

## **Synergistic effect of cobalt in a Pd/Co catalyzed Suzuki-Miyaura cross-coupling in water**

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# Electronic Supporting Information

## Experimental Section

### General procedure for synthesis of $\text{CoPd}_2(\text{HBPDC})_2\text{Cl}_4 \cdot (\text{H}_2\text{O})_4$ (**1**) and $\text{Pd}(\text{H}_2\text{BPDC})\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**2**)

#### Synthesis of $\text{Pd}_2\text{Co}(\text{HBPDC})_2\text{Cl}_4 \cdot (\text{H}_2\text{O})_4$ (**1**)

A mixture containing  $\text{K}_2\text{PdCl}_4$  (0.2 mmol),  $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 mmol),  $\text{H}_2\text{BPDC}$  (0.2 mmol), water (8 mL) and  $0.01 \text{ mol} \cdot \text{L}^{-1}$  NaOH (1 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at  $95 \text{ }^\circ\text{C}$  for 96 hr and then cooled to room temperature. Yellow thin sheet crystals of **1** were obtained and picked out, washed with distilled water and dried in air (Yield: 40.6% based on Pd). Elemental analysis Calcd (%) for  $\text{C}_{24}\text{H}_{22}\text{Cl}_4\text{N}_4\text{O}_{12}\text{Pd}_2\text{Co}$  (**1**): C 30.63; H 2.34; N 5.95. Found: C 31.01; H 2.51; N 6.23. IR (KBr,  $\text{cm}^{-1}$ ): 3448w, 1719m, 1638s, 1550s, 1356s, 1258w, 1235w, 767m.

#### Synthesis of $\text{Pd}(\text{H}_2\text{BPDC})\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**2**)

A mixture of  $\text{K}_2\text{PdCl}_4$  (0.2 mmol),  $\text{H}_2\text{BPDC}$  (0.2 mmol) and water (10 mL) was stirred for 20 min in the air, transferred to a 23 mL Teflon reactor and kept at  $120 \text{ }^\circ\text{C}$  for 20 hr under autogenous pressure, then cooled to room temperature at a rate of  $10 \text{ }^\circ\text{C h}^{-1}$ . Yellow crystals of **2** were obtained in 32% yield based on Pd. Elemental analysis Calcd (%) for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_5\text{Pd}$ : C, 32.73; H, 2.31; N, 6.33%. Found: C, 32.79; H, 2.29; N, 6.37%. IR (KBr) ( $\text{cm}^{-1}$ ): 3628(s), 3392(s), 3199(s), 3076(s), 1729(s), 1696(s), 1558(m), 1410(s), 1373(m), 1272(m), 1237(m), 1208(s), 1141(m), 1068(w), 930(w), 817(m), 765(m), 749(w), 662(m), 536(m).<sup>1</sup>

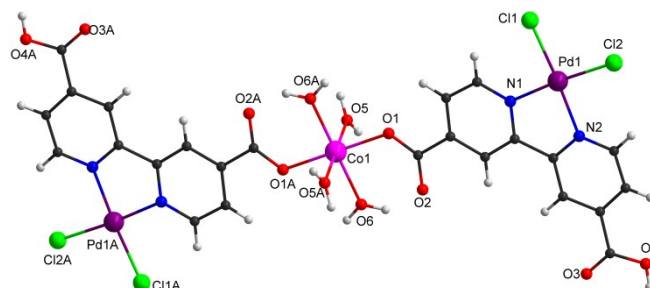
### General procedure for the Suzuki-Miyaura coupling reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), base (2.0 mmol),  $\text{H}_2\text{O}$  (6 mL), and Co/Pd catalyst was stirred and heated in air for the desired time, at the selected reaction temperature (Table 1). At the end of the reaction, the mixture was extracted with ethyl acetate (20 mL), washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The product was further purified by column chromatography on silica gel and identified by gas chromatography-mass spectroscopy (GC-MS) and  $^1\text{H}$  NMR spectra. Yields, calculated from GC, were based on the amount of aryl halide employed.

