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Supporting Information for:

Chelation-directed C-H activation/C-C bond forming reactions catalyzed by Pd(II) nanoparticles supported on multiwalled carbon nanotubes

Table of Contents:

I.	General Procedures	2
П.	Synthesis of solid-supported Pd(II)/MWCNT catalyst	2
III.	Synthesis of the $[Ph_2I]BF_4$ Arylation Reagent	4
IV.	C-H activation/C-C bond forming reactions with the $[Ph_2I]BF_4$ Arylation Reagent	5
V.	Synthesis of [Mes-I-Ar] Arylation Reagent	8
VI.	C-H activation/C-C bond forming reactions with [Mes-I-Ar] Arylation Reagents	. 12
VII.	Procedure for Recycling Experiments	. 18
VIII.	. Procedure for Residual Palladium Measurement Experiment	. 18
IX.	Procedure for Hot Filtration Experiment	. 19
Х.	Calculation of Turnover Frequencies (TOF)	. 19
XI.	Scale up of reactions with heterogeneous catalyst	. 20
XII.	References	. 20
XIII.	NMR Spectra	. 21

I. General Procedures

All the reactions were carried out in vials sealed with Teflon lined caps under ambient atmosphere. Palladium (II) acetate (98% reagent grade) and multi-walled carbon nanotubes (cat. #: 724769) were purchased from Sigma-Aldrich. Substrates, boronic acids, and PhI(OAc)₂ were purchased from Sigma-Aldrich, TCI, or Chem-Impex. All solvents were purchased from VWR and other chemicals were purchased from Sigma-Aldrich and all were used without distillation or purification. Analytical Thin Layer Chromatography (TLC) was performed using silica gel GHLF plates (Analtech Inc., DE, USA). Flash chromatography was performed on TELEDYNE ISCO CombiFlash® Rf instrument using RediSep Rf Normal-phase Flash Columns (4-gm, 12-gm, 24-gm or 40-gm). NMR spectra were recorded on a Bruker 400 MHz instrument operating at 400 MHz for ¹H and 125 MHz for ¹³C acquisitions. Electrospray ionization (ESI) mass spectra were obtained from Perkin Elmer Flexar UPLC/AxION2 TOF Mass Spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 using a monochromatic AI KR X-ray. The Pd content in the Pd nanoparticles supported on carbon nanotubes before and after reaction was determined using an Inductively Coupled Plasma equipped with Mass Spectrometry (ICP-MS, Varian 820-MS).

II. Synthesis of solid-supported Pd(II)/MWCNT catalyst

Palladium (II) acetate (0.110 g, 0.49 mmol) and multi-walled carbon nanotubes (0.500 g) were loaded in a 45 ml zirconia grinding vial. Two 12.77 mm diameter zirconia balls are also placed in the vial before sealing. The container is then placed in an 8000 M Spex Mixer/Mill. The contents in the mixer were shaken back and forth 5.9 cm and

side-to-side 2.5 cm for 10 minutes at room temperature at 115 volts (1060 cycles/minute). The resulting solid was collected, characterized by XPS (see below), and used directly in reactions.

XPS Analysis of solid-supported Pd(II)/MWCNTs





B. XPS of catalysts after use in reactions



C. Pd(II)/Pd(0) rations of catalyst before and after reactions

	Pd(II)	Pd(0)
Before Reaction	40.18%	59.82%
After Reaction	57.68%	42.32%

While the catalyst used in this study is a mixture of Pd(II) and Pd(0), we have named it the "Pd(II)/MWCNT" catalyst because we believe that Pd(II) is the active metal for the C-H activation/C-C bond forming reactions. Pd(0) has not been reported to catalyze these oxidative types of reactions and the Pd(0) content decreases after the reaction and is converted to Pd(II). While it is possible that Pd(0) is contributing in some manner to the reactions reported here, Pd(II) is likely the active catalyst.

