Supporting Information for:
Regioselective Electrophilic Borylation of Haloarenes.
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General Considerations:

All manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox unless otherwise stated. Glassware was dried in a hot oven overnight. Haloarenes, DMTol (N,N,4-trimethylaniline), 2,6-lutidine and Et$_3$N were distilled from CaH$_2$ prior to use unless otherwise stated. All other materials were purchased from commercial vendors and used as received. DMTol-BCl$_3$ was prepared following the reported procedure.$^1$ NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz $^1$H; 101 MHz $^{13}$C; 128 MHz $^{11}$B; 376 MHz $^{19}$F; 62 MHz, $^{27}$Al 104 MHz).

$^1$H NMR chemical shifts values are reported in ppm relative to protio impurities in the deuterated solvents (e.g. CHCl$_3$ in CDCl$_3$ $\delta$H = 7.27; CH$_2$Cl$_2$ in CD$_2$Cl$_2$ $\delta$H = 5.32) as internal standards and $^{13}$C NMR using the centre line of CDCl$_3$ ($\delta$C = 77.0) or CD$_2$Cl$_2$ ($\delta$C = 54.0) as appropriate as internal standard. All coupling constants ($J$) are reported in Hertz (Hz). $^{11}$B NMR spectra were referenced to external BF$_3$:Et$_2$O, $^{19}$F to CFCl$_3$ and $^{27}$Al to Al(NO$_3$)$_3$ in D$_2$O (Al(D$_2$O)$_6$$^{3+}$). Unless otherwise stated all NMR are recorded at 293 K. Elemental analysis of air sensitive compounds were performed by London Metropolitan University service. Broad features in the $^{11}$B and $^{27}$Al NMR spectra are due to materials present in the spectrometer probe/NMR tube glass. Resonances for the carbon directly bonded to boron are not observed in the $^{13}$C($^1$H) NMR spectra.

GC spectra for borylated bromobenzene were recorded on a Thermo Finnigan Focus GC with Flame Ionisation Detector. The column employed was an Agilent Technologies J&W DB-Wax (polyethylene glycol) of dimension: length, 15 m; internal diameter 0.32 mm; film, 0.25 µm. The following temperature program was used: Initial temperature: 70 °C, held at temperature for 2 min, increase temperature at a rate: 5 °C/min until temperature: 150 °C, then increase temperature at a rate: 20 °C/min until final temperature: 250 °C. The temperature of injector and detector were maintained at 250 °C.

GC spectra for borylated 2-fluorotoluene were recorded on a Thermo Scientific Trace 1310 GC with Flame Ionisation Detector The column employed was a Zebron ZB-SemiVolatiles w/10m GUARDIAN (5% Phenyl-Arylene 95% Dimethylpolysiloxane) of dimension: length, 30 m; internal diameter 0.25 mm; film, 0.25 µm. The following temperature program was used: Initial temperature: 70 °C, held at temperature for 2 min, increase temperature at a rate: 5 °C/min until temperature: 200 °C, then increase temperature at a rate: 20 °C/min until final temperature: 300 °C. The temperature of injector and detector were maintained at 300 °C.

New aryl boronate ester compounds were identified by X-ray diffraction studies and/or 1D / 2D NMR spectroscopy.
General procedure A (Borylation of haloarene with DMTol-BCl$_3$/AlCl$_3$ in a 1 : 2 ratio):

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with DMTol-BCl$_3$ (200 mg, 0.79 mmol), powdered AlCl$_3$ (211 mg, 1.58 mmol) and anhydrous haloarene (0.8 ml). The NMR tube was sealed, removed from the glovebox and the reaction mixture was heated with initial shaking to ensure complete dissolution of solids. Periodically the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. After the reaction was judged to be finished, the mixture was cooled to room temperature and transferred dropwise via cannula under a positive pressure of nitrogen to a mixture of pinacol (300 mg, 2.54 mmol) and Et$_3$N (1.7 ml) in CH$_2$Cl$_2$ (10 ml) at 0 °C (pinacol, Et$_3$N and CH$_2$Cl$_2$ were used without any purification), with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH$_2$Cl$_2$ (2 × 2 ml) the mixture was stirred at 20 °C for 14 hours. All further manipulations were performed without using Schlenk line techniques and dried solvents. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (100 mL) and the solid removed by filtration through celite, upon washing with further hexane (2 × 150 ml) the extracts were combined and the volatiles removed in vacuo.

General procedure B (Borylation of haloarene with [Cl$_2$Py-BCl$_2$][AlCl$_4$]/AlCl$_3$ in a 1 : 1 ratio):

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with [Cl$_2$Py-BCl$_2$][AlCl$_4$] (319 mg, 0.80 mmol), powdered AlCl$_3$ (107 mg, 0.80 mmol) and anhydrous haloarene (0.8 ml). The NMR tube was sealed, removed from the glovebox and the reaction mixture was heated with initial shaking to ensure complete dissolution of solids. Periodically, the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. After the reaction was judged to be finished, the mixture was cooled to room temperature and transferred dropwise via cannula under a positive pressure of nitrogen to a mixture of pinacol (300 mg, 2.54 mmol) and Et$_3$N (1.7 ml) in CH$_2$Cl$_2$ (10 ml) at 0 °C (pinacol, Et$_3$N and CH$_2$Cl$_2$ were used without any purification), with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH$_2$Cl$_2$ (2 × 2 ml) the mixture was stirred at 20 °C for 14 hours. All further manipulations were performed without using Schlenk line techniques and dried solvents. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (100 mL) and the solid removed by filtration through celite, upon washing with further hexane (2 × 150 ml) the extracts were combined and the volatiles removed in vacuo.
Borylation of 1,2-dichlorobenzene with DMTol-BCl₃/AlCl₃ in a 1:2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 24 hours.

Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a pale yellow oil (173 mg, 80%).

Elemental analysis Found: C, 52.40; H, 5.69. Calc. for C₁₂H₁₅BCl₂O₂: C, 52.80; H, 5.54.

The ¹H and ¹³C NMR data are identical to that previously reported.² Representative NMR spectra are shown below.

¹H NMR (400 MHz,CDCl₃) δ = 7.87 (d, J = 1.5 Hz, 1 H), 7.60 (dd, J = 1.5, 7.9 Hz, 1 H), 7.45 (d, J = 7.9 Hz, 1 H), 1.35 (s, 12 H).

¹³C{¹H} NMR (101MHz,CDCl₃) δ = 136.6, 135.5, 133.7, 132.3, 130.0, 84.3, 24.8.

¹¹B NMR (128 MHz,CDCl₃) δ = 30.3.

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²Representative NMR spectra are shown below.
Borylation of bromobenzene with DMTol-BCl/AlCl₃ in a 1:2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 2 hours.

Purification: The crude product was absorbed on silica and purified by chromatography on silica gel (eluent hexane : CH₂Cl₂ 1:9 to hexane : CH₂Cl₂ = 2:8). The product was dried at 20 °C at 4x10⁻² torr to remove residual DMTol giving 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8 : 1 ratio) as colourless solid (202 mg, 80%).

Following the general procedure A; Temperature: 100 °C; Reaction time: 6 hours.

Purification: The crude product was absorbed on silica and purified by chromatography on silica gel (eluent hexane : CH₂Cl₂ 1:9 to hexane : CH₂Cl₂ = 2:8). The product was dried at 20 °C at 4x10⁻² torr to remove residual DMTol giving 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23 : 1 ratio) as colourless solid (132 mg, 59%).

Elemental analysis Found: C, 51.38; H, 5.61. Calc. for C₁₂H₁₆BBrO₂: C, 50.94; H, 5.70.

The NMR spectra are identical to that previously reported. Representative spectra are shown below.

H NMR (400MHz,CDCl₃) δ = 7.67 (d, J = 8.2 Hz, 2 H), 7.51 (d, J = 8.2 Hz, 2 H), 1.35 (s, 12 H).

C¹H NMR (101 MHz,CDCl₃) δ = 136.3, 130.9, 126.2, 84.0, 24.8.

B NMR (128 MHz,CDCl₃) δ = 30.8.
Borylation of fluorobenzene with DMTol-BCl/AlCl$_3$ in a 1:2 ratio:

Following the general procedure A; Temperature: 100 °C; Reaction time: 2 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH$_2$Cl$_2$. The product was dried at 20 °C at 4x10$^{-3}$ torr to remove DMTol giving 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 3 % of others isomers as pale yellow oil (94 mg, 53 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported.$^4$ Representative spectra are shown below.

$^1$H NMR (400MHz,CDCl$_3$) $\delta$ = 7.82 (tdd, J = 2.2, 6.3, 8.6 Hz, 2 H), 7.06 (tdd, J = 2.2, 8.6, 9.2 Hz, 2 H), 1.35 (s, 12 H).

$^{13}$C NMR (101MHz,CDCl$_3$) $\delta$ = 165.1 (d, J = 251.0 Hz), 137.0 (d, J = 8.3 Hz), 114.8 (d, J = 220.3 Hz), 83.9, 24.8.

$^{11}$B NMR (128MHz,CDCl$_3$) $\delta$ = 30.6.

$^{19}$F NMR (376MHz,CDCl$_3$) $\delta$ = 108.4 (tt, J = 6.2, 9.2 Hz).
Borylation of chlorobenzene with DMTol-BCl/AlCl₃ in a 1:2 ratio:

with 10 equivalents

Following the general procedure A using 0.8 ml (10 equivalents) of chlorobenzene; Temperature: 100 °C; Reaction time: 7 hours.

Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as pale yellow oil (148 mg, 78 %).

with 5 equivalents

Following the general procedure A using 0.4 ml (5 equivalents) of chlorobenzene; Temperature: 100 °C; Reaction time: 7 hours.

Purification: The crude material was dissolved in 20 ml of hexane and washed with HCl (6 N, 20 ml). The aqueous phase was extracted with hexane (2 x 20 ml). The combined organic layers were washed with brine (10 ml) and dried over MgSO₄. Removal of volatiles at 20 °C at 4x10⁻² torr gave 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as pale yellow oil (138 mg, 73 %).

Elemental analysis Found: C, 60.70; H, 6.81. Calc. for C_{12}H_{16}BClO₂: C, 60.43; H, 6.76.

The NMR spectra are identical to that previously reported.² Representative NMR spectra are shown below.

Selected NMR data for 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

¹H NMR (400 MHz,CDCl₃) δ = 7.74 (td, J = 1.8, 8.3 Hz, 2 H), 7.35 (td, J = 1.9, 8.3 Hz, 2 H), 1.35 (s, 12 H).

¹³C{¹H} NMR (101MHz,CDCl₃) δ = 137.5, 136.1, 128.0, 84.0, 24.8.

¹¹B NMR (128 MHz,CDCl₃) δ = 30.6.
$^{11}$B NMR
Borylation of 1-chloro-2-fluorobenzene

with DMTol-BCl\textsubscript{3}/AlCl\textsubscript{3} in a 1 : 2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 21 hours.

