

Supporting Information

MOF-253-Pd(OAc)₂: A Recyclable MOF for Transition-Metal Catalysis in Water

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General Experimental Details

Nitrogen physisorption isotherms were recorded in a Micromeritics 3Flex surface characterization analyzer at 77 K. MOF samples (ca. 100 mg) were degassed under vacuum ($\sim 5 \times 10^{-5}$ Torr) at 200 °C for 12 h prior to analysis. Powder X-ray diffraction (PXRD) patterns of the MOFs were obtained on a STOE Stadi P powder diffractometer using Cu K α radiation (40

kV, 40 mA, $\lambda = 0.1541$ nm). MOFs were dried under vacuum (ca. 30 mTorr) at 150 °C for 12 h prior to PXRD analysis. Inductively coupled plasma-mass spectroscopy was performed on a Thermo Scientific X Series II ICP-MS to determine the palladium content in bpy-UiO-Pd(OAc)₂ and MOF-253-Pd(OAc)₂. Prior to ICP-MS measurements, bpy-UiO-Pd(OAc)₂ and MOF-253-Pd(OAc)₂ were dissolved in boiling aqua regia.

All reactions were performed under air unless otherwise noted. Reactions involving air-sensitive reagents were conducted under inert atmosphere in a nitrogen-filled dry box or by standard Schlenk techniques. Glassware for moisture sensitive reactions was dried at 140 °C in an oven for at least one hour prior to use. Aqueous sodium trifluoroacetate solutions were prepared by dissolving the sodium trifluoroacetate in deionized water. The aqueous solutions were adjusted to pH 8.2 by dropwise addition of concentrated HCl. Flash column chromatography was performed on Siliflash® P60 silica gel (230-400 mesh) using hexane/ethyl acetate mixtures as the eluent. Products were visualized on TLC by UV light and/or by staining with 2,4-dinitrophenylhydrazine.

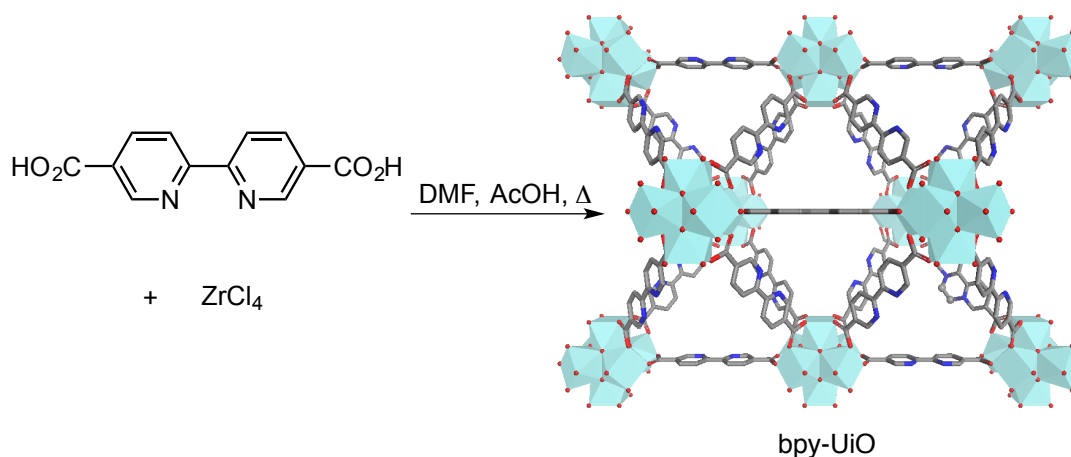
NMR spectra were acquired on Varian MR-400 and Bruker Avance III 600 spectrometers at the Iowa State Chemical Instrumentation Facility. Chemical shifts are reported in ppm relative to a residual solvent peak (CDCl₃ = 7.26 ppm for ¹H and 77.1 ppm for ¹³C). ¹⁹F NMR shifts are reported in ppm relative to trifluorotoluene as an external standard (F₃CC₆H₅ = -63.72 ppm). Coupling constants are reported in hertz.

Materials

3-Methylcyclohex-2-en-1-one **1a**, 3-methylcyclopent-2-en-1-one **1b**, and 4-methylpent-3-en-2-one **1c** were purchased from TCI and used without further purification. 4-Methylphenylboronic acid, 4-trifluoromethylphenylboronic acid, and 3-chlorophenylboronic acid

were purchased from Frontier Scientific and used without further purification. 2-Methoxyphenylboronic acid and palladium acetate were purchased from Sigma-Aldrich and used with further purification. Phenylboronic acid, 3-methoxyphenylboronic acid, and 4-methoxyphenylboronic acid were purchased from AK Scientific and used without further purification. 2,2'-Bipyridine-5,5'-dicarboxylic acid was synthesized according to a literature procedure.¹ bpy-UiO and MOF-253 were synthesized according to a literature procedures.^{2,3} Palladium acetate was purchased from Oakwood Chemical and used without further purification. Zirconium chloride and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Acros Organics Chemicals and used without further purification.

