Supporting Information for

Origin of the Difference in Reactivity between Ir Catalysts for the Borylation of C-H Bonds

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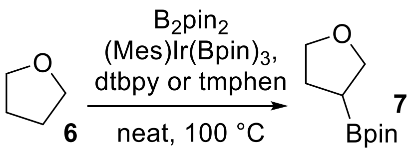
A. General Experimental Details

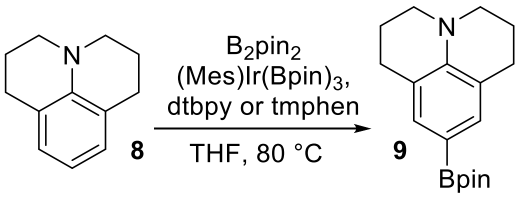
All reactions requiring an inert atmosphere were conducted in a nitrogen-filled glove box. When vials were used as the reaction vessel, they were sealed with Teflon-lined caps. THF used as solvent for the borylation reactions was degassed with nitrogen for 30 minutes, dried with a solvent purification system using a 1 m column containing activated alumina, and stored over molecular sieves. All solvents were purchased from Fisher Chemical. 3,4,7,8-Tetramethylphenanthroline and 4,4-di-tert-butyl-2,2-dipyridyl were purchased from Aldrich. Iridium complexes were obtained from Johnson-Matthey or Strem. 2,7-dimethylbenzoimidazole[1], (tmphen)Ir(COE)$(BPin)_3$[2], (dtbpy)Ir(COE)$(BPin)_3$[2], and (Mes)Ir$(BPin)_3$[3] were prepared according to known procedures. All chemicals were used as received, unless otherwise noted. Silica gel chromatography was performed with Silicycle SiliaFlash T60 TLC-grade silica gel, or with a Teledyne ISCO CombiFlash RF 200, equipped with Gold-Top silica columns. Products were visualized on TLC plates using a 254 nm UV lamp. GC analysis was performed on an HP 6890 GC equipped with an HP-5 column (25 m x 0.20 mm x 0.33 μm film) and an FID detector. Quantitative GC analysis was performed by adding dodecane as an internal standard at the beginning of each reaction. Response factors relative to dodecane were determined for the acquisition of kinetic data and for the determination of GC yields. NMR spectra were acquired on 300, 400, 500, and 600 MHz Bruker instruments at the University of California, Berkeley NMR facility. Chemical shifts were reported relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm for ^1H and 77.2 ppm for ^{13}C; THF-d_8 = 3.58 ppm for ^1H and 67.2 ppm for ^{13}C; C_6D_6 = 7.16 ppm for ^1H and 128.06 ppm for ^{13}C). The resonances for carbon atoms attached to boron were not observed due to the boron quadrupole. Mass spectrometric analyses were performed at the

University of California, Berkeley Mass Spec Center using EI and ESI ionization techniques with a Thermo Finnigan LTQ FT Instrument. ESI spectra were acquired using positive ionization unless otherwise noted. IR spectra were acquired on a Thermo Scientific iS5 IR spectrometer. Samples for IR spectroscopy were prepared either as a solution in THF, or as a nujol mull.

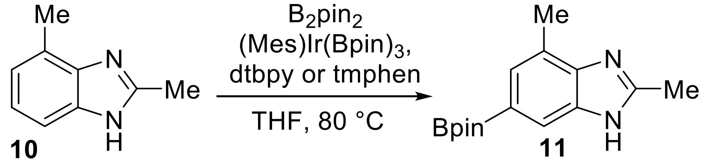
B. Catalytic borylation reactions



In a nitrogen-filled glovebox, a 4 mL vial was charged with (Mes)Ir(Bpin)$_3$ (5.9 mg, 0.0085 mmol)), dtbpy (2.3 mg, 0.0085 mmol) or tmphen (2.0 mg, 0.0085 mmol), B$_2$pin$_2$ (43 mg, 0.17 mmol), dodecane (internal standard), and THF (0.36 mL). The vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 100 °C for 24 h. The reaction mixture was cooled to room temperature, and the yield (103% with Ir-tmphen; 5% with Ir-dtbpy) was determined by GC. To isolate the product, the solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography with 5-20% EtOAc in hexanes as eluent. ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.98 (t, J = 8.0 Hz, 1H), 3.80 (m, J = 8.0, 4.0 Hz, 1H), 3.70 (m, J = 8.0, 7.0 Hz, 1H), 3.61 (m, J = 9.7, 8.0 Hz, 1H), 2.07 (m, 1H), 1.85 (m, 1H), 1.60 (m, 1H), 1.24 (s, 12H).). ^{13}C NMR (126 MHz, CDCl$_3$) δ 83.4, 70.4, 68.5, 28.7, 24.9. ^{11}B NMR (193 MHz, CDCl$_3$) δ 33.31. The NMR spectra matched those in the literature.[4] GC-MS: m/z 189.1

