Supplementary Information

Tackling Poison and Leach: Catalysis by Dangling Thiol-Palladium Functions within a Porous Metal-Organic Solid

Bo Gui, ^{†a} Ka-Kit Yee, ^{†b} Yan-Lung Wong,^b Shek-Man Yiu,^b Matthias Zeller,^c Cheng Wang,^{*a} and Zhengtao Xu^{*b}

^a Key Laboratory of Biomedical Polymers (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
^b Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China
^c Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, OH 44555, USA

Experimental details

General procedure for synthesis of SM1 to SM5 (devised and conducted at Wuhan University). 4-methoxyl carbonylphenylboronic acid (97%) was purchased from AK Scientific, Inc.. Ally bromide, 1,4-Diazabicyclo[2.2.2]octane and dimethylcarbamothioic chloride was purchased from TCI. Pd(PPh₃)₄ was bought from Aladdin. 1,4-dibromo-2,5-dimethoxybenzene was synthesized according to the literature (K.-S. Lee; J.-S. Lee,

Chem. Mater. 2006, 18, 4519-4525).

Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on Mercury VX-300 spectrometers, with working frequencies of 300 MHz for ¹H, and 75 MHz for ¹³C nuclei, respectively. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents.

General procedure for the conversion of SM5 into H₂DMTD, preparation and characterization of ZrDMTD, and property studies (devised and conducted at City University of Hong Kong). Starting materials, reagents, and solvents were purchased from Aldrich and used without further purification. The CHN elemental analyses were performed with a Vario Micro CUBE CHN elemental analyzer. The quantification of the

metal ions was conducted with a PerkinElmer Optima 2100 DV ICP (Inductively Coupled Plasma) optical emission spectrometer. Solution ¹H NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 3 °C/min with an empty Al₂O₃ crucible being used as the reference.

FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. FT-Raman spectra were obtained using a NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software. Powder X-ray diffraction data for the Zr-based MOF samples were collected in the reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-K α 1 (λ = 1.5406 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA.

The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. The ZrDMTD sample was outgassed at 0.03 torr, heated with a 2 °C/min ramp to 100 °C, and held at 100 °C for 12 hours. The sample was then kept under vacuum until the analysis was run. Pore analysis was performed using CO₂ at 298 K (P range of 8×10^{-3} to 780 mmHg).



Scheme S1. The synthetic steps for H₂DMTD.

Synthesis of SM1: 1,4-dibromo-2,5-dimethoxybenzene (2.00 g, 6.76 mmol), 4methoxyl carbonylphenyl boronic acid (3.04 g, 16.89 mmol), K₂CO₃ (2 M aqueous solution, 25 mL) and Pd(PPh₃)₄ (0.35 g, 3.5 mol%) were added to flask containing THF (50 mL). The reaction mixture was refluxed at 80 °C under nitrogen atmosphere for 15 h. After cooling down, DCM (100 mL) was added. The organic layer was washed with brine and dried over Na₂SO₄. After that, the solvents were evaporated under reduced pressure and the resulting residue was subjected to column chromatography (80% DCM in petrol). The product **SM1** was isolated as white gray solid (1.23 g, 45%, yield). ¹H NMR (300 MHz, CDCl₃): δ = 8.11 (d, *J* = 7.9 Hz, 4H), 7.66 (d, *J* = 7.9 Hz, 4H), 6.99 (s, 2H), 3.95 (s, 6H), 3.81 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ = 167.0, 150.7, 142.8, 130.0, 129.43, 129.39, 128.8, 114.5, 56.4, 52.1.

Synthesis of SM2: 10 mL of BBr₃ was slowly added to a solution of compound **SM1** (3.0 g) in 50 mL DCM under nitrogen atmosphere. The reaction was stirred at room

temperature for 48 h. After that, H₂O (100 mL) was added. The precipitate was filtered, washed extensively with H₂O (1 L), and dried under vacuum. Compound **SM2** was isolated as a green yellow solid (2.5 g, 97%, yield). ¹H NMR (300 MHz, DMSO- d_6): 12.93 (s, 2H), 9.24 (s, 2H), 7.99 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 8.4 Hz, 4H), 6.94 (s, 2H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 167.3$, 147.3, 142.7, 129.1, 129.0, 128.8, 127.0, 117.5.

