Supporting Information for

A Self-Assembled Pd_6L_8 Nanoball for Suzuki-Miyaura Coupling Reactions in both Homogeneous and Heterogeneous Formats

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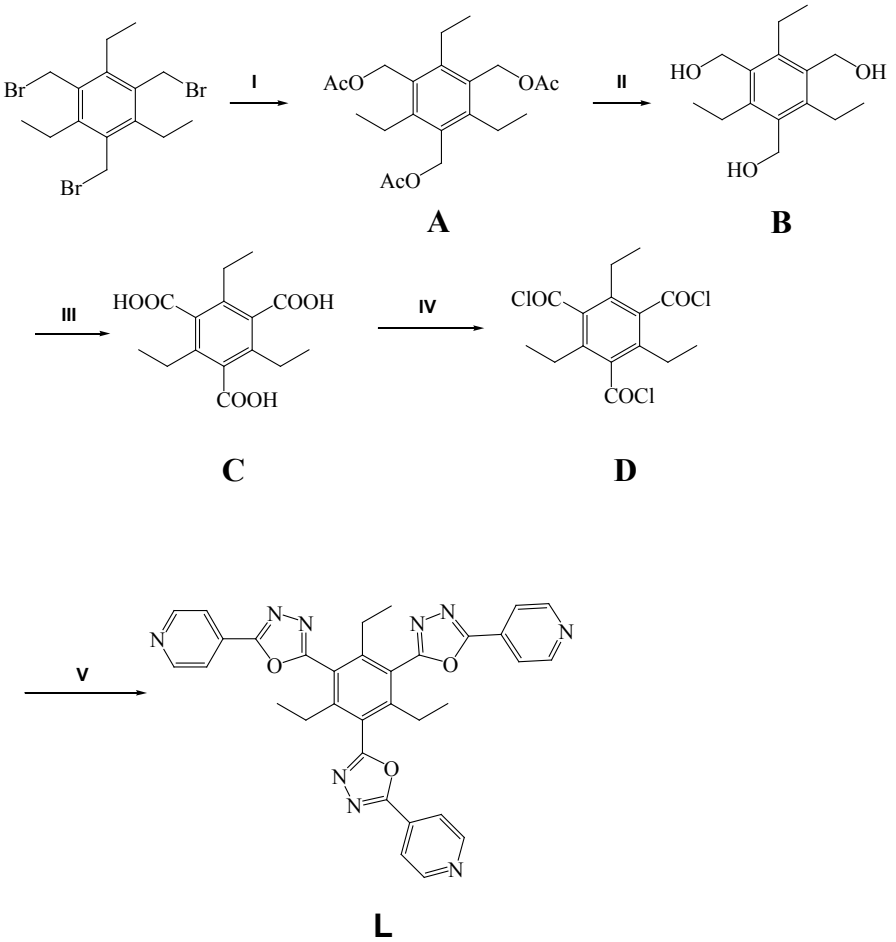
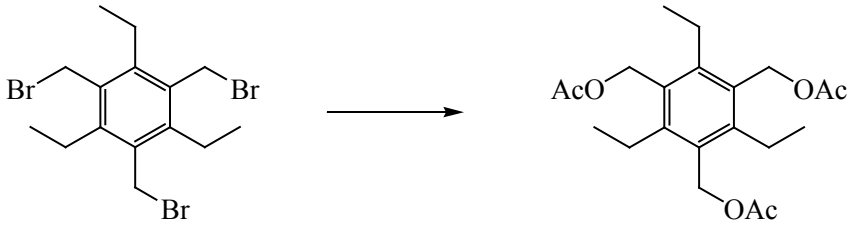
Materials and Methods. All chemical reagents were purchased without further purification. Infrared spectroscopy (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000-400 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^1H NMR data were collected using a AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Element analyses were performed on a Perkin-Elmer Model 240C analyzer. CSI-MS was performed on a JMS T100CS. DOSY-NMR was performed on a Bruker AVANCE 600. TEM image was obtained on a JEM-1011. TLC analysis was performed on Merck silica gel 60 F254. Column chromatography was carried out on silica gel (Wakogel C-200).

Synthesis of L and Its Single-Crystal Structure

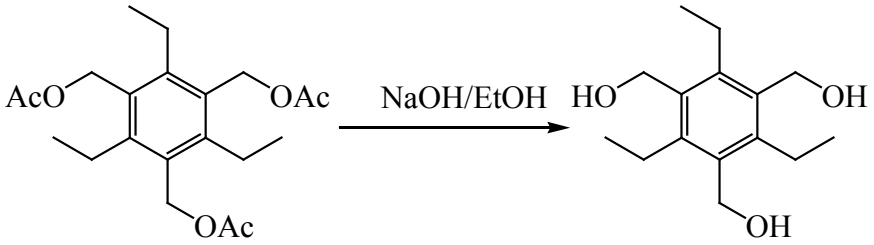


Scheme 1. Synthesis of **L**. I. NaOAc, acetic acid, 120°C, 12 h (90%), II. NaOH, EtOH, reflux, 5 h (93%), III. CrO_3, H_2SO_4, acetone, r. t., 2 h (81%), IV. $SOCl_2$, reflux (100%), V. 5-(4-pyridyl)-1H-tetrazole, pyridine, 120°C, 2 h (56%).



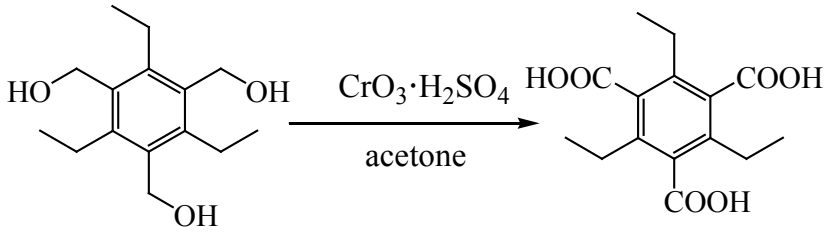
A

A mixture of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (11.88 g, 4.26 mmol), NaOAc (2g, 28.6 mmol) and HOAc (40 mL) was heated to 120°C for 12 h. The reaction was cooled to room temperature. After addition of water (100 mL), the white solid was filtered off, washed with water and dried in air to give 1.45 g (90 %) of **A** as white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 5.36 (s, 6H, CH_2), 2.55 (q, J = 7.7 Hz, 6H, C_2H_5), 2.03 (s, 9H, CH_3), 1.21 (t, J = 7.7 Hz, 9H, C_2H_5). IR (KBr pellet) [(cm^{-1})]: 2967(m), 2931(m), 2874(w), 1730(s), 1571(w), 1375(m), 1222(s), 1101(w), 1020(m), 949(m), 918(m), 766(w), 604(w). Anal. Calcd for $C_{21}H_{30}O_6$: C, 66.64; H, 7.99. Found: C, 66.67; H, 5.32.