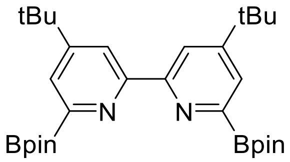


In a nitrogen-filled glovebox, a 4 mL vial was charged with (Mes)Ir(Bpin)$_3$ (4.3 mg, 0.0063 mmol), dtbpy (1.7 mg, 0.0063 mmol) or tmphen (1.5 mg, 0.0063 mmol), B$_2$pin$_2$ (32 mg, 0.125 mmol), Julolidine (21.7 mg, 0.125 mmol) 1,3,5-trimethoxybenzene (internal standard), and THF (0.5 mL). The vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated with a rotary evaporator. The reaction yield (91% with Ir-tmphen; 31% with Ir-dtbpy) was determined by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25 (s, 2H), 3.19–3.16 (m, 4H), 2.74 (t, J = 6.2 Hz, 4H), 1.97–1.91 (m), 1.31 (s, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.52, 133.79, 120.38, 83.20, 50.06, 27.63, 24.64, 21.96. ^{11}B NMR (193 MHz, CDCl$_3$) δ 33.81. The NMR spectra matched those in the literature.[5] GC-MS m/z: 299.2.



In a nitrogen-filled glovebox, a 4 mL vial was charged with (Mes)Ir(Bpin)$_3$ (4.3 mg, 0.0063 mmol), dtbpy (1.7 mg, 0.0063 mmol) or tmphen (1.5 mg, 0.0063 mmol), B$_2$pin$_2$ (32 mg, 0.125 mmol), 2,7-dimethylbenzoimidazole (18.3 mg, 0.125 mmol), 1,3,5-trimethoxybenzene (internal standard), and THF (0.5 mL). The vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated with a rotary evaporator.

MeOH (0.5 mL) was added, and the resulting mixture was stirred for 30 min. The reaction yield (88% with Ir-tmphen; 30% with Ir-dtbpy) was determined by ^{1}H-NMR spectroscopy. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.78 (s, 1H), 7.45 (s, 1H), 2.55 (s, 3H), 2.54 (s, 3H), 1.33 (s, 12H). 13C NMR (126 MHz, CDCl$_3$) δ 151.7, 141.3, 137.3, 128.5, 124.3, 121.9, 118.3, 83.4, 24.6, 16.8, 14.6. ^{11}B NMR (193 MHz, CDCl$_3$) δ 33.89. The NMR spectra matched those in the literature.[1] GC-MS: m/z 272.2



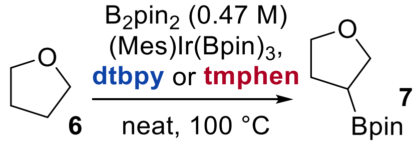
In a nitrogen-filled glovebox, a 20 mL vial was charged with [Ir(COD)(OMe)]$_2$ (6.2 mg, 0.009 mmol), dtbpy (100 mg, 0.37 mmol), and B$_2$pin$_2$ (190 mg, 0.74 mmol). Hexane (2 mL) was added and the vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated in the glovebox under reduced pressure. Pentane was added, and the solution was cooled at -30 °C overnight. A colorless solid formed, and this solid was isolated by filtration in the glovebox. ^{1}H NMR (600 MHz, Benzene-d_6) δ 9.27 (d, *J* = 2.1 Hz, 2H), 8.23 (d, *J* = 2.1 Hz, 2H), 1.15 (s, 24H), 1.09 (s, 18H). ^{13}C NMR (151 MHz, Benzene-d_6) δ 159.17, 158.02, 120.62, 84.16, 34.78, 30.52, 25.04. ^{11}B NMR (193 MHz, Benzene-d_6) δ 31.25. The NMR spectra matched those in the literature.[6]

C. Synthesis of [(tmphen)Ir(Bpin)$_3$(CO)] (5)

In an argon-filled glovebox, a 20 mL vial was charged with [Ir(COD)OMe]$_2$ (66.5 mg, 0.100 mmol), cyclohexane (4 mL), and a magnetic stir bar. The mixture was stirred, and to the mixture was added cis-cyclooctene (182 μL, 1.40 mmol). To the resulting solution was added pinacolborane (230 µL, 1.60 mmol), at which point the mixture became orange/red. The solution was stirred for 5 min. A separate 4 mL vial was charged with tmphen (47.3 mg, 0.200 mmol) and THF (4 mL). The solution of ligand in THF was heated at 65 °C for 10 minutes to dissolve the ligand and transferred to the 20 mL vial containing the orange/red solution. The color of the solution instantly changed from orange/red to dark red. The mixture was transferred to a 50 mL round-bottom flask with an airless valve. The flask was sealed with a threaded Teflon stopper and brought outside of the glovebox. The flask was cooled at -78 °C and evacuated to ~500 mtorr. The flask was removed from the cold bath and was backfilled with carbon monoxide. The flask was warmed to RT, and the mixture was stirred for 20 min. The solvents were evaporated, and the flask was brought back into the glovebox. The residue was washed with pentane and then extracted with 4 x 2 mL of Et_2O and filtered through a pipet, packed with a glass wool plug and Celite. The solvents were evaporated, yielding complex **5** (23.0 mg, 14% yield) as a grey green solid. ^1H NMR (500 MHz, $CDCl_3$) δ 9.67 (d, *J* = 102.3 Hz, 2H), 8.01 (s, 2H), 2.73 (s, 6H), 2.55 (s, 6H), 1.33 (s, 24H), 0.62 (s, 12H). ^{11}B NMR (160 MHz, $CDCl_3$) δ 46.6, 33.1. IR ν_{CO}(THF) = 1971 cm^{-1}, (nujol mull, cm^{-1}) 1966, 1618, 1521, 1210, 1146, 1110, 1058, 964, 862, 722. Anal. Calcd (%) for $C_{35}H_{52}B_3IrN_2O_7$: C, 50.20; H, 6.26; N, 3.35; Found: C, 49.99; H, 6.35; N, 3.28.

