 13540 | 341.6 | 12634.17 |
| 289.4 | 6017.5 | 534.4 | 13690 | 341.4 | 12963.33 |
| 289.2 | 6050 | 534.2 | 13830 | 341.2 | 13519.17 |
| 289 | 5960 | 534 | 13936.67 | 341 | 13634.17 |
| 288.8 | 5937.5 | 533.8 | 14058.33 | 340.8 | 14074.17 |
| 288.6 | 5965.834 | 533.6 | 14499.17 | 340.6 | 14193.33 |
| 288.4 | 5980.834 | 533.4 | 14533.33 | 340.4 | 14605.83 |
| 288.2 | 5956.667 | 533.2 | 15107.5 | 340.2 | 14765 |
| 288 | 5995 | 533 | 15256.67 | 340 | 14956.67 |
| 287.8 | 5999.167 | 532.8 | 15625.83 | 339.8 | 15211.67 |
| 287.6 | 6005 | 532.6 | 15999.17 | 339.6 | 15250 |
| 287.4 | 6066.667 | 532.4 | 16163.33 | 339.4 | 15209.17 |
| 287.2 | 6153.334 | 532.2 | 16899.17 | 339.2 | 15042.5 |
| 287 | 6123.334 | 532 | 17340.83 | 339 | 15020.83 |
| 286.8 | 6163.334 | 531.8 | 17851.67 | 338.8 | 14826.67 |
| 286.6 | 6156.667 | 531.6 | 18189.17 | 338.6 | 14461.67 |
| 286.4 | 6394.167 | 531.4 | 18382.5 | 338.4 | 14232.5 |
| 286.2 | 6494.167 | 531.2 | 18662.5 | 338.2 | 13786.67 |
| 286 | 6639.167 | 531 | 19050.83 | 338 | 13345.83 |
| 285.8 | 6899.167 | 530.8 | 19116.67 | 337.8 | 12935 |
| 285.6 | 7281.667 | 530.6 | 19215.83 | 337.6 | 12510.83 |
| 285.4 | 7675 | 530.4 | 19257.5 | 337.4 | 12282.5 |
| 285.2 | 8194.167 | 530.2 | 19090.83 | 337.2 | 12028.33 |
| 285 | 9004.167 | 530 | 18940 | 337 | 12216.67 |
| 284.8 | 9843.334 | 529.8 | 18528.33 | 336.8 | 12385.83 |
| 284.6 | 10788.33 | 529.6 | 18233.33 | 336.6 | 12352.5 |
| 284.4 | 11883.33 | 529.4 | 17491.67 | 336.4 | 12487.5 |
| 284.2 | 13196.67 | 529.2 | 17153.33 | 336.2 | 13239.17 |
| 284 | 14970 | 529 | 16755.83 | 336 | 13639.17 |
| 283.8 | 16214.17 | 528.8 | 16029.17 | 335.8 | 14240.83 |
| 283.6 | 17755.83 | 528.6 | 15718.33 | 335.6 | 14607.5 |
| 283.4 | 18878.33 | 528.4 | 15034.17 | 335.4 | 15040.83 |
| 283.2 | 20021.67 | 528.2 | 14521.67 | 335.2 | 15348.33 |
| 283 | 21010.83 | 528 | 13875.83 | 335 | 15672.5 |
| 282.8 | 21364.17 | 527.8 | 13731.67 | 334.8 | 16191.67 |
| 282.6 | 21127.5 | 527.6 | 13366.67 | 334.6 | 16464.17 |
| 282.4 | 21227.5 | 527.4 | 12879.17 | 334.4 | 16631.67 |
| 282.2 | 20037.5 | 527.2 | 12729.17 | 334.2 | 16335.83 |
| 282 | 18890.83 | 527 | 12508.33 | 334 | 16343.33 |
| 281.8 | 17190 | 526.8 | 12390 | 333.8 | 16086.67 |
| 281.6 | 15304.17 | 526.6 | 12153.33 | 333.6 | 15685.83 |
| 281.4 | 13625.83 | 526.4 | 11985 | 333.4 | 15363.33 |
| 281.2 | 11865 | 526.2 | 11773.33 | 333.2 | 14594.17 |
| 281 | 9889.167 | 526 | 11640.83 | 333 | 14235 |
| 280.8 | 8352.5 | 525.8 | 11607.5 | 332.8 | 13608.33 |
| 280.6 | 7100 | 525.6 | 11375.83 | 332.6 | 12610 |
| 280.4 | 6002.5 | 525.4 | 11417.5 | 332.4 | 11840 |
| 280.2 | 5343.334 | 525.2 | 11416.67 | 332.2 | 10994.17 |
### Atomic Concentration Table

| C1s   | O1s   | Pd3d  |
|-------|-------|-------|
| 0.314 | 0.733 | 5.637 |
| 58.955| 137.649| 1198.860 |
| 73.84%| 22.35%| 3.80% |