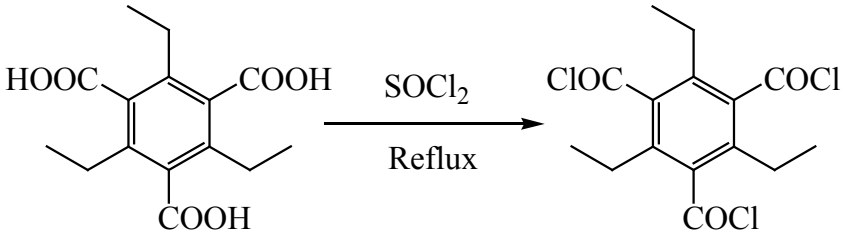
A **B**

A (22.30 g, 6.1 mmol) and NaOH (1g, 24.4 mmol) were dissolved in EtOH (20 mL). The mixture was refluxed for 5 h. The reaction was cooled to room temperature. After addition of water (20 mL), the yellow solid was filtered off, washed with water and dried in air to give **B** in 93 % yield. ^{1}H NMR (300 MHz, DMSO, 25°C, TMS): 4.70 (s, 3H, OH), 4.49 (s, 6H, CH_2), 2.80 (m, 6H, C_2H_5), 1.13 (t, J = 6.7 Hz, 9H, C_2H_5). IR (KBr pellet) [(cm^{-1})]: 3219(s), 2965(s), 2872(m), 1654(w), 1572(w), 1457(m), 1377(m), 1226(w), 1094(m), 990(s), 968(s), 771(m). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.41; H, 9.56.



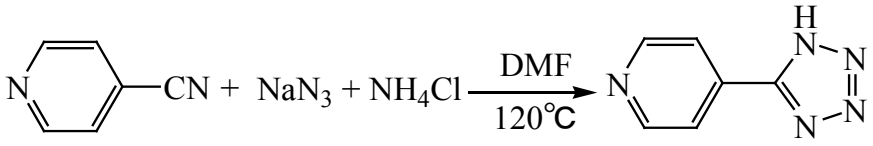
B **C**

CrO_3/H_2SO_4 (CrO_3, (7.7 g, 77 mmol) and H_2SO_4 (7.7 mL)) was added to a mixture of **B** (32.2 g, 8.73 mmol) and actone (40 mL) at 4°C within 30 min. The mixture was stirred for 2 h at room temperature. The reaction mixture was poured onto 80 mL of ice water and extracted with ether (50 mL X 3). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated on the rotovap to afford a colorless crystalline solid of **C**. Yield 2.1g (81 %). ^{1}H NMR (300 MHz, DMSO, 25°C, TMS): 13.37 (s, 3H, COOH), 2.57 (q, J = 7.5 Hz, 6H, C_2H_5), 1.11 (t, J = 7.5 Hz, 9H, C_2H_5). IR (KBr pellet) [(cm^{-1})]: 3354(m), 2979(m), 2636(m), 1715(s), 1573(m), 1475(w), 1264(m), 1147(m), 1069(w), 930(w), 678(w). Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.19; H, 6.20.



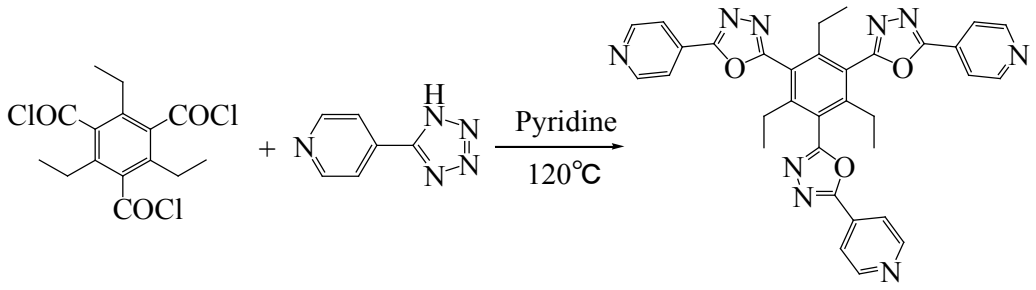
C **D**

A mixture of **C** (42.94 g, 10 mmol) and $SOCl_2$ (20 mL) was refluxed to generate yellow solid (**D**) which was stored in dried flask.



A mixture of 4-cyanopyridine (10.41 g, 100 mmol), NaN_3 (7.15 g, 110 mmol) and NH_4Cl (5.89 g, 110 mmol) in 100 mL of DMF was heated to 120°C for two days. The reaction mixture was cooled to room temperature, and removed the solvent under vacuum. After

addition of 100 mL of water, the pH value was adjusted at 5 by the addition of HCl. The white solids were filtered off to yield 12.5 g of 5-(4-pyridyl)-1H-tetrazole[1]. Yield 12.5 g, 86 %.



D **L**

A mixture of **D** (9.0 mmol), 5-(4-pyridyl)-1H-tetrazole (4.41 g, 30 mmol), pyridine (10 mL) was heated to 120°C for 2 h. The reaction mixture was cooled to room temperature, and 100 mL of water was added. The filtered solid was purified on a purified by column chromatrography on silica gel using EtOAc as an eluent. After purification a light yellow solid of **L** was obtained. Yield 3.4 g, 56%. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.88 (d, J = 7.9 Hz, 6H, C_5NH_4), 7.97 (d, J = 7.9 Hz, 6H, C_5NH_4), 2.45 (q, J = 7.4 Hz, 6H, C_2H_5), 1.15 (t, J = 7.4 Hz, 9H, C_2H_5). IR (KBr pellet) [(cm^{-1})]: 3044(w), 2978(m), 2880(w), 1723(w), 1609(s), 1572(s), 1474(m), 1413(s), 1215(m), 1099(s), 965(m), 875(s), 800(w), 695(s), 517(w). Anal. Calcd for $C_{33}H_{27}O_3N_9$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.35; H, 4.53; N, 21.13.