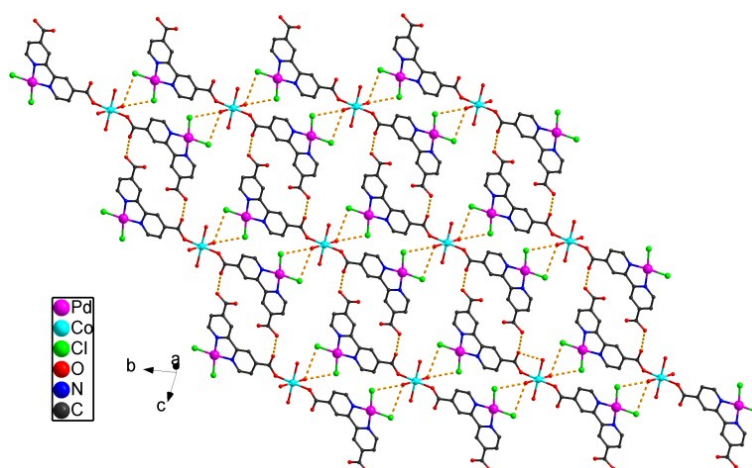
### Physical measurements

The elemental analyses (C, H, and N) were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR

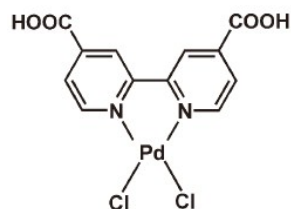
spectra were recorded on a Nicolet IR-470 spectrometer using KBr pellets. Crystallographic data was obtained on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation (0.71073 Å) at 293 K in the  $\omega$ - $2\theta$  scan mode. Powder X-ray diffraction (PXRD) patterns of the samples were recorded using an X-ray diffractometer (BRUKER D8 ADVANCE) with Cu  $K\alpha$  radiation. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument applying a heating rate of 10 °C min<sup>-1</sup>.



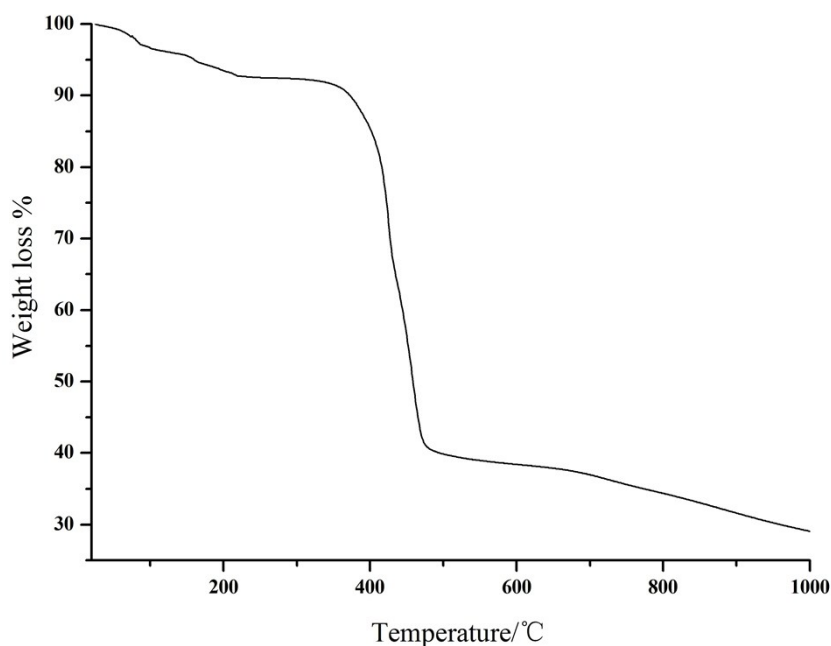
**Fig. S1** View of the coordination environments of Pd(II) and Co(II) ions in complex **1**. Symmetry codes: A 1-x, -y, 2-z



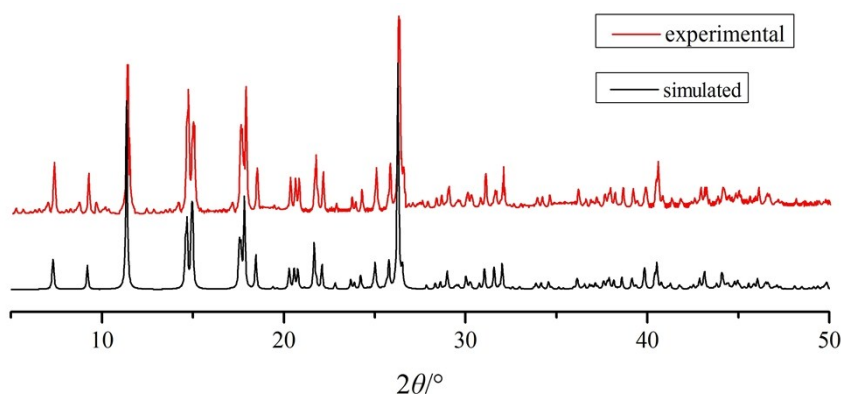
**Fig. S2** Two-dimensional layer formed by H-bond interactions of complex **1**.



