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Undirected *ortho*-selectivity in C–H borylation of arenes catalyzed by NHC platinum(0) complexes

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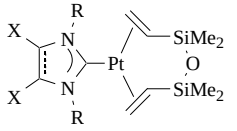
General information

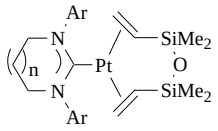
All reactions were carried out using standard Schlenk technique under argon atmosphere. Tetrahydrofuran and toluene were distilled over sodium-benzophenone under Ar. Chemicals and solvents were obtained from commercial sources and used without further purification. Bis(pinacolato)diboron was crystallized from dry pentane and dried in vacuum.[S1] NMR spectra were obtained on a Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t" or ''m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation ''br" is given for broadened signals.

All (NHC)Pt(dvtms) complexes were prepared according to the literature procedure.[S2]

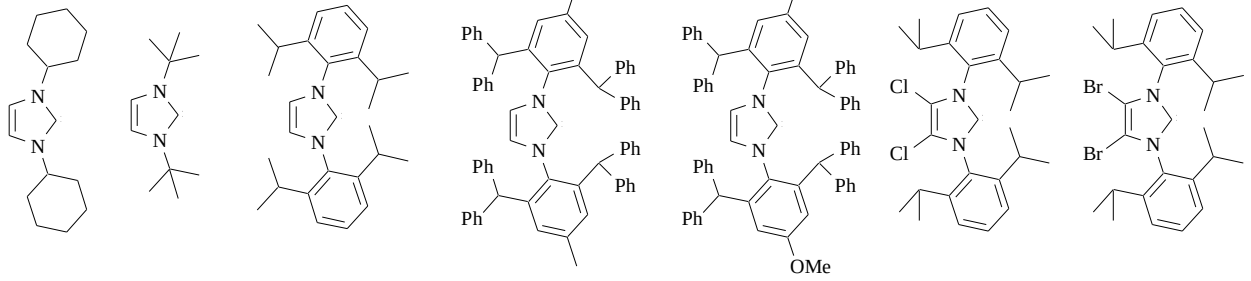
Scheme S1. Structures of NHC ligands



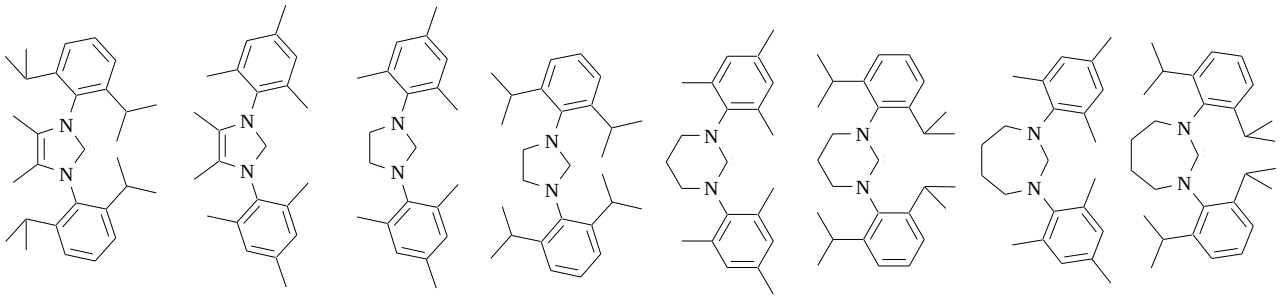
1a-k



1l-o

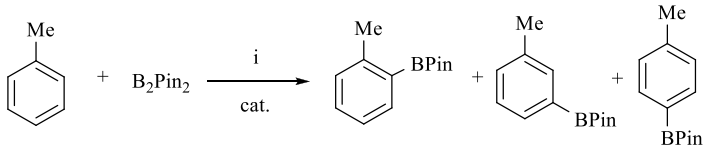


ICy (in **1a**) ItBu (in **1b**) IPr (in **1c**) IPr* (in **1d**) IPr*OMe (in **1e**) IPrCl(in **1f**) IPrBr(in **1g**)

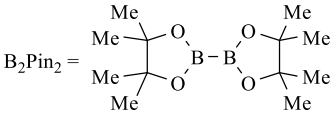


IPrMe(in **1h**) IMesMe(in **1i**) SIMes (in **1j**) SIPr (in **1k**) 6-Mes (in **1l**) 6-Dipp (in **1m**) 7-Mes (in **1n**) 7-Dipp (in **1o**)

General procedure for the catalytic C-H borylation of arenes with B_2Pin_2



o-**2** *m*-**2** *p*-**2**



CAUTION: the reaction mixture may be heated above the boiling point of the substrate in a closed vessel. To avoid the risks, the equipment intended for elevated pressure operations should be applied, a J-Young type stopper is recommended.

A 10 ml Schlenk flask equipped with a magnetic stirring bar was charged with B_2Pin_2 (76 mg, 0.3 mmol) and (NHC)Pt(dvtms) (1 mol.%). The flask was evacuated and filled with argon, and the cycle was repeated twice, followed by addition of dry arene (1 ml). The solution was degassed using 3 freeze-pump-thaw cycles and then placed into a preheated oil bath at specified temperature and stirred for 20 h. The mixture was then filtered through a pad of Celite® and evaporated to dryness. The residue was analyzed by ^{1}H NMR.

The composition of a mixture of products was determined using characteristic signals of aryl pinacol arylboronates (those not overlapping with signals from other compounds, marked in bold). Yields were determined using ferrocene (Fc) as an internal standard.

Borylation of toluene is highly sensitive to temperature of the reaction (IPrPt(dvtms), **2c** as catalyst):

110°C – no product

120°C – 69%, *o:m:p* = 4.9:2.2:1.

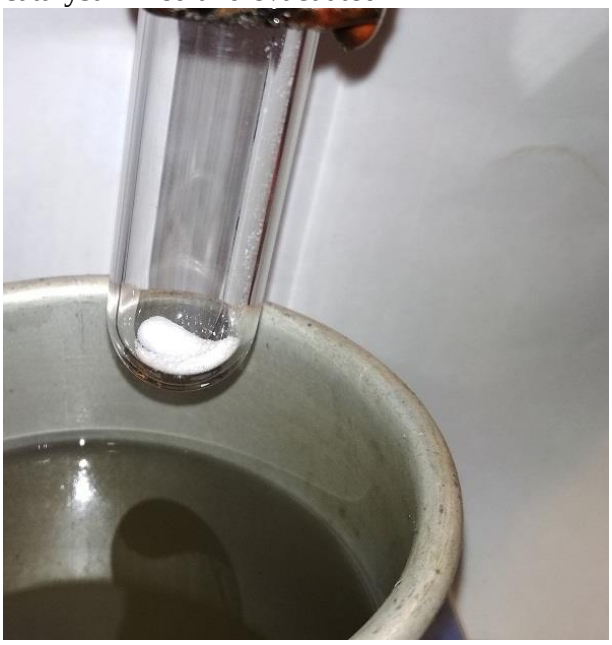
130°C – 74%, *o:m:p* = 5.3:2.3:1.