The target ligand **L** was synthesized as above in an overall 38% yield. In addition, the ligand **L** has been characterized by the single-crystal X-ray diffraction analysis. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[2] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[2] None of the crystals showed evidence of crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique. The crystal data and structure refinement for **L** is listed in Table S1. From the crystal structure, the three oxadiazole arms and three ethyl groups of **L**

adopt a cis-configuration respectively, but the three ethyl groups point to the same and inverse directions vs three 4-(pyridyl)oxadiazole arms with a 1 : 1 ratio, as shown in Figure S1.

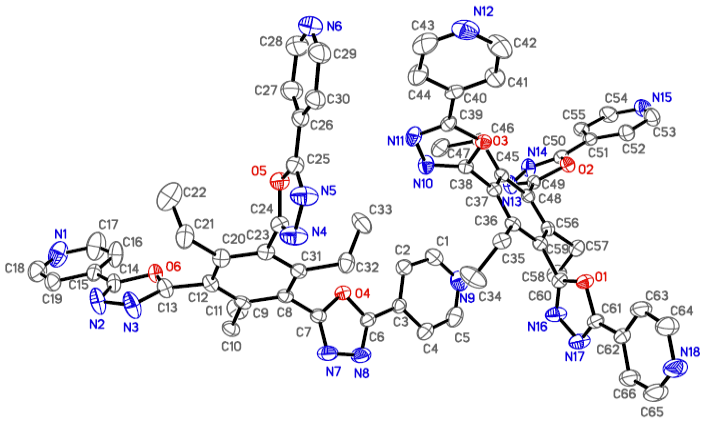


Fig. S1 The crystal structure of **L**. (H atoms have been omitted for clarity)

Table S1. Crystal data and structure refinement for **L.**

Identification code	**L**
Empirical formula	C33 H27 N9 O3
Formula weight	597.64
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 16.032(4) Å alpha = 90 deg. b = 11.544(3) Å beta = 90.772(4) deg. c = 32.695(7) Å gamma = 90 deg.
Volume	6051(2) A^3
Z, Calculated density	8, 1.312 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	2496
Crystal size	0.30 x 0.16 x 0.15 mm
Theta range for data collection	1.25 to 25.60 deg.
Limiting indices	-17<=h<=19, -13<=k<=14, -39<=l<=39
Reflections collected / unique	31454 / 11327 [R(int) = 0.0532]
Completeness to theta = 25.60	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11327 / 1 / 817
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1361
R indices (all data)	R1 = 0.1221, wR2 = 0.1631
Largest diff. peak and hole	0.527 and -0.212 $e.A^{-3}$

Synthesis and Characterization of $Pd_6L_8(NO_3)_{12}$ (1)

A mixture of **L** (79.6 mg, 10 mmol) and palladium nitrate (23.0 mg, 10 mmol) was dissolved in DMSO (4 mL). This mixture was heated to 70℃ for 2 h. After cooled to room temperature, dichloromethane (4 mL) and diethyl ether (20 mL) were added to the reaction system. The resulting precipitate was collected by centrifugation as white powder. Yield 97.5 mg, 98 %. ^{1}H NMR (300 MHz, DMSO, 25°C, TMS): 9.65 (d, J = 5.1 Hz, 48H, C_5NH_4), 8.36 (d, J = 5.6 Hz, 48H, C_5NH_4), 2.13 (48H, C_2H_5), 0.81 (t, J = 7.2 Hz, 72H, C_2H_5). IR (KBr pellet) [(cm^{-1})]: 2979(m), 1624(m), 1541(m), 1482(m), 1384(s), 1219(w), 1101(w), 1058(m), 966(w), 836(m), 709(w), 531(w). Anal. Calcd for $Pd_6C_{264}H_{216}O_{60}N_{84}$: Pd, 10.36; C, 51.44; H, 3.53; N, 19.09. Found: Pd, 10.39; C, 51.45; H, 3.50; N, 19.11.

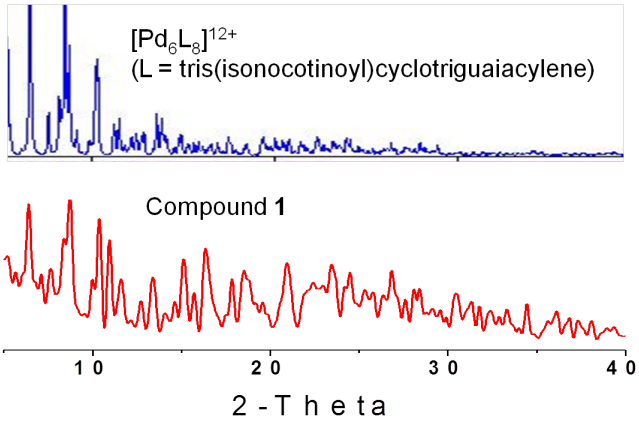
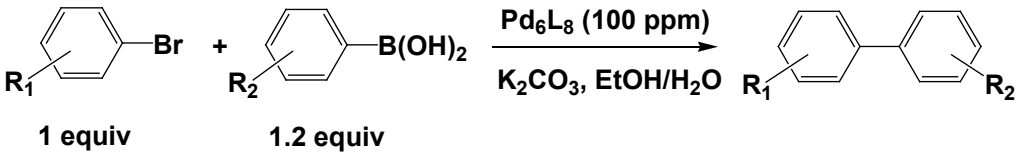


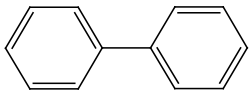
Fig. S2 The XRPD pattern of **1** is almost identical to that of $[Pd_6L_8]^{12+}$ obtained from a similar C_3-symmetric tripod tris(isonocotinoyl)cyclotriguaiacylene, which could be additional evidence for the formation of Pd_6L_8 nanoball. Blue: simulated XRPD pattern based on Pd_6L_8 (L = tris(isonocotinoyl)cyclotriguaiacylene). Red: measured XRPD pattern based on **1**. We hypothesize that the the slight peak shifts are caused by a different rotational disorder of the attached substituted groups on ligand.[3]

Experimental Procedure for Suzuki-Miyaura Cross-Coupling Catalyzed by 1

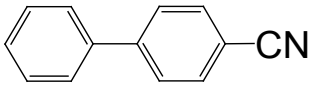
1. Cross-coupling homogeneously catalyzed by **1** (60°C, 100 ppm) in H_2O/EtOH in air



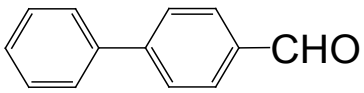
A mixture of ArBr (10 mmol), $ArB(OH)_2$ (12 mmol), K_2CO_3 (10 mmol) were dissolved in a mixed-solvent system of H_2O/EtOH (10 mL, 1:1). After addition of **1** (1 mg, 100 ppm), the reaction mixture was heated to 60°C for 1 or 10 h. After addition of water (5 mL), the mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with water, dried over Mg_2SO_4, and purified by column chromatography on silica gel to afford the corresponding coupling products as crystalline solids.