III. Synthesis of the [Ph₂I]BF₄ Arylation Reagent



Diphenyliodonium tetrafluoroborate ([Ph₂I]BF₄)¹: Under nitrogen, phenylboronic acid (0.4 mmol) was dissolved in DCM (0.1 M), cooled to 0 °C. To this, BF₃OEt₂ (0.4 mmol) was added. The reaction mixture was stirred at 0 °C for 15 min. This was followed by the addition of diacetoxyiodobenzene (0.4 mmol) dissolved in DCM (0.1 M) to the above reaction mixture. It was stirred at 0 °C for 1.5 h under nitrogen. To this, saturated solution of aqueous NaBF₄ (1.5 mL) was added, the reaction was stirred for 30 min. The reaction mixture was extracted with DCM, washed with water and filtered over MgSO₄. The organic layer was dried, washed with hexanes:DCM (3:1). The precipitate was collected, washed with hexanes and dried to afford pure product in 84% yield (119.5 mg, 0.3 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.24 (d, *J* = 7.56 Hz, 4H), 7.66 (t, *J* = 7.45 Hz, 2H), 7.53 (t, *J* = 7.76 Hz, 4H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 135.12, 132.02, 131.73, 116.44.

IV. C-H activation/C-C bond forming reactions with the [Ph₂I]BF₄ Arylation Reagent

General Procedure A for arylation using [Ph₂I]BF₄: Substrate (0.05 mmol) was added to acetic-acid (0.12 M) followed by the addition of arylating agent [Ph₂I]BF₄ (0.08 mmol) and Pd(II)-MWCNT catalyst (5 mol%). The reaction mixture was heated at 100 °C for 3 h. It was then cooled to room temperature, diluted with DCM, washed with saturated aqueous NaHCO₃, brine, and filtered over celite and MgSO₄. The organic layer was dried and purified over silica using 20% EtOAc-hexanes unless otherwise noted.



2-([1,1'-biphenyl]-2-yl)-3-methylpyridine (1a)²: General procedure A was followed on substrate 3-methyl-2-phenylpyridine (**1**), and purified using 5% EtOAc-DCM to afford the product in 90% yield (19.5 mg, 0.08 mmol). ¹H NMR (400 MHz, (CDCl₃) δ 8.49 (dd, J = 4.9 Hz, 1H), 7.42-7.50 (m, 3H), 7.38-7.41 (m, 1H), 7.28-7.30 (m, 1H), 7.08-7.17 (m, 6H), 1.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.63, 146.65, 141.28, 140.87, 139.58, 137.64, 131.82, 130.04, 129.87, 129.43, 128.51, 127.93, 127.57, 126.78, 122.24, 18.95.



1-(2-(pyridin-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (2a)³: General procedure A was followed on substrate 1-(3-(pyridin-2-yl)phenyl)ethan-1-one (**2**) to afford the product in 80% yield (11.1 mg, 0.04 mmol). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.60-8.62 (m, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.10 (dd, *J* = 8.1Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (td, *J* = 7.7 Hz, 1H), 7.27-7.30 (m, 3H), 7.21-7.25 (m, 1H) 7.17-7.19 (m, 2H), 6.98 (dt, *J* =

7.9 Hz, 1H), 2.66 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 197.49, 159.32, 150.40, 145.86, 141.48, 140.98, 137.27, 136.30, 131.67, 131.50, 130.25, 129.07, 128.79, 128.22, 125.91, 122.73, 26.81.

1-(7-phenylindolin-1-yl)ethan-1-one (3a)³: General procedure A was followed on substrate 1-(indolin-1-yl)ethan-1-one (**3**), using a mixture of 1:1 CH₃COOH: (CH₃CO)₂CO as the solvent, and purified using 10% acetone-EtOAc to afford the product in 27% yield (6 mg, 0.03 mmol). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.38-7.48 (m, 4H), 7.16-7.31 (m, 4H), 4.24 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.76 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 142.25, 141.63, 137.65, 129.75, 129.64, 128.17, 127.75, 125.98, 124.63, 51.16, 22.82.



1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one (4a)⁴: General procedure A was followed on substrate 1-phenylpyrrolidin-2-one (**4**), and purified using 10% acetone-EtOAc to afford the product in 32% yield (7 mg, 0.03 mmol). ¹H NMR (400 MHz, (CDCl₃) δ 7.31-7.42 (m, 9H), 3.21 (t, *J* = 6.7 Hz, 2H), 2.41 (t, *J* = 7.9 Hz, 2H), 1.83-1.90 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 175.72, 139.87, 139.36, 136.58, 131.01, 128.71, 128.56, 128.17, 127.73, 50.35, 31.35, 29.85, 19.15.