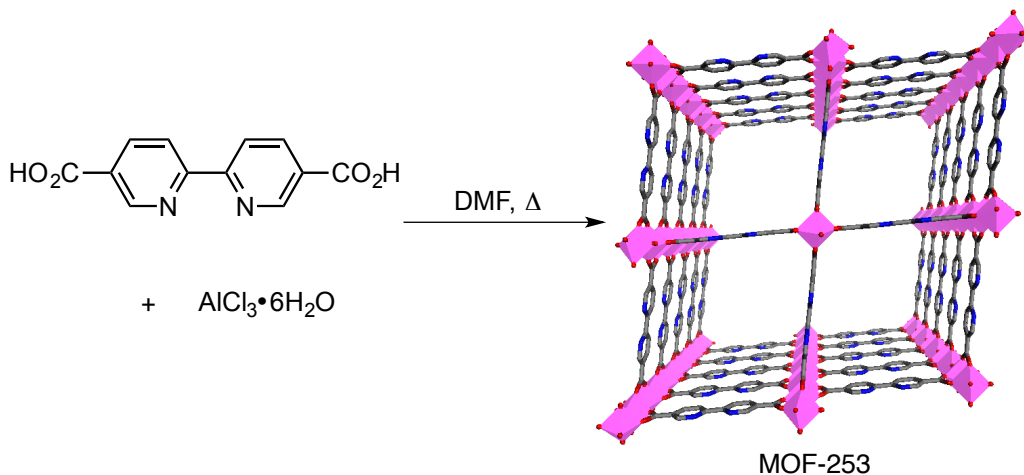
Synthesis and Metalation of Metal-Organic Frameworks



Scheme S1. Synthesis of bpy-UiO. Cyan octahedra represent Zr clusters. Red, blue, and grey spheres represent O, N, and C atoms. H atoms are omitted for clarity.

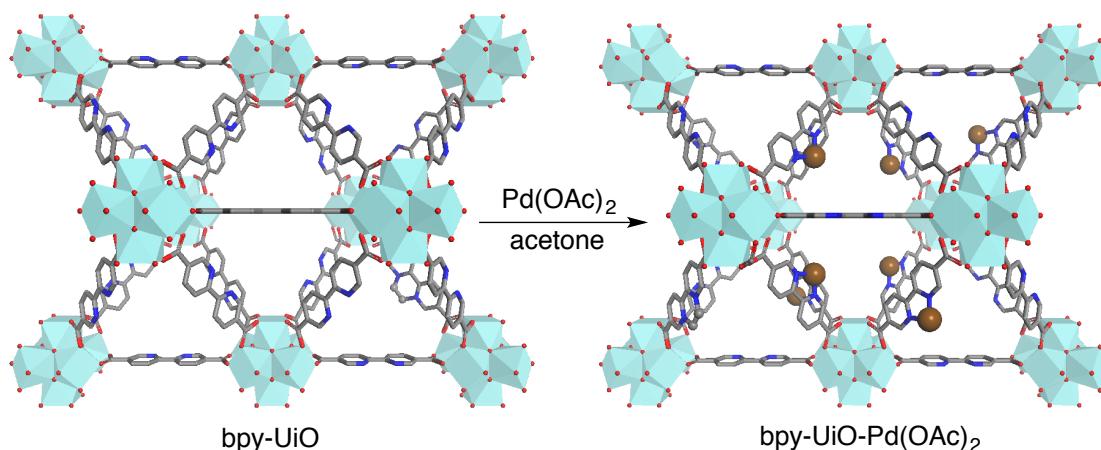
Synthesis of bpy-UiO MOF (Scheme S1). ZrCl_4 (300 mg, 1.28 mmol) and 2,2'-bipyridine-5,5'-dicarboxylic acid (300 mg, 1.23 mmol) were dissolved in 120 mL of *N,N'*-dimethylformamide (DMF) by sonication in a 480 mL Teflon PFA wide mouth jar. Glacial acetic acid (5.6 mL) was added as a modulator. The jar was capped and placed in a pre-heated oven at 120 °C for 3 days. After cooling to ambient temperature, the solid bpy-UiO MOF was collected via centrifugation and washed with DMF (3x) and ethanol (3x) every 12 hours. Finally, bpy-UiO was activated at

150 °C under vacuum (30 mTorr) for 12 hours prior to experimental use (380 mg, 1.033 mmol, 84% yield).