140°C –78%, *o:m:p* = 4.6:2.2:1.

Experimental set

Schlenk flask, glass stopper, Teflon coated stirring bar and stainless-steel Keck-clip

Freshly recrystallized $B_2(Pin)_2$ and platinum catalyst mixed and evacuated

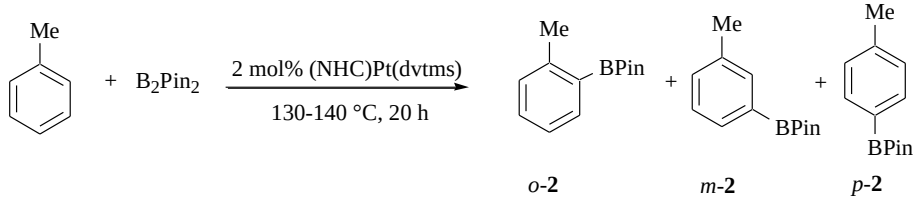


Toluene (1 ml) was added. The vessel was degassed using freeze-pump-thaw technique, and then heated to r.t. under dry argon atmosphere. Oil bath preheated to 120°C.

The reaction vessel was sealed and immersed in the preheated oil bath. The level of reaction mixture is below the level of heated oil.

The reaction mixture after 20 h of heating.

Borylation of toluene



(*o*-2) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.78** (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.16 – 7.20 (m, 2H), 2.56 (s, 3H), 1.36 (s, 12H)[S3]

(*m*-2) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.65** (s, 1H) 7.63 (t, *J* = 4.3 Hz, 1H), 7.31-7.27 (m, 2H), 2.37 (s, 3H), 1.36 (s, 12 H)[S4]

(*p*-2) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.72** (m, *J* = 7.9 Hz, 2H), 7.20 (m, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.35 (s, 12H)[S3]

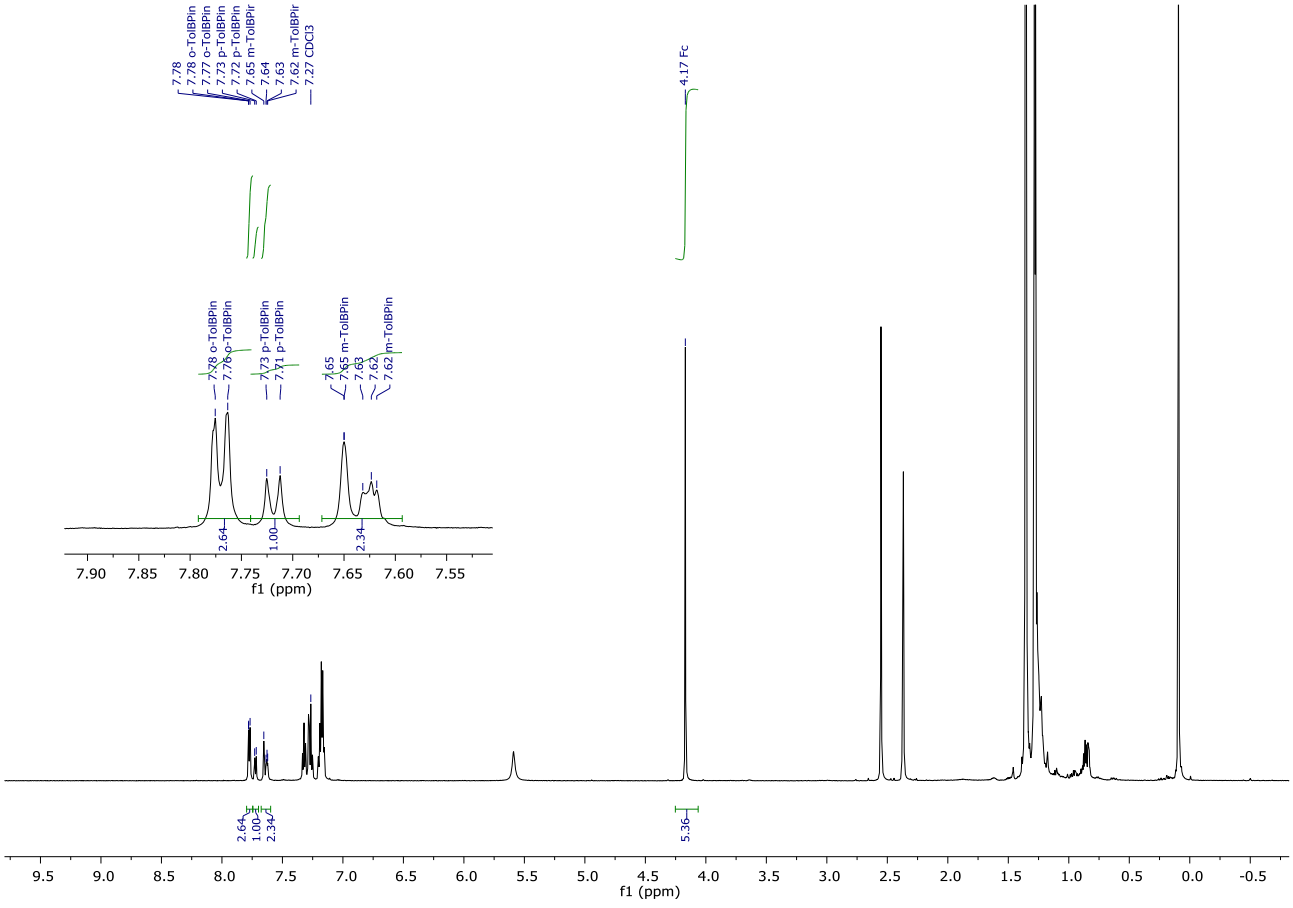


Figure S1 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of toluene with IPrPt(dvtms) (**1c**) at 130 °C.