Purification: The crude material was dissolved in 20 ml of hexane and washed with HCl (6 N, 20 ml). The aqueous phase was extracted with hexane (2 x 20 ml). The combined organic layers were washed with brine (10 ml) and dried over MgSO\textsubscript{4}. Removal of volatiles at 20 °C at 4x10\textsuperscript{-2} torr gave a mixture of 2-(3-chloro-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-chloro-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.2 : 1 ratio) and less than 5 % of another isomer as pale yellow oil (153 mg, 75%).

with [Cl\textsubscript{3}Py-BCl\textsubscript{2}][AlCl\textsubscript{4}]/AlCl\textsubscript{3} in a 1 : 1 ratio:

Following the general procedure B; Temperature: 140 °C; Reaction time: 41 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH\textsubscript{2}Cl\textsubscript{2}. Removal of volatiles at 60 °C at 50 torr gave a mixture of 2-(3-chloro-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-chloro-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.4 : 1 ratio) and less than 5 % of another isomer as pale yellow oil (152 mg, 74 %).

Elemental analysis Found: C, 56.65; H, 6.26. Calc. for C\textsubscript{12}H\textsubscript{15}BClFO\textsubscript{2}: C, 56.19; H, 5.89.

Representative NMR spectra are shown below.

Selected NMR data for 2-(3-chloro-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:
The $^1$H NMR data is identical to that previously reported.$^5$

\begin{align*}
^1\text{H NMR} (400 MHz, CDCl\textsubscript{3}) & \delta = 7.85 (dd, J = 1.5, 8.1 Hz, 1 H), 7.67 (ddd, J = 1.5, 5.2, 8.1 Hz, 1 H), 7.13 (dd, J = 8.2, 9.2 Hz, 1 H), 1.35 (s, 12 H), 1.34 (s, 12 H). \\
^13\text{C} (^1\text{H}) \text{ NMR} (101 MHz, CDCl\textsubscript{3}) & \delta = 160.2 (d, J = 235.1 Hz), 137.2, 134.8 (d, J = 8.1 Hz), 120.8 (d, J = 16.9 Hz), 116.2 (d, J = 19.8 Hz), 84.2, 24.8. \\
^19\text{F} \text{ NMR} (376 MHz, CDCl\textsubscript{3}) & \delta = 111.2 (dt, J = 5.1, 8.5 Hz). \\
^11\text{B} \text{ NMR} (128 MHz, CDCl\textsubscript{3}) & \delta = 30.3.
\end{align*}

Selected NMR data for 2-(4-chloro-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:
The $^1$H NMR data is identical to that previously reported.$^6$

\begin{align*}
^1\text{H NMR} (400 MHz, CDCl\textsubscript{3}) & \delta = 7.55 (dd, J = 1.3, 9.6 Hz, 1 H), 7.50 (dd, J = 1.3, 7.8 Hz, 1 H), 7.40 (dd, J = 7.1, 7.8 Hz, 1 H), 1.35 (s, 12 H), 1.34 (s, 12 H). \\
^13\text{C} (^1\text{H}) \text{ NMR} (101 MHz, CDCl\textsubscript{3}) & \delta = 157.8 (d, J = 240.7 Hz), 131.0 (d, J = 3.7 Hz), 130.2, 124.1 (d, J = 17.6 Hz), 122.2 (d, J = 19.1 Hz), 84.3, 24.8. \\
^19\text{F} \text{ NMR} (376 MHz, CDCl\textsubscript{3}) & \delta = 111.2 (dd, J = 7.2, 9.2 Hz). \\
^11\text{B} \text{ NMR} (128 MHz, CDCl\textsubscript{3}) & \delta = 30.3.
\end{align*}
Borylation of 1-bromo-2-fluorobenzene

with DMTol-BCl/AlCl₃ in a 1 : 2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 24 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving a mixture of 2-(3-bromo-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-bromo-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.8 : 1 ratio) and less than 5 % of another isomer as pale yellow oil (191 mg, 80 %).

with [Cl₂Py-BCl₂][AlCl₄]/AlCl₃ in a 1 : 1 ratio:

Following the general procedure B; Temperature: 140 °C; Reaction time: 24 hours.

Purification: The crude product was absorbed on silica and purified by chromatography on silica gel (eluent hexane : EtOAc 1 : 9 to hexane : EtOAc 3 : 7). Removal of volatiles at 60 °C at 50 torr gave a mixture of 2-(3-bromo-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-bromo-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.3 : 1 ratio) and less than 5 % of another isomers pale yellow oil (189 mg, 78 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (albeit containing two major isomers). Representative NMR spectra are shown below. Isomers were identified by comparison to the known related chloro isomers (see above) and by J couplings, NOESY and HBQC NMR.

Selected NMR data for 2-(3-bromo-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

- **¹H NMR (400MHz, CDCl₃)**: δ = 8.01 (dd, J = 1.5, 7.3 Hz, 1 H), 7.72 (dd, J = 1.6, 5.3, 8.2 Hz, 1 H), 7.11 (dd, J = 8.2, 8.8 Hz, 1 H), 1.35 (s, 12 H).
- **¹³C{¹H} NMR (101 MHz, CDCl₃)**: δ = 161.1 (d, J = 251.6 Hz), 140.1, 135.6 (d, J = 8.1 Hz), 116.1 (d, J = 21.3 Hz), 108.9 (d, J = 19.8 Hz), 84.2, 24.8.
- **¹⁹F NMR (376 MHz, CDCl₃)**: δ = -102.9 (ddd, J = 5.3, 7.3, 8.8 Hz).
- **¹¹B NMR (128 MHz, CDCl₃)**: δ = 30.1.

Selected NMR data for 2-(4-bromo-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

- **¹H NMR (400 MHz, CDCl₃)**: δ = 7.59 - 7.50 (m, 2 H), 7.43 (dd, J = 1.5, 7.8 Hz, 1 H), 1.35 (s, 12 H).
- **¹³C{¹H} NMR (101 MHz, CDCl₃)**: δ = 158.8 (d, J = 248.7 Hz), 133.1, 131.3 (d, J = 3.7 Hz), 122.0 (d, J = 20.5 Hz), 112.5 (d, J = 20.8 Hz), 84.3, 24.8.
- **¹⁹F NMR (376 MHz, CDCl₃)**: δ = -108.78 (dd, J = 6.8, 8.9 Hz).
- **¹¹B NMR (128 MHz, CDCl₃)**: δ = 30.1.
Borylation of 1,3-dichlorobenzene with DMTol-BCl/AlCl₃ in a 1 : 2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 40 hours.

Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving 2-(2,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 3 % of other isomers as pale yellow oil (109 mg, 50 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported. Representative NMR spectra are shown below.

**¹H NMR (400MHz, CDCl₃)** δ = 7.56 (d, J = 8.0 Hz, 1 H), 7.30 (d, J = 1.8 Hz, 1 H), 7.15 (dd, J = 1.8, 8.0 Hz, 1 H), 1.29 (s, 12 H).

**¹³C{¹H} NMR (101MHz, CDCl₃)** δ = 140.4, 137.4, 137.3, 129.4, 126.2, 84.3, 24.8.

**¹¹B NMR (128MHz, CDCl₃)** δ = 30.4.

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Borylation of 1,3-difluorobenzene with DMTol-BCl/AlCl₃ in a 1 : 2 ratio:

Following the general procedure A; Temperature: 140 °C; Reaction time: 17 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving 2-(2,4-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 3 % of other isomers as pale yellow oil (85 mg, 45 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported. Representative NMR spectra are shown below.

\( ^1H \) NMR (400 MHz, CDCl₃) \( \delta = 7.74 \text{ (q, } J = 7.3 \text{ Hz, } 1 \text{ H}), 6.87 \text{ (dt, } J = 2.1, 8.3 \text{ Hz, } 1 \text{ H}), 6.77 \text{ (dt, } J = 2.1, 9.5 \text{ Hz, } 1 \text{ H}), 1.36 \text{ (s, } 12 \text{ H}).

\( ^13C\{^1H\} \) NMR (101 MHz, CDCl₃) \( \delta = 167.8 \text{ (dd, } J = 11.7, 253.8 \text{ Hz}), 165.5 \text{ (dd, } J = 12.5, 253.1 \text{ Hz}), 138.2 \text{ (t, } J = 10.3 \text{ Hz}), 111.1 \text{ (dd, } J = 3.7, 20.2 \text{ Hz}), 103.7 \text{ (dd, } J = 24.2, 27.9 \text{ Hz}), 83.9, 24.8.\)

\( ^19F \) NMR (376 MHz, CDCl₃) \( \delta = -98.7 \text{ (dt, } J = 7.2, 10.0 \text{ Hz}), -105.1 \text{ (tt, } J = 9.5, 8.3 \text{ Hz}).

\( ^11B \) NMR (128 MHz, CDCl₃) \( \delta = 29.9.\)
$^{11}$B NMR

29.88
Borylation of 1-chloro-3-fluorobenzene:

Following the general procedure A; Temperature: 140 °C; Reaction time: 40 hours.

Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH₂Cl₂. The product was dried at 20 °C at 4x10⁻² torr to remove DMTol giving 2-(4-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of another isomer as a colourless solid (131 mg, 64 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (with only visible impurity due to a minor isomer). HRMS (APCI) Found: 257.0896. Calc. for C₁₂H₁₅BClFO₂ (M + H⁺): 257.0918.

Product characterised by combined NMR spectroscopy / X-ray diffraction studies. Representative NMR spectra are shown below.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta = 7.67 \text{ (dd, } J = 6.7, 7.9 \text{ Hz, 1 H)}, \text{ 7.14 (dd, } J = 2.0, 8.0 \text{ Hz, 1 H)}, \text{ 7.07 (dd, } J = 1.8, 9.0 \text{ Hz, 1 H)}, \text{ 1.36 (s, 12 H)}. \]

\[ ^13C\{^1H\} \text{ NMR (101 MHz, CDCl}_3) \delta = 167.0 \text{ (d, } J = 254.6 \text{ Hz)}, \text{ 138.4 (d, } J = 10.3 \text{ Hz)}, \text{ 137.6 (d, } J = 9.5 \text{ Hz)}, \text{ 124.2 (d, } J = 2.9 \text{ Hz)}, \text{ 116.1 (d, } J = 27.1 \text{ Hz)}, \]

84.1, 24.8.

\[ ^19F \text{ NMR (376 MHz, CDCl}_3) \delta = -100.5 \text{ (dd, } J = 6.6, 9.0 \text{ Hz)}. \]

\[ ^11B \text{ NMR (128 MHz, CDCl}_3) \delta = 29.9. \]
$^{11}\text{B NMR}$
Borylation of 1-bromo-3-fluorobenzene:

Following the general procedure A; Temperature: 140 °C; Reaction time: 48 hours.

Purification: The crude material was dissolved in 30 ml of hexane/\(\text{CH}_2\text{Cl}_2\) (2 : 1) and washed with HCl (6 N, 20 ml). The aqueous phase was extracted with hexane (2 x 20 ml). The combined organic layers were washed with brine (10 ml) and dried over MgSO\(_4\). Removal of volatiles at 20 °C at 4x10\(^{-2}\) torr gave 2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of another isomer as colourless solid (159 mg, 67 %).

Elemental analysis Found: C, 49.17; H, 4.97. Calc. for C\(_{12}\)H\(_{15}\)BBrFO\(_2\): C, 47.89; H, 5.02.

HRMS (APCI) Found: 301.0395. Calc. for C\(_{12}\)H\(_{15}\)BBrFO\(_2\) (M + H\(^+\)): 301.0413.