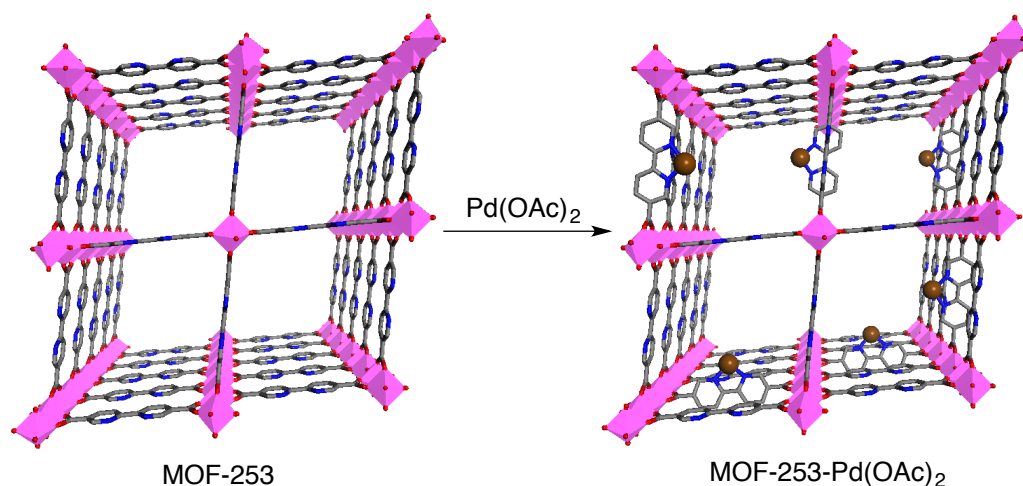
Scheme S2. Synthesis of MOF-253. Pink octahedra represent Al cluster. Red, blue, and grey spheres represent O, N, and C atoms. H atoms are omitted for clarity.

Synthesis of MOF-253 (Scheme S2). $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (151 mg, 0.625 mmol) and 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) were dissolved in 10 mL of *N,N'*-dimethylformamide (DMF) in a 20 mL scintillation vial. The vial was placed in a pre-heated oven at 130 °C for 24 hours. After cooling to ambient temperature, MOF-253 was collected as a white solid via centrifugation and thoroughly washed with DMF (3x) and methanol (3x) every 12 hours. Finally, MOF-253 was activated at 150 °C under vacuum (30 mTorr) for 12 hours prior to experimental use (150 mg, 0.531 mmol, 85% yield).



Scheme S3. Synthesis of bpy-UiO-Pd(OAc)₂ C1 (Scheme S3). Cyan octahedra represent Zr clusters. Brown spheres represent Pd(OAc)₂ species. Red, blue, and grey spheres represent O, N, and C atoms. H atoms are omitted for clarity.

Metalation of bpy-UiO with Pd(OAc)₂ (Scheme S3). Activated bpy-UiO (200 mg) was dispersed in acetone (6 mL) and was sonicated for 30 min to achieve a homogeneous dispersion. Palladium acetate (47 mg) in acetone (6 mL) was added dropwise to the dispersion of bpy-UiO with vigorous stirring (800 rpm). After 24 hours of stirring at ambient temperature, the as-prepared bpy-UiO-Pd(OAc)₂ was washed with acetone (3x) every 12 hours to completely remove the palladium salts not bound to the bipyridine linkers. Finally, the solid was dried at 50 °C, under vacuum to produce bpy-UiO-Pd(OAc)₂ **C1** (8.1 weight % Pd). An analogous procedure can be followed to produce **C1** (5.0 weight % Pd) by adding 23.5 mg of palladium acetate, rather than 47 mg of palladium acetate.



Scheme S4. Synthesis of MOF-253-Pd(OAc)₂ C2 (Scheme S4). Pink octahedra represent Al clusters. Brown spheres represent Pd(OAc)₂ species. Red, blue, and grey spheres represent O, N, and C atoms. H atoms are omitted for clarity.

Metalation of MOF-253 with Pd(OAc)₂ (Scheme S4). Activated MOF-253 (200 mg) was dispersed in acetone (6 mL) and was sonicated for 30 min to achieve a homogenous dispersion. Palladium acetate (23.5 mg) in acetone (6 mL) was added dropwise to the dispersion of MOF with vigorous stirring (800 rpm). After 24 hours of stirring at ambient temperature, the as-prepared MOF-253-Pd(OAc)₂ was washed with acetone (3x) every 12 hours to completely remove the palladium salts not bound to the bipyridine linkers. Finally, the solid was dried at 50 °C under vacuum to produce MOF-253-Pd(OAc)₂ **C2** (8.4 weight % Pd).