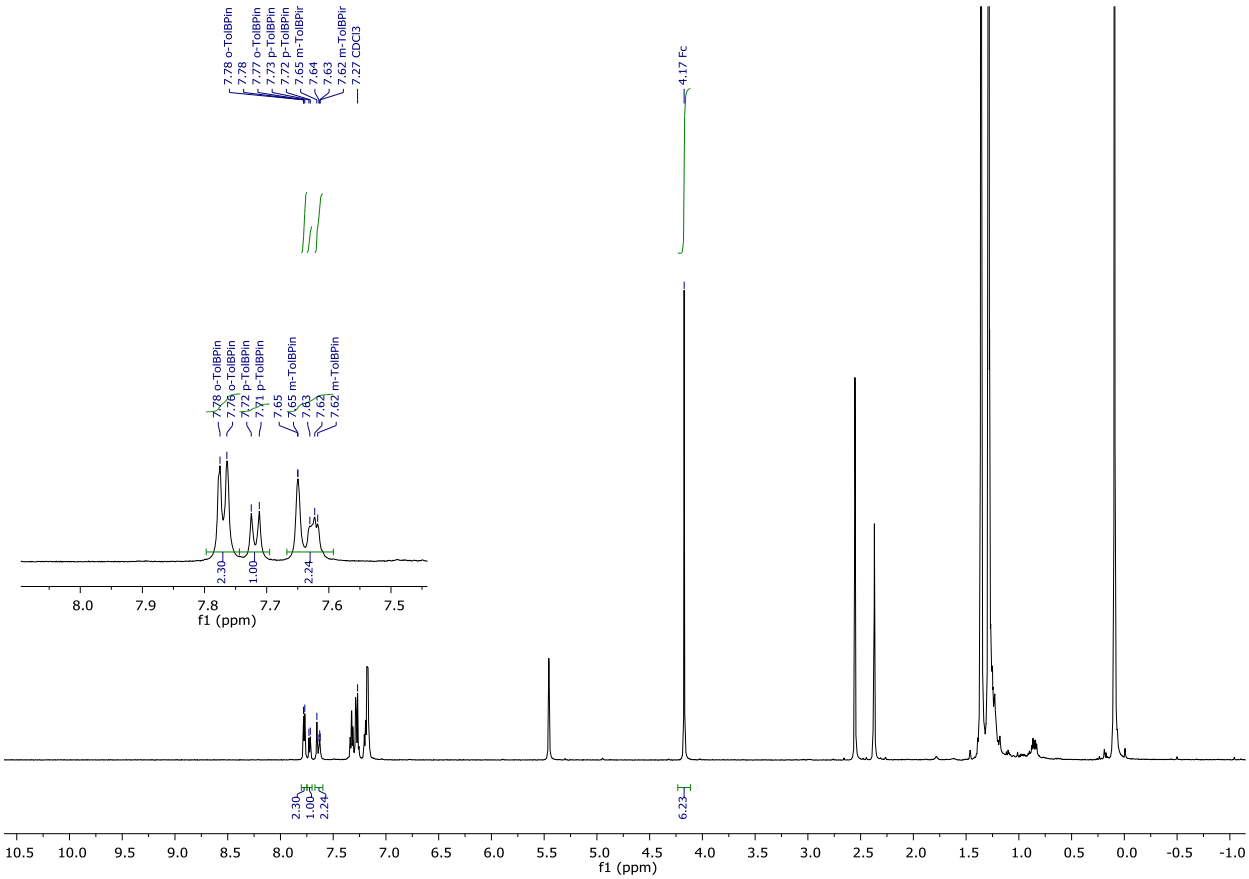
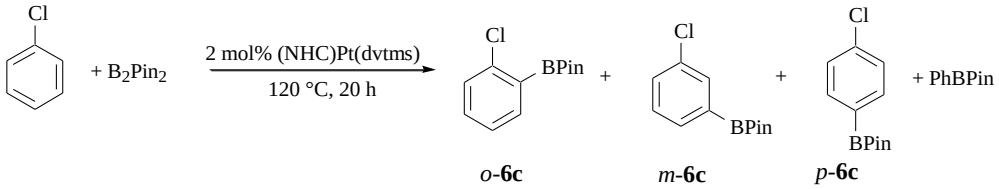


Figure S2 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of toluene with IPrPt(dvtms) (**1c**) at 140 °C.

Borylation of chlorobenzene



o-**6c** *m*-**6c** *p*-**6c**

(*o*-6c) ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm **7.71 – 7.66** (m, 1H), 7.35 – 7.32 (m, 2H), 7.23 (ddd, *J* = 7.3, 5.6, 3.1 Hz, 1H), 1.37 (s, 12H)[S4]

(*m*-6c) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.78** (dd, *J* = 2.3, 1.1 Hz, 1H), 7.66 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.42 (ddd, *J* = 7.7, 2.3, 1.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 1.34 (s, 12H)[S4]

(*p*-6c) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm **7.74 – 7.72** (d, *J* = 8.3 Hz, 2H), 7.35 – 7.34 (d, *J* = 8.3 Hz, 2H), 1.34 (s, 12H)[S5]

(PhBPin) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.81** (d, *J* = 7.0 Hz, 2H), 7.45 (m, 1H), 7.36 (m, 2H), 1.34 (s, 12H)[S6]