Synthesis of SM3: A mixture of compound SM2 (2.0 g) and concentrated sulfuric acid (2 mL) was dissolved in EtOH (100 mL). The reaction mixture was refluxed for 12 h. After that, the solvents was evaporated by vacuum and H₂O (50 mL) was added. The precipitate was filtered, washed extensively with H₂O (300 mL), and dried under vacuum. Compound SM3 was isolated (2.0 g, 90%, yield) as white solid. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 9.29 (s, 2H), 8.0 (d, *J* = 8.4 Hz, 4H), 7.72 (d, *J* = 8.4 Hz, 4H), 6.94 (s, 2H), 4.34 (q, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ¹³CNMR (75 MHz, DMSO-*d*₆): δ = 167.0, 150.7, 142.8, 130.0, 129.43, 129.38, 128.8, 114.5, 56.4, 52.1.

Synthesis of SM4: Compound SM3 (1.40 g, 3.4 mmol) and DABCO (2.38 g, 19.0 mmol) were dissolved in dry DMF (50 mL) at 0 °C under a nitrogen atmosphere. A solution of dimethylthiocarbamoyl chloride (2.70 g, 19.0 mmol) in dry DMF (20 mL) was added directly to the reaction in an hour. The reaction mixture was allowed to warm up to room temperature, before being stirred for an additional 15 h. During the reaction, a large amount of off-white solid precipitated out. The solid was filtered and washed with water and finally dried in vacuum. Compound SM4 was isolated (980 mg, 49%, yield) as white solid. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.04$ (d, J = 8.2 Hz, 4H), 7.67 (d, J = 8.2 Hz, 4H), 7.33 (s, 2H), 4.34 (q, 4H), 3.25(s, 12H), 1.34(t, J = 7.1 Hz, 6H). ¹³C NMR (75

MHz, CDCl₃): δ = 186.9, 166.4, 148.2, 141.0, 134.4, 129.7, 129.4, 129.1, 126.4, 61.1, 43.3, 38.7, 14.4.

Synthesis of SM5: A Pyrex glass tube was charged with compound SM4 (1.0 g, 1.72 mmol) and sealed under nitrogen atmosphere. The tubes were heated in muffle furnace for 3 h under 240 °C. After cooling down, the brown solid was collected by dissolving in CH₂Cl₂ (10 mL). The solvents were evaporated under reduced pressure and the resulting residue was subjected to column chromatography (5% ethyl acetate in DCM) to afford SM5 as white solid (640 mg, yield, 64%). ¹H NMR (300 MHz, CDCl₃): δ = 8.04 (d, *J* = 8.4 Hz, 4H), 7.63 (s, 2H), 7.55 (d, *J* = 8.4 Hz, 4H), 4.36 (q, 4H), 2.88 (d, J = 9.4 Hz, 12H), 1.36 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ = 166.6, 165.8, 145.4, 144.4, 139.4, 129.7, 129.5, 129.0, 128.9, 61.0, 37.0, 14.4.

Synthesis of H₂DMTD. Compound SM5 (50 mg, 0.086 mmol) was placed in a 10 mL two neck flask charged with a magnetic stir bar. The flask was evacuated and was refilled by N₂ for 3 times to ensure the flask was under N₂ atmosphere. KOH solution (1.3 M, 1.2 mL in EtOH/H₂O, v:v=1:1) was bubbled by N₂ for 5 minutes and then transferred to the two neck flask via cannula under N₂ protection. The mixture was refluxed under an inert atmosphere for 12 hours. The reaction mixture was cooled to room temperature and HCl (10%, 3 mL) was added. A white precipitate was formed, filtered, and washed extensively with water, yielding H₂DMTD as white solid (20.5 mg, 62.4%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.04 (d, *J* = 8.1, 4H), 7.57 (d, *J* = 8.1, 4H), 7.47 (s, 2H).