**Fig. S3** Structure of Pd(H<sub>2</sub>BPDC)Cl<sub>2</sub>·H<sub>2</sub>O (**2**)



**Fig. S4** TGA curves of complex **1**



**Fig. S5** The simulated and experimental PXRD patterns of complex **1**

### TG analysis and PXRD

Thermogravimetric (TG) analysis was performed, in a nitrogen atmosphere, on polycrystalline sample of **1**. As shown in Fig. S4, the first weight loss of **1** occurring from 25 °C to 235°C is about 7.45%, corresponding to the loss of the coordinated water molecules (calcd: 7.40%). The catalyst is stable up to 300 °C and decomposes above this temperature. Powder X-ray diffraction (PXRD) analysis of **1** was performed at room temperature (Fig. S5). The pattern for **1** is in good agreement with the calculated ones obtained from the single-crystal structures, indicating that the single-crystal structure is really representative for the main constituent of the corresponding sample.

### Single crystal X-ray crystallographic study

The collection of single crystal crystallographic data was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation (0.71073 Å) at 293 K in the  $\omega$ - $2\theta$  scan mode. An

empirical absorption correction was applied to the data using the SADABS program.<sup>2</sup> The structures were solved by direct methods and refined by full matrix least-squares methods on  $F^2$  using the SHELXTL crystallographic software package.<sup>3,4</sup> All non-H atoms were refined anisotropically. The H atoms were placed in calculated positions and refined using a riding mode. The crystallographic data, selected bond lengths and angles for **1** are listed in Table S1 and Table S2, respectively. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC: 1516139.

**Table S1** Crystal Data and Structure Refinement for **1**.

|                                  |                                   |
|----------------------------------|-----------------------------------|
| formula                          | $C_{24}H_{22}Cl_4N_4O_{12}Pd_2Co$ |
| fw                               | 971.99                            |
| temp/K                           | 293 (2)                           |
| cryst syst                       | Triclinic                         |
| space group                      | $P-1$                             |
| $a/\text{\AA}$                   | 5.3010(11)                        |
| $b/\text{\AA}$                   | 12.470(3)                         |
| $c/\text{\AA}$                   | 12.610(3)                         |
| $\alpha/^\circ$                  | 76.80(3)                          |
| $\beta/^\circ$                   | 79.55(3)                          |
| $\gamma/^\circ$                  | 81.30(3)                          |
| $V/\text{\AA}^3$                 | 792.8(3)                          |
| Z                                | 1                                 |
| $D_c/\text{mg cm}^{-3}$          | 2.036                             |
| $F(000)$                         | 477                               |
| $\vartheta$ range / $^\circ$     | 3.36 - 27.57                      |
| Reflns collected/unique          | 8006 / 3591                       |
| $R_{\text{int}}$                 | 0.0696                            |
| data/restraints/params           | 3591 / 0 / 214                    |
| GOF on $F^2$                     | 1.067                             |
| $R_1, wR_2$ ( $I > 2\sigma(I)$ ) | 0.0753, 0.1825                    |
| $R_1, wR_2$ (all data)           | 0.1136, 0.2171                    |

**Table S2** Bond lengths [ $\text{\AA}$ ] and angles [deg] for compounds **1**.

|                   |           |                     |            |
|-------------------|-----------|---------------------|------------|
| Pd(1)-N(1)        | 2.039(7)  | Pd(1)-N(2)          | 2.055(7)   |
| Pd(1)-Cl(1)       | 2.299(3)  | Pd(1)-Cl(2)         | 2.302(3)   |
| Co(1)-O(5)        | 2.057(6)  | Co(1)-O(5)#1        | 2.057(6)   |
| Co(1)-O(1)        | 2.092(5)  | Co(1)-O(1)#1        | 2.092(5)   |
| Co(1)-O(6)        | 2.144(6)  | Co(1)-O(6)#1        | 2.144(6)   |
| N(1)-Pd(1)-Cl(1)  | 94.10(2)  | N(2)-Pd(1)-Cl(1)    | 175.53(18) |
| N(1)-Pd(1)-Cl(2)  | 175.60(2) | N(2)-Pd(1)-Cl(2)    | 94.00(19)  |
| Cl(1)-Pd(1)-Cl(2) | 90.35(10) | O(5)-Co(1)-O(5)#1   | 180.00(1)  |
| N1-Pd1-N2         | 81.60(3)  | O(5)#1-Co(1)-O(1)#1 | 92.80(3)   |
| O(5)-Co(1)-O(1)   | 92.80(3)  | O(5)#1-Co(1)-O(1)   | 87.20(3)   |
| O(1)#1-Co(1)-O(1) | 180.00(2) | O(5)-Co(1)-O(6)     | 91.90(3)   |