Product characterised by combined NMR spectroscopy / X-ray diffraction studies. Representative NMR spectra are shown below.

\[^1\text{H} \text{NMR} (400 \text{MHz}, \text{CDCl}_3) \ \delta = 7.61 \text{ (dd, } J = 6.8, 7.8 \text{ Hz, 1 H}), 7.29 \text{ (dd, } J = 1.5, 7.8 \text{ Hz, 1 H}), 7.24 \text{ (dd, } J = 1.5, 8.8 \text{ Hz, 5 H}), 1.36 \text{ (s, 12 H).}\]

\[^{13}\text{C} \{^1\text{H}\} \text{ NMR (101 MHz, CDCl}_3\) \ \delta = 166.9 \text{ (d, } J = 256.0 \text{ Hz), 137.8 \text{ (d, } J = 8.8 \text{ Hz), 127.1(d, } J = 3.7 \text{ Hz), 126.4(d, } J = 10.3 \text{ Hz), 119.0(d, } J = 27.9 \text{ Hz), 84.1, 24.7.}\]

\[^{19}\text{F NMR (376 MHz, CDCl}_3\) \ \delta = -100.2 \text{ (dd, } J = 6.8, 8.8 \text{ Hz).}\]

\[^{11}\text{B NMR (128 MHz, CDCl}_3\) \ \delta = 30.1.\]
Borylation 2-fluorotoluene

with DMTol-BCl/AlCl₃ in a 1 : 2 ratio:

Following the general procedure A; Temperature: 100 °C; Reaction time: 1 hour.

Purification: The crude material was dissolved in 30 ml of hexane/CH₂Cl₂ (2 : 1) and washed with HCl (6 N, 20 ml). The aqueous phase was extracted with hexane (2 x 20 ml). The combined organic layers were washed with brine (10 ml) and dried over MgSO₄. Removal of volatiles at 20 °C at 4x10⁻² torr gave a mixture of 2-(4-fluoro-3-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(3-fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 1 : 5 ratio as pale yellow oil (140 mg, 75 %)

with [Cl₂Py-BCl₂][AlCl₄]/AlCl₃ in a 1 : 1 ratio:

Following the general procedure B; Temperature: 100 °C; Reaction time: 1 hour.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH₂Cl₂. Removal of volatiles at 60 °C at 50 torr gave a mixture of 2-(4-fluoro-3-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(3-fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 1 : 5 ratio as pale yellow oil (143 mg, 76 %).

A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (albeit as a mixture of two isomers).

Selected NMR data for 2-(4-fluoro-3-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

Product characterised by COSY and NOESY NMR.

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta = 7.60 - 7.51 (m, 2 H), 6.92 (dd, J = 8.2, 10.0 Hz, 1 H), 2.20 (d, J = 1.8 Hz, 3 H), 1.26 (s, 12 H). \]

\[ \text{\textsuperscript{13}C{\textsuperscript{1}H} NMR (101 MHz, CDCl\textsubscript{3}) } \delta = 163.7 \text{ (d, J = 163.7 Hz), 138.3 (d, J = 5.1 Hz), 134.3 (d, J = 8.8 Hz), 124.2 (d, J = 16.1 Hz), 114.5 (d, J = 21.3 Hz), 83.8, 24.8, 14.3 (d, J = 3.7 Hz) \]

\[ \text{\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) } \delta = -112.9 \text{ (m).} \]

\[ \text{\textsuperscript{11}B NMR (128 MHz, CDCl\textsubscript{3}) } \delta = 30.7. \]

Selected NMR data for 2-(3-fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

The \textsuperscript{1}H NMR data is identical to that previously reported.⁹

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta = 7.41 - 7.30 (m, 2 H), 7.11 (t, J = 7.4 Hz, 1 H), 2.22 (d, J = 1.8 Hz, 3 H), 1.26 (s, 12 H). \]

\[ \text{\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) } \delta = -119.0 \text{ (qdd, J = 1.7, 7.8, 10.0 Hz).} \]

\[ \text{\textsuperscript{11}B NMR (128 MHz, CDCl\textsubscript{3}) } \delta = 30.7. \]
Borylation of biphenyl with DMTol-BCl/AlCl₃ in a 1:2 ratio:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d₆ capillary was charged with DMTol-BCl₃ (200 mg, 0.79 mmol), powdered AlCl₃ (211 mg, 1.58 mmol), biphenyl (40 mg, 0.26 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and rotated for 30 min. The reaction mixture was heated at 100 °C and shaken until no more solid was present. Periodically the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. After 24 hours, the mixture was cooled to room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (400 mg, 3.38 mmol) and Et₃N (1.7 ml) in CH₂Cl₂ (10 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH₂Cl₂ (2 × 2 ml) the mixture was stirred at 20 °C for 14 hours. All further manipulations were performed without using Schlenk line techniques and dried solvents. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (100 mL) and the solids removed by filtration, upon washing with further hexane (2 × 150 ml) the extracts were combined and the volatiles removed in vacuo to give the crude product which was purified by chromatography on silica gel (eluent hexane : CH₂Cl₂ 2 : 8 to CH₂Cl₂) giving 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl as colourless solid (59 mg, 56 %).

The NMR spectra are identical to that previously reported. Representative NMR spectra are shown below.