D. Kinetic Studies

Catalytic Borylation of THF. In a nitrogen-filled glovebox, a 4 mL vial was charged with (η^6-mes)Ir(Bpin)$_3$ (5.9 mg, 0.0085 mmol), tmphen or dtbpy (0.0085 mmol), and a 0.472 M stock solution of B_2pin_2 in THF (0.360 mL, 0.170 mmol). To the vial was added a magnetic stir bar and dodecane as an internal standard, and the vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 100 °C. At various time points, aliquots were taken from the mixture and analyzed by gas chromatography.



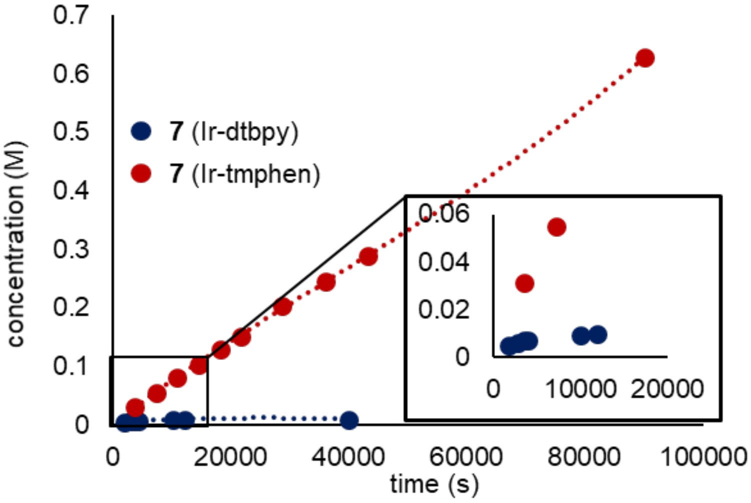


Figure S1. Borylation of THF catalyzed by (Mes)Ir(Bpin)$_3$ (5 mol%) and dtbpy (blue) or tmphen (red).

Catalytic C-H Borylation of 9 and 11. In a nitrogen-filled glovebox, a 4 mL vial was charged with the arene or heteroarene (0.063 mmol) and 1,3,5-trimethoxybenzene (internal standard). A solution of (Mes)Ir(Bpin)$_3$ (2.2 mg, 0.0032 mmol), dtbpy (0.8 mg, 0.0032 mmol) or tmphen (0.7 mg, 0.0032 mmol), and B$_2$pin$_2$ (16 mg, 0.063 mmol) in THF-d_8 (0.45 mL) was added. The red solution was transferred to a J. Young NMR tube and the NMR tube was sealed. The reaction mixture was heated at 100 °C. At various time points, ^{1}H NMR spectra were recorded.

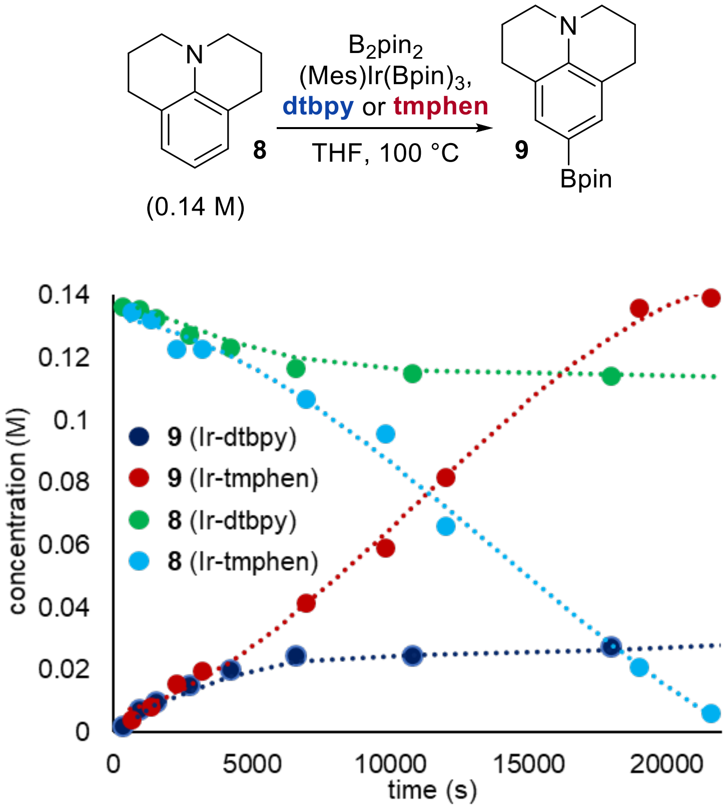


Figure S2: Borylation of Julolidine (9) catalyzed by $(Mes)Ir(Bpin)_3$ (5 mol%) and dtbpy (blue) or tmphen (red). The lines are not fits to a kinetic equation; they are intented to help guide the eye.