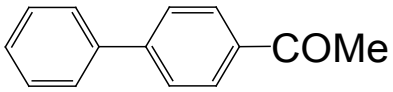
Product **1**[4]: White solid. Eluent: hexane/dichloromethane = 10/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS) 7.59 (d, J = 7.2 Hz, 4H, C_6H_5), 7.44 (t, J = 7.4 Hz, 4H, C_6H_5), 7.34 (t, J = 7.3 Hz, 2H,). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 140.67, 129.36, 128.08, 127.13. Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54; Found: C, 93.47; H, 6.54. MS-EI, m/z 154 (M^+).



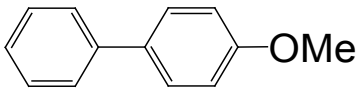
Product **2**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.73 (d, J = 8.2 Hz, 2H, C_6H_4), 7.68 (d, J = 8.5 Hz, 2H, C_6H_4), 7.59 (d, J = 7.8 Hz, 2H, C_6H_5), 7.48 - 7.51 (m, 2H, C_6H_5), 7.42-7.48 (m, 1H, C_6H_5). ^{13}C NMR (151 MHz, $CDCl_3$, 25°C, TMS): 145.63, 139.14, 132.58, 129.14, 128.70, 127.71, 127.22, 118.93, 110.94. Anal. Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82; Found: C, 87.12; H, 5.05; N, 7.82. MS-EI, m/z 179 (M^+).



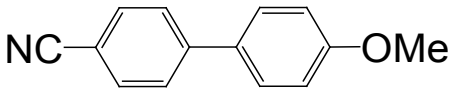
Product **3**[6]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 10.06 (s, 1H, CHO), 7.96 (d, *J* = 8.3 Hz, 2H, C_6H_4), 7.76 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.63-7.65 (m, 2H, C_6H_5), 7.46-7.51 (m, 2H, C_6H_5), 7.39-7.44 (m, 1H, C_6H_5). ^{13}C NMR (151 MHz, $CDCl_3$, 25°C, TMS): 191.80, 147.09, 139.68, 135.27, 130.24, 129.01, 128.48, 127.66, 127.36. Anal. Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53; Found: C, 85.71; H, 5.52. MS-EI, m/z 182 (M^+).



Product **4**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.03 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.70 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.63 (d, *J* = 7.4 Hz, 2H, C_6H_5), 7.45-7.50 (t, *J* = 7.4 Hz, 2H, C_6H_5), 7.37-7.42 (m, 1H, C_6H_5), 2.64 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 197.65, 145.75, 135.90, 132.68, 128.95, 128.90, 128.23, 127.26, 127.20, 26.60. Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16; Found: C, 85.67; H, 6.16. MS-EI, m/z 196 (M^+).

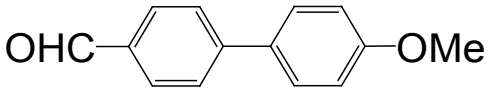


Product **5**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.53 (dd, *J* = 9.3, 5.4 Hz, 4H, C_6H_5), 7.42 (t, *J* = 7.5 Hz, 2H, C_6H_4), 7.30 (t, *J* = 7.3 Hz, 1H, C_6H_5), 6.99 (d, *J* = 8.7 Hz, 2H, C_6H_4), 3.85 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 159.24, 140.89, 133.84, 128.75, 128.18, 126.76, 126.68, 114.28, 55.34. Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57; Found: C, 84.77; H, 6.58. MS-EI, m/z 184 (M^+).

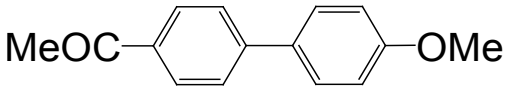


Product **6**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): 7.69 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.64 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.53 (d, *J* = 8.8 Hz, 2H, C_6H_4), 7.00 (d, *J* = 8.8 Hz, 2H, C_6H_4), 3.86 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$,

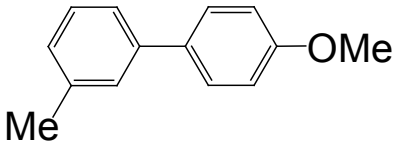
25°C, TMS): 160.26, 145.18, 132.53, 131.45, 128.66, 126.66, 119.06, 114.12, 110.11, 55.38. Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69; Found: C, 80.34; H, 5.30; N, 6.70. MS-EI, m/z 209 (M^+).



Product **7:** White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 10.32 (s, 1H, CHO), 7.91 (d, J = 8.4 Hz, 2H, C_6H_4), 7.60 (d, J = 8.2 Hz, 2H, C_6H_4), 7.57 (d, J = 8.8 Hz, 2H, C_6H_4), 6.99 (d, J = 8.8 Hz, 2H, C_6H_4), 3.86 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 191.85, 160.08, 146.72, 134.64, 131.99, 130.28, 128.47, 127.01, 114.45, 55.36. Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70; found: C, 79.25; H, 5.69. MS-EI, m/z 212 (M^+).

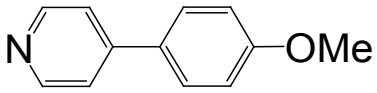


Product **8**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.00 (d, J = 8.4 Hz, 2H, C_6H_4), 7.63 (d, J = 8.4 Hz, 2H, C_6H_4), 7.57 (d, J = 8.8 Hz, 2H, C_6H_4), 7.00 (d, J = 8.8 Hz, 2H, C_6H_4), 3.86 (s, 3H, OCH_3), 2.62 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 197.61, 159.95, 145.34, 135.33, 128.92, 128.34, 127.94, 126.58, 114.43, 55.35, 26.54. Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; Found: C, 79.63; H, 6.24. MS-EI, m/z 226 (M^+).