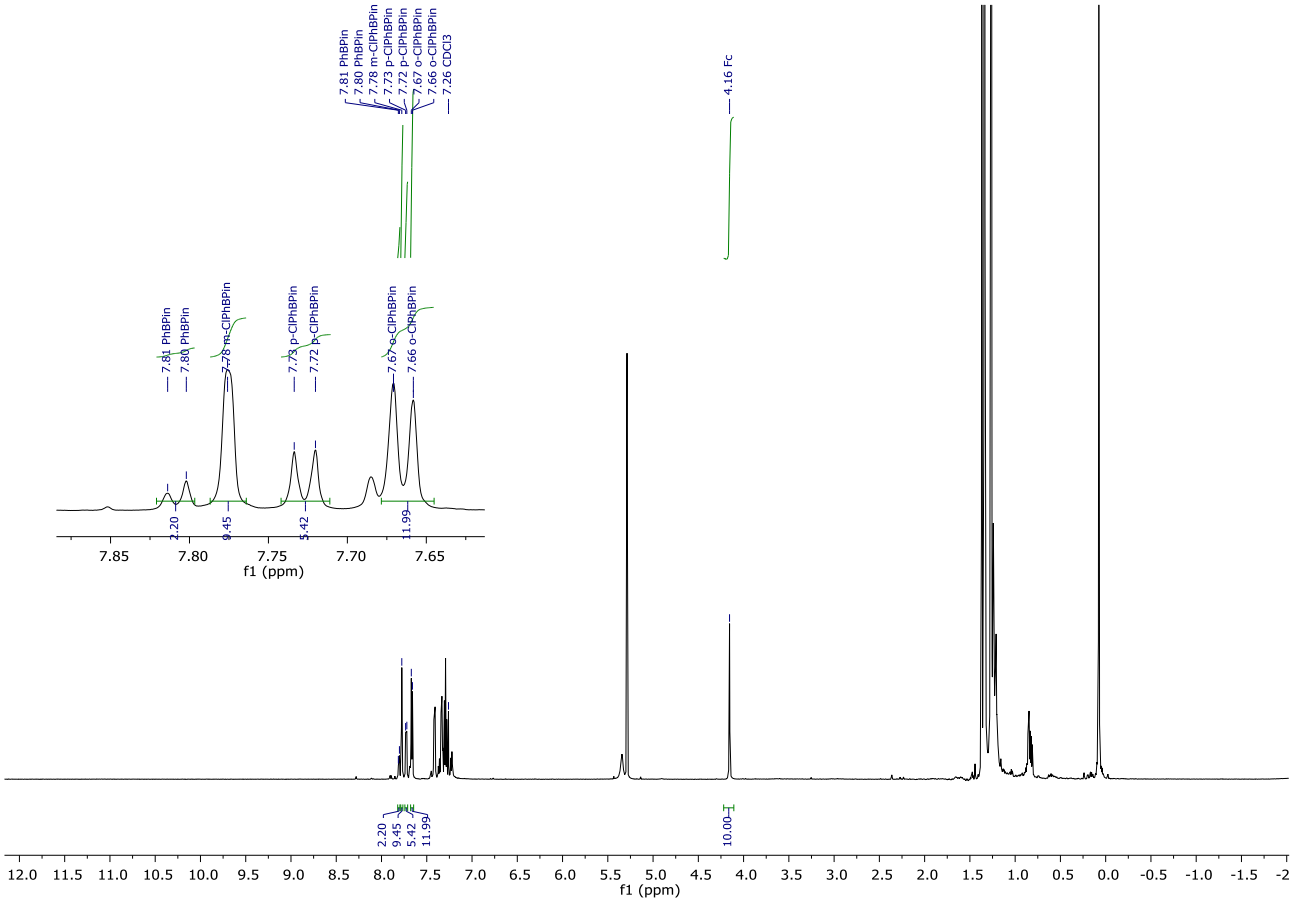
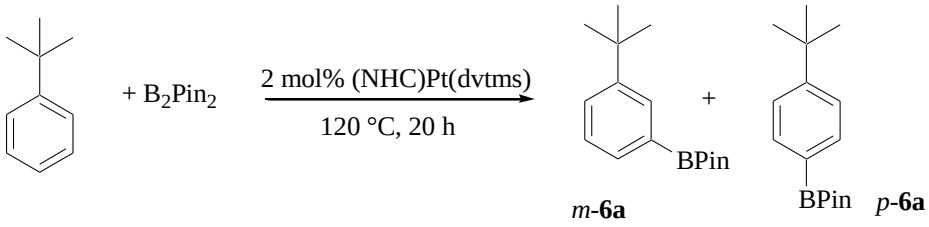


Figure S3 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of PhCl with (7-Dipp)Pt(dvtms) (**1o**) at 120°C

Borylation of tert-butylbenzene



(*m*-6a) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **7.86** (s, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52 (ddd, *J* = 7.9, 2.0, 1.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 1.36 (s, 21H)[S7]

(*p*-6a) ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm **7.79 – 7.76** (d, *J* = 8.3 Hz, 2H), 7.43 – 7.41 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 12H), 1.34 (s, 9H)[S5]

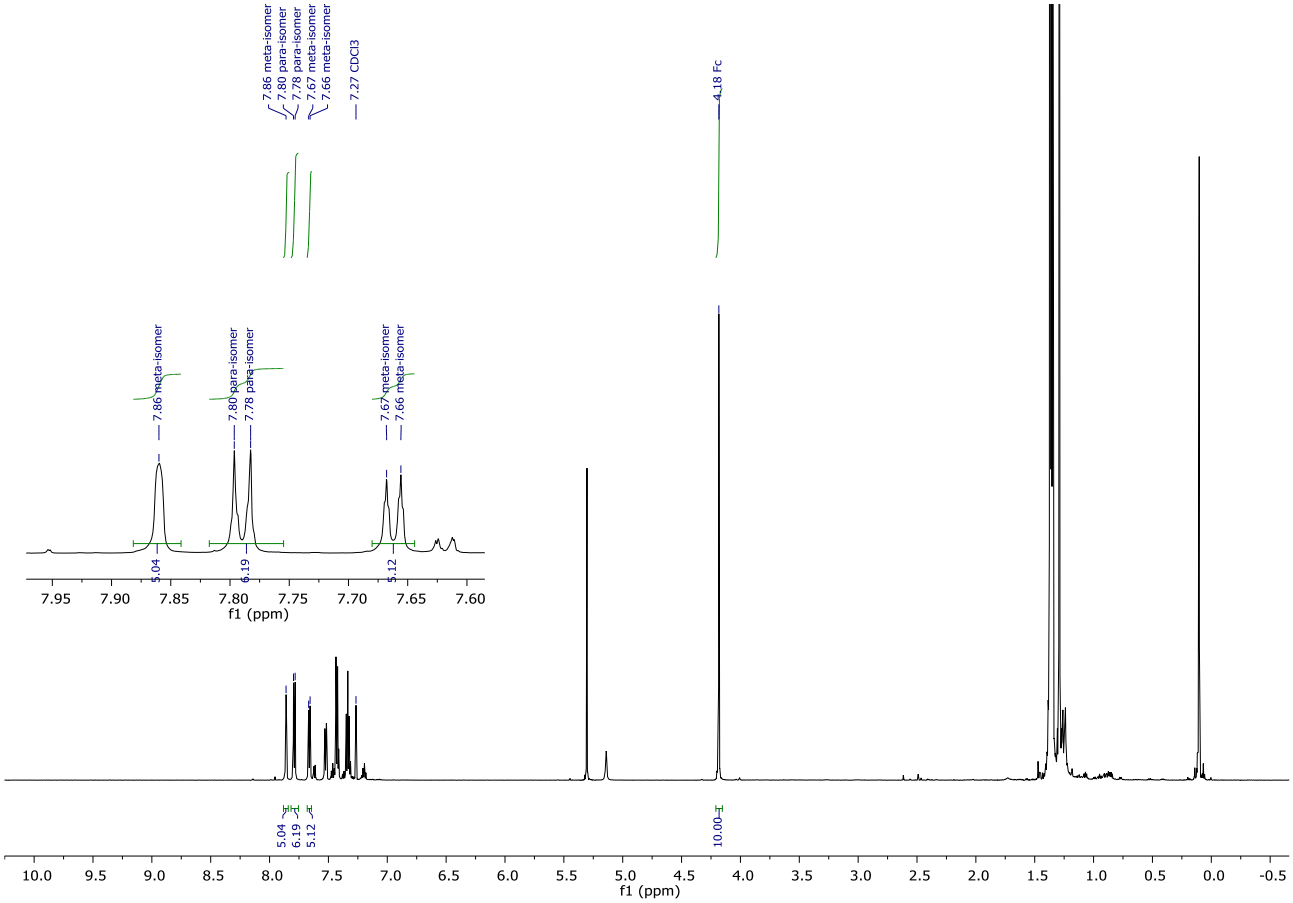
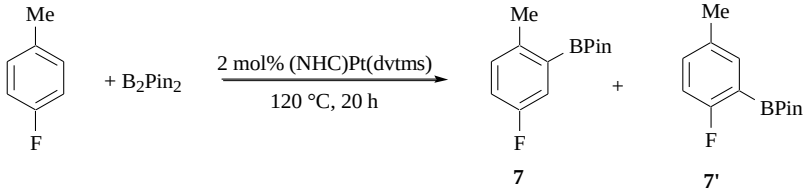