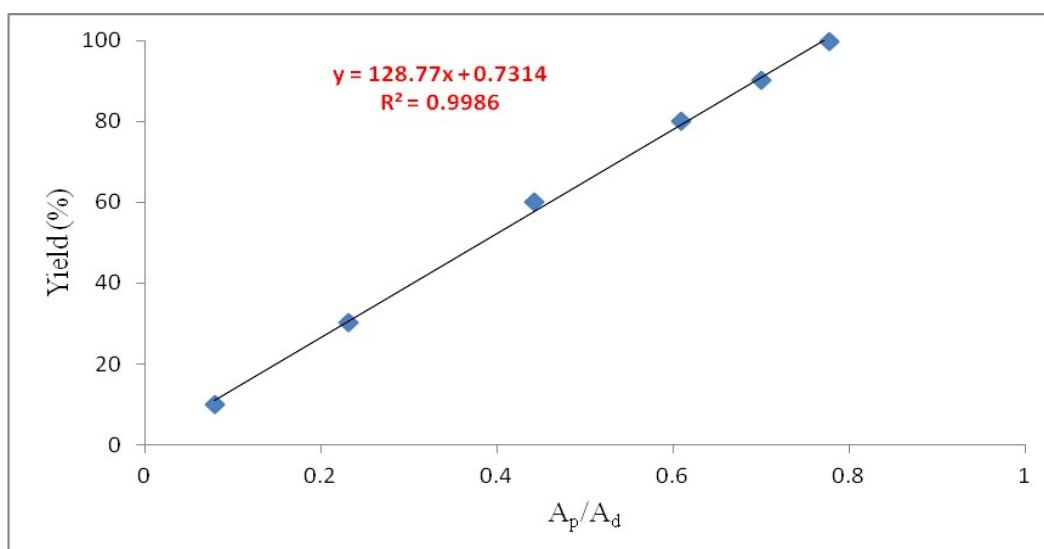
|                     |          |                     |           |
|---------------------|----------|---------------------|-----------|
| O(5)#1-Co(1)-O(6)   | 88.10(3) | O(1)#1-Co(1)-O(6)   | 86.50(2)  |
| O(1)-Co(1)-O(6)     | 93.50(2) | O(5)-Co(1)-O(6)#1   | 88.10(3)  |
| O(5)#1-Co(1)-O(6)#1 | 91.90(3) | O(1)#1-Co(1)-O(6)#1 | 93.50(2)  |
| O(1)-Co(1)-O(6)#1   | 86.50(2) | O(6)-Co(1)-O(6)#1   | 180.00(1) |
| O(5)-Co(1)-O(1)#1   | 87.20(3) |                     |           |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2

### GC-yield standard curve

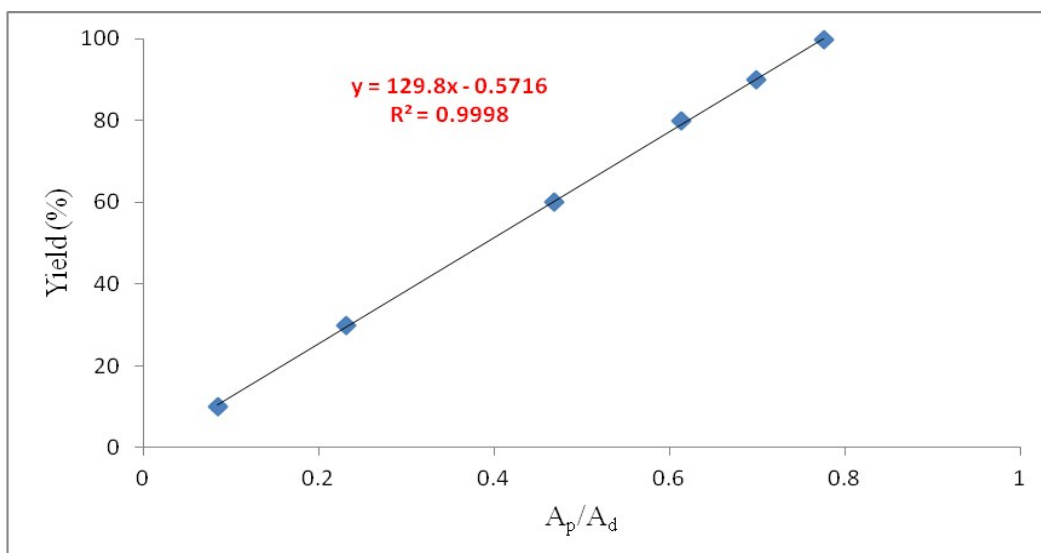
The response peak area ratios of product of biphenyl, 4-phenyltoluene, or 4-phenylacetophenone and internal standard *n*-hexadecane ( $A_p/A_d$ ) were obtained from Agilent 7890A GC spectrometer. All the GC-yields were calculated by the formula of curve fitting.