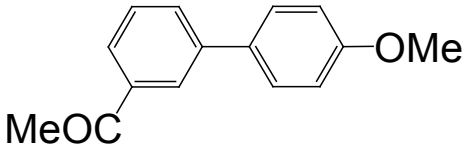


Product **9**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.55 (d, J = 8.6 Hz, 2H, C_6H_4), 7.35-7.46 (m, 2H, C_6H_4), 7.32 (d, J = 7.6 Hz, 1H, C_6H_4), 7.07-7.19 (m, 1H, C_6H_4), 7.00 (d, J = 8.6 Hz, 2H, C_6H_4), 3.87 (s, 3H, OCH_3), 2.44 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 159.15, 140.87, 138.28, 133.95, 128.66,

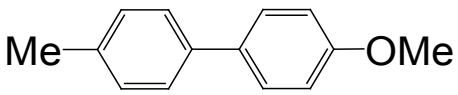
128.18, 127.58, 127.44, 123.89, 114.19, 55.33, 26.97. Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.79; H, 7.11. MS-EI, m/z 198 (M^+).



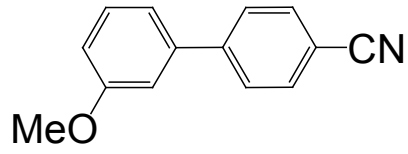
Product **10**: White solid. Eluent: dichloromethane /ethyl acetate = 1/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.62 (s, 2H, C_5NH_4), 7.60 (d, J = 8.7 Hz, 2H, C_6H_4), 7.48 (d, J = 4.4 Hz, 2H, C_5NH_4), 7.00 (d, J = 8.7 Hz, 2H, C_6H_4), 3.86 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 160.56, 150.07, 147.79, 130.25, 128.09, 120.98, 114.54, 55.32. Anal. Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56; Found: C, 77.85; H, 5.98; N, 7.58. MS-EI, m/z 185 (M^+).



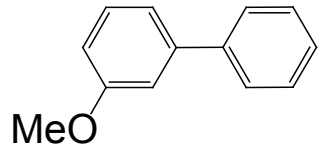
Product **11**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.14 (s, 1H, C_6H_4), 7.88 (d, J = 7.7 Hz, 1H, C_6H_4), 7.75 (d, J = 7.7 Hz, 1H, C_6H_4), 7.47-7.57 (m, 3H, C_6H_4), 7.00 (d, J = 8.7 Hz, 2H, C_6H_4), 3.85 (s, 3H, OCH_3), 2.64 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 198.11, 159.52, 141.21, 137.56, 132.54, 131.22, 128.98, 128.18, 126.60, 126.35, 114.34, 55.31, 26.73. Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; Found: C, 79.64; H, 6.23. MS-EI, m/z 226 (M^+).



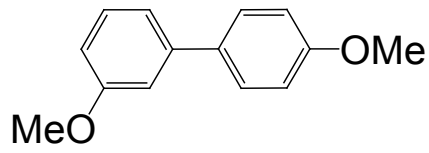
Product **12**[5]: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.48 (dd, J = 18.3, 8.4 Hz, 4H, C_6H_4), 7.23 (d, J = 8.7 Hz, 2H, C_6H_4), 6.96 (d, J = 8.7 Hz, 2H, C_6H_4), 3.85 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 158.93, 137.96, 136.34, 133.74, 129.44, 127.95, 126.58, 114.16, 55.33, 21.06. Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.82; H, 7.11. MS-EI, m/z 198 (M^+).



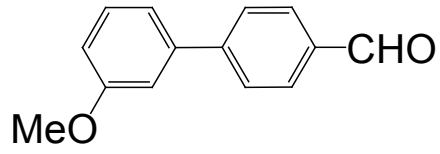
Product **13**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.70 (q, J = 8.4 Hz, 4H, C_6H_4), 7.39 (t, J = 7.9 Hz, 1H, C_6H_4), 7.16 (d, J = 7.7 Hz, 1H, C_6H_4), 7.10 (s, 1H, C_6H_4), 6.97 (dd, J = 8.2, 2.3 Hz, 1H, C_6H_4), 3.87 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 160.12, 145.46, 140.57, 132.53, 130.15, 127.74, 119.62, 118.91, 113.86, 113.07, 110.99, 55.36. Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.36; H, 5.30; N, 6.69; Found: C, 80.39; H, 5.31; N, 6.67. MS-EI, m/z 209 (M^+).



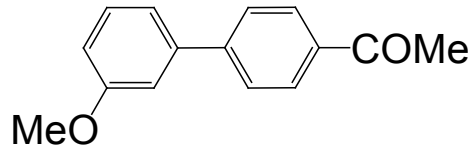
Product **14**[7]: Colorless oil. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.60 (d, J = 7.3 Hz, 2H, C_6H_5), 7.45 (t, J = 7.4 Hz, 2H, C_6H_5), 7.30-7.41 (m, 2H, C_6H_4 ,C_6H_5), 7.20 (d, J = 7.7 Hz, 1H, C_6H_4), 7.15 (d, J = 2.2 Hz, 1H, C_6H_4), 6.92 (dd, J = 7.9, 2.1 Hz, 1H, C_6H_4), 3.88 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 160.27, 142.96, 141.33, 129.96, 128.94, 127.61, 127.38, 119.86, 113.17, 112.90, 55.34. Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57; Found: C, 84.78; H, 6.59. MS-EI, m/z 184 (M^+).



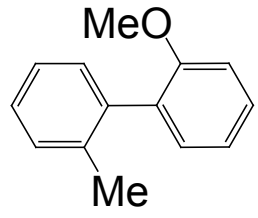
Product **15**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.53 (d, J = 8.8 Hz, 2H, C_6H_4), 7.33 (t, J = 7.9 Hz, 1H, C_6H_4), 7.09-7.15 (m, 2H, C_6H_4), 6.98 (d, J = 8.8 Hz, 2H, C_6H_4), 6.84-6.87 (m, 1H, C_6H_4), 3.86 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 160.03, 159.33, 142.39, 133.61, 129.79, 128.23, 119.31, 114.24, 112.58, 112.06, 55.33, 55.27. Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59; Found: C, 78.51; H, 6.60. MS-EI, m/z 214 (M^+).