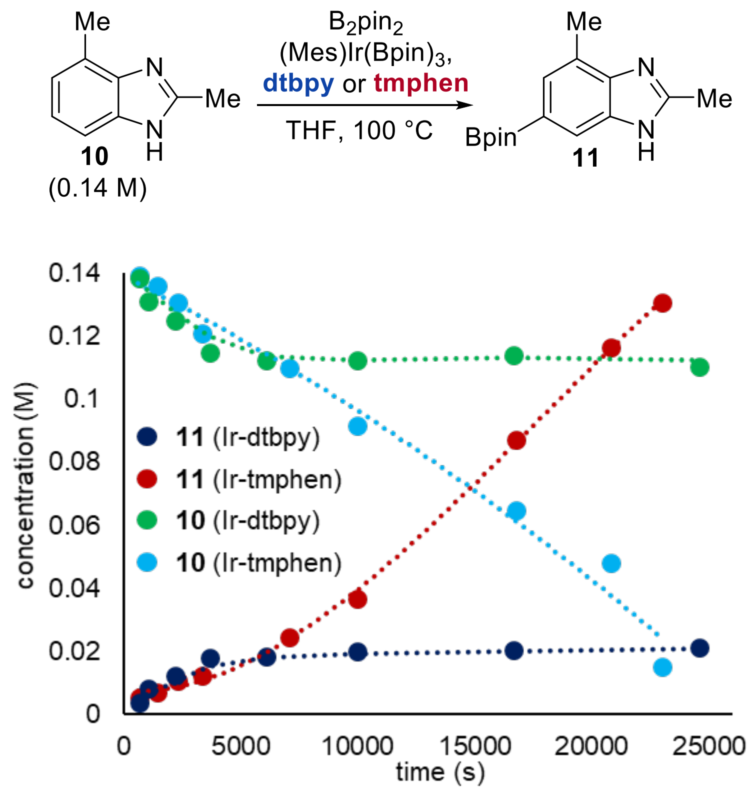


Figure S3: Borylation of 2,7-dimethylbenzoimidazole (11) catalyzed by (Mes)Ir(Bpin)$_3$ (5 mol%) and dtbpy (blue) or tmphen (red). The lines are not fits to a kinetic equation; they are intented to help guide the eye.

Catalytic C-H Borylation of o-xylene, dtbpy and tmphen.

In a nitrogen-filled glovebox, a 4 mL vial was charged with the arene (0.045 mmol) and dodecahydrotriphenylene (DHT, internal standard). A solution of $[Ir(COD)(OMe)]_2$ (0.7 mg, 0.001 mmol), dtbpy (0.6 mg, 0. 0.002 mmol) or tmphen (0.7 mg, 0.002 mmol), and B_2pin_2 (23 mg, 0.090 mmol) in THF-d_8 (0.45 mL) was added. The solution was transferred to a J. Young NMR tube, and the tube was sealed. The reaction mixture was heated at 70 °C. At various time points, ^{1}H NMR spectra were recorded.

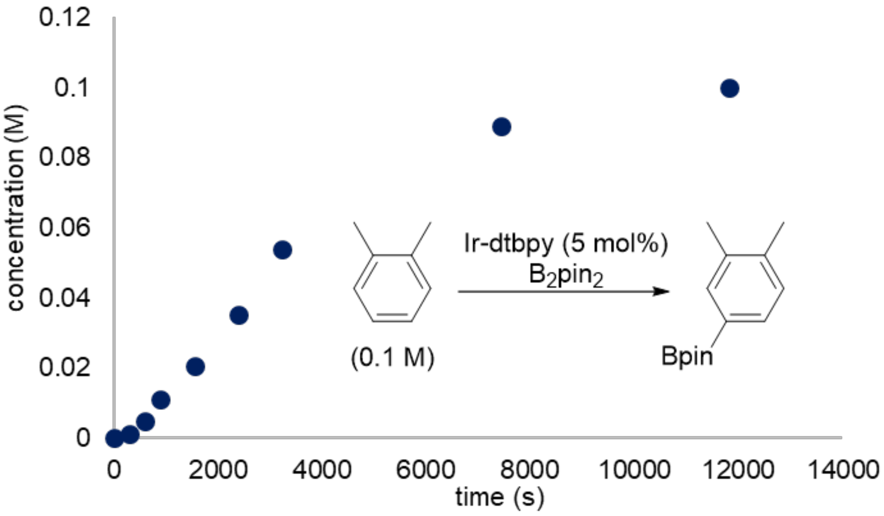


Figure S4. Borylation o-xylene catalyzed by [Ir(COD)(OMe)]$_2$ (2.5 mol%) and dtbpy (5 mol%)