10-phenylbenzo[*h*]**quinoline** (5a)⁵: General procedure A was followed on substrate benzo[h]quinolone (5) to afford the product in 19% yield (4.3 mg, 0.02 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.43 (m, 1H), 8.09 (dd, *J* = 8.08 Hz, 1H), 7.92 (d, *J* = 8.39 Hz, 1H), 7.86 (d, *J* = 8.63 Hz, 1H), 7.69 (d, *J* = 7.93 Hz, 2H), 7.55 (dd, *J* = 7.23 Hz, 1H), 7.31-7.40 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 148.85, 146.43, 147.75, 135.14, 134.99, 131.46, 129.05, 128.72, 128.27, 127.91, 127.33, 127.22, 127.00, 125.90, 125.64, 121.03.

V. Synthesis of [Mes-I-Ar] Arylation Reagent

General procedure B for the synthesis of asymmetrical arylating agents: Under nitrogen, substituted phenylboronic acid (0.7 mmol) was suspended/dissolved in DCM (0.1 M), cooled to 0 °C. To this, BF_3OEt_2 (0.8 mmol) was added. The reaction mixture was stirred at 0 °C for 15 min. This was followed by the addition of iodomesitylene diacetate (0.8 mmol) dissolved in DCM (0.3 M) to the above reaction mixture. It was warmed to room temperature, and stirred for 2 h under nitrogen. To this, saturated solution of aqueous NaBF₄ (3.0 mL) was added, the reaction was stirred for 30 min. The reaction mixture was extracted with DCM, washed with water, filtered over MgSO₄. Organic layer was dried, washed with Et₂O to afford pure product.



Mesityl(p-tolyl)iodonium tetrafluoroborate ([Mes-I-*p*-Me-Ph]BF₄)⁶: General procedure B was followed on substrate 4-tolyl boronic acid to afford the product in 70% yield (217.2 mg, 0.51 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 7.85 (d, J = 8.36 Hz, 2H), 7.30 (d, J = 8.44 Hz, 2H), 7.20 (s, 2H), 2.59 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 142.99, 142.23, 141.44, 134.43, 132.45, 129.71, 122.68, 110.83, 26.24, 20.73, 20.45.



(4-fluorophenyl)(mesityl)iodonium tetrafluoroborate ([Mes-I-*p*-F-Ph]BF₄)⁶: General procedure B was followed on substrate 4-fluorophenyl boronic acid to afford the product in 75% yield (229.6 mg, 0.54 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.02-8.04 (m, 2H), 7.36 (t, *J* = 8.91 Hz, 2H), 7.21 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 143.16, 141.47, 137.21, 137.12, 129.77, 122.94, 119.31, 119.08, 108.62, 30.62, 26.22, 20.47.



Mesityl(4-methoxyphenyl)iodonium tetrafluoroborate ([Mes-I-*p***-OMe-Ph]BF₄)⁷: General procedure B was followed on substrate 4-methoxyphenyl boronic acid to afford the product in 85% yield (251.2 mg, 0.57 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) \delta 7.91 (d,** *J* **= 9.1 Hz, 2H), 7.19 (s, 2H), 7.03 (d,** *J* **= 9.25 Hz, 2H), 3.78 (s, 3H), 2.60 (s, 6H), 2.29 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) \delta 161.69, 142.83, 141.27, 136.46, 129.62, 123.01, 117.47, 103.32, 55.63, 26.17, 20.41.**



(4-Ethoxyphenyl)(mesityl)iodonium tetrafluoroborate ([Mes-I-*p*-OEt-Ph]BF₄): General procedure B was followed on substrate 4-ethoxyphenyl boronic acid to afford the product in 95% yield (142.1 mg, 0.31 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 7.66 (d, *J* = 9.35 Hz, 2H), 7.26 (s, 1H), 7.09 (s, 2H), 6.91 (d, *J* = 9.39 Hz, 2H), 4.02 (q, *J* = 7.18 Hz, 6.93 Hz, 2H), 2.65 (s, 6H), 2.35 (s, 3H), 1.39 (t, *J* = 6.97 Hz, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 160.99, 142.85, 141.29, 136.48, 129.64, 123.04, 117.86, 103.15, 63.75, 26.19, 20.43, 14.30. HRMS [C₁₇H₂₀IO]⁺ Expected:367.0553, Found: 367.0544