Single crystal sample of ZrDMTD. $ZrCl_4$ (3.6 mg, 0.0155 mmol), H_2DMTD (6.3 mg, 0.017 mmol), benzoic acid (35.7 mg, 0.29 mmol, about 18.9 molar equivalents to $ZrCl_4$; used as a modulator to promote the crystal growth process), and DMF/DEF (v:v=1:1,

0.45 mL) were loaded in a Pyrex glass tube. The tube was then sealed under a vacuum (with the reagents being frozen in liquid nitrogen) and heated at 120 °C in an oven for 24 h, followed by natural cooling to room temperature, during which light yellow octahedron shape single crystals suitable for single-crystal X-ray diffraction were formed. The crystals were suspended in DMF (10 mL) at 60 °C for 2 hours to remove unreacted substrate. The solvent was decanted and the crystals was washed with DMF (20 mL) and CH₃CN (20 mL). The obtained crystals were dried in air to give the as-made product as light yellow octahedron crystals (7.3 mg, 74.4%, based on ZrCl₄). Elemental analyses on the as-made sample found [C (44.46%), H (3.95%), N (2.92%)]; A fitting formula can be determined to be $Zr_6O_4(OH)_2(L)_6(DMF)_7(H_2O)_{18}$ (mw 3798), which gives a calculated profile as [C (44.59%), H (4.27%), N (2.58%)].

Pd (II) uptake by ZrDMTD. In a 3.5 mL glass vial, ZrDMTD (30 mg, 7.9×10^{-3} mmol) was placed in a solution containing excess Pd(CH₃CN)₂Cl₂ (123 mg, 0.475 mmol) in a 7 mL CH₃CN. The color of the crystal was changed from light yellow to deep red immediately. After 12 hours, the supernatant was decanted and the crystals were soaked in hot acetonitrile (about 70°C, 10 mL x 3 — each time, the crystals were allowed to soak for 3 hours before the CH₃CN was decanted) to remove residual unbound Pd(II) species. The obtained deep red crystals were dried in air to give the ZrDMTD-Pd sample (37.8 mg, 93.1%, based on ZrDMTD). Elemental analyses on the ZrDMTD-Pd sample found [C (31.53%), H (4.32%), N (1.15%)]; ICP indicated a Zr/Pd ratio of 1:0.70. A fitting formula can be determined to be Zr₆O₄(OH)₂(L)₆(DMF)₄(PdCl₂)_{4.2}(H₂O)₆₁ (mw 5146), which gives a calculated profile as [C (31.74%), H (4.43%), N (1.09%)]. The ZrDMTD-Pd was soaked in CH₃CN for long term storage.



Scheme S2. The synthetic steps for the bulky substrate M.

Synthesis of 5-amino-isophthalic acid dibutyl ester (C1). A 50-ml round-bottom flask were loaded with a magnetic stirring bar, 5-amino-isophthalic acid dimethyl ester (500 mg, 2.39 mmol), n-butanol (15 ml) and concentrated H₂SO₄ (0.5 mL). The flask was then connected to a condenser, and the mixture was refluxed for 24 hours and then cooled back down to room temperature. The mixture was then poured into 50 mL of water and extracted with dichloromethane (3 x 30 mL). The combined organic layer was dried over K₂CO₃. The organic layer was concentrated in vacuo (using n-hexane to azeotrope the n-butanol). The residue was purified by column chromatography (silica gel, 5:1 hexane/ethyl acetate as the eluent) to provide a yellowish oily product (310.0 mg, yield 44.2% based on 5-amino-isophthalic acid dimethyl ester). ¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1 H), 7.49 (s, 2 H), 4.30 (t, 4 H), 1.73 (quin, 4H), 1.45 (m, 4H), 0.96 (t, 6H).

Synthesis of bulky substrate of M. A mixture of 5-bromo-isophthalic acid (110 mg, 0.45 mmol), thionyl chloride (2.0 mL), and 5 drops of DMF was added in a round bottom flask and was refluxed for one day, after which the excess of thionyl chloride was removed in vacuo and the residual yellowish oily product was mixed with **C1** (310 mg,

1.06 mmol), triethylamine (0.12 mL) and dichloromethane (10 mL). The mixture was stirred at room temperature for 2 hours. After removing the solvent in vacuo, a yellowish oily crude product was obtained and this yellowish crude product was purified by column chromatography (silica gel, with 10:1 hexane/ethyl acetate as the eluent) to provide a white solid product (280.0 mg, 79.0% yield based on 5-bromo-isophthalic acid). ¹H NMR (400 MHz, CDCl₃): δ 8.44 (s, 4H), 8.36 (s, 1H), 8.32 (s, 2H), 8.04 (s, 2H), 4.28 (t, 8H), 1.70 (quin, 8H), 1.43 (m, 8H), 0.94 (t, 12H).