Characterization Data for bpy-UiO, MOF-253, bpy-UiO-Pd(OAc)₂ C1 and MOF-253-Pd(OAc)₂ C2

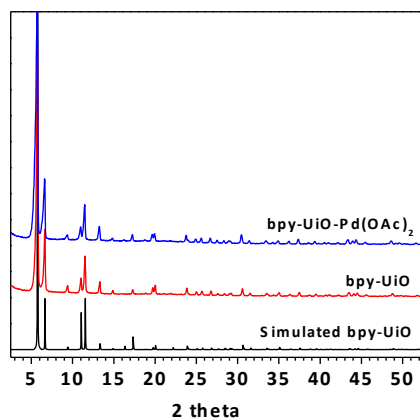


Figure S1. PXRD patterns of simulated bpy-UiO, pristine bpy-UiO and bpy-UiO-Pd(OAc)₂ C1.

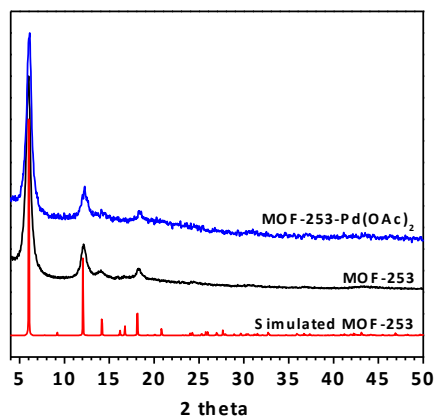


Figure S2. PXRD patterns of simulated MOF-253, pristine MOF-253 and MOF-253-Pd(OAc)₂ C2.

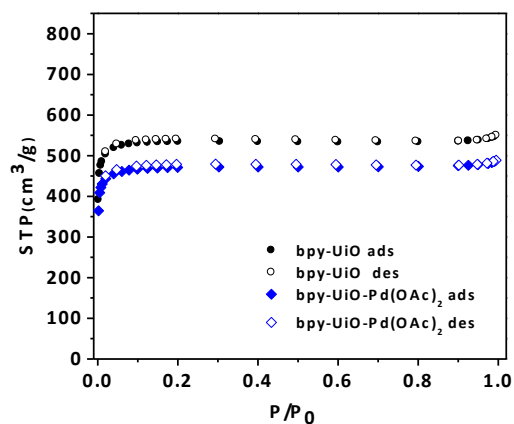


Figure S3. Nitrogen adsorption/desorption isotherms of the bpy-UiO (BET surface area 2209.0 ± 7.3 m²/g) and bpy-UiO-Pd(OAc)₂ C1 (BET surface area 1900.0 ± 3.7 m²/g).

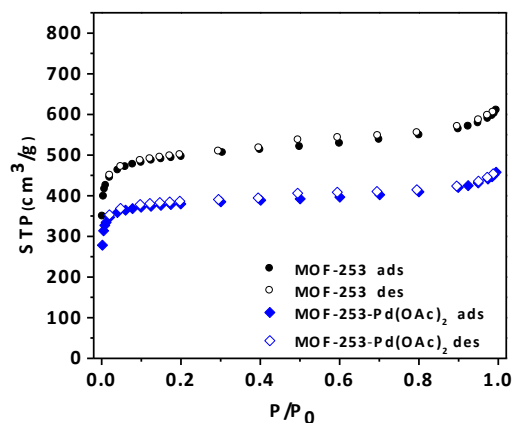


Figure S4. Nitrogen adsorption/desorption isotherms of the as-synthesized MOF-253 (BET surface area $1949.3 \pm 10.0 \text{ m}^2/\text{g}$) and MOF-253-Pd(OAc)₂ C2 (BET surface area $1515.0 \pm 6.7 \text{ m}^2/\text{g}$).

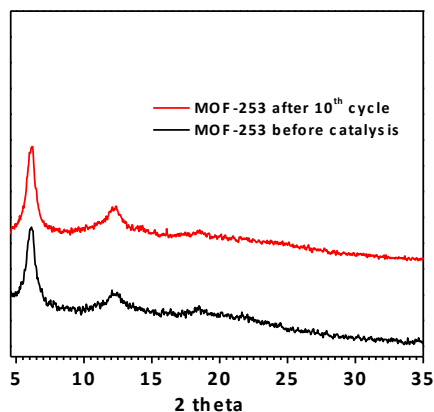


Figure S5. PXRD patterns of as-synthesized MOF-253-Pd(OAc)₂ C2 and used MOF-253-Pd(OAc)₂ C2 after 10 cycles.

