Supporting Information

[Electronic Supplementary Information to accompany] Highly Active, Separable and Recyclable Bipyridine Iridium Catalysts for C-H Borylation Reactions

Hind Mamlouk,¹ Jakkrit Suriboot,² Praveen Kumar Manyam,¹ Ahmed AlYazidi,¹ David Bergbreiter^{2,*} and Sherzod T. Madrahimov^{1,*}

¹Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar ²Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

* <u>bergbreiter@chem.tamu.edu;</u> * <u>sherzod.madrahimov@qatar.tamu.edu</u>,

Table of Contents

S1.	General information	<i>S1</i>
S2.	General procedures for direct C-H borylation of arenes	<i>S2</i>
S3.	Catalyst recycling and ICP-OES analysis of Iridium PIB ₁₀₀₀ -bpy –catalyst	S26
S4.	References	S27

S1. General information

All reactions involving air and moisture sensitive conditions were carried out in a glovebox under argon atmosphere. Heptane was dried on activated 4Å molecular sieves before use. Arenes, pinacolatodiboron and all iridium precursors were purchased from Sigma-Aldrich and used without further purification. PIB₁₀₀₀-bpy ligand was prepared according to a previously reported procedure (S1). The ¹H NMR spectrum of PIB₁₀₀₀-bpy is shown below in Figure 1. All glassware was oven-dried before use.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 and 600 (400 MHz for ¹H, 101 MHz for ¹³C and 600 MHz for ¹H and 151 MHz for ¹³C) spectrometer and referenced to the residual solvent peak. ¹H NMR data are reported as follows: chemical shift (multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet and m = multiplet), coupling constant and integration). ¹H and ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was conducted on a Thermo ICPi 6500 that is equipped to cover the spectral range from 175 to 785 nm. Samples (5 mg) were digested by heating at 150° C in 1mL of conc. HNO₃ in a microwave reactor for 20 min, followed by addition of 1 mL of conc. H₂SO₄ and further heating at 150° C in a microwave reactor for 20 min whereupon the solution became clear. The clear solution was diluted to 10 mL with distilled water in a 10 mL volumetric flask and the iridium content of this solution was measured at emission wavelengths of 205.2, 212.6, and 224.2 nm. The iridium content was then estimated based on the calibration curve with an R² value of 0.999 obtained from standardized solutions containing 5, 10, 15, 20, 25, 30, 35, 40, and 50 ppm of Ir (prepared from commercially available ICP standard solutions). The same procedure was applied to the borylated products obtained after each of the first three cycles.



Figure 1: ¹H NMR spectrum of PIB₁₀₀₀-bpy

S2. General procedure for direct C-H borylation of arenes

In a glovebox, a 20 mL vial containing $[Ir(OMe)(COD)]_2$ (10.0 mg, 0.015 mmol) or $[IrCl(COE)_2]_2$ (13.4 mg, 0.015 mmol) or $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), PIB₁₀₀₀-bpy (51.0 mg, 0.03 mmol), Pinacolatodiboron, pin₂B₂, (280.0 mg, 1.1 mmol) was charged with dry heptane (3 mL) and arenes (2 mmol). The reaction mixture was then allowed to magnetically stir at 25 °C or at 80°C for 18h. After the completion of 18h, the reaction mixture was concentrated under reduced pressure and 2 mL of acetonitrile was added which resulted in precipitation of the PIB-bound catalyst forming a biphasic mixture. This biphasic mixture was centrifuged (Speed: 10000 rpm/min) for 15 min which leads to complete separation of the nonpolar catalyst from the product containing acetonitrile phase. The product containing acetonitrile phase was collected and this biphasic separation procedure was repeated 3 more times to ensure complete separation of the product from the catalyst. The product was collected after removing the acetonitrile under reduced pressure.

Borylation reaction of benzene

In a glove box, a 20 mL vial containing $[Ir(OMe)(COD)]_2$ (10.0 mg, 0.015 mmol), PIB₁₀₀₀-BPY (51.0 mg, 0.03 mmol), and Pinacolatodiboron, pin₂B₂, (280.0 mg, 1.1 mmol) was charged with benzene (5 ml, 30 mmol). The reaction mixture was then allowed to magnetically stir at 80°C for 18h. After the completion of 18h, the reaction mixture was concentrated under reduced pressure and 2 mL of acetonitrile was added which resulted in precipitation of the PIB-bound catalyst forming a biphasic mixture. This biphasic mixture was centrifuged (Speed: 10000 rpm/min) for 15 min which leads to complete separation of the nonpolar catalyst from the product containing acetonitrile phase. The product containing acetonitrile phase was collected and this biphasic separation procedure was repeated 3 more times to ensure complete separation of the product from the catalyst. The product was collected after removing the acetonitrile under reduced pressure.

1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1).