Mesityl(4-nitrophenyl)iodonium tetrafluoroborate ([Mes-I-*p*-NO₂-Ph]BF₄): General procedure B was followed on substrate 4-nitrophenyl boronic acid. The isolated product was used directly in the arylation reaction. ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.15-8.27 (m, 4H), 7.97(d, *J* = 8.19 Hz, 2H), 7.56 (d, *J* = 8.64 Hz, 2H), 7.25 (s, 2H), 2.59 (s, 6H), 2.31 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 149.23, 143.49, 141.67, 135.35, 132.12, 129.91, 126.16, 122.91, 121.09, 120.96, 26.24, 20.48. HRMS [C₁₅H₁₅INO₂]⁺ Expected:368.0142, Found: 368.0131.



Mesityl(2-nitrophenyl)iodonium tetrafluoroborate ([Mes-I-*m***-NO₂-Ph]BF₄):** General procedure B was followed on substrate 2-nitrophenyl boronic acid to afford the product in 79% yield (241 mg, 0.53 mmol). ¹H NMR (400 MHz, $(CD_3)_2SO$) δ 8.59 (d, *J* = 8.09 Hz, 1H), 7.79-7.90 (m, 2H), 7.41 (s, 2H), 7.03 (d, *J* = 8.04 Hz, 1H), 2.56 (s, 6H), 2.42 (s, 3H); ¹³C NMR (125 MHz, $(CD_3)_2SO$) δ 145.93, 144.72, 142.95, 138.08, 132.23, 130.41, 130.22, 127.87, 120.58, 108.39, 26.15, 20.72. HRMS [C₁₅H₁₅INO₂]⁺ Expected:368.0142, Found: 368.0132



Mesityl(2-nitrophenyl)iodonium tetrafluoroborate ([Mes-I-o-NO₂-Ph]BF₄)⁸: General procedure B was followed on substrate 3-nitrophenyl boronic acid. The isolated product was used directly in the arylation reaction. ¹H NMR (400 MHz, $(CD_3)_2SO$) δ 8.83 (t, J = 2.01 Hz, 1H), 8.40-8.43 (m 1H), 8.18 (d, J = 8.7 Hz, 1H), 8.10 (d, J = 1.95 Hz, 1H), 7.90-7.93 (m, 1H), 7.33-7.77 (m, 2H), 7.40 (t, J = 7.82 Hz, 1H), 7.27 (s, 2H), 2.60 (s, 6H), 2.32 (s, 3H). ¹³C NMR (125 MHz, $(CD_3)_2SO$) δ 148.56, 143.59, 141.86, 139.68, 138.17, 132.92, 129.95, 128.89, 127.76, 126.42, 125.21, 122.67, 120.16, 114.14, 26.34, 20.55.



(4-Formylphenyl)(mesityl)iodonium tetrafluoroborate ([Mes-I-*p*-CHO-Ph]BF₄): General procedure B was followed on substrate 4-formylphenyl boronic acid to afford the product in 69% yield (101 mg, 0.23 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 10.00 (s, 1H), 8.15 (d, *J* = 8.48 Hz, 2H), 7.95 (d, *J* = 8.48 Hz, 2H), 7.24 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 192.32, 143.27, 141.58, 137.74, 134.85, 131.85, 129.83, 122.91, 120.71, 26.24, 20.46. HRMS [C₁₆H₁₆IO]⁺ Expected:351.0240, Found: 351.0236.