Figure S4 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of Bu^{t}Ph with (7-Dipp)Pt(dvtms) (**1o**) at 120°C

Borylation of 4-fluorotoluene



(**7**) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.42** (dd, *J* = 9.4, 2.5 Hz, 1H), 7.11 (dd, *J* = 8.6, 4.9 Hz, 1H), 6.96-7.01 (m, 1H), 1.36 (s, 12H)[S8]

(7') ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **7.52** (dd, *J* = 5.5, 2.3 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.91 (t, *J* = 8.7 Hz, 1H), 1.36 (s, 12H)[S8]

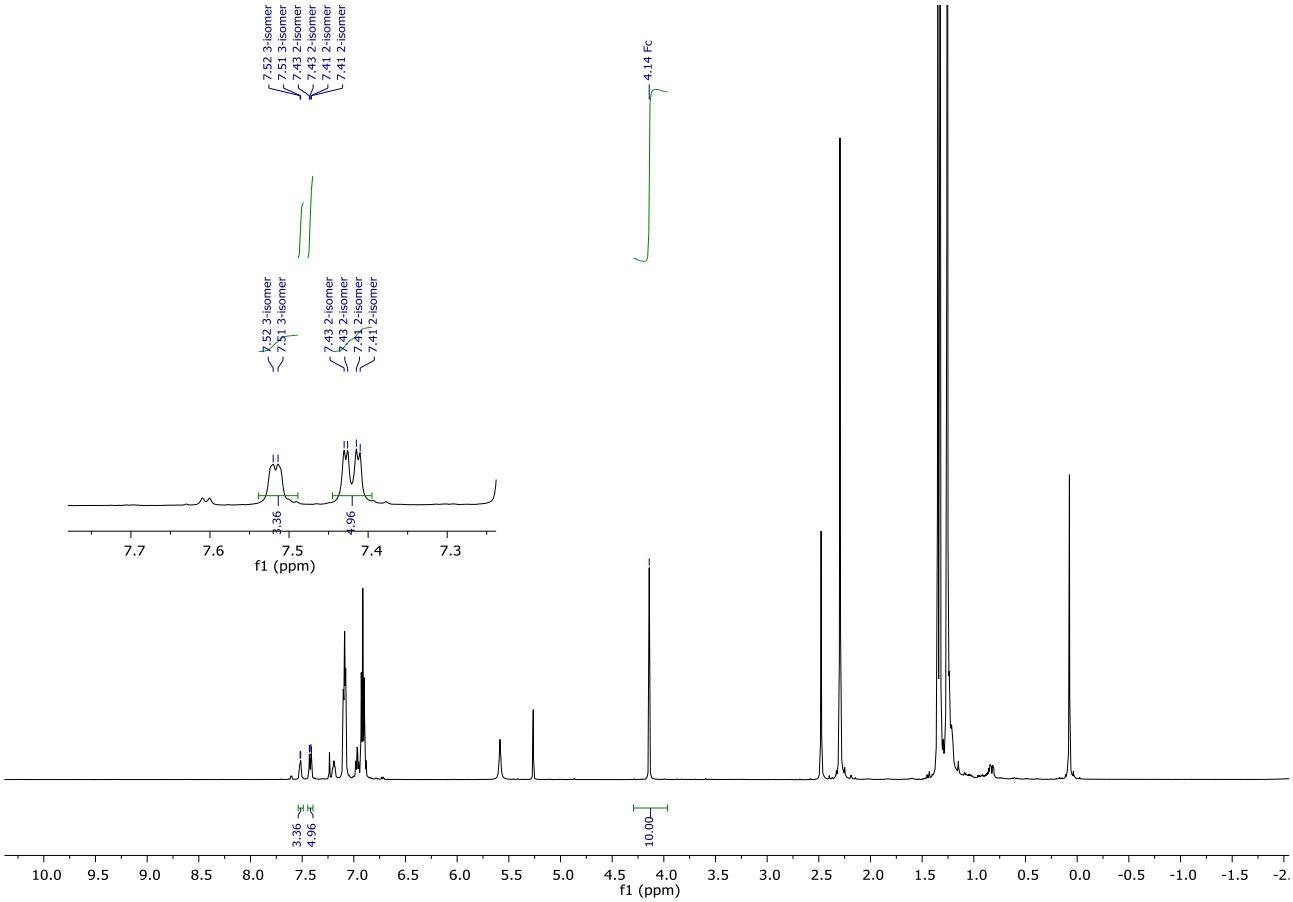
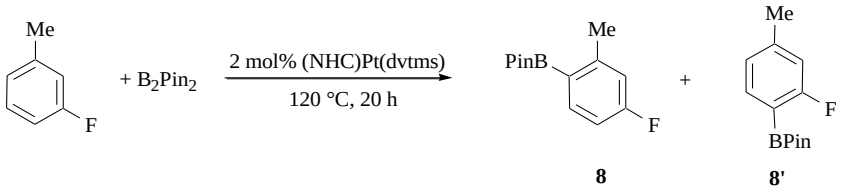


Figure S5 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of 4-fluorotoluene with (7-Dipp)Pt(dvtms) **(1o)** at 120 °C

Borylation of 3-fluorotoluene



8 **8'**

(8) ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm **7.75** (t, *J* = 7.5 Hz, 1H), 6.87-6.83 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H)[S9]

(**8'**) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **7.61** (t, *J* = 7.4 Hz, 1H), 7.00 – 6.92 (m, 1H), 6.85 (d, *J* = 10.3 Hz, 1H), 2.35 (s, 3H), 1.35 (s, 12H)[S9]