Transparent oil. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 1.5 Hz, 1H), 7.59 (dd, J = 7.9, 1.5 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 1.34 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 136.55, 135.49, 133.74, 132.26, 130.00, 84.33, 24.84. GC-MS: RT=13. 97 min, M⁺ = 272.1, vs MW= 272.96 g.mol⁻¹.





GC-MS Chromatogram of 1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1).



2-Chloro-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2).

Reddish oil. Yield: 92% (*p*-isomer: *m*-isomer = 2a:2b = 40:60)¹H NMR (600 MHz, CDCl₃) δ (*p*-isomer) 7.68 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 6H), 1.33 (s, 24H); (*m*-isomer) 7.78 (s, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 6H), 1.33 (s, 24H); ¹³C NMR (151 MHz, CDCl₃) δ 139.07, 137.61, 137.21, 135.82, 135.13, 135.08, 134.11, 133.39, 132.77, 130.81, 130.39, 128.91, 128.41, 126.97, 126.45, 83.85, 83.83, 82.86, 24.72, 24.39, 20.16, 19.64. GC-MS: 2a: RT=13.04 min, M⁺ = 252.1 vs MW= 252.55 g.mol⁻¹; 2b: RT= 13.18 min, M⁺ = 252.1, vs MW= 252.55 g.mol⁻¹.





GC-MS Chromatogram of 2-Chloro-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2).



1,4-dichloro-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3 a).

Transparent crystals. Yield: 70%. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 1.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 1.37 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 137.75, 136.04, 132.12, 131.70, 130.70, 84.51, 24.78. GC-MS: RT=13.67 min, M⁺ = 272 vs MW= 272.96 g.mol⁻¹.

ĊI





GC-MS Chromatogram of 1,4-dichloro-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene



1,4-dichloro-2,5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3 b). White solid. Yield: 6 % (49 mg). ¹H NMR (600 MHz, CDCl₃) δ 7.63 (s, 2H), 1.36 (s, 24H). ¹³C NMR (151 MHz, CDCl₃) & 137.16, 136.78, 84.52, 24.79.





3-Chloro-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (4).

White solid. Yield: 86%. ¹H NMR (600 MHz, CD₂Cl₂) δ 7.52 (s, 1H), 7.46 (s, 1H), 7.26 (s, 1H), 2.33 (s, 3H), 1.32 (s, 12H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 139.10, 133.17, 133.03, 131.26, 130.90, 83.67, 24.25, 20.33. GC-MS: RT=13.07 min, M⁺ = 252.1 vs MW= 252.55 g.mol⁻¹.











3-Chloro-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (5).

Transparent oil. Yield: 87%. ¹H NMR (600 MHz, CDCl₃) δ 7.37 (s, 1H), 7.22 – 7.16 (m, 1H), 6.99 (s, 1H), 3.82 (s, 3H), 1.34 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 159.88, 134.57, 126.84, 117.71, 117.43, 84.15, 55.52, 24.82. GC-MS: RT=14.55 min, M⁺ = 268.1 vs MW= 268.54 g.mol⁻¹.





GC-MS Chromatogram of 3-Chloro-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (5).



(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (6).

Transparent oil. Yield: 82% (*m*-isomer: 3,5-*Bis*-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene: *p*-isomer= 6a: 6b:6c= 60:5:35).¹H NMR (600 MHz, Acetone-*d*₆) δ (*m*-isomer) 7.58 (m, 8H), 7.56 (d, *J* = 7.0 Hz, 9H), 7.27 (dt, *J* = 14.6, 7.4 Hz, 17H), 2.34 (s, 40H), 1.32 (s, 66H); (*m*-*p*-isomer) 8.05 (s, 1H), 7.68 (m, 2H), 2.36 (s, 4H), 1.34 (s, 32H); (*p*-isomer) 7.66 (d, 10H), 7.19 (d, *J* = 7.5 Hz, 10H), 1.33 (s, 95H); ¹³C NMR (151 MHz, Acetone-*d*₆) δ 206.00, 138.93, 137.70, 136.12, 135.60, 132.73, 132.57, 129.25, 128.47, 84.46, 84.39, 84.30, 25.28, 25.01, 21.77, 21.40, 21.29. GC-MS: 6a: RT=10.82 min, M⁺ = 218.2 vs MW= 218.10 g.mol⁻¹; 6b: RT=17.97 min, M⁺ = 344.2 vs MW= 344.07 g.mol⁻¹; 6c: RT=10.94 min, M⁺ = 218.2 vs MW= 218.10 g.mol⁻¹.







GC-MS Chromatogram of (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (6).



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) -o-xylene (7).

Transparent oil. Yield: 81%. ¹H NMR (600 MHz, CDCl₃) δ 7.58 (s, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 1.34 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 140.09, 135.91, 135.83, 132.38, 129.13, 83.51, 24.82, 19.98, 19.44; GC-MS: RT=12.52 min, M⁺ = 232.2 vs MW= 232.13 g.mol⁻¹.









GC-MS Chromatogram 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) -o-xylene (7).

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (8).