Product **16:** White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 10.05 (s, 1H, CHO), 7.95 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.73 (d, *J* = 8.2 Hz, 2H, C_6H_4), 7.39 (t, *J* = 7.9 Hz, 1H, C_6H_4), 7.22 (d, *J* = 7.7 Hz, 1H, C_6H_4), 7.15 (d, *J* = 2.0 Hz, 1H. C_6H_4), 6.96 (dd, *J* = 8.1, 2.2 Hz, 1H, C_6H_4), 3.87 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 191.85, 160.06, 146.97, 141.13, 135.29, 130.20, 130.04, 127.69, 119.80, 113.75, 113.14, 55.33. Anal. Calcd. for $C_{14}H_{12}O2$: C, 79.22; H, 5.70; Found: C, 79.21; H, 5.68. MS-EI, m/z 212 (M^+).

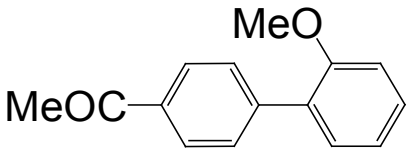


Product **17**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.02 (d, *J* = 8.3 Hz, 2H, C_6H_4), 7.67 (d, *J* = 8.3 Hz, 2H, C_6H_4), 7.38 (t, *J* = 7.9 Hz, 1H, C_6H_4), 7.22 (t, *J* = 9.3 Hz, 1H, C_6H_4), 7.15 (s, 1H, C_6H_4), 6.93 (dd, *J* = 8.2, 2.3 Hz, 1H, C_6H_4), 3.87 (s, 3H, OCH_3), 2.63 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 197.57, 160.03, 145.48, 141.24, 135.91, 129.98, 128.85, 127.18, 119.67, 113.48, 113.03, 55.27, 26.59. Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; Found: C, 79.65; H, 6.22. MS-EI, m/z 226 (M^+).

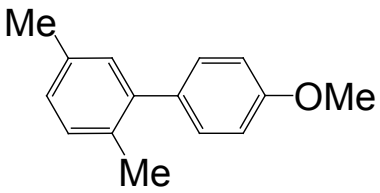


Product **18**[7]: Light yellow oil. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.36 (t, *J* = 7.8 Hz, 1H, C_6H_4), 7.14-7.28 (m, 5H, C_6H_4), 7.04 (d, *J* = 7.4 Hz, 1H, C_6H_4), 6.98 (d, *J* = 8.4 Hz, 1H, C_6H_4), 3.78 (s, 3H, OCH_3), 2.16 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 156.74, 138.78, 136.90, 131.11, 131.02, 130.11, 129.67,

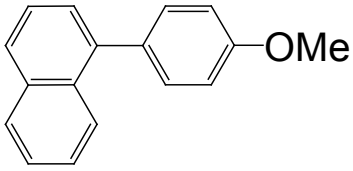
128.65, 127.38, 125.53, 120.56, 110.81, 55.46, 20.01. Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.80; H, 7.14. MS-EI, m/z 198 (M^+).



Product **19**: Colorless oil. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.00 (d, J = 8.2 Hz, 2H, C_6H_4), 7.63 (d, J = 8.2 Hz, 2H, C_6H_4), 7.30-7.39 (m, 2H, C_6H_4), 7.02 (dd, J = 17.4, 7.9 Hz, 2H, C_6H_4), 3.82 (s, 3H, OCH_3), 2.63 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 197.84, 156.44, 143.58, 135.47, 130.69, 129.71, 129.49, 129.41, 128.06, 120.95, 111.33, 55.54, 26.64. Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; Found: C, 79.64; H, 6.23. MS-EI, m/z 226 (M^+).

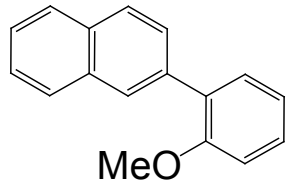


Product **20**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.47 (d, J = 8.7 Hz, 1H, C_6H_3), 7.23(s, 1H, C_6H_3), 7.13 (d, J = 8.0 Hz, 1H, C_6H_3), 7.04 (d, J = 6.5 Hz, 2H, C_6H_4), 6.95(d, J = 8.5 Hz, 2H, C_6H_4), 3.85 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 158.42, 141.33, 135.13, 134.48, 130.62, 130.19, 127.71, 127.63, 114.14, 113.42, 55.27, 20.90, 20.02. Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60; Found: C, 84.89; H, 7.62. MS-EI, m/z 212 (M^+).

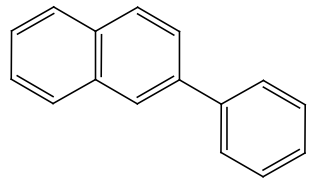


Product **21**[8]: Light yellow solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.91 (d, J = 8.2 Hz, 2H, $C_{10}H_7$), 7.76-7.87 (m, 1H, $C_{10}H_7$), 7.46-7.63 (m, 2H, $C_{10}H_7$), 7.41 (dd, J = 8.6, 5.4 Hz, 4H, $C_{10}H_7$, C_6H_4), 7.03 (d, J = 8.6 Hz, 2H, C_6H_4), 3.90

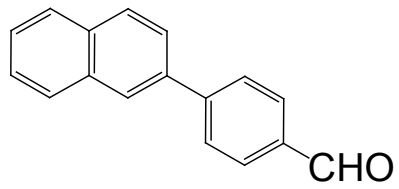
(s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 156.98, 136.61, 133.78, 132.78, 131.45, 130.96, 129.10, 128.45, 127.92, 127.52, 126.23, 126.10, 121.26, 111.62, 55.77. Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02; Found: C, 87.18; H, 6.03. MS-EI, m/z 234 (M^+).



Product **22**: White solid. Eluent: hexane/dichloromethane = 6/1. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.97 (s, 1H, Ar), 7.88 (d, J = 7.7 Hz, 3H, Ar), 7.69 (dd, J = 8.5, 1.4 Hz, 1H, Ar), 7.40-7.60 (m, 3H, Ar), 7.29-7.39 (m, 1H, Ar), 7.05 (dd, J = 18.1, 7.9 Hz, 2H, Ar), 3.78 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 159.15, 139.69, 133.96, 132.64, 131.52, 131.29, 128.76, 128.16, 127.70, 127.24, 126.64, 126.36, 126.27, 126.00, 125.77, 114.39, 55.62. Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02; Found: C, 87.16; H, 6.01. MS-EI, m/z 234 (M^+).