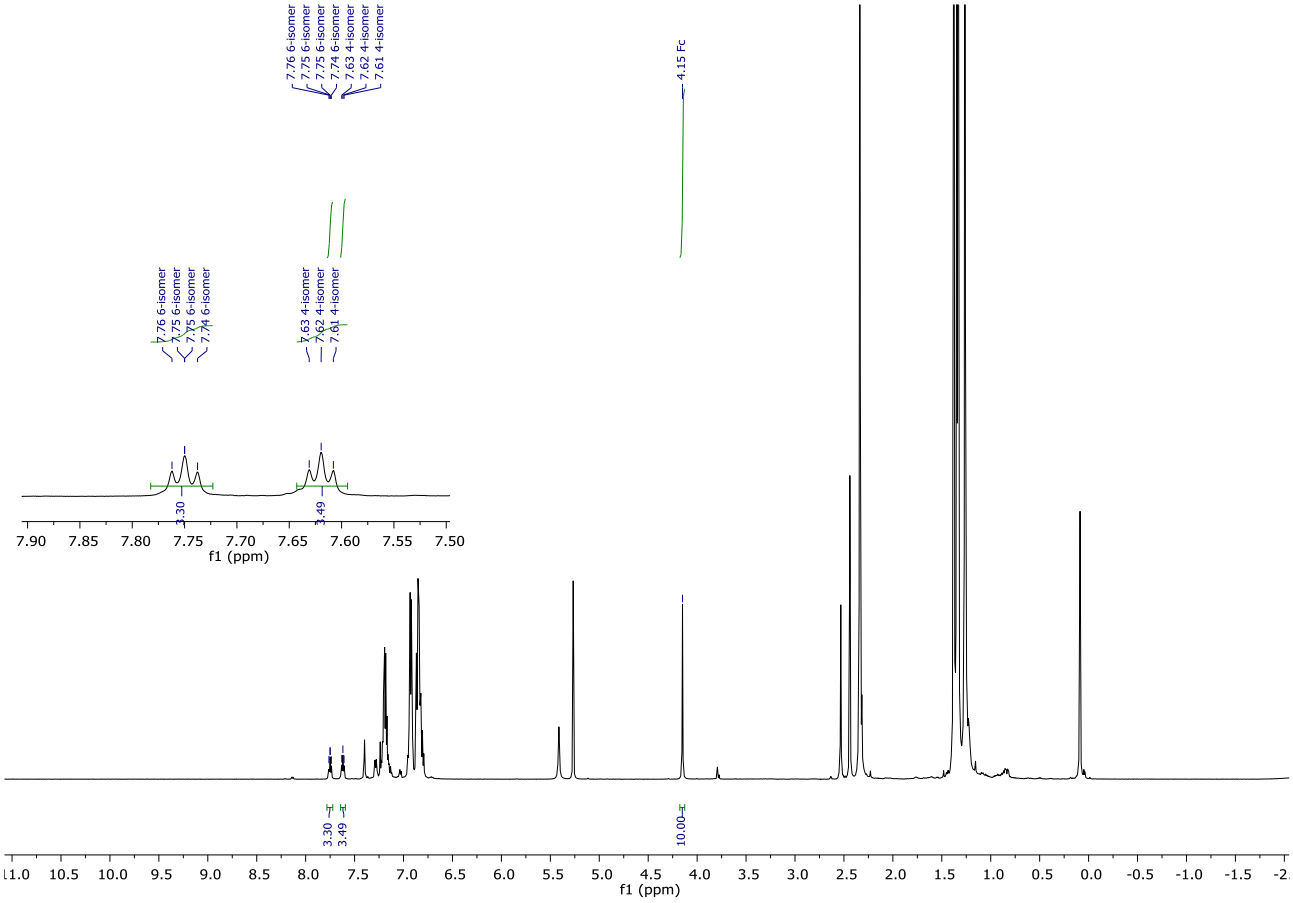
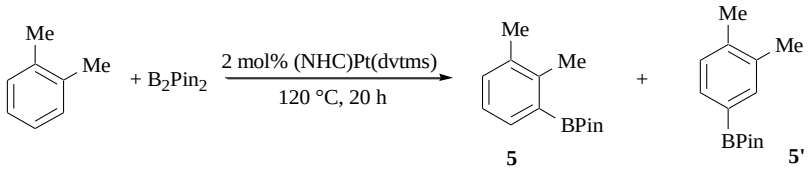


Figure S6 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of 3-fluorotoluene with (7-Dipp)Pt(dvtms) (**1o**) at 120°C

Borylation of o-xylene



(5) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm **7.63 – 7.62** (d, *J* = 7.3 Hz, 1H), 7.23 – 7.22 (m, 1H), 7.12 – 7.09 (t, *J* = 7.4 Hz, 1H), 2.49 (s, 3H), 2.29 (s, 3H), 1.36 (s, 12H)[S5]

(5') ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **7.60** (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.35 (s, 12H)[S7]