(2-Formylphenyl)(mesityl)iodonium tetrafluoroborate ([Mes-I-o-CHO-Ph]BF₄): General procedure B was followed on substrate 2-formylphenyl boronic acid to afford the product in 30% yield (86 mg, 0.2 mmol. ¹H NMR (400 MHz, $(CD_3)_2SO$) δ 10.32 (s, 1H), 8.43 (dd, *J* = 7.5 Hz, 1H), 7.91 (td, *J* = 7.28 Hz, 1H), 7.79 (td, *J* = 7.85 Hz, 1H), 7.39 (s, 2H), 6.90 (d, *J* = 8.29 Hz, 1H), 3.32 (s, 9H), 2.42 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 195.04, 144.41, 143.05, 138.48, 138.41, 132.97, 131.57, 130.05, 128.92, 116.99, 110.14, 25.99, 20.68. HRMS $[C_{16}H_{16}IO]^{+}$ Expected:351.0240, Found: 351.0229

VI. C-H activation/C-C bond forming reactions with [Mes-I-Ar] Arylation Reagents

General procedure C for arylation using asymmetrical arylating agents: Substrate (0.05 mmol) was added to acetic-acid (0.12 M) followed by the addition of asymmetrical arylating agent [Mes-I-Ar]BF₄ (0.08 mmol) and Pd(II)-MWCNT catalyst (5 mol%). The reaction mixture was heated at 100 °C for 3 h. It was then cooled to room temperature, diluted with DCM, washed with saturated aqueous NaHCO₃, brine, and filtered over celite and MgSO₄. The organic layer was dried and purified over silica using 20% EtOAc-hexanes unless otherwise noted.



3-methyl-2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine (1b)³: General procedure C was followed on substrate 3-methyl-2-phenylpyridine (1), using [Mes-I-*p*-Me-C₆H₅]BF₄ to afford the product in 87% yield (20 mg, 0.08 mmol). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.43 (dd, J = 4.9 Hz, 1H), 7.38-7.49 (m, 4H), 7.32-7.34 (m, 1H), 7.15 (q, 1H), 6.98-7.03 (m, 4H), 2.66 (s, 3H), 1.74 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 160.66, 147.33, 141.47, 140.83, 139.27, 138.04, 137.09, 132.10, 130.86, 130.35, 129.92, 129.36, 129.02, 127.82, 123.02, 20.99, 19.00.



2-(4'-fluoro-[1,1'-biphenyl]-2-yl)-3-methylpyridine (1c)³: General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*p*-F-C₆H₅]BF₄ to afford the product in 79% yield (18.5 mg, 0.07 mmol). ¹H NMR (400 MHz, (CD₃)₂CO) δ 8.43 (dd, *J* = 4.99 Hz, 1H), 7.42-7.52 (m, 4H), 7.34-7.37 (m, 1H), 7.13-7.19 (m, 3H), 6.92-6.97 (m, 2H), 1.78 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 163.94, 161.51, 160.26, 147.40, 140.88, 140.50, 138.43, 138.22, 132.12, 131.96, 131.88, 130.86, 130.39, 129.14, 128.23, 123.17, 115.51, 115.30, 18.97.



2-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-methylpyridine (1d)⁹: General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*m*-NO₂-C₆H₅]BF₄ to afford the product in 33% yield (8.1 mg, 0.03 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (dd, *J* = 5.09 Hz, 1H), 7.38-7.46 (m, 4H), 7.31 (dd, *J* = 8.1 Hz, 1H), 7.10 (q, 1H), 7.02-7.04 (m, 2H), 6.69-6.71 (m, 2H), 3.75 (s, 3H), 1.75 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.81, 158.63, 146.65, 140.46, 139.41, 137.74, 133.75, 131.86, 130.49, 130.03, 129.71, 128.50, 127.18, 122.21, 113.48, 55.29, 18.95.



2-(4'-ethoxy-[1,1'-biphenyl]-2-yl)-3-methylpyridine (1e): General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*p*-OEt-C₆H₅]BF₄ to afford the product in 79% yield (20.3 mg, 0.07 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 4.85 Hz, 1H), 7.37-7.47 (m, 4H), 7.30 (d, *J* = 7.59 Hz, 1H), 7.10 (q, 1H), 7.01 (d, *J* = 8.64 Hz, 2H), 6.68 (d, *J* = 8.64 Hz, 2H), 3.96 (q, *J* = 6.9 Hz, 7.1 Hz, 2H), 1.74 (s, 3H), 1.38 (t, *J* = 7.01 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.85, 157.99, 146.66, 140.51, 139.44, 137.67, 133.60, 131.83, 130.46, 130.01, 129.67, 128.46, 127.12, 122.17, 114.01, 63.45, 18.93, 14.96. HRMS C₂₀H₁₉NO [M+H]⁺ Expected: 290.1540, Found: 290.1563.