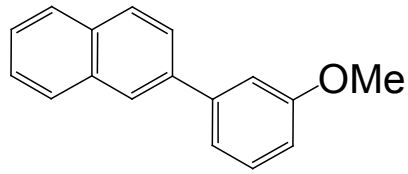


Product **23**[6]: White solid. Eluent: hexane/dichloromethane = 6/1. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.05 (s, 1H, Ar), 7.80-7.99 (m, 3H, Ar), 7.64-7.79 (m, 3H, Ar), 7.45-7.59 (m, 4H, Ar), 7.39 (t, J = 7.3 Hz, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 141.19, 138.62, 133.77, 132.70, 128.94, 128.50, 128.29, 127.73, 127.51, 127.44, 126.36, 126.02, 125.88, 125.68. Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; Found: C, 94.11; H, 5.93. MS-EI, m/z 204 (M^+).

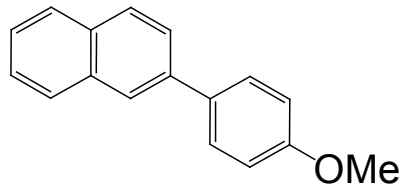


Product **24**: White solid. Eluent: hexane/dichloromethane = 6/1. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 10.08 (s, 1H, CHO), 8.11 (s, 1H, Ar), 7.98 (t, J = 6.3 Hz, 3H, Ar), 7.89 (d, J = 8.3

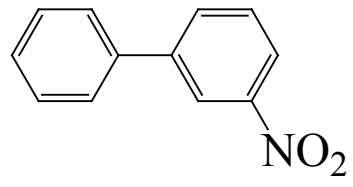
Hz, 3H, Ar), 7.64-7.83 (m, 2H, Ar), 7.51-7.59 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 191.89, 147.06, 136.95, 135.19, 133.51, 133.09, 130.31, 129.89, 129.20, 128.78, 128.39, 127.89, 127.70, 126.63, 125.11. Anal. Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21; Found: C, 87.88; H, 5.20. MS-EI, m/z 232 (M^+).



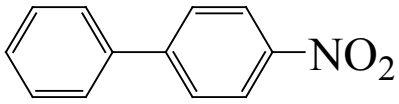
Product **25**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 8.05 (s, 1H, Ar), 7.84-7.98 (m, 3H, Ar), 7.55 (dd, J = 8.6, 1.1 Hz, 1H, Ar), 7.51 (dd, J = 9.2, 5.6 Hz, 2H, Ar), 7.42 (t, J = 7.8 Hz, 1H, Ar), 7.33(d, J = 7.7 Hz, 1H), 7.26 (d, J = 5.5 Hz, 1H), 6.96 (dd, J = 8.0, 1.3 Hz, 1H, Ar), 3.91 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 160.11, 142.70, 138.48, 133.71, 132.79, 129.93, 128.47, 128.29, 127.72, 126.37, 126.06, 125.94, 125.67, 120.01, 113.24, 112.82, 55.37. Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02; found: C, 87.17; H, 6.02. MS-EI, m/z 234 (M^+).



Product **26**: White solid. Eluent: hexane/dichloromethane = 6/1. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.99 (s, 1H, Ar), 7.88 (dd, J = 12.0, 7.9 Hz, 3H, Ar), 7.58-7.77 (m, 3H, Ar), 7.38-7.58 (m, 2H, Ar), 7.03 (d, J = 8.7 Hz, 2H, Ar), 3.88 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): 159.33, 138.21, 133.84, 133.66, 132.39, 128.47, 128.40, 128.12, 127.68, 126.28, 125.69, 125.48, 125.07, 114.39, 55.38. Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02; found: C, 87.13; H, 6.01. MS-EI, m/z 234 (M^+).



Product **27**: Yield 96%. Light yellow solid. Eluent: cyclohexane/dichloromethane = 9 / 1. ^{1}H NMR (600 MHz, $CDCl_3$, 25°C, TMS): 8.44 (d, J = 1.1 Hz, 1H), 8.18 (dd, J = 8.2, 0.6 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.66 – 7.55 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.46 – 7.37 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, 25°C, TMS) 148.69, 142.82, 138.61, 133.00, 129.69, 129.14, 128.52, 127.12, 122.00, 121.94. Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; Found: C, 72.38; H, 4.56; N, 7.00. MS-EI, m/z 199 (M^+).



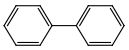
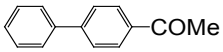
Product **28**: Yield 94%. Light yellow solid. Eluent: cyclohexane/dichloromethane = 6 / 1. ^{1}H NMR (600 MHz, $CDCl_3$, 25°C, TMS) 8.28 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.49 (dd, J = 8.1, 6.7 Hz, 2H), 7.44 (ddd, J = 7.5, 3.7, 1.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, 25°C, TMS) 147.58, 147.05, 138.72, 129.14, 128.91, 127.76, 127.36, 124.07. Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; Found: C, 72.36; H, 4.53; N, 7.01. MS-EI, m/z 199 (M^+).

2. Different catalyst loading for homogeneous catalytic cross-coupling in EtOH/H_2O system in air

For exploration the catalytic activity of **1**, typical Suzuki-Miyaura reactions were performed with different amount of catalyst. A mixture of PhBr (10/20/50/100 mmol), $PhB(OH)_2$ (12/24/50/120 mmol), K_2CO_3 (10/20/50/100 mmol) were dissolved in a mixed-solvent system of H_2O/EtOH (5/10/50/100 mL, 1:1). After addition of **1** (1 mg, 100 ppm), the reaction mixture was heated to 60°C for 1/5/12/24 h, respectively. After addition of water, the mixture was extracted with EtOAc (10 mL×3). The combined organic layers were washed with water, dried over Na_2SO_4, and purified by column chromatography on silica gel to afford the corresponding coupling products as crystalline solids.

3. Homogeneous catalytic cross-coupling based on $PhB(OH)_2$ carried out at room temperature in air

Table S2. Cross-coupling reactions catalyzed by **1** at room temperature.

Substrate	Product	Time	%Yield[a]
PhBr		4 h	99
4-BrPhCOMe		4 h	98

[a] Isolated yield.

A mixture of ArBr (10 mmol), $ArB(OH)_2$ (12 mmol), K_2CO_3 (10 mmol) were dissolved in a mixed-solvent system of H_2O/EtOH (10 mL, 1:1). After addition of **1** (1 mg, 100 ppm), the reaction mixture was stirred at room temperature for 4 h. After addition of water (5 mL), the mixture was extracted with EtOAc (10 mL×3). The combined organic layers were washed with water, dried over Na_2SO_4, and purified by column chromatography on silica gel to afford the corresponding coupling products as crystalline solids.