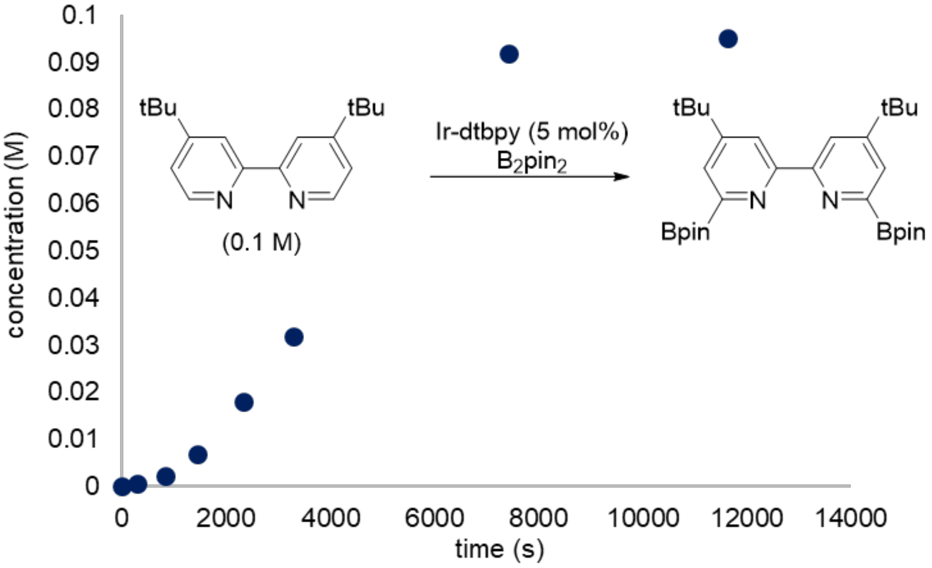


Figure S5. Borylation of dtbpy catalyzed by [Ir(COD)(OMe)]$_2$ (2.5 mol%) and dtbpy (5 mol%)

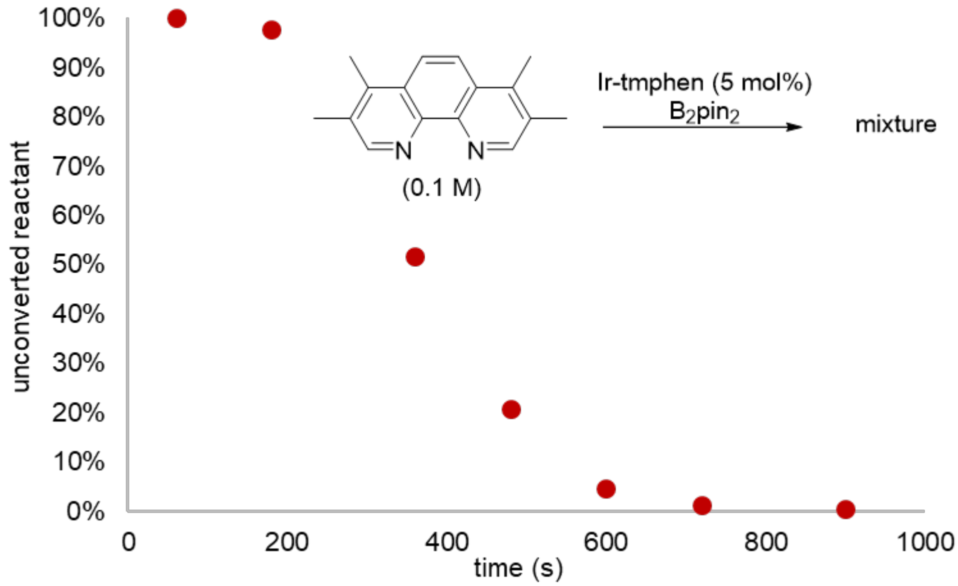


Figure S6. Borylation of tmphen catalyzed by $[Ir(COD)(OMe)]_2$ (2.5 mol%) and tmphen (5 mol%)

Stoichiometric Borylation of arenes

In a nitrogen-filled glovebox, a 4 mL vial was charged with (dtbpy)Ir(COE)$(Bpin)_3$ or (tmphen)Ir(COE)$(Bpin)_3$ (0.0053 mmol), dodecahydrotriphenylene (DHT, internal standard), arene (0.080 mmol), and cyclohexane-d_{16} (0.5 mL). The solution was transferred to a J. Young NMR tube, and the tube was sealed. At various time points, ^{1}H-NMR spectra were recorded.