Corrected RSF
Table S3: XRD data for isolated palladium colloids

| # Strongest 3 peaks | 2Theta | d (Å) | I/I1 | FWHM | Intensity (Counts) | Integrated Int (Counts) |
|---------------------|--------|------|------|------|-------------------|------------------------|
| no. peak            | 2Theta | d (Å) | I/I1 | FWHM | Intensity (Counts) | Integrated Int (Counts) |
| 1 26                | 40.0000 | 2.25221 | 100  | 3.44000 | 172 | 21520 |
| 2 25                | 39.0400 | 2.30535 | 76   | 0.00000 | 131 | 0 |
| 3 24                | 37.8800 | 2.37324 | 41   | 1.60000 | 71  | 7997 |

| # Peak Data List | 2Theta | d (Å) | I/I1 | FWHM | Intensity (Counts) | Integrated Int (Counts) |
|------------------|--------|------|------|------|-------------------|------------------------|
| no. peak         | 2Theta | d (Å) | I/I1 | FWHM | Intensity (Counts) | Integrated Int (Counts) |
| 1 4.6333         | 18.24828 | 11   | 0.53330 | 19 | 489 |
| 2 7.2025         | 12.26352 | 8    | 0.27500 | 13 | 225 |
| 3 8.0200         | 11.01521 | 12   | 0.72000 | 21 | 984 |
| 4 9.4200         | 9.34104 | 26   | 1.39000 | 44 | 3039 |
| 5 10.6950        | 8.26537 | 9    | 0.37000 | 15 | 303 |
| 6 11.4850        | 7.69855 | 4    | 0.23000 | 7  | 119 |
| 7 12.4266        | 7.13724 | 3    | 0.17330 | 5  | 60  |
| 8 13.6900        | 6.46313 | 4    | 0.06000 | 7  | 81  |
| 9 14.4200        | 6.05402 | 4    | 0.06000 | 7  | 47  |
| 10 16.4433       | 5.38660 | 6    | 0.27330 | 10 | 225 |
| 11 18.3925       | 4.81990 | 5    | 0.09500 | 8  | 97  |
| 12 19.1200       | 4.63812 | 5    | 0.12000 | 9  | 162 |
| 13 20.3200       | 4.36684 | 5    | 0.20000 | 8  | 258 |
| 14 21.6400       | 4.10336 | 4    | 0.08000 | 7  | 91  |
| 15 22.7300       | 3.90899 | 3    | 0.10000 | 5  | 59  |
| 16 23.3700       | 3.80337 | 6    | 0.18000 | 10 | 161 |
| 17 24.1650       | 3.68001 | 3    | 0.09000 | 6  | 51  |
| 18 25.3433       | 3.51152 | 5    | 0.12670 | 8  | 111 |
| 19 26.1000       | 3.41141 | 4    | 0.16000 | 7  | 90  |
| 20 27.6663       | 3.22130 | 3    | 0.06330 | 5  | 36  |
| 21 33.8800       | 2.64372 | 4    | 0.12000 | 7  | 116 |
| 22 35.8500       | 2.50283 | 11   | 0.46000 | 13 | 520 |
| 23 36.8400       | 2.43781 | 23   | 0.92000 | 40 | 1554 |
| 24 37.8800       | 2.37324 | 41   | 1.60000 | 71 | 7997 |
| 25 39.8400       | 2.30525 | 76   | 0.00000 | 131 | 0 |
| 26 40.0000       | 2.25221 | 100  | 3.44000 | 172 | 21520 |
| 27 42.8200       | 2.11018 | 12   | 0.40000 | 21 | 701 |
| 28 45.4050       | 1.99587 | 4    | 0.11000 | 7  | 107 |
| 29 47.2350       | 1.92723 | 3    | 0.15000 | 5  | 57  |
| 30 51.1900       | 1.78307 | 3    | 0.10000 | 5  | 38  |
| 31 52.4500       | 1.74317 | 3    | 0.06000 | 5  | 48  |
| 32 53.6950       | 1.70565 | 5    | 0.21000 | 8  | 109 |
| 33 54.8600       | 1.67215 | 4    | 0.32000 | 7  | 187 |
| 34 55.5300       | 1.65355 | 6    | 0.30000 | 10 | 192 |
| 35 56.4200       | 1.62956 | 5    | 0.28000 | 8  | 216 |
| 36 57.7666       | 1.59625 | 3    | 0.09330 | 5  | 43  |
| 37 58.6150       | 1.57366 | 3    | 0.17000 | 5  | 74  |
| 38 59.2700       | 1.55782 | 4    | 0.14000 | 7  | 69  |
| 39 62.4800       | 1.48028 | 4    | 0.12000 | 7  | 78  |
| 40 63.0500       | 1.47321 | 3    | 0.06000 | 5  | 34  |
| 41 64.3600       | 1.44675 | 4    | 0.09330 | 5  | 32  |
| 42 65.5900       | 1.42218 | 4    | 0.18000 | 7  | 134 |