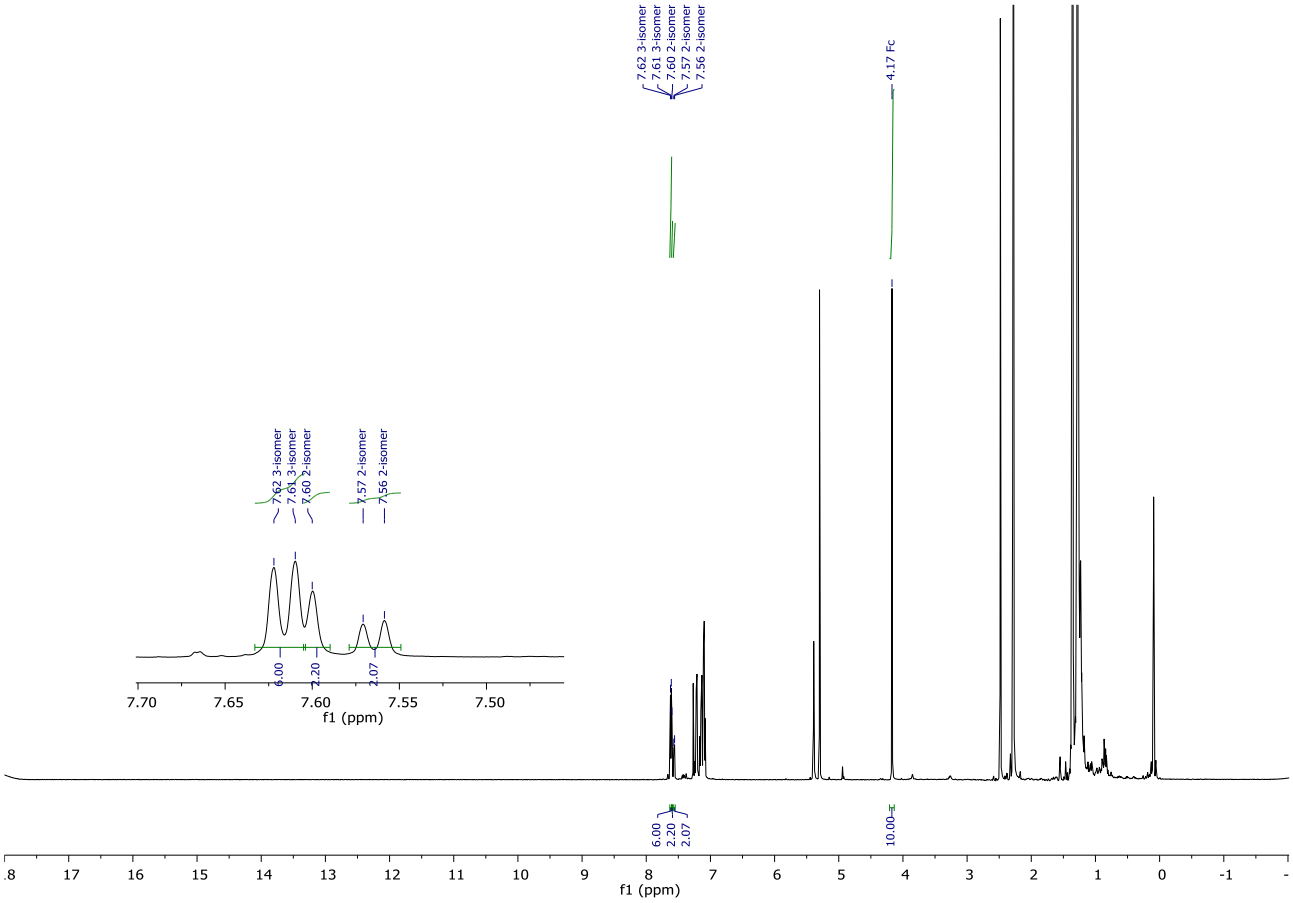
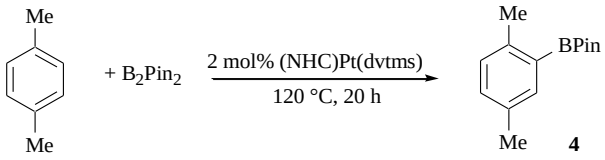


Figure S7 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of *o*-xylene with (7-Dipp)Pt(dvtms) **(1o)** at 120°C

Borylation of p-xylene



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(**4**) ^{1}H NMR (399.78 MHz, $CDCl_3$) δ ppm **7.57** (d, *J* = 1.4 Hz, 1H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 2.49 (s, 3H), 2.30 (s, 3H), 1.34 (s, 12H)[S10, 11]

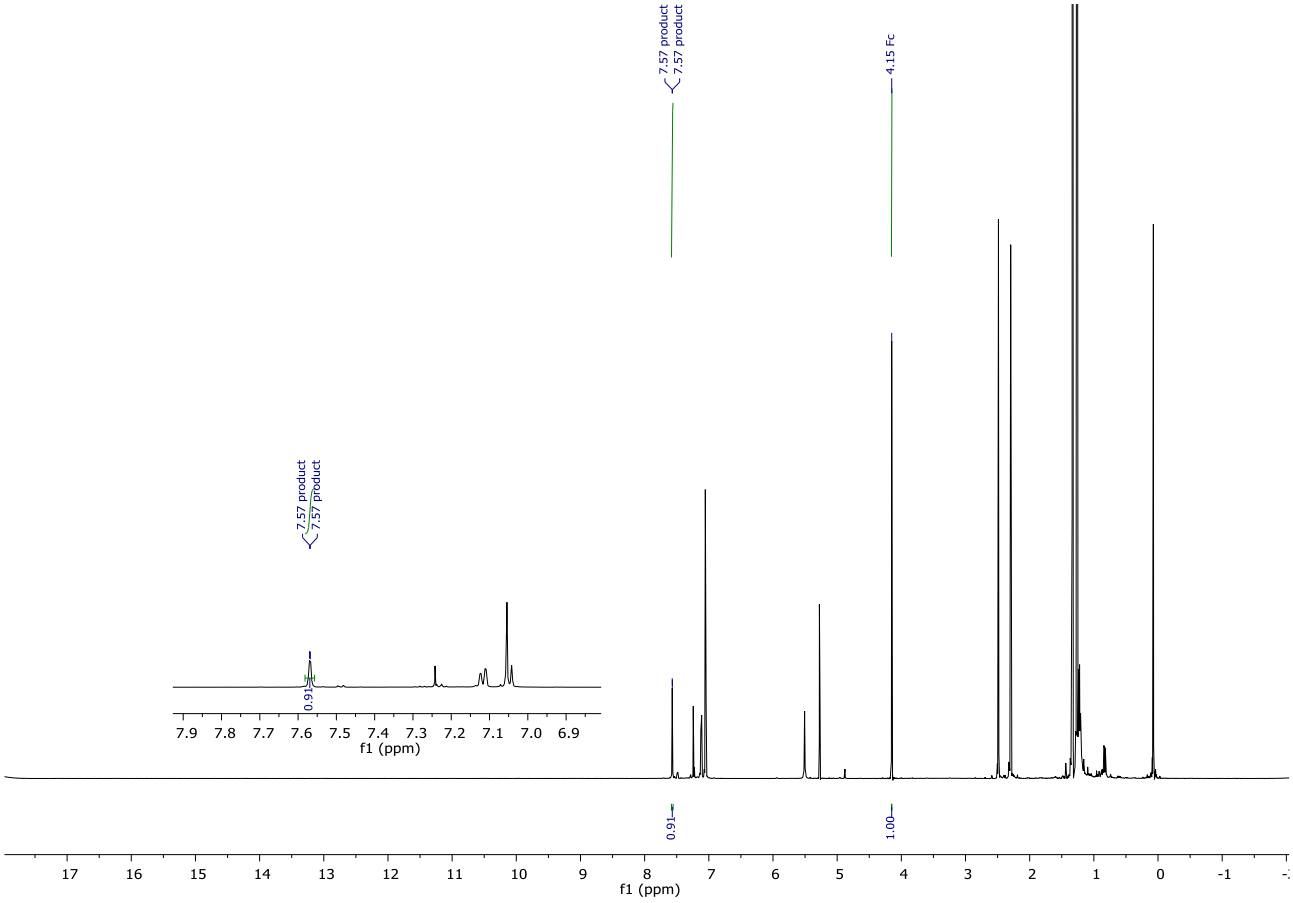
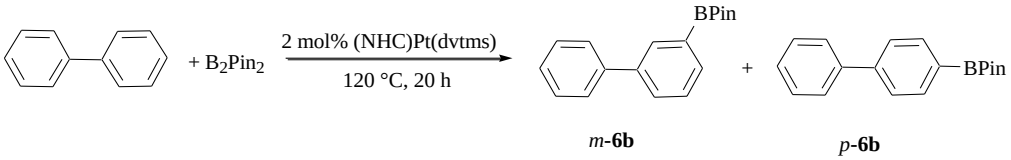