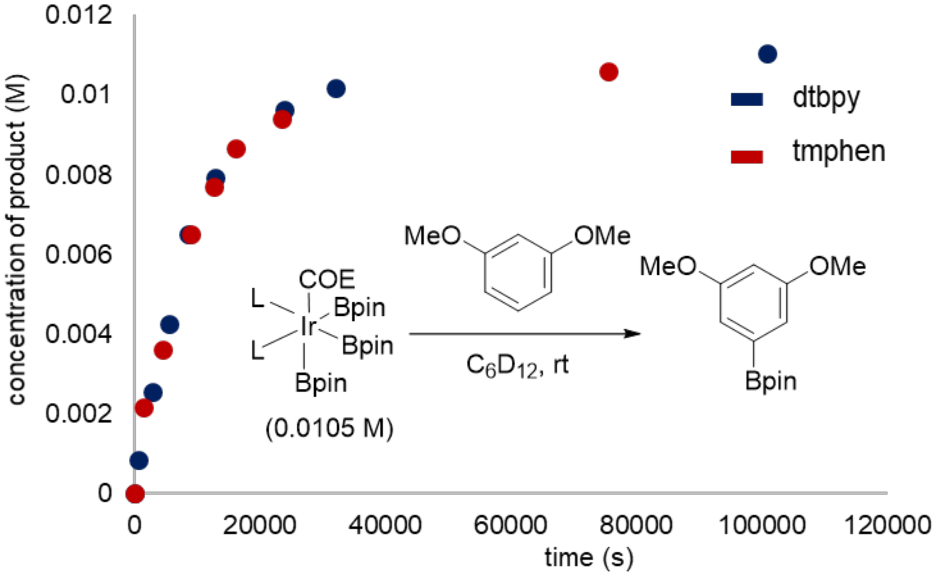


Figure S7. Reaction profile for the stoichiometric borylation of *m*-dimethoxybenzene with Ir complexes (10.5 μM) 1 (blue) and 2 (red) ligated by dtbpy and tmphen.

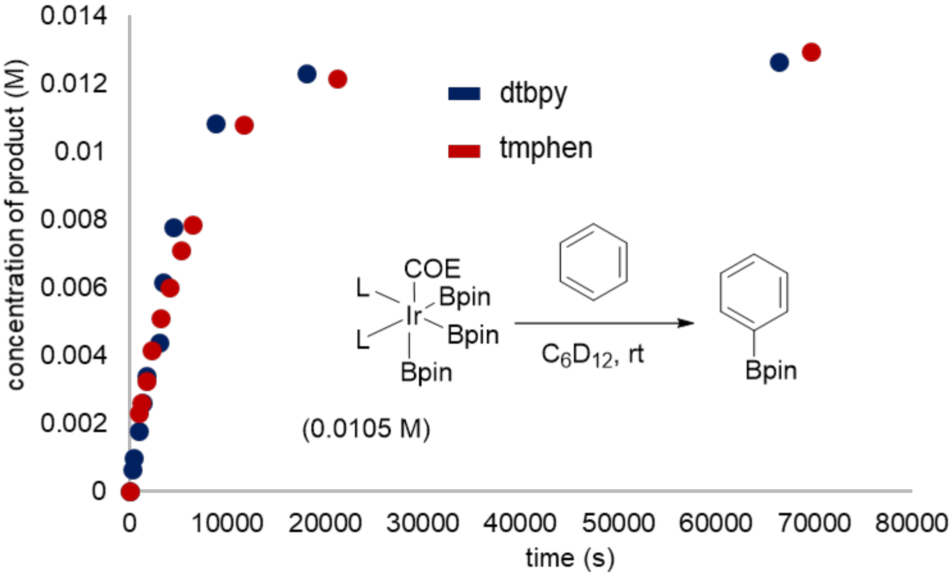


Figure S8. Reaction profile for the stoichiometric borylation of benzene with Ir complexes (10.5 μM) 1 (blue) and 2 (red) ligated by dtbpy and tmphen.

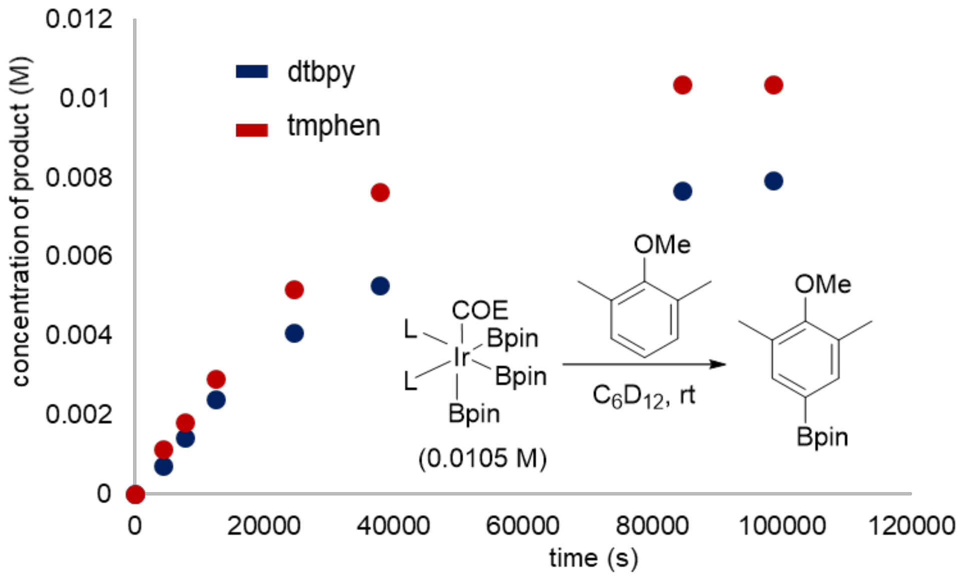


Figure S9. Reaction profile for the stoichiometric borylation of 2-methoxy-1,3-dimethylbenzene with Ir complexes (10.5 µM) 1 (blue) and 2 (red) ligated by dtbpy and tmphen.