Orange oil. Yield: 90%. (*m*-isomer: 3,5-*bis*-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole: *p*-isomer = 8a:8b:8c = 65:20:15).¹H NMR (600 MHz, CDCl₃) δ (*m*-isomer:8a) 7.40 (d, 8Hz, 1H), 7.32 (d, 2.8 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, 2.8 Hz, 8Hz, 1H), 3.83 (s, 3H), 1.33 (s, 12H); (*m*-*m*-isomer) 7.87 (s, 1H), 7.43 (s, 2H), 3.83 (s, 3H), 1.33 (s, 24H); (*p*-isomer: 8c) 7.75 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H); ¹³C NMR (151 MHz, CDCl₃) δ 159.04, 136.50, 133.61, 128.92, 127.18, 122.81, 118.72, 117.89, 113.31, 83.82, 83.77, 55.33, 55.25, 24.86, 24.81; GC-MS: **8 a**: RT=12.82 min, M⁺ = 234.2 vs MW= 234.1 g.mol⁻¹; **8b**: RT=19.19 min, M⁺ = 360.2 vs MW= 360.06 g.mol⁻¹; **8c**: RT=12.55 min, M⁺ = 234.1 vs MW= 234.1 g.mol⁻¹.









GC-MS Chromatogram of (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (8).

1,3-dichloro-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (9).

Light yellow oil. Yield: 84%. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 2.0 Hz, 2H), 7.43 (t, *J* = 2.0 Hz, 1H), 1.34 (s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 134.71, 132.69, 131.07, 84.50, 24.83; GC-MS: RT=13.56 min, M+ = 272.0 vs MW= 272.96 g.mol⁻¹.







(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (10).

Transparent oil. Yield = 90 %. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.77 – 7.69 (m, 2H), 7.47 – 7.39 (m, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 1.31 (s, 12H); ¹³C NMR (101 MHz, CD₂Cl₂) δ 135.14, 131.71, 128.23, 84.34, 25.24; GC-MS: RT=9.50 min, M⁺ = 204.1 vs MW= 204.08 g.mol⁻¹.







GC-MS Chromatogram of (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (10).

S3. Catalyst recycling and ICP-OES analysis of Iridium PIB₁₀₀₀-BPY –catalyst in the borylation reaction of 1,2-dichlorobenzene

Procedure:

In a glove box, to a mixture of the isolated (PIB₁₀₀₀-bpy)Ir(COD)(Bpin)₃ (45 mg, mmol) and Pin₂B₂ (210 mg, 0.825 mmol) in dry heptane (2.26 mL) was added 1,2-dichlorobenzene (170 μ L, 1.5 mmol) at room temperature for 18 h. After the completion of 18h, the reaction mixture was concentrated under reduced pressure and 2 mL of acetonitrile was added which resulted in precipitation of the PIB-bound catalyst forming a biphasic mixture. This biphasic mixture was centrifuged (Speed: 10000 rpm/min) for 15 min which leads to complete separation of the nonpolar catalyst from the product containing acetonitrile phase. The product containing acetonitrile phase was collected and this biphasic separation procedure was repeated 3 more times to ensure complete separation of the product from the catalyst. The product was collected after removing the acetonitrile under reduced pressure.





Cycle	Yield (%)	Mass of the iridium PIB ₁₀₀₀ -bpy catalyst (mg) after reaction	Mass of the iridium PIB ₁₀₀₀ -bpy catalyst (mg) before reaction	Ir containing ^c in iridium PIB ₁₀₀₀ -bpy catalyst (C _{Theoretical} = 43.5 ppm)	Ir containing in the product (ppm)
1	95	60	10 mg of Ir and 51 mg of ligand	49 ppm	0.6
2	94	45	45 mg	42 ppm	0.2
3	94	37	36 mg	44 ppm	0.1

^a Iridium PIB₁₀₀₀-bpy catalyst was regenerated from direct C-H borylation conditions and isolated by centrifuge.

^b The 3 cycles were performed at room temperature for 18 h with 1,2-dichlorobenzene (2 mmol), bis(pinacolato)diboron (1,1 mmol), and recycled catalyst.

^c ICP-OES analysis of Iridium PIB₁₀₀₀-bpy catalyst.



- S5. References
- (S1) Priyadarshani N., Liang Y., Suriboot J., Bazzi H. S., Bergbreiter D. E., ACS Macro Lett. 2013, 2, 571-574.
- (S2) Boebel T. A., Hartwig J. F., Organometallics 2008, 27, 6013–6019.
- (S3) Maegawaa Y., Inagaki S., Dalton Trans. 2015, 44, 13007–13016.
- (S4) Tajuddin A., Harrisson P., Bitterlich B., Collings J. C., Sim N., Batsanov A. S., Cheung M. S., Kawamorita S., Maxwell A.C., Shukla L., Morris J., Lin Z., Marder T. B., Steel P. G., *Chem. Sci.*, **2012**, *3*, 3505-3515.

S27