Figure S8 ^{1}H NMR (600 MHz, $CDCl_3$). Borylation of *p*-xylene with (7-Dipp)Pt(dvtms) **(1o)** at 120°C

Borylation of biphenyl



(*m*-6b) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **8.05** (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.33 (dd, *J* = 7.7, 7.7 Hz, 1H), 1.36 (s, 12H)[S12]

(*p*-6b) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm **7.89** (d, *J* = 8.3 Hz, 2H), 7.63-7.60 (m, 4H), 7.46-7.42 (m, 2H), 7.35 (tt, *J* = 7.4, 1.3 Hz, 1H), 1.36 (s, 12H)[S12]

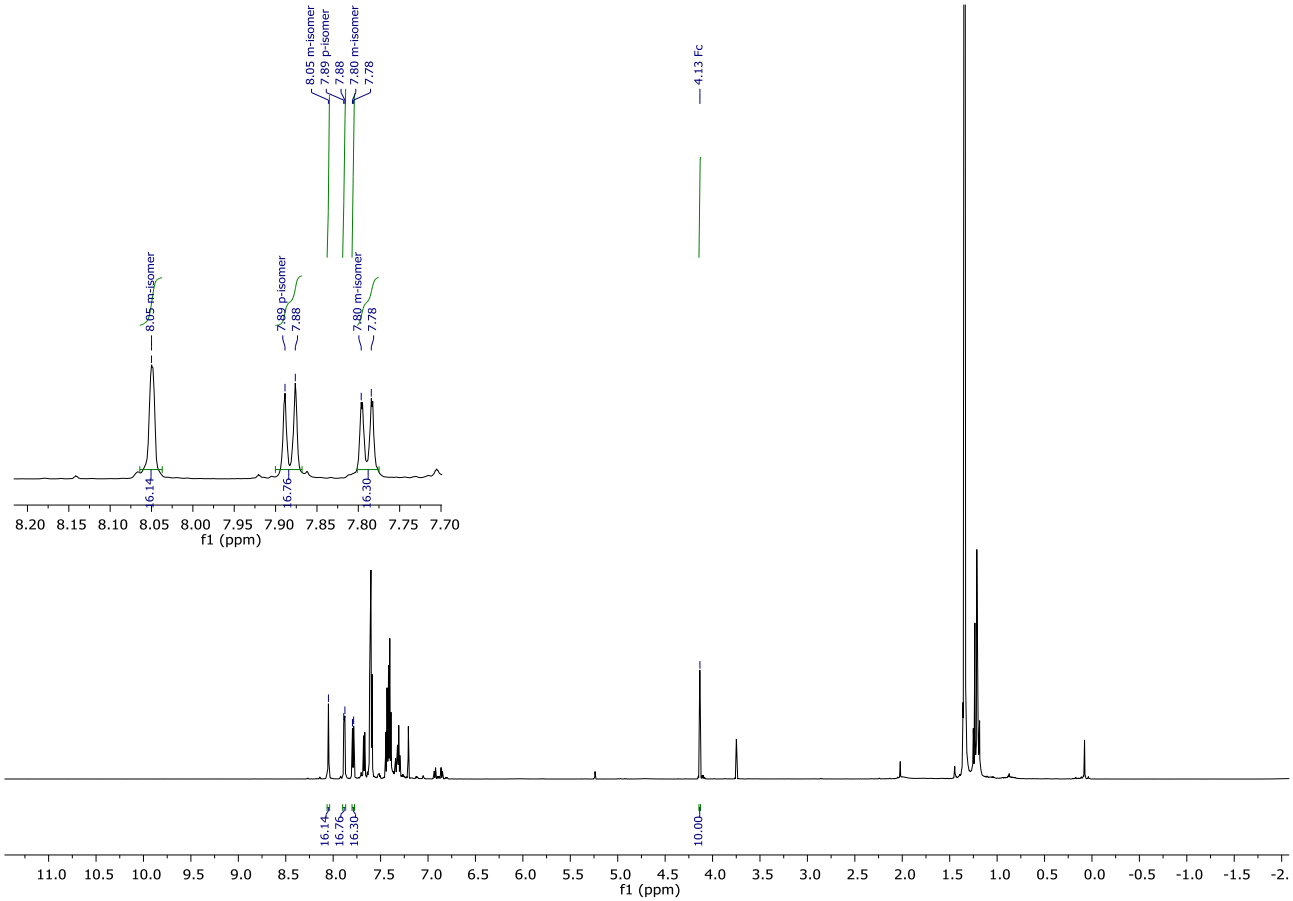
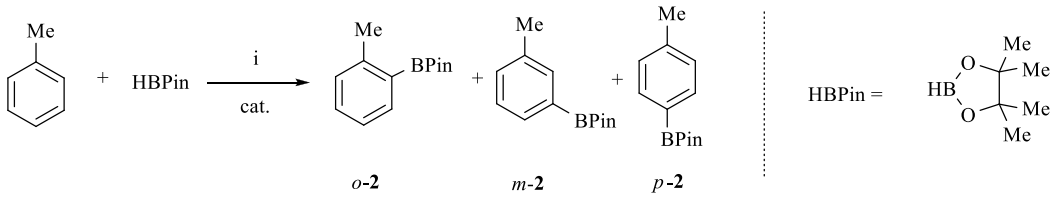


Figure S9 ^{1}H NMR (600 MHz, Chloroform-*d*). Borylation of biphenyl with (7-Dipp)Pt(dvtms) **(1o)** at 120°C

General procedure for the catalytic borylation of toluene with HBPin



CAUTION: the reaction mixture may be heated above the boiling point of the substrate in a closed vessel. To avoid the risks, the equipment intended for elevated pressure operations should be applied, a J-Young type stopper is recommended).

A 10 ml Schlenk flask equipped with a magnetic stir bar was charged with toluene (2.3 ml) and (NHC)Pt(dvtms) (1 mol%). The solution was degassed using 3 freeze-pump-thaw cycles, HBPin (100 µl, 0.69 mmol) was added. %The flask was placed into a preheated oil bath at specified temperature and stirred for 20 h. The reaction mixture was filtered through a pad of Celite®, evaporated to dryness and analyzed by ^{1}H NMR using ferrocene (Fc) as the internal standard.

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