Elemental analyses and TGA on the as-made ZrDMTD sample. Elemental analyses on the as-made sample found [C (44.46%), H (3.95%), N (2.92%)]. For better characterizing the composition, thermogravimetirc (TG) data were also measured (see Figure S2 below for the TGA plot). The formula $Zr_6O_4(OH)_4$ ·(L)_n·(DMF)_m·(H₂O)_y was used to fit the elemental analysis data and the TGA data. It was found that when n=6 (i.e., the linker sites are fully occupied), the elemental and TGA data can be readily fitted. For example, $Zr_6O_4(OH)_4$ ·(L)₆·(DMF)₇·(H₂O)₁₈ is calculated to give [C (44.59%), H (4.27%), N (2.58%)], matching closely the measured data [C (44.46%), H (3.95%), N (2.92%)]. The water content of 272/3798=7.2% is closely consistent with the first stage of weight loss in the TGA (100-93.0=7.0%), The DMF content calculated from the water-free formula $Zr_6O_4(OH)_4$ ·(L)₆·(DMF)₇ equals 511/3526=14.5%, which is closely consistent with the second stage of weight loss in the TGA [(93-80)/0.93%=14.0%]; see Figure S2). Moreover, the ZrO₂ content from $Zr_6O_4(OH)_4$ ·(L)₆·(DMF)₇ equals 739/3526=21.0%, matching the residual weight percentage found in TGA (19.6/0.93% = 21.1%).

General procedure of Suzuki-Miyaura Coupling Reaction Catalyzed by ZrDMTD-Pd (with No Stirring Applied). In air, aryl halide (0.12 mmol), boronic acid (0.18 mmol), and triethylamine (24 mg, 0.24 mmol) were loaded in a 7.5 mL glass vial containing 1 mL ethanol. The ZrDMTD-Pd crystals (ca. 1.0 mg, ca. 8.2×10^{-4} mmol Pd) were then loaded to the solution (note: the crystal sample being immersed in ethanol, its mass was estimated from the sample volume as follows. The crystals/ethanol mixture was dropped into a narrow glass tube to settle the crystals to the bottom, from the height of the settled sample and the diameter of the tube one obtains the volume. The density of the crystals had been previously estimated from weighing a freshly dried trial sample of known volume). The mixture was heated at 80 °C for several hours. After the reaction was completed (monitor by TLC), the supernatant was collected. The catalyst was soaked in 70 °C ethanol (2 mL) for 10 minutes to ensure all the soluble organic substrate was removed from the catalyst. The supernatant and ethanol portion were combined and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the product.

General procedure for recycling ZrDMTD-Pd. After the catalytic reaction, the supernatant was removed by centrifugation (with care taken to avoid direct contact between the catalyst crystals and air, i.e., by means of leaving a small amount of liquid to cover the crystals). The catalyst in the glass vial was soaked in 70 °C ethanol (2 mL) for 10 minutes to remove the residual soluble organic substrates from the catalyst host. The supernatant was decanted and a new batch of reactants and reagents were loaded to the vial for the next catalytic cycle.

Comparison experiment using H₂DMTD with PdCl₂(CH₃CN)₂ as the catalyst. Under air atmosphere, PdCl₂(CH₃CN)₂ (0.21 mg, 8.2×10^{-4} mmol Pd) and H2L (0.45 mg, 1.2×10^{-3} mmol) were loaded in a 7.5 mL glass vial containing 1 mL ethanol. To this solution, aryl halide (0.12 mmol), 4-methoxycarbonylphenylboronic acid (32 mg, 0.18 mmol) and triethylamine (24 mg, 0.24 mmol) were added and the mixture was stirred at 80 °C for several hours. The reaction was stopped and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the product.

Comparison experiment using degraded ZrDMTD-Pd as catalyst. The ZrDMTD-Pd crystals was collected after the catalytic reaction, and then exposed to air for 2 days to effect the degradation. The formation of Pd particle on the ZrDMTD-Pd sample thus degraded was indicated from the XRD pattern (Figure 2, pattern f). Under air atmosphere, the degraded ZrDMTD-Pd (1 mg, 8.2×10^{-4} mmol Pd), iodobenzene (24 mg, 0.12 mmol), 4-methoxycarbonylphenylboronic acid (32 mg, 0.18 mmol) and triethylamine (24 mg, 0.24 mmol) were loaded in a 7.5 mL glass vial containing 1 mL ethanol. The mixture was heated at 80 °C for 5 hours. The reaction was stopped after 5 hours and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the product as white solid (5.6 mg, 32.4% yield base on iodo-benzene) after flash chromatography using 2:1 hexane/dichloromethane as eluent.