4. Suzuki-Miyaura homogeneous catalytic cross-coupling based on PhX (X = I, Br, Cl, F) in H_2O/EtOH

A mixture of PhX (X = I and Br) (10 mmol), $PhB(OH)_2$ (12 mmol), K_2CO_3 (10 mmol) were dissolved in a mixed-solvent system of H_2O/EtOH (5 mL, 1:1). After addition of **1** (1 mg, 100 ppm), the reaction mixture was stirred at 60°C for 1 h. After addition of water (5 mL), the mixture was extracted with CH_2Cl_2 (10 mL × 3). The yields were determined by HPLC.

A mixture of PhX (X = Cl and F) (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), K_2CO_3 (0.5 mmol) were dissolved in a mixed-solvent system of H_2O/EtOH (2 mL, 1:1). After addition of **1** (10 mg, 2 mol %), the reaction mixture was stirred at 60°C for 30 h. After addition of water (3 mL), the mixture was extracted with CH_2Cl_2 (5 mL×3). The yields were determined by HPLC.

5. Control experiment to demonstrate the cross-coupling reactoin catalyzed by **1** in *o*-xylene being a heterogeneous process.

A mixture of PhBr (2.0 mmol), $PhB(OH)_2$ (2.2 mmol), K_2CO_3 (2.2 mmol) were added to *o*-xylene (10 mL). After addition of **1** (2 mg), the reaction mixture was stirred at 130°C. The reaction was finished in around 24 h (monitored by HPLC). After filtration, additional $PhB(OH)_2$ (2.0 mmol), PhBr (2.0 mmol) and K_2CO_3(2.2 mmol) were added to the filtrate, and the reaction mixture was stirred at 130°C again, no more Ph-Ph product was detected on HPLC

analysis (Fig. S2). Moreover, no Pd(II)-species was detected in the filtrate by XPS measurement (Fig. S2), which further confirms above reaction is a heterogenerous process.

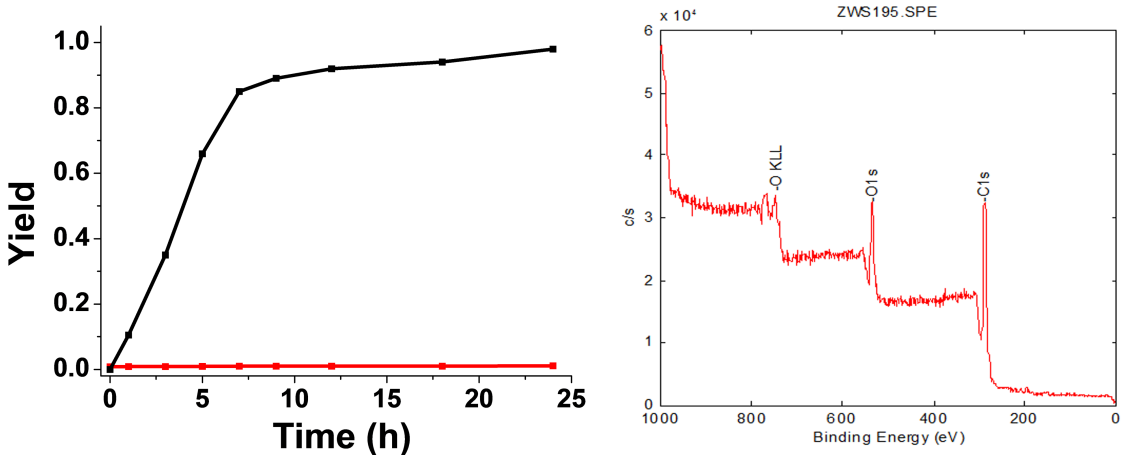


Fig. S3 Left: The changes conversion with time going on base on HPLC. Black line: PhBr (2.0 mmol), $PhB(OH)_2$ (2.2 mmol), K_2CO_3 (2.2 mmol) and **1** (2mg) in *o*-xylene (10 mL) at 130°C. Red line: $PhB(OH)_2$ (2.0 mmol), PhBr (2.0 mmol) and K_2CO_3(2.2 mmol) in the filtrate at 130°C. Right: XPS spectrum performed on the filtrate.

6. Cross-coupling heterogeneously catalyzed by **1** in *o*-xylene.

A mixture of PhBr (2.0 mmol), $PhB(OH)_2$ (2.2 mmol), K_2CO_3 (2.2 mmol) were added to o-xylene (10 mL). After addition of **1** (100 or 2500 ppm), the reaction mixture was stirred at 130°C for 20 or 24 h, respectively. The yields were determined by HPLC. Catalyst was easily recycled by filtration after each run.

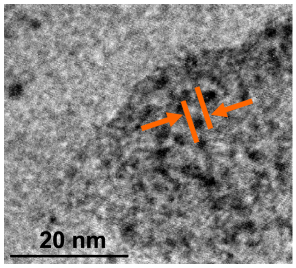
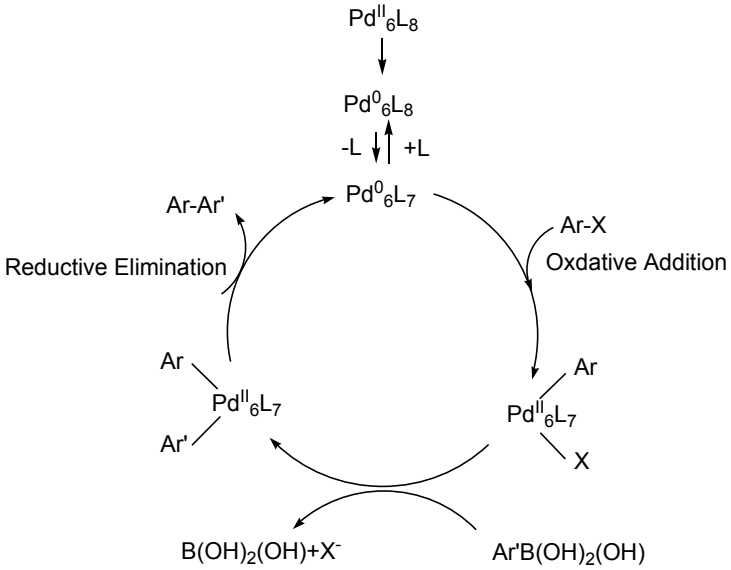


Fig. S4 TEM image of **1** after second recycle.

Supposed Catalytic Mechanism



Scheme 2 Supposed catatlytic mechanism based on **1**.[9]

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