**¹H NMR** (400MHz, CDCl₃) δ = 7.90 (d, J = 7.8 Hz, 4 H), 7.65 (d, J = 8.0 Hz, 4 H), 1.38 (s, 24 H).

**¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 143.6, 135.2, 126.5, 83.8, 24.9.

**¹¹B NMR** (128 MHz, CDCl₃) δ = 30.7.
Large scale borylation outside glovebox

An additional 0.5 equivalents of AlCl₃ / amine are used in these reactions due to reaction with protic impurities (e.g., H₂O) in the unpurified solvent/reagent generating ammonium[AlCl₄]

Borylation of chlorobenzene with DMTol-BCl₃/DMTol/AlCl₃ in a 1 : 0.5 : 2.5 ratio:

An oven dried 100 ml Schlenk tube fitted with a J. Youngs valve was flushed with N₂ and charged with AlCl₃ (6.67 g, 50 mmol) and non-purified (as received from commercial vendor) chlorobenzene (40 ml, 394 mmol). After stirring for 30 minutes, DMTol (1.44 ml, 10 mmol) was added and stirred for an additional 30 minutes. Then DMTol-BCl₃ (5.05 g, 20 mmol) was added, the Schlenk tube was sealed and the mixture heated at 100 °C with vigorous stirring. After 24 hours, the mixture was cooled to room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (8.5 g, 72 mmol) and Et₃N (45 ml) in CH₂Cl₂ (150 ml) at 0 °C with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the Schlenk tube with CH₂Cl₂ (2 x 10 ml) the mixture was stirred at 20 °C for 14 hours. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (500 ml) and the solids removed by filtration through celite, upon washing with further hexane (2 x 300 ml) the extracts were combined and the volume reduced to ca. 200 ml. The solution was washed with HCl (6 M, 200 ml). The aqueous phase was extracted with hexane (2 x 100 ml). The combined organic layers were dried over MgSO₄ and volatiles removed at 20 °C at 4x10⁻² torr yielding 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as colourless solid (3.89 g, 81 %).

Representative ¹H NMR spectra are shown below.
Borylation of bromobenzene with DMTol/BCl/AlCl$_3$ in a 1.5 : 1 : 2.5 ratio:

An oven dried 80 ml Schlenk tube fitted with a J. Youngs valve was flushed with N$_2$ and charged with AlCl$_3$ (3.35 g, 25 mmol) and non-purified (used as received from commercial vendor) bromobenzene (25 ml, 238 mmol). After stirring for 30 minutes, DMTol (2.16 ml, 15 mmol) was added and stirred for an additional 30 minutes. Then BCl$_3$ (1 M in heptanes, 10 ml, 10 mmol) was added, the Schlenk tube was sealed and the mixture heated at 100 °C with vigorous stirring. After 24 hours, the mixture was cooled at room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (4.25 g, 36 mmol) and Et$_3$N (25 ml) in CH$_2$Cl$_2$ (75 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (EXOTHERMIC REACTION!). After washing the Schlenk tube with CH$_2$Cl$_2$ (2 x 10 ml) the mixture was stirred at 20 °C for 14 hours. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (250 ml) and the solids removed by filtration through celite, upon washing with further hexane (2 x 200 ml) the extracts were combined and the volume reduced to ca. 100 ml. The solution was washed with HCl (6 N, 100 ml). The aqueous phase was extracted with hexane (2 x 100 ml). The combined organic layers were dried over MgSO$_4$ and volatiles removed at 20 °C at 4x10$^{-2}$ torr yielding 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as colourless solid (2.05 g, 72 %).

Representative $^1$H NMR spectra are shown below.

![1H NMR spectra](image-url)
Synthesis of [Cl₂Py-BCl₂][AlCl₄]:

In the glove box, an oven dried Schlenk tube was charged with 2,6-dichloropyridine (1.480 g, 10.0 mmol) and AlCl₃ (1.333 g, 10.0 mmol). The Schlenk tube was removed from glovebox and BCl₃ (1.0 M in CH₂Cl₂, 11 ml, 11.0 mmol) was added, under inert atmosphere, to the solid mixture and stirred for 10 min. The precipitated product was decanted, washed with anhydrous CH₂Cl₂ (2 mL) and dried at 20 °C at 4x10⁻² torr for 2 h to give [Cl₂Py-BCl₂][AlCl₄] (2.3 g, 58 %) as colourless solid.

Elemental analysis Found: C, 15.14; H, 0.81; N, 3.66. Calc. for C₃H₂AlBCl₈N: C, 15.07; H, 0.76; N, 3.52.

Dissolution of 50 mg of solid in 0.8 ml of CH₂Cl₂ showed that [Cl₂Py-BCl₂][AlCl₄] is in equilibrium with BCl₃ and [(Cl₂Py)₂AlCl₄][AlCl₄]. NMR spectra were recorded using a DMSO-d₆ capillary as lock solvent.
\[ ^{11}\text{B NMR} \]

- **BCl\textsubscript{3}**
- \([\text{Cl}_2\text{Py-BCl}_2]^+\)

\[ ^{27}\text{Al NMR} \]

- 102.79
- 98.96
Synthesis of [(Cl\textsubscript{2}Py)\textsubscript{2}AlCl\textsubscript{2}][AlCl\textsubscript{4}]:

In the glovebox, an oven dried Schlenk tube was charged with 2,6-dichloropyridine (148mg, 1.0mmol) and AlCl\textsubscript{3} (133 g, 1.0 mmol). The Schlenk tube was removed from glovebox and CH\textsubscript{2}Cl\textsubscript{2} (5 ml) was added to the solid mixture and the reaction mixture stirred for 1 hour. Then the solution was filtered with a filter cannula and layered with pentane and stored at -20 °C. After the slow diffusion of pentane / CH\textsubscript{2}Cl\textsubscript{2} finished colourless crystals suitable for X-ray analysis were obtained. The solution was removed and the crystals dried in vacuo yielding [(Cl\textsubscript{2}Py)\textsubscript{2}AlCl\textsubscript{2}][AlCl\textsubscript{4}] as colourless solid (236 mg, 84 %). The product was contaminated with ~7 % of [Cl\textsubscript{2}Py-CH\textsubscript{2}Cl][AlCl\textsubscript{4}] (from solvent activation) and ~15 % of another species assigned as [Cl\textsubscript{2}Py-H][AlCl\textsubscript{4}] frustrating attempts to obtain accurate elemental analysis.