Catalytic activity test of the reaction supernatant. After the catalytic reaction, the catalyst was removed by simple filtration. The supernatant was collected and new batch of reactants (Iodobenzene, 4-methoxycarbonylphenylboronic acid and triethylamine) were added to the supernatant. A drop of this solution was taken out and added to 0.5 mL $CDCl_3$ for ¹H NMR measurement. The remaining solution was sealed in a glass vial and heated at 80 °C for 5 hours. The mixture was cooled to room temperature and a drop of

the reaction solution was taken out and added to another 0.5 mL CDCl₃ for another ¹H NMR measurement. The ratio between 4-methoxycarbonylphenylboronic acid and biphenyl-4-carboxylic acid methyl ester was unchanged after heating at 80 °C for 5 hours, suggesting no catalytic activity for the isolated supernatant.

Palladium leaching study. After the reaction was completed, the supernatant was collected. The organic solvent in the supernatant was evaporated under reduced pressure. 65% HNO₃ (2 mL) was added to the residue and heated at 90 °C for 30 minutes to digest all the metal species. The resultant solution was cooled to room temperature and diluted to 10.0 mL with deionized H₂O. The diluted solution was subjected to the ICP analysis for the determination of the Pd concentration. The Pd concentrations of the supernatants for the 1st, 2nd, 3rd and 8th cycles were found to be 0.0095 ppm, 0.0004 ppm, -0.0009 ppm and 0.0033 ppm, respectively--all below the detection limit (0.015 ppm), indicating negligible leaching of palladium from the solid catalyst. Furthermore, the ZrDMTD-Pd crystals after the 3rd and 8th catalytic cycles were collected and dissolved in a hot (about 80 °C) HNO₃ (65%)/H₂SO₄ (95%) mixture (v:v=2:1, 0.5 mL). The resultant solution was cooled to room temperature, and diluted to 5.0 mL with deionized H_2O . The diluted solution was then subjected to the ICP analysis, Zr/Pd ratio of ZrDMTD-Pd samples after 3rd and 8th cycle were found to be 1:0.67 and 1:0.68, respectively. The persistent Pd contents thus found further indicate the absence of leaching.

Test on molecules M and bfbn for confirming the heterogeneous nature of ZrDMTD-Pd. In air, the small substrate 4-bromo-2-fluorobenzonitrile (bfbn, 24 mg, 0.12 mmol), the bulky bromide molecule M (95 mg, 0.12 mmol), 4-methoxycarbonylphenylboronic acid (64 mg, 0.36 mmol) and triethylamine (48 mg, 0.48

mmol) were loaded in a 7.5 mL glass vial containing 2 mL ethanol. Freshly prepared ZrDMTD-Pd crystals (1 mg, ca. 8.2×10^{-4} mmol Pd) were then added to the solution. After the reaction mixture was heated at 80 °C for 12 hours, bfbn was found by TLC monitoring to have completely reacted (to form methyl 4'-cyano-3'-fluoro-[1,1'-biphenyl]-4-carboxylate, see Figure S13 below). By contrast, the bulky molecule **M** was found by the same TLC test to be unreacted (Figure S13), and can be recovered by column chromatography (e.g., see Figure S15 for the NMR spectra).

Test on the iodo version of M and iodobenzene for confirming the heterogeneous nature of ZrDMTD-Pd. In air, the small substrate iodobenzene (24 mg, 0.12 mmol), the iodo version of M (100 mg, 0.12 mmol), 4-methoxycarbonylphenylboronic acid (64 mg, 0.36 mmol) and triethylamine (48 mg, 0.48 mmol) were loaded in a 7.5 mL glass vial containing 2 mL ethanol. Freshly prepared ZrDMTD-Pd crystals (1 mg, ca. 8.2×10^{-4} mmol Pd) were then added to the solution. After the reaction mixture was heated at 80 °C for 4 hours, iodobenzene was found by TLC monitoring to have completely reacted (see Figure S13 below). By contrast, the iodo version of M was found by the same TLC test to be unreacted (Figure S14), and can be recovered by column chromatography (e.g., see Figure S16 for the NMR spectra).