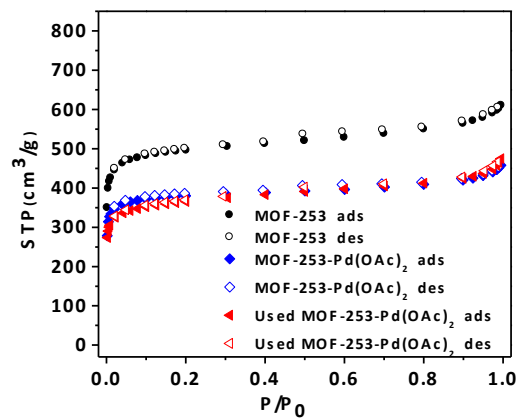
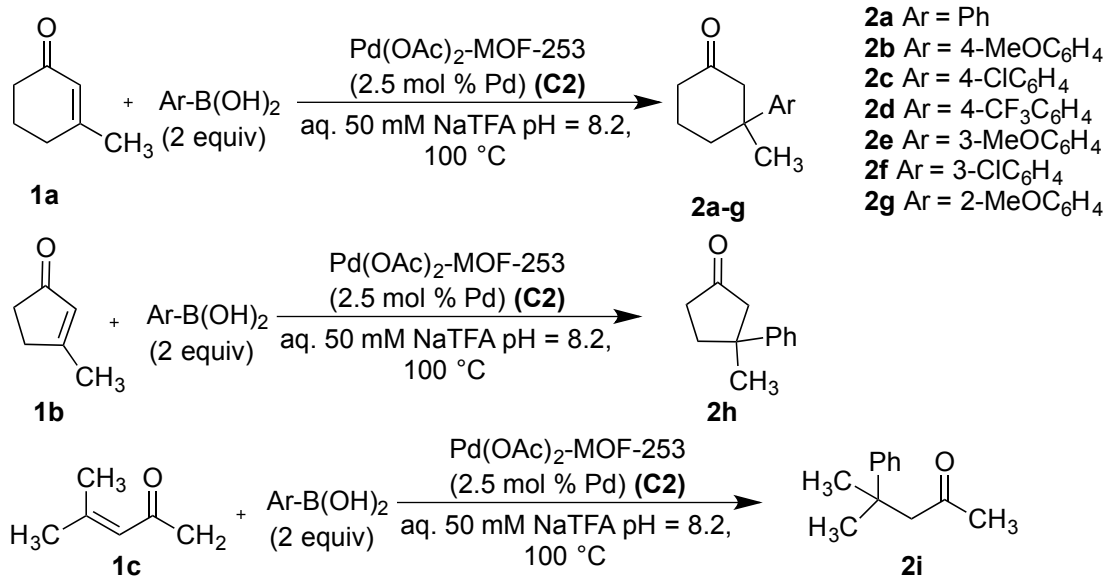


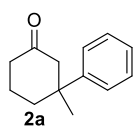
Figure S6. Nitrogen adsorption/desorption isotherms of the bare MOF-253 (BET surface area $1949.3 \pm 10.0 \text{ m}^2/\text{g}$), as-synthesized MOF-253-Pd(OAc)₂ C2 (BET surface area $1515.0 \pm 6.7 \text{ m}^2/\text{g}$) and used MOF-253-Pd(OAc)₂ C2 (BET surface area $1423.0 \pm 2.3 \text{ m}^2/\text{g}$) after 10 cycles.

**General Procedure A: Conjugate Additions of Arylboronic Acids to Enones 1a-1c
Catalyzed by MOF-253-Pd(OAc)₂ C2**

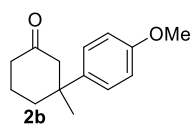


To a 1 dram vial was added the appropriate arylboronic acid (1.00 mmol, 2.00 equiv), MOF-253-Pd(OAc)₂ **C2** (0.013 mmol, 0.025 equiv), enone **1a-c** (0.50 mmol, 1.00 equiv) and 50 mM aqueous sodium trifluoroacetate solution (333 μ L, pH = 8.2). The vial was sealed with a PFTE/silicone-lined septum cap. The reaction mixture was heated to 100 $^{\circ}$ C. The resulting biphasic mixture was allowed to stir at this temperature (2-18 h) until the reaction was judged to be complete by TLC analysis. The mixture was allowed to cool to room temperature, diluted with EtOAc (3 mL), and filtered through a pad of silica gel. The silica gel was washed with EtOAc (3 x 10 mL). The resulting organic layer was washed with brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was dissolved in CDCl₃ (0.70 mL) and CH₂Br₂ (17.6 μ L, 0.250 mmol) was added as an internal standard. NMR yields were determined by ¹H NMR spectroscopy of the crude reaction mixture. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane:EtOAc) to yield the desired ketones **2a-2i**.

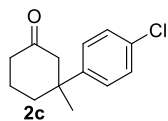
Characterization Data for Ketones 2a-2i



3-Methyl-3-phenylcyclohexan-1-one (2a): Prepared according to General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) and phenylboronic acid (122 mg, 1.00 mmol) (reaction time = 3 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2a** (85 mg, 0.452 mmol, 90%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.33 (s, 3H), 1.64-1.71 (m, 1H), 1.85-1.95 (m, 2H), 2.17-2.21 (m, 1H), 2.32 (app t, J = 7.0 Hz, 2H), 2.44 (d, J = 14.0 Hz, 1H), 2.88 (d, J = 14.0 Hz, 1H), 7.19-7.22 (m, 1H), 7.22 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 22.1, 29.9, 38.0, 40.9, 42.9, 53.2, 125.7, 126.3, 128.6, 147.5, 211.5.