| 43 67.4566       | 1.38729 | 3    | 0.24670 | 6  | 149 |
| 44 69.1700       | 1.35705 | 3    | 0.22000 | 6  | 110 |
| 45 69.3500       | 1.35397 | 3    | 0.14000 | 6  | 75  |
| 46 69.9200       | 1.34432 | 3    | 0.08000 | 5  | 47  |
| 47 70.5900       | 1.33319 | 4    | 0.22000 | 7  | 106 |
| 48 71.2000       | 1.32526 | 3    | 0.24000 | 6  | 85  |
| 49 72.1050       | 1.30886 | 3    | 0.21000 | 6  | 84  |
| 50 74.1550       | 1.27767 | 4    | 0.31000 | 7  | 137 |
| 51 75.0000       | 1.26536 | 3    | 0.12000 | 5  | 58  |
| 52 75.6300       | 1.23556 | 3    | 0.09000 | 5  | 31  |
| 53 76.9050       | 1.23869 | 5    | 0.21000 | 9  | 139 |
| 54 77.6000       | 1.22933 | 4    | 0.20000 | 7  | 125 |
Figure S37: TEM for Pd colloids at 100 °C
Figure S38: TEM for Pd colloids using Cs$_2$CO$_3$ as the base
Figure S39: TEM analysis of reaction using Na$_2$CO$_3$ as the base
The X-ray absorption experiments were performed at the beam line BL-14B2 of SPring8, Japan. The samples for Extended X-ray Absorption Fine Structure (EXAFS) experiments were prepared by mixing BN with sample of interest and then homogenizing it in a mortar by a pestle. The samples were packed very tightly in an aluminum cell of 10 mm diameter, taking care that no air is trapped. The sample was secured in the cell by applying scotch tape on both sides of the cell. The ratio of sample to BN was chosen in such a way that the theoretical absorption jump (as calculated by software supplied by SPring-8) was about 1 unit at Pd K-edge. Spectrometric data were collected in the range of 24033 – 25346 eV in the absorption mode using a fixed-exit double crystal Si (311) monochromator. The samples were irradiated with an X-ray beam with a cross-section area of aa X bb mm (width X height) and the intensity of transmitted x-ray were monitored by ionizing chambers that were filled with Ar gas at XX mbar (composition of gas). The energy calibration at the Pd-K edge was monitored by using a Pd foil as a reference material, and measured before and after the samples were done. Athena (Demeter) software was used for processing the raw data obtained above, which implement the FEFF6 and IFEFFIT codes. The AUTOBK method was used to isolate the k-space EXAFS data from the raw data. The energy calibration was done using reference Pd-foil collected simultaneously.

The fitting was performed using Artemis software of Demeter 0.9.22, copyrights Bruce Ravel. The data were fit from 2.1 to 3.0 Å in R-space and 3.0 to 13.0 Å⁻¹ in k weighing, with multiple k weighing. The path degeneracy (N), energy correction (∆E₀), adjustment in half path length (∆R) and mean square displacement (σ²), were used as variable parameters for fitting. For calibration purpose, energy of Pd-foil was used as reference.

For fitting purposes, Pd metal and Pd(OAc)₂ were used as theory. By fitting Pd-foil, the amplitude reduction factor calculated was 0.84 units, which was kept constant during the fitting. The SO² value was defined as amp*N where amp is set at 0.84 and N was kept variable (guess) for fitting. The rest of the values such as ∆E₀, ∆R and σ² were also kept variable (guess).

![FT magnitude vs Radial distance](image1)

(a) FT in R-space b) k-space, of best fit and sample of Pd nanoparticles

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