X-ray Structure Determination of ZrDMTD. A crystal of dimensions $0.32 \times 0.22 \times 0.13$ mm coated with paratone-N and mounted on a nylon cryoloop was used for X-ray diffraction analysis. X-ray diffraction data were collected using ω -scan mode at 173 K on an Oxford Diffraction Gemini S Ultra 4-circle kappa diffractometer with a 92 mm diagonal Sapphire CCD detector using monochromatized Cu-K α radiation ($\lambda = 1.5418$ Å).

The data were processed and absorption correction was done by multi-scan method using CrysAlis¹. The structure was solved using direct methods with the program SHELXS-97² and refined using full-matrix least-squares based on F^2 with Shelxl-2013³ using the graphical interface Shelxle. Zirconium and several non-hydrogen atoms were located during structure solution and the positions of other non-hydrogen atoms were determined from difference density maps. In the final stage of refinement, all non-hydrogen atoms were refined anisotropically. Due to the low resolution of the data, all benzene ring C-C bond distances were restrained to 1.39(2) Å and all C, O and S atoms were restrained to be approximately isotropic in behavior. The central benzene ring is disordered around the intersection of two two-fold axes and mirror planes with half occupancy for the carbon atoms. The attached sulfur atom is additionally 1:1 disordered with a carbon bound hydrogen atom. For refinement reasons, the moiety was modeled as half a benzene ring with one SH unit with all atoms one quarter occupied, and with two of the carbon atoms being symmetry equivalents of each other (C7 and C8). To overcome correlation, all benzene ring C atoms (and their opposite side counterparts) were constrained to lie within one common plane that did also include the S atom (esd 0.001 \AA^2). C7 and C8 were constrained to have identical ADPs, and C6, C7, C8 and S1 were subjected to a rigid bond restraint (RIGU restraint in Shelxl-2013, esd 0.004 Å²). The C7-S1 bond was restrained to 1.76(2) Å.

The position of oxygen atom O1 was split and refined as half hydroxy and half oxy with slightly different Zr-O distances (shorter for the oxy-Zr bonds). Associated with the hydroxy unit is half a hydrogen bonded water molecule. The water H atoms were omitted from the refinement. All other H atoms were placed in calculated positions with C-H

distances of 0.95 Å, an O-H distance of 1.0 Å and an S-H distance of 1.2 Å and refined using a riding model with thermal parameters equal to 1.2 times (1.5 times for H atoms in thiol groups) that of the associated C, O or S atoms, and these are included in the calculation of final R-indices.

1. CrysAlis, Oxford Diffraction Ltd., Version 1.171.33.66, 2010.

2. Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution; University of Göttingen: Germany, 1997.

3. Sheldrick, G. M. SHELXL-2013, Program for Crystal Structure Refinement; University of Göttingen: Germany, 2013.

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Entry	Aryl halide	Boronic acid	Time (hr)	Product	Yield (%)	TON ^b
1	<>−ı	(HO)2B- S	5		83.6	123
2	< <u></u> →-ı	(HO) ₂ B-C-OMe	5	$\bigcirc - \bigcirc$	80.7	118
3	, ○-{ }-I	(HO)2 ^B - OMe	5	,º-{\$}-{\$}-{\$}_{OMe}^O	80.2	118
4	ر ا	(HO) ₂ B-,O OMe	5		86.0	126
5	⟨ → Br	(HO)2B-COMe	12		85.6	125
6	FBr	(HO) ₂ B-C-COMe	12	F-	80.4	118
7	F NC - Br	(HO)2B-COCOMe	12	NC - OMe	84.2	123

Table S1. Efficiencies of Suzuki-Miyaura reactions catalyzed by ZrDMTD-Pd crystals ^a



^a Reaction conditions: Aryl halide (0.1196 mmol), phenylboronic acid (0.1794 mmol), triethylamine (0.2392 mmol) and ZrDMTD-Pd (1.0 mg, 8.16×10^{-4} mmol Pd) in 1.0 mL ethanol was heated at 80 °C for several hours. ^b TON defined as the molar ratio between product and Pd.

NMR Data of Coupled Products of Suzuki Reaction.



Biphenyl-4-carboxylic acid methyl ester. White solid. ¹H NMR (400 MHz, CDCl₃): δ

8.11 (d, 2H), 7.68-7.62 (m, 4H), 7.47 (t, 2H), 7.40 (t, 1H), 3.95 (s, 3H).