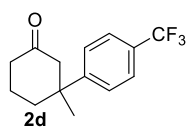


3-(4-Methoxyphenyl)-3-methylcyclohexan-1-one (2b): Prepared according to General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) and 4-methoxyphenylboronic acid (152 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2b** (87 mg, 0.399 mmol, 80%) as a clear, yellow oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.30 (s, 3H), 1.61-1.70 (m, 1H), 1.83-1.92 (m, 2H), 2.13-2.18 (m, 1H), 2.30 (app t, J = 6.8, 2H), 2.41 (d, J = 14.0 Hz, 1H), 2.85 (d, J = 14.0 Hz, 1H), 3.78 (s, 3H), 6.85 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 22.1, 30.2, 38.1, 40.9, 42.4, 53.4, 55.3, 113.9, 126.7, 139.5, 157.8, 211.6.



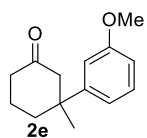
3-(4-Chlorophenyl)-3-methylcyclohexan-1-one (2c): Prepared according to General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) 4-chlorophenylboronic acid (156 mg, 1.00 mmol) (reaction time = 5 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2c** (100 mg, 0.450 mmol,

90%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.30 (s, 3H), 1.59-1.68 (m, 1H), 1.83-1.94 (m, 2H), 2.12-2.18 (m, 1H), 2.31 (app t, *J* = 6.8 Hz, 2H), 2.43 (d, *J* = 14.0 Hz, 1H), 2.84 (d, *J* = 14.0 Hz, 1H), 7.23-7.29 (m, 4H). ¹³CNMR (100 MHz, CDCl₃): δ 22.0, 30.0, 38.0, 40.8, 42.7, 53.1, 127.2, 128.7, 132.1, 145.9, 211.0.



3-Methyl-3-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (2d): Prepared

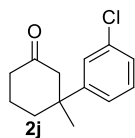
according to General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) 4-trifluoromethylphenylboronic acid (190mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2d** (111 mg, 0.434 mmol, 87%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.33 (s, 3H), 1.58-1.68 (m, 1H), 1.85-1.99 (m, 2H), 2.18-2.23 (m, 1H), 2.31-2.35 (m, 2H), 2.47 (d, *J* = 14.4 Hz, 1H), 2.88 (d, *J* = 14.4 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 22.0, 29.9, 37.9, 40.8, 43.2, 52.9, 124.2 (q, *J* = 270 Hz), 125.6 (q, *J* = 3.0 Hz), 126.1, 128.63 (q, *J* = 33.0 Hz), 151.5, 210.8. ¹⁹F NMR (376.05 MHz, CDCl₃): δ -64.8 (s, 3F).



3-(3-Methoxyphenyl)-3-methylcyclohexan-1-one (2e): Prepared according to

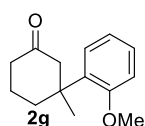
General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) and 3-methoxyphenylboronic acid (152 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2e** (99 mg, 0.454 mmol, 91%) as a clear, yellow oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 3H), 1.64-1.72 (m, 1H), 1.83-1.94 (m, 2H), 2.14-2.20 (m, 1H), 2.31 (app t, *J* = 6.8 Hz, 2H), 2.43 (d, *J* = 14.0 Hz, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 3.80 (s, 3H), 6.75 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.87 (m, 1H), 6.90 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.25

(dd, $J = 8.0, 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 22.1, 29.8, 38.0, 40.9, 42.9, 53.2, 55.2, 111.0, 112.2, 118.1, 129.5, 149.3, 159.7, 211.4.



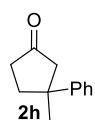
3-(3-Chlorophenyl)-3-methylcyclohexan-1-one (2f): Prepared according to

General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) and 3-chlorophenylboronic acid (156 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2f** (101 mg, 0.455 mmol, 91%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ^1H NMR (400 MHz, CDCl_3): δ 1.29 (s, 3H), 1.62-1.71 (m, 1H), 1.83-1.94 (m, 2H), 2.11-2.18 (m, 1H), 2.31 (app t, $J = 6.8$ Hz, 2H), 2.42 (d, $J = 14.0$ Hz, 1H), 2.82 (d, $J = 14.0$ Hz, 1H), 7.16-7.19 (m, 2H), 7.24 (d, $J = 7.6$, 1H), 7.29 (app t, $J = 2.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 29.6, 37.8, 40.8, 42.9, 53.0, 123.9, 126.0, 126.5, 129.9, 134.6, 149.7, 210.8.