3-methyl-2-(4'-nitro-[1,1'-biphenyl]-2-yl)pyridine (1f): General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*p*-NO₂-C₆H₅]BF₄ to afford the product in 61% yield (15.6 mg, 0.05 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.47 (dd, *J* = 4.96 Hz, 1H), 8.03 (dt, *J* = 8.95 Hz, 2H), 7.43-7.54 (m, 4H), 7.36 (d, *J* = 7.53 Hz, 1H), 7.26-7.29 (m, 2H), 7.14 (q, 1H), 1.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.49, 147.96, 146.81, 146.61, 139.58, 138.49, 137.85, 131.45, 130.16, 130.01, 129.56, 128.79, 128.64, 123.07, 122.56, 18.85. HRMS C₁₈H₁₄N₂O₂ [M+H]⁺ Expected: 291.1128, Found: 291.1110.



3-methyl-2-(3'-nitro-[1,1'-biphenyl]-2-yl)pyridine (1g)¹⁰: General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*m*-NO₂-C₆H₅]BF₄ to afford the product in 69% yield (17.7 mg, 0.06 mmol). ¹H NMR (400 MHz, CDCl₃) *δ* 8.48 (dd, J = 4.94 Hz, 1H), 8.01-8.05 (m, 2H), 7.41-7.55 (m, 5H), 7.37 (d, J = 7.7 Hz, 1H), 7.31 (td, J = 7.9 Hz, 1H), 7.13 (q, 1H), 1.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) *δ* 158.58, 148.10, 146.93, 142.88, 139.63, 138.42, 138.08, 135.45, 131.66, 130.23, 129.78, 128.92, 128.81, 128.76, 1224.17, 122.73, 121.78, 19.03. HRMS C₁₈H₁₄N₂O₂ [M+H]⁺ Expected: 291.1128, Found: 291.1108.



3-methyl-2-(2'-nitro-[1,1'-biphenyl]-2-yl)pyridine (1h): General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*m*-NO₂-C₆H₅]BF₄ to afford the product in 58% yield (14.9 mg, 0.05 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, J = 4.7 Hz, 1H), 7.72 (dd, J = 8.1 Hz, 1H), 7.29-7.49 (m, 8H), 7.03 (q, 1H), 2.09 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.59, 148.95, 146.21, 138.33, 137.16, 136.06, 133.64, 132.41, 132.03, 129.92, 129.67, 128.44, 128.10, 127.96, 124.09, 122.31, 19.10. HRMS C₁₈H₁₄N₂O₂ [M+H]⁺ Expected: 291.1128, Found: 291.1141.



2'-(3-methylpyridin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (1i)¹⁰: General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*p*-CHO-C₆H₅]BF₄ to afford the product in 77% yield (18.5 mg, 0.07 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.94 (s, 1H), 8.47 (dd, *J* = 4.90 Hz, 1H), 7.68 (d, *J* = 8.53 Hz, 2H), 7.42-7.52 (m, 4H), 7.33 (d, *J* = 7.86 Hz, 1H), 7.28 (d, *J* = 8.13 Hz, 2H), 7.12 (q, 1H), 1.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 192.07, 158.90, 147.65, 146.78, 139.58, 137.95, 134.78, 131.74, 130.26, 130.03, 129.75, 129.40, 128.72, 128.55, 122.58, 18.97. HRMS C₁₉H₁₅NO [M+H]⁺ Expected: 274.1227, Found: 274.1253.