4-Methylsulfanyl-biphenyl. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, 2H),

7.53 (d, 2H), 7.44 (t, 2H), 7.36-7.32 (m, 3H), 2.53 (s, 3H).



Biphenyl. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, 4H), 7.45 (t, 4H), 7.37 (t,

4H).



4'-Cyano-3'-fluoro-biphenyl-4-carboxylic acid methyl ester. White solid. ¹H NMR



4'-Cyano-3',5'-difluoro-biphenyl-4-carboxylic acid methyl ester. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, 2H), 7.63 (d, 2H), 7.30 (d, 2H).



4'-Fluoro-biphenyl-4-carboxylic acid methyl ester. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, 1H), 7.62-7.59 (m, 2H), 7.15 (t, 2H), 3.94 (s, 3H).



Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, 1H), 7.62 (d, 1H), 7.58 (d, 1H), 7.00 (d, 1H), 3.93 (s, 3H), 3.86 (s, 3H).



Methyl 4'-(methylthio)-[1,1'-biphenyl]-4-carboxylate. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, 1H), 7.64 (d, 1H), 7.56 (d, 1H), 7.34 (d, 1H), 3.94 (s, 3H), 2.53 (s, 3H).



Figure S1. Thermogravimetric analysis (TGA) plots of an as made ZrDMTD sample.



Figure S2. The Raman spectra of (a) an as-made sample of ZrDMTD and (b) ZrDMTD-Pd (crystalline sample freshly loaded with Pd(II), with no exposure to air).



Figure S3. The IR spectra of (a) an as-made sample of ZrDMTD, and (b) ZrDMTD -Pd.



Figure S4. PXRD patterns: (a) calculated from the single-crystal structure of ZrDMTD; (b) asmade ZrDMTD; (c) as-made ZrDMTD placed in air for 10 mins; (d) ZrDMTD-Pd; (e) the sample of (d) after 8 cycles of catalytic reaction; and (f) the sample of (e) after being placed in air for 2 days. Patterns a, b, d and e were taken with crystals covered by a thin layer of DMF to prevent solvent.



Figure S5. CO_2 sorption isotherm at 273 K for an activated ZrDMTD sample (previously activated by Soxhlet extraction in methanol and evacuating at 100 °C for 12 hours).



Figure S6. Photographs of (a) an as-made sample of ZrDMTD, (b) ZrDMTD-Pd (freshly loaded with Pd(II), before being used in the catalytic cycles), (c) ZrDMTD-Pd after one catalytic cycle and (d) ZrDMTD-Pd after 8 catalytic cycles. The scale bar is 500 µm.



Figure S7. X-ray photoelectron spectroscopy (XPS) peaks of the $3d_{5/2}$ states of the Pd in a) ZrDMTD-Pd and b) ZrDMTD-Pd after the catalytic process.



Figure S8. SEM images (720 magnification) a crystal of (a) freshly prepared ZrDMTD-Pd (i.e., freshly loaded with Pd(II), before being used in the catalytic process) and (b) ZrDMTD-Pd after being used as a catalyst for the Suzuki-Miyaura Reaction.



Figure S9. Stirring gives over 90% conversion within one hour—as indicated by an ¹H NMR for between spectrum monitoring а reaction iodobenzene and (4-(methoxycarbonyl)phenyl)boronic acid (the tetramethylbenzene was added as an internal standard). The two asterisked peaks are likely due to the boroxine formed from the excess boronic acid. Procedure: in air, iodobenzene (24 mg, 0.12 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (32 mg, 0.18 mmol), and triethylamine (24 mg, 0.24 mmol) were loaded in a 7.5-mL glass vial containing absolute ethanol (1.0 mL). The ZrDMTD-Pd crystals (ca. 1.0 mg, ca. 8.2×10^{-4} mmol Pd) were then added and the reaction mixture was stirred by a magnetic bar at 80 °C for 1 hour. After the catalyst solid was removed by centrifugation, the solution was evaporated in vacuo and the residue was dissolved in dichloromethane. The dichoromethane solution was washed by DI water (3 x 10 mL) and evaporated in vacuo. The residual solid was dissolved in CDCl₃ for NMR measurement, with 1,2,4,5-tetramethylbenzene added as the internal standard, and about 93% of the iodobenzene was thus found to be converted to the product (TON for the single run: 136). Similar activities were consistently observed in all the 8 cycles of catalysis conducted.