3-(2-Methoxyphenyl)-3-methylcyclohexan-1-one (2g): Prepared according to

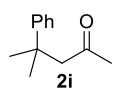
General Procedure A from 3-methylcyclohex-2-en-1-one **1a** (55 mg, 0.50 mmol) and 2-methoxyphenylboronic acid (152 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2g** (37 mg, 0.339 mmol, 34%) as a clear, yellow oil. Characterization data is consistent with previously reported data.⁴ ^1H NMR (400 MHz, CDCl_3): δ 1.40 (s, 3H), 1.60-1.70 (m, 1H), 1.80-1.92 (m, 2H), 2.31 (app t, $J = 6.8$ Hz, 2H), 2.45 (d, $J = 14.4$ Hz, 1H), 2.54-2.61 (m, 1H), 2.99 (d, $J = 14.4$ Hz, 1H), 3.84 (s, 3H), 6.89 (app d, $J = 8.0$ Hz, 2H), 7.20 (app d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 22.2, 26.4, 35.0, 41.0, 42.9, 53.5, 55.0, 111.8, 120.7, 127.5, 127.8, 134.9, 157.9, 212.5.



3-Methyl-3-phenylcyclopentan-1-one (2h): Prepared according to General Procedure

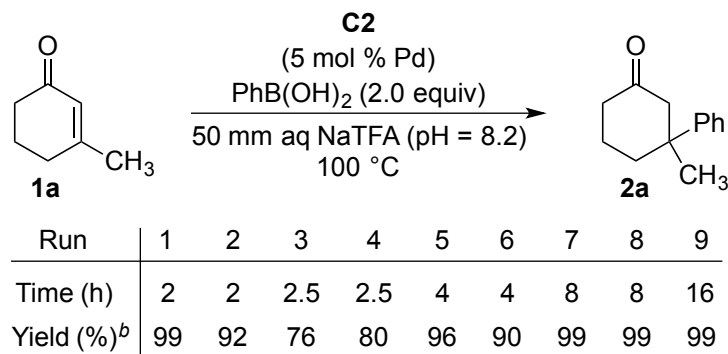
A from 3-methylcyclopent-2-en-1-one **1b** (48 mg, 0.50 mmol) and phenylboronic acid (122 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash

chromatography (90:10 hexane: EtOAc) to yield **2h** (83 mg, 0.476 mmol, 95%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.39 (s, 3H), 2.26-2.44 (m, 4H), 2.48 (d, *J* = 17.2 Hz, 1H), 2.66 (d, *J* = 17.2 Hz, 1H), 7.21-7.25 (m, 1H), 7.29-7.37 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 29.5, 35.8, 36.8, 43.9, 52.3, 125.5, 126.4, 128.6, 148.5, 218.6.



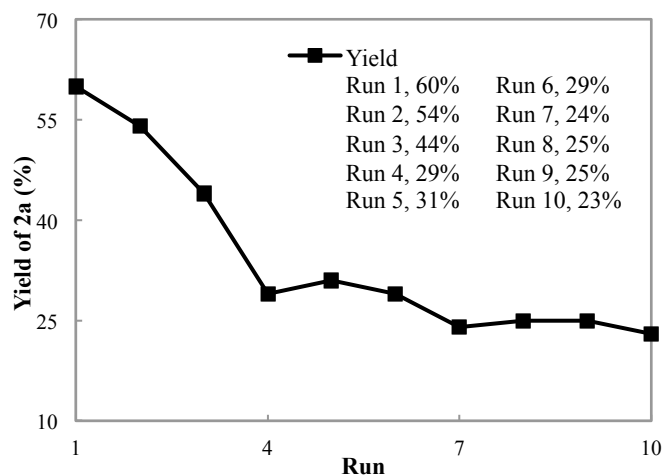
4-Methyl-4-phenylpentan-2-one (2i): Prepared according to General Procedure A from 4-methylpent-3-en-2-one **1c** (49 mg, 0.50 mmol) and phenylboronic acid (122 mg, 1.00 mmol) (reaction time = 16 h). The crude product was purified by flash chromatography (90:10 hexane: EtOAc) to yield **2i** (74 mg, 0.417 mmol, 83%) as a colorless oil. Characterization data is consistent with previously reported data.⁴ ¹H NMR (400 MHz, CDCl₃): δ 1.43 (s, 6H), 1.80 (s, 3H), 2.74 (s, 2H), 7.20 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.31-7.34 (m, 2H), 7.37-7.39 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 29.0, 31.9, 37.4, 57.1, 125.6, 126.0, 128.4, 148.2, 208.2.