2'-(3-methylpyridin-2-yl)-[1,1'-biphenyl]-2-carbaldehyde (1j): General procedure C was followed on substrate 3-methyl-2-phenylpyridine (**1**), using [Mes-I-*m*-NO₂-C₆H₅]BF₄ to afford the product in 18% yield (2.8 mg, 0.01 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.94 (s, 1H), 8.34 (s, 1H), 7.82 (d, *J* = 7.75 Hz, 1H), 7.30-7.54 (m, 7H), 7.18 (d, *J* = 7.58 Hz, 1H), 7.00-7.03 (m, 1H), 1.91 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 192.02, 158.19, 146.63, 144.72, 140.62, 137.81, 137.04, 133.98, 132.82, 131.57, 131.41, 129.90, 128.50, 128.10, 127.69, 126.95, 122.43, 29.85, 19.14. HRMS C₁₉H₁₅NO [M+H]⁺ Expected: 274.1227, Found: 274.1246.



10-(p-tolyl)benzo[*h*]**quinoline (5b)**¹¹: General procedure C was followed on substrate benzo[h]**quinolone (5)** to afford the product in 15% yield (3.6 mg, 0.013 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.43 (m, 1H), 8.09 (dd, *J* = 8.08 Hz, 1H), 7.92 (d, *J* = 8.39 Hz, 1H), 7.86 (d, *J* = 8.63 Hz, 1H), 7.69 (d, *J* = 7.93 Hz, 2H), 7.55 (dd, *J* = 7.23 Hz, 1H), 7.31-7.40 (m, 6H); ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.38 (dd, *J* = 4.19 Hz 1H), 8.32 (dd, *J* = 8.23 Hz, 1H), 8.06 (dd, *J* = 8.08 Hz, 1H), 8.00 (d, *J* = 8.68 Hz, 1H), 7.88 (d, *J* = 8.83 Hz, 1H), 7.73 (t, *J* = 7.53 Hz, 1H), 7.43-7.48 (m, 2H), 7.14-7.15 (m, 4H), 2.39 (s, 3H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 146.72, 142.99, 141.02, 135.56, 134.68, 134.29, 131.39, 128.32, 128.11, 127.90, 127.84, 127.16, 126.89, 126.08, 121.48, 20.83.



10-(4-florophenyl)benzo[*h*]**quinoline (5c)**¹²: General procedure C was followed on substrate benzo[h]**quinolone (5)** to afford the product in 35% yield (8.3 mg, 0.03 mmol). ¹H NMR (400 MHz, (CD₃)₂SO) δ 8.40 (dd, *J* = 4.43 Hz 1H), 8.34 (dd, *J* = 7.97 Hz, 1H), 8.08 (dd, *J* = 8.35 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.85 Hz, 1H), 7.75 (t, *J* = 7.35 Hz, 1H), 7.46-7.49 (m, 2H), 7.15-7.28 (m, 4H); ¹³C NMR (125 MHz, (CD₃)₂SO) δ 161.96, 159.57, 146.85, 145.78, 142.14, 142.11, 139.89, 135.70, 134.65, 131.27, 130.19, 130.11, 128.30, 128.11, 127.21, 126.98, 126.22, 121.58, 114.05, 113.84.

VII. Procedure for Recycling Experiments

To a solution of 2-phenyl-3-methylpyridine (14.9 mg, 0.088 mmol) in acetic acid (0.74 mL) in 10 mL reaction vial, was added [Ph₂I]BF₄ (38 mg, 0.103 mmol) and Pd(II)/MWCNT (5 mg, 5 mol%). The vial was sealed and the reaction mixture was heated at 100 °C for 12 hours. Upon the completion of the reaction period, the mixture was diluted with 2 mL acetic acid and shaken. The entire mixture was centrifuged and the solvent above the Pd/MWCNT nanoparticles was decanted. The washing and centrifugation were repeated for two additional times to ensure the removal of the organic products from the surface of the catalyst. The Pd/MWCNT nanoparticles was then reused for the subsequent reaction using fresh reagents (2-phenyl-3-methylpyridine, [Ph₂I]BF₄, and acetic acid). This procedure was applied for each recycling experiment and the percent conversion to the products was determined by GC-MS.