E. HPLC-MS Analysis of the Products from Borylation of tmphen and Subsequent Oxidation

In a nitrogen-filled glovebox, a 4 mL vial was charged with $[Ir(COD)(OMe)]_2$ (1.4 mg, 0.0012 mmol), dtbpy (1.2 mg, 0. 0.0023 mmol), B_2pin_2 (23 mg, 0.090 mmol), arene (0.0045 mmol), DHT (internal standard) and THF (0.5 mL). The vial was sealed with a Teflon-lined cap and heated at 70 °C. After 2 h, the reaction mixture was cooled to 0 °C. A 2:1 mixture of NaOH (3 M) and H_2O_2 (30% in H_2O) was added dropwise, and the mixture was stirred at room temperature for 2 h. The solvents were evaporated under reduced pressure, and the crude products were analyzed by reversed-phase HPLC-MS.

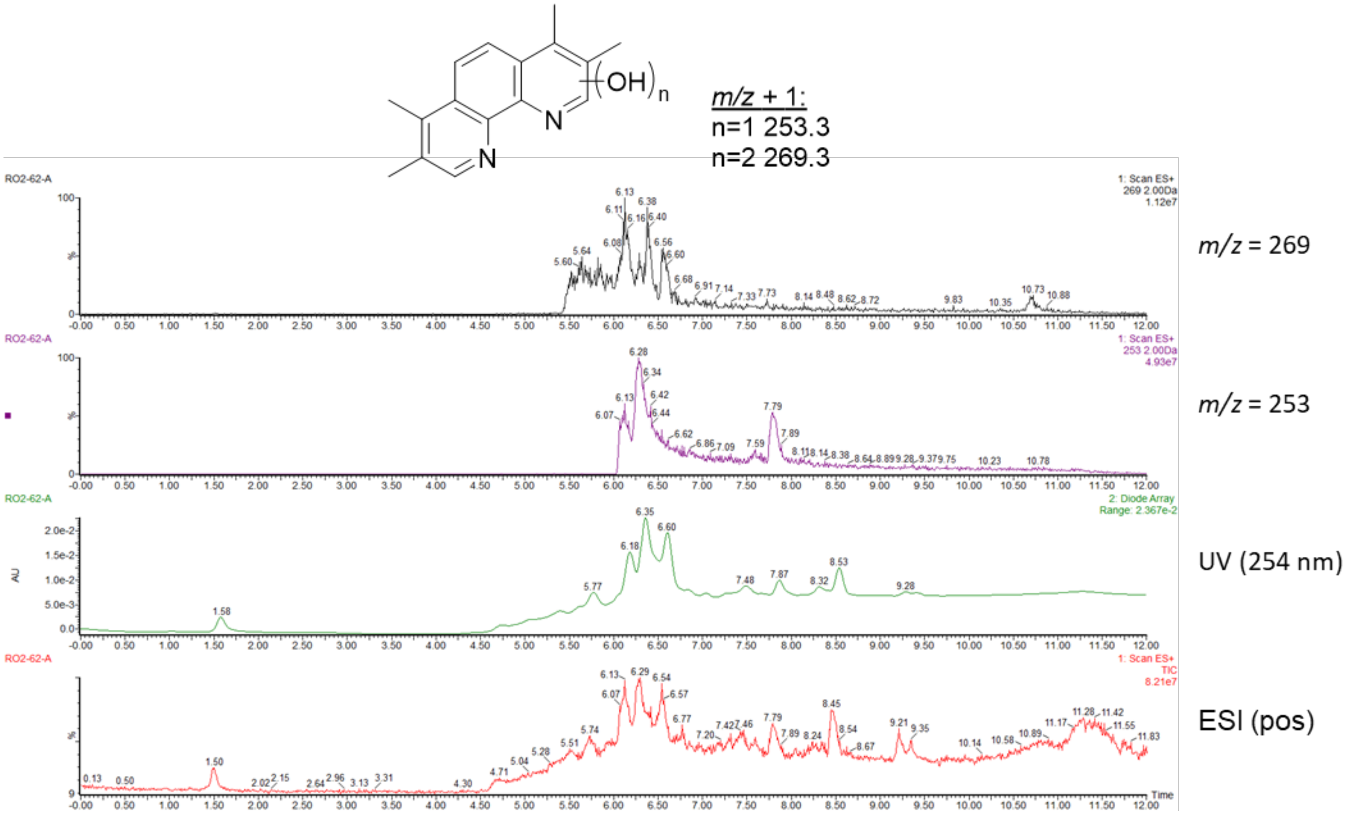
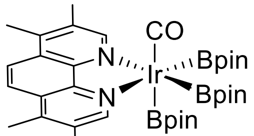


Figure S10. HPLC-MS trace of the products from stoichiometric borylation of tmphen, followed by oxidation with H_2O_2/$^{-}$OH, showing the formation of multiple reaction products.