GC-yield standard curve of biphenyl:



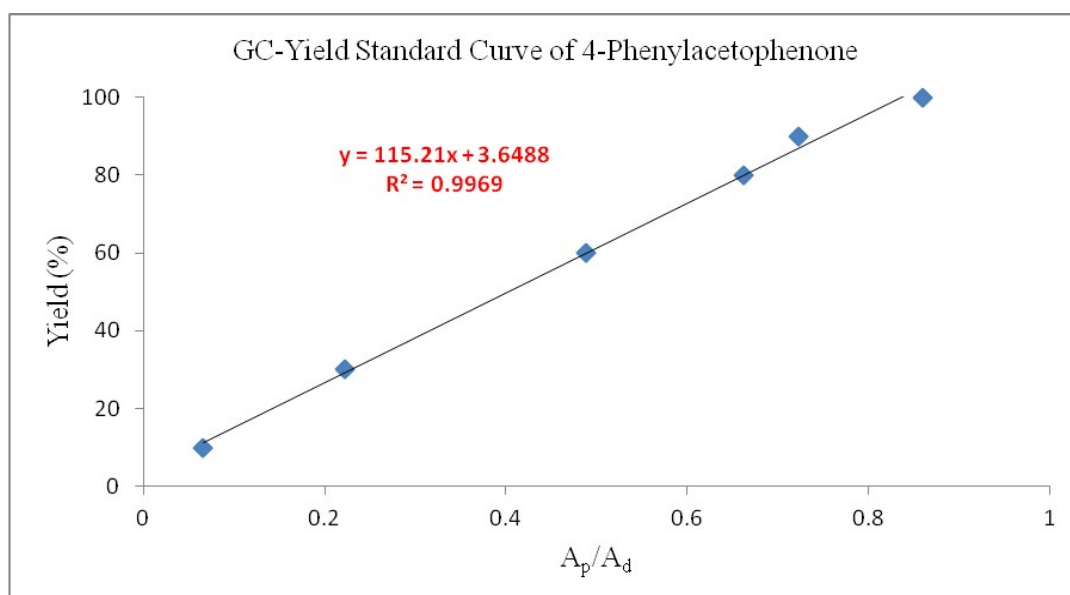
|           |        |        |        |        |        |        |
|-----------|--------|--------|--------|--------|--------|--------|
| $A_p/A_d$ | 0.0798 | 0.2310 | 0.4421 | 0.6101 | 0.7005 | 0.7777 |
| Yield (%) | 10.05  | 30.15  | 59.98  | 80.08  | 90.14  | 99.86  |

GC-yield standard curve of 4-phenyltoluene:

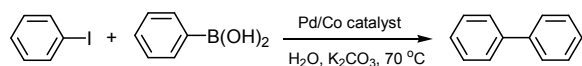


|           |        |        |        |        |        |        |
|-----------|--------|--------|--------|--------|--------|--------|
| $A_p/A_d$ | 0.0854 | 0.2323 | 0.4689 | 0.6136 | 0.6998 | 0.7771 |
| Yield (%) | 10.10  | 30.02  | 60.03  | 79.95  | 90.06  | 99.86  |

GC-yield standard curve of 4-phenylacetophenone:

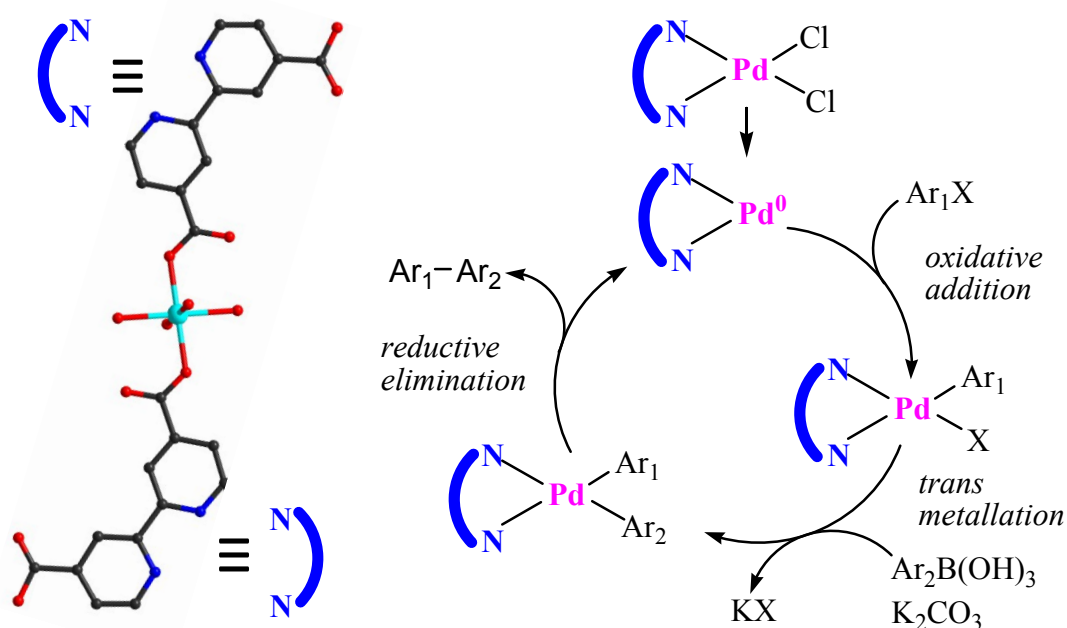


|           |        |        |        |        |        |        |
|-----------|--------|--------|--------|--------|--------|--------|
| $A_p/A_d$ | 0.0661 | 0.2220 | 0.4878 | 0.6625 | 0.7229 | 0.8596 |
| Yield (%) | 9.94   | 30.06  | 60.13  | 80.00  | 89.94  | 99.87  |

**Table S3** Effect of Co/Pd catalyst loading and reaction time on TON and TOF.<sup>a</sup>

| Entry | Co/Pd catalyst (mol% Pd) | Time/h | Yield <sup>b</sup> (%) | TON <sup>a,c</sup>   | TOF/h <sup>-1a,d</sup> |
|-------|--------------------------|--------|------------------------|----------------------|------------------------|
| 1     | 1×10 <sup>-3</sup>       | 5      | 95                     | 9.50×10 <sup>4</sup> | 1.90×10 <sup>4</sup>   |
| 2     | 1×10 <sup>-3</sup>       | 3      | 67                     | 6.70×10 <sup>4</sup> | 2.23×10 <sup>4</sup>   |
| 3     | 1.5×10 <sup>-3</sup>     | 5      | 97                     | 6.47×10 <sup>4</sup> | 1.29×10 <sup>4</sup>   |
| 4     | 5×10 <sup>-4</sup>       | 5      | 62                     | 1.24×10 <sup>5</sup> | 2.48×10 <sup>4</sup>   |

<sup>a</sup> TON (= turnover number) and TOF (= turnover frequency) were determined for substrate (aryl halide) to catalyst (Pd) molar ratio 10<sup>5</sup>. <sup>b</sup> Yields were determined by GC and GC–MS analysis. <sup>c</sup> TON (mol product per mol Pd). <sup>d</sup> TOF (TON per hour)

**Scheme S1** Proposed reaction mechanism of Suzuki-Miyaura cross-coupling catalyzed by Pd/Co catalyst

<sup>1</sup>H NMR data for the products of the C–C coupling reactions

Biphenyl: <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  = 7.35 (t, 2H), 7.45(t, 4H), 7.64 (d, 4H)

4-Aceyl-1,1'-biphenyl: <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  = 2.60 (s, 3H), 7.42 (t, 2H), 7.50 (t, 2H), 7.73 (d, 2H), 7.82 (d, 2H), 8.03(d, 2H)

4-Methyl-1,1'-biphenyl: <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  = 2.33 (s, 3H), 7.26 (d, 2H), 7.32 (t, 1H), 7.43 (t, 2H), 7.53 (d, 2H), 7.61 (d, 2H).

## References

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