VIII. Procedure for Residual Palladium Measurement Experiment

To a solution of 2-phenyl-3-methylpyridine (14.9 mg, 0.088 mmol) in acetic acid (0.74 mL) in 10 mL reaction vial, was added [Ph₂I]BF₄ (38 mg, 0.103 mmol) and Pd(II)/MWCNT (5 mg, 5 mol%). The vial was sealed and the reaction mixture was heated at 100 °C for 12 hours. Upon the completion of the reaction period, the reaction mixture was then hot filtered over celite and the filtrate solution was subjected to ICP-MS analysis. The amount of Pd content was determined to be 38.4 ppm. This amount of palladium is 5.6% of the total palladium loaded on the surface of the catalyst (calculated as 686.5 ppm, based on 5 mol% loading of 10 wt% catalyst).

IX. Procedure for Hot Filtration Experiment

To a solution of 2-phenyl-3-methylpyridine (14.9 mg, 0.088 mmol) in acetic acid (0.74 mL) in 10 mL reaction vial, was added [Ph₂I]BF₄ (38 mg, 0.103 mmol) and Pd(II)/MWCNT (5 mg, 5 mol%). The vial was sealed and the reaction mixture was heated at 100 °C for 12 hours. Upon the completion of the reaction period, the reaction mixture was then hot filtered over celite and percent conversion was measured by GC-MS. Fresh reagents [2-phenyl-3-methylpyridine (14.9 mg, 0.088 mmol), [Ph₂I]BF₄ (38 mg, 0.103 mmol)] were added to the filtrate solution, the mixture was heated at 100 °C for additional 12 hours. No further catalytic activity was observed in this mixture by GC-MS spectroscopy.

X. Calculation of Turnover Frequencies (TOF)

Turnover frequencies (TOF) were calculated as moles of product/moles of Pd(II)/hour. For the solidsupported catalyst, the moles of Pd(II) were calculated using the catalyst loading and the XPS data (Before Reaction) in Section II.

To allow a direct comparison with the reactions using homogeneous catalyst and substrates **1** and **2** were repeated at different time points than reported in the literature:

Substrate **1** (0.015 g, 0.09 mmol) was added to acetic-acid (0.74 ml, 0.12 M) followed by the addition of arylating agent [Ph₂I]BF₄ (0.038 g, 0.10 mmol) and Pd(OAc)₂ catalyst (1 mg, 5 mol%). The reaction mixture was heated at 100 °C for 3 h. It was then cooled to room temperature, diluted with DCM, washed with saturated aqueous NaHCO3, brine, and filtered over celite and MgSO4. The organic layer was dried and purified over silica using 5% EtOAc-DCM to afford the product in 88% yield (19 mg, 0.08 mmol). The TOF was calculated as described above (see Table 4, entry 1).

Substrate **2** (0.010 g, 0.05 mmol) was added to acetic-acid (0.44 ml, 0.12 M) followed by the addition of arylating agent $[Ph_2I]BF_4$ (0.028 g, 0.08 mmol) and $Pd(OAc)_2$ catalyst (0.6 mg, 5 mol%). The reaction mixture was heated at 100 °C for 24 h. It was then cooled to room temperature, diluted with DCM,

washed with saturated aqueous NaHCO3, brine, and filtered over celite and MgSO4. The organic layer was dried and purified over silica using 20% EtOAc-hexanes to afford the product in 80% yield (11 mg, 0.04 mmol). The TOF was calculated as described above (see Table 4, entry 2).

XI. Scale up of reactions with heterogeneous catalyst

To demonstrate that the catalysts can be used on larger scale, scale-up experiments were performed on substrate $\mathbf{1}$ with two different arylating reagents:



2-([1,1'-biphenyl]-2-yl)-3-methylpyridine (1a): General procedure A was followed on substrate 3methyl-2-phenylpyridine (**1**, 250 mg, 1.47 mmol), and purified using 5% EtOAc-DCM to afford the product in 89% yield (322 mg, 1.31 mmol).



3-methyl-2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine (1b): General procedure C was followed on

substrate 3-methyl-2-phenylpyridine (1, 250 mg, 1.47 mmol), using [Mes-I-p-Me-C₆H₅]BF₄, and

purified using 20% EtOAc-hexanes to afford the product in 85% yield (324 mg, 1.25 mmol).

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XIII. NMR Spectra





































































