F. ^{1}H NMR Spectrum of [(tmphen)Ir(Bpin)$_3$(CO)] (5)



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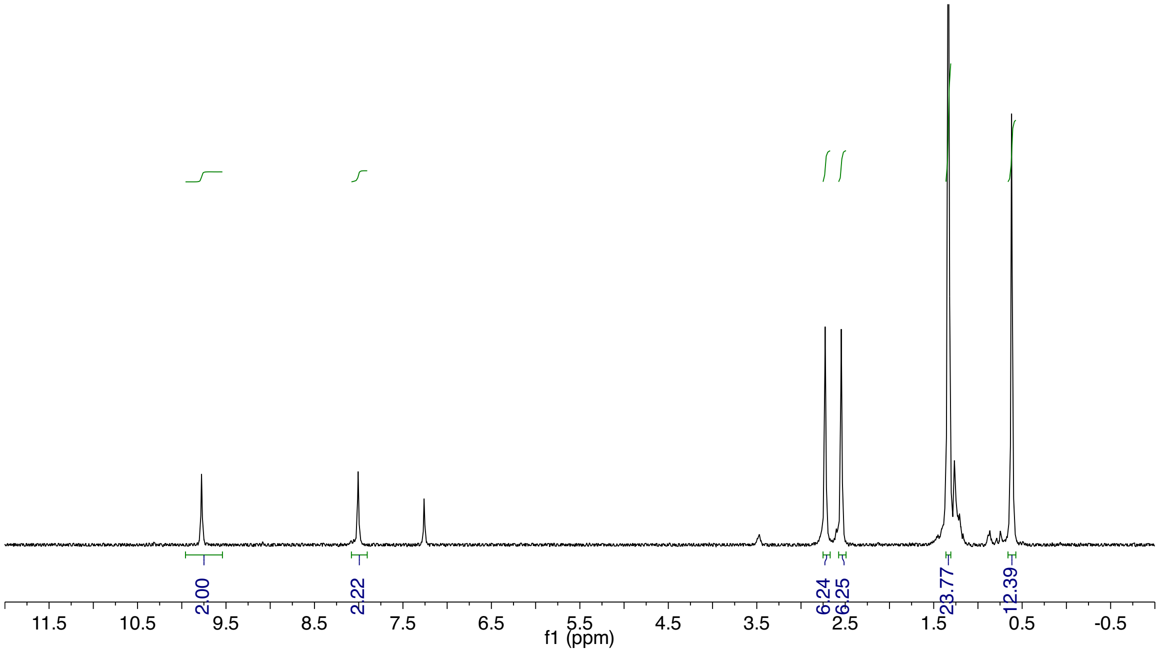
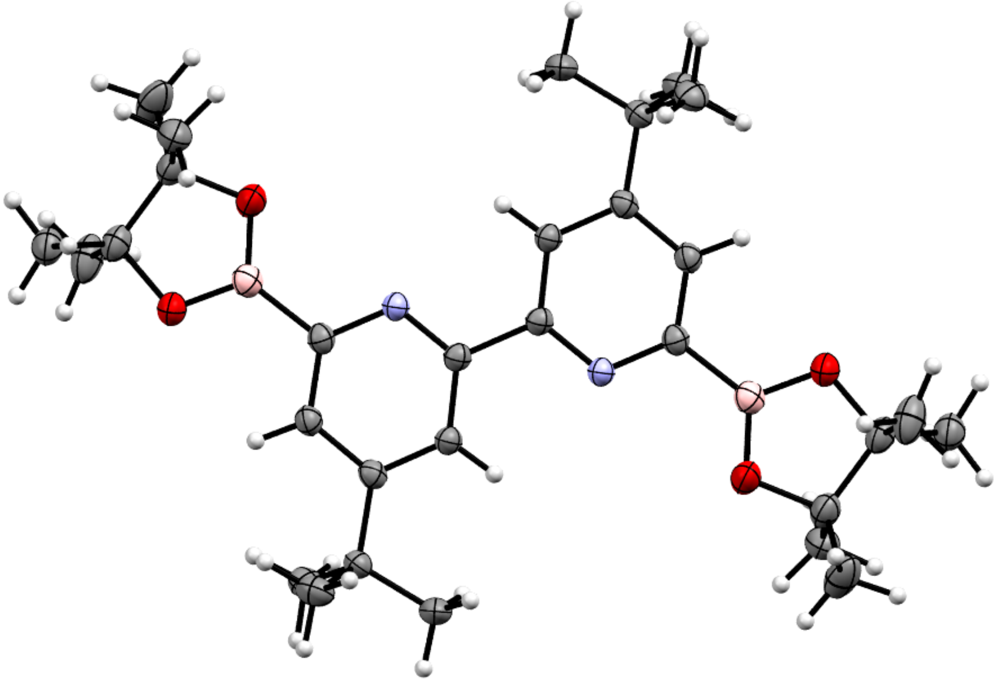


G. X-ray Crystallographic Data of $(Bpin)_2$-dtbpy (13)



Empirical formula	C30 H46 B2 N2 O4	
Formula weight	520.31	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 14.0153(3) Å	α= 90°.
	b = 11.1661(3) Å	β= 90°.
	c = 19.0586(5) Å	γ = 90°.
Volume	2982.60(13) Å^3	
Z	4	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	0.586 mm^{-1}	
F(000)	1128	
Crystal size	0.220 x 0.070 x 0.060 mm^3	
Theta range for data collection	4.640 to 68.251°.	
Index ranges	-16<=h<=16, -13<=k<=13, -22<=l<=22	
Reflections collected	13276	

Independent reflections	2726 [R(int) = 0.0621]
Completeness to theta = 68.000°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.52404
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2726 / 0 / 179
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1595
R indices (all data)	R1 = 0.0645, wR2 = 0.1665
Extinction coefficient	n/a
Largest diff. peak and hole	0.309 and -0.297 e.Å^{-3}

H. References

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