Recycling Studies of C2 in Conjugate Addition Phenylboronic Acid to Enone 1a



To a 1 dram vial was added phenylboronic acid (3.00 mmol, 2.00 equiv), MOF-253-Pd(OAc)₂ **C2** (0.075 mmol, 0.050 equiv), enone **1a** (1.5 mmol, 1.00 equiv) and 50 mM aqueous sodium trifluoroacetate solution (1 mL, pH = 8.2). The vial was sealed with a PFTE/silicone-lined septum cap. The reaction mixture was heated to 100 °C and allowed to stir at this temperature (2-16 h). The mixture was allowed to cool to room temperature, diluted with EtOAc (3 mL), and the mixture was centrifuged at 5000 RPM for 5 minutes. The organic layer was separated from the aqueous layer, and the aqueous layer was extracted twice more with EtOAc (3 mL). The combined organics were washed with brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was dissolved in CDCl₃ (0.70 mL) and CH₂Br₂ (52.8 μL, 0.750 mmol) was added as an internal standard. NMR yields were determined by ¹H NMR spectroscopy of the crude reaction mixture. Following the final extraction, the aqueous layer was removed from the vial, and fresh reagents and reaction medium were added to the MOF-253-Pd(OAc)₂ for the next cycle.

Low Conversion Recycling Studies for Conjugate Addition of Phenylboronic Acids to Enone **1a Catalyzed by MOF-253-Pd(OAc)₂ **C2****



To a 1 dram vial was added phenylboronic acid (3.00 mmol, 2.00 equiv), MOF-253-Pd(OAc)₂ **C2** (0.075 mmol, 0.050 equiv), enone **1a** (1.5 mmol, 1.00 equiv) and 50 mM aqueous sodium trifluoroacetate solution (1 mL, pH = 8.2). The vial was sealed with a PFTE/silicone-lined septum cap. The reaction mixture was heated to 100 °C and allowed to stir at this temperature for 1 hour. The mixture was allowed to cool to room temperature, diluted with EtOAc (3 mL), and the mixture was centrifuged at 5000 RPM for 5 minutes. The organic layer was separated from the aqueous layer, and the aqueous layer was extracted twice more with EtOAc (3 mL). The combined organics were washed with brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was dissolved in CDCl₃ (0.70 mL) and CH₂Br₂ (52.8 μL, 0.750 mmol) was added as an internal standard. NMR yields were determined by ¹H NMR spectroscopy of the crude reaction mixture. Following the final extraction, the aqueous layer was removed from the vial, and fresh reagents were added to the MOF-253-Pd(OAc)₂ for the next cycle.

Leaching Test for Conjugate Addition of Phenylboronic Acid to Enone **1a Catalyzed by MOF-253-Pd(OAc)₂ **C2****

To a 1 dram vial was added phenylboronic acid (3.00 mmol, 2.00 equiv), MOF-253-Pd(OAc)₂ **C2** (0.075 mmol, 0.050 equiv), and 50 mM aqueous sodium trifluoroacetate solution (1 mL, pH = 8.2). The vial was sealed with a PTFE/silicone-lined septum cap. The reaction mixture was heated to 100 °C and allowed to stir at this temperature for 2 hours. The mixture was centrifuged at 5000 RPM for 1 minute and the aqueous layer was immediately removed from the reaction mixture and added to a new vial containing fresh phenylboronic acid (3.00 mmol, 2.00 equiv), and enone **1a** (1.50 mmol, 1.00 equiv). This vial was stirred at 100 °C for 2 hours. The mixture was allowed to cool, diluted with EtOAc (3 mL), and the mixture centrifuged at 5000 RPM for 5 minutes. The organic layer was separated from the aqueous layer, and the aqueous layer was extracted twice more with EtOAc (3 mL). The combined organics were washed with brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was dissolved in CDCl₃ (0.70 mL) and CH₂Br₂ (52.8 μL, 0.750 mmol) was added as an internal standard. The yield of ketone **2a** was determined to approximately 1% by ¹H NMR spectroscopy.

ICP-MS Leaching Test for Conjugate Addition of Phenylboronic Acids to Enone **1a Catalyzed by MOF-253-Pd(OAc)₂ **C2****

To a 1 dram vial was added phenylboronic acid (3.00 mmol, 2.00 equiv), MOF-253-Pd(OAc)₂ **C2** (0.075 mmol, 0.050 equiv), and 50 mM aqueous sodium trifluoroacetate solution (1 mL, pH = 8.2). The vial was sealed with a PTFE/silicone-lined septum cap. The reaction mixture was heated to 100 °C and allowed to stir at this temperature for 2 hours. The mixture was centrifuged at 5000 RPM for 1 minute and the aqueous layer was immediately removed from the mixture.

ICP-MS analysis was performed to determine Pd content revealing 16 µg (0.6% of the original palladium content in the reaction) had leached into the aqueous supernatant.

References

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