\[ \begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2})} & \quad \delta = 8.18 (t, J = 8.1 \text{ Hz}, 1 \text{ H}), 7.74 (d, J = 8.1 \text{ Hz}, 2 \text{ H}), \\
\text{\textsuperscript{27}Al NMR (104 MHz, CD\textsubscript{2}Cl\textsubscript{2})} & \quad \delta = 103.8, 99.8.
\end{align*} \]

\[ \begin{align*}
\text{\textsuperscript{1}H NMR} & \quad \begin{array}{c}
\text{peak} \\
\delta (\text{ppm})
\end{array} \\
0.07 & \quad 0.14 & \quad 1.17 & \quad 0.31 & \quad 2.00 & \quad 0.14
\end{align*} \]

[Diagram of chemical structures]
$^{27}\text{Al NMR}$
Equimolar combination of \( \text{Cl}_2 \text{Py} \), \( \text{BCl}_3 \) and \( \text{AlCl}_3 \) in \( \text{CH}_2\text{Cl}_2 \):

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-\( \text{d}_6 \) capillary was charged with \( \text{AlCl}_3 \) (67 mg, 0.50 mmol). The NMR tube was removed from the glovebox and under inert atmosphere anhydrous \( \text{CH}_2\text{Cl}_2 \) (0.5 ml), 2,6-dichloropyridine (74 mg, 0.50 mmol) and \( \text{BCl}_3 \) (1 M in \( \text{CH}_2\text{Cl}_2 \), 0.5 ml, 0.50 mmol) were added. The NMR tube was shaken until all \( \text{AlCl}_3 \) dissolved.
$^{27}$Al NMR
Synthesis of [Cl₂Py-BCl₂][Al₂Cl₇]

An oven dried J. Young’s NMR tube fitted with a DMSO-d₆ capillary, under inert atmosphere, was charged with 2,6-dichloropyridine (111 mg, 0.75mmol) and BCl₃ (1 M in CH₂Cl₂, 0.9 ml, 0.90 mmol). The NMR tube was sealed, transferred in the glovebox and powdered AlCl₃ (200 mg, 1.50mmol) was added to the mixture. The NMR tube was shaken until all AlCl₃ dissolved. Repeated attempts to generate crystalline material from this reaction mixture failed.

¹H NMR (400 MHz, CH₂Cl₂ with DMSO-d₆ capillary) δ = 8.74 (t, J = 8.3 Hz, 2 H), 8.22 (d, J = 8.3 Hz, 4 H).

¹¹B NMR (128 MHz, CH₂Cl₂ with DMSO-d₆ capillary) δ = 43.0, 45.8 (free BCl₃).

²⁷Al NMR (104 MHz, CH₂Cl₂ with DMSO-d₆ capillary) δ = 103.8, 99.8.
$^{11}\text{B NMR}$

- $45.80$
- $43.03$
- $[\text{Cl}_2\text{Py-BCl}_2]^+$

$^{27}\text{Al NMR}$

- $103.10$
Borylation of 2-fluorotoluene with DMTol-BCl₃/AlCl₃ monitored at different times:

In the glovebox, an oven dried 5 ml Schlenk tube fitted with a J. Youngs valve was charged with DMTol-BCl₃ (505 mg, 2.0 mmol), AlCl₃ (534 mg, 4.0 mmol) and 4 ml of fluorotoluene. The ampoule was sealed, removed from the glovebox and heated at 100 °C with vigorous stirring. At selected times (see table S1), the reaction mixture was cooled to 0 °C and an 0.5 ml aliquot was taken with a syringe under inert atmosphere. The aliquot was added dropwise to a mixture of pinacol (200 mg, 1.69 mmol) and Et₃N (1 ml) in CH₂Cl₂ (10 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After the mixture was stirred at 20 °C for 14 hours, the volatiles were removed in vacuo and the resulting solid was suspended in hexane (50 mL) and the solids removed by filtration through celite, upon washing with further hexane (2 × 50 ml) the extracts were combined and the volatiles removed in vacuo. The crude material was dissolved in CH₂Cl₂ (5 ml), passed through a plug of silica gel and the plug washed with CH₂Cl₂. After removal of volatiles at 20 °C at 4x10⁻² torr, a sample for GC was prepared.

Borylation of 2-fluorotoluene with [Cl₂Py-BCl₂][AlCl₄]/AlCl₃ at different times:

In the glove box, an oven dried 5 ml Schlenk tube fitted with a J. Youngs valve was charged with [Cl₂Py-BCl₂][AlCl₄] (797 mg, 2.0 mmol), AlCl₃ (267 mg, 2.0 mmol) and 4 ml of fluorotoluene. The ampoule was sealed, removed from the glovebox and heated at 100 °C with vigorous stirring. At selected times (see table S1), the reaction mixture was cooled to 0 °C and an 0.5 ml aliquot was taken with syringe under inert atmosphere. The aliquot was added dropwise to a mixture of pinacol (200 mg, 1.69 mmol) and Et₃N (1 ml) in CH₂Cl₂ (10 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!!!). After the mixture was stirred at 20 °C for 14 hours, the volatiles were removed in vacuo and the resulting solid was suspended in hexane (50 mL) and the solids removed by filtration through celite, upon washing with further hexane (2 × 50 ml) the extracts were combined and the volatiles removed in vacuo. The crude material was dissolved in CH₂Cl₂ (5 ml), passed through a plug of silica gel and the plug washed with CH₂Cl₂. After removal of volatiles at 20 °C at 4x10⁻² torr, a sample for GC was prepared.
Table S1. Isomer distribution of borylated 2-fluorotoluene at different times.