Figure S10. The supernatant test: solution ¹H NMR spectra indicate no catalysis from the supernatant. (A) the isolated supernatant (containing the product biphenyl-4-carboxylic acid) after the addition of a new batch of reactants of iodobenzene and 4-methoxycarbonylphenylboronic acid; (B) the sample of (A) after heating at 80 °C for 5 hours. Selected NMR peaks from the reactants/product are labelled.



Figure S11. Hot filtration test: ¹H NMR spectra indicate no further catalysis from the filtrates. (A) the isolated filtrate upon filtration; and (B) the sample of (A) after heating at 80 °C for 5 hours. Selected NMR peaks from the reactants/product are labelled. Procedure: in air, iodobenzene (24 mg, 0.12 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (32 mg, 0.18 mmol), and triethylamine (24 mg, 0.24 mmol) were loaded in a 7.5-mL glass vial containing absolute ethanol (1.0 mL). The ZrDMTD-Pd crystals (ca. 1.0 mg, ca. 8.2×10^{-4} mmol Pd) were then loaded to the solution. The mixture was stirred at 80 °C for 15 mins. After 15 mins (about 15.2 % conversion), the catalyst was separated by hot filtration and the filtrate was further stirred at 80 °C for another 5 hours.



Figure S12. Testing the poison effect of unmetallated, as-made ZrDMTD crystals (containing free-standing thiol functions): a) a TLC plate indicates minimal poisoning--the iodobenzene reactant disappeared after 1.5 hrs (with stirring); b) a photograph of the reaction mixture at the very beginning of the reaction (showing the colorless as-made crystals and the red, metallated crystals); c) a photograph of the reaction mixture after the reaction (no stirring was applied for preserving the crystal shape; the reaction completed within 5 hrs). No color change occurred in the as-made crystals, consistent with the absence of Pd leaching from the colored metallated crystals. Procedure: iodobenzene (24)0.12 mmol). in air. mg, (4-(methoxycarbonyl)phenyl)boronic acid (32 mg, 0.18 mmol), and triethylamine (24 mg, 0.24 mmol) were loaded in a 7.5-mL glass vial containing absolute ethanol (1.0 mL). The ZrDMTD-Pd crystals (ca. 1.0 mg, ca. 8.2×10^{-4} mmol Pd) and as-made ZrDMTD crystals (ca. 10.0 mg, containing ca. 0.032 mmol -SH; added as the "quasi-poison") were then loaded to the solution. The mixture was stirred at 80 °C for 1.5 hour. After 1.5 hours, the TLC test was conducted, which was developed by 1:1 hexane/dichloromethane. The slightly longer reaction time (vs. 1.0 hr in the absence of the as-made ZrDMTD crystals) could be ascribed to the trapping of the reactants in the pores of the as-made ZrDMTD crystals.



Figure S13. A photograph (taken under a UV lamp) of the TLC plate for monitoring the reaction between 4-methoxycarbonylphenylboronic acid (marked as S1) and the two substrates of different sizes: the bulky bromide molecule **M** (marked as S2 in this TLC test) and the slender 4-bromo-2-fluorobenzonitrile (bfbn, marked as 1). The reaction was conducted using freshly prepared ZrDMTD-Pd crystals as the catalyst, and the TLC plate was developed by 5:1 hexane/ethyl acetate.



Figure S14. A photograph (taken under a UV lamp) of the TLC plate for monitoring the reaction between 4-methoxycarbonylphenylboronic acid (marked as S1) and the two substrates of different sizes: the bulky iodo version of \mathbf{M} (marked as S2 in this TLC test) and the slender iodobenzene (marked as 1). The reaction was conducted using freshly prepared ZrDMTD-Pd crystals as the catalyst, and the TLC plate was developed by 5:1 hexane/ethyl acetate.



Figure S15. Solution ¹H NMR spectra of (a) molecule **M**; and (b) the isolated second highest spot from the reaction mixture. Both of the samples were dissolved in DMSO- d_6 for the NMR measurement.



Figure S16. Solution ¹H NMR spectra of (a) the iodo version of **M**; and (b) the isolated second highest spot from the reaction mixture. Both of the samples were dissolved in DMSO- d_6 for the NMR measurement.