\[
\begin{align*}
\text{Of} & \quad \text{[AlCl}_4\text{]} + \text{AlCl}_3 \\
\text{N} \quad \text{BCI}_2 & \quad \text{3.2 eq Pinacol Et}_3\text{N} \\
\text{F} & \quad 100^\circ\text{C} \\
\text{F} & \quad \text{3.2 eq Pinacol Et}_3\text{N} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time</th>
<th>([\text{Cl}_3\text{Py-BCl}_2][\text{AlCl}_4]/\text{AlCl}_3)</th>
<th>(\text{DMTol-BCl}/\text{AlCl}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>10 min</td>
<td>92.74</td>
<td>7.26</td>
</tr>
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<td>30 min</td>
<td>92.39</td>
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</tr>
<tr>
<td>7 d</td>
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</table>
Synthesis $[\text{Cl}_2\text{B}(2,6\text{-lutidine})][\text{AlCl}_4]$:

An oven dried Schlenk tube, under inert atmosphere, was charged with a solution of $\text{BCl}_3$ (1 M in $\text{CH}_2\text{Cl}_2$, 12 ml, 12.0 mmol) and the solution was cooled at 0 °C. 2,6-Lutidine (1 ml, 8.6 mmol) was added dropwise over 15 minutes. The reaction mixture was warmed to room temperature and stirred for 1 hour. Then, the reaction mixture was transferred over 5 minutes via cannula under a positive pressure of argon to an oven dried Schlenk tube charged with $\text{AlCl}_3$ (1.15 g, 8.6 mmol). The former Schlenk tube was washed with anhydrous $\text{CH}_2\text{Cl}_2$ (3 ml) and the washings were transferred to the Schlenk tube containing the reaction mixture. After stirring the reaction mixture for 2 hours the volume was reduced to ~10 ml. Then the solution was filtered with a filter cannula, layered with pentane and stored at -20 °C. After the slow diffusion of pentane in $\text{CH}_2\text{Cl}_2$ finished the solution was removed and the solid dried in vacuo yielding $[\text{Cl}_2\text{B}(2,6\text{-lutidine})][\text{AlCl}_4]$ with ~ 5% of $[2,6\text{-lutidine-H}][\text{AlCl}_4]$ as pale brown solid (2.94 g, 96 %).

Elemental analysis Found: C, 23.62; H, 2.50; N, 3.97. Calc. for $\text{C}_7\text{H}_9\text{AlBCl}_6\text{N}$: C, 15.07; H, 0.76; N, 3.52.

The NMR data are identical to that previously reported.$^1$

$^1\text{H}$ NMR (CD$_2$Cl$_2$) $\delta = 8.49$ (t, $J = 8.0$ Hz, 1 H), 7.89 (d, $J = 8.0$ Hz, 2 H), 2.93 (s, 6 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD$_2$Cl$_2$) $\delta = 153.2$, 149.2, 128.0, 22.7.

$^{11}\text{B}$ NMR (CD$_2$Cl$_2$) $\delta = 46.8$. 

![1H NMR](image-url)
Attempt to borylate 1,2-dichlorobenzene with [2,6-lutidine-BCl₂][AlCl₄]:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d₆ capillary was charged with [2,6-lutidine-BCl₂][AlCl₄] (80 mg, 0.22 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and heated at 140 °C. The NMR tube was occasionally shaken and the reaction was monitored by NMR spectroscopy. After 21 hours, the ¹¹B NMR spectrum showed no arene borylation although ¹H NMR spectrum showed that almost all 2,6-lutidine was protonated.

[¹H NMR]
$^{11}$B NMR

$\text{BCl}_3$
Attempt to borylate 1,2-dichlorobenzene with an equimolar mixture of DMTol-BCl$_3$ and AlCl$_3$:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with DMTol-BCl$_3$ (200 mg, 0.79 mmol), AlCl$_3$ (105 mg, 0.79 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and heated at 140 °C. The NMR tube was occasionally shaken and the reaction was monitored by NMR spectroscopy. After 46 hours, NMR spectroscopy showed almost all the DMTol was protonated but only a small amount of borylated 1,2-dichlorobenzene (53.4 ppm in the $^{11}$B NMR spectrum) was present.
Attempt to borylate 1,2-dichlorobenzene with the mixture of Et$_3$N-BCl$_3$ and AlCl$_3$:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with Et$_3$N-BCl$_3$ (53 mg, 0.24 mmol), AlCl$_3$ (39 mg, 0.29 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and heated at 140 °C. After 150 minutes, the $^{11}$B NMR spectrum showed no arene borylation although $^1$H NMR spectrum showed that almost all Et$_3$N was protonated.
Attempt to borylate 1,2-dichlorobenzene with \([\text{Cl}_2\text{Py}-\text{BCl}_2][\text{AlCl}_4]\):

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with \([\text{Cl}_2\text{Py}-\text{BCl}_2][\text{AlCl}_4]\) (100 mg, 0.25 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and heated at 140 °C. The NMR tube was occasionally shaken and the reaction was monitored by NMR spectroscopy. After 7 days, $^{11}$B NMR spectrum showed extremely minor amounts of arene borylation.
Borylation of 1,2-dichlorobenzene with 2,6-lutidine-BCl$_3$/AlCl$_3$ in a 1 : 2 ratio:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with 2,6-lutidine-BCl$_3$ (200 mg, 0.89 mmol), powdered AlCl$_3$ (250 mg, 1.87 mmol) and anhydrous 1,2-dichlorobenzene (1 ml). The NMR tube was sealed, removed from the glovebox and the reaction mixture was heated with initial shaking to ensure complete dissolution of solids. Periodically the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. After 72 hours, the mixture was cooled to room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (421 mg, 3.56 mmol) and Et$_3$N (2 ml) in CH$_2$Cl$_2$ (5 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH$_2$Cl$_2$ (2 x 2 ml) the mixture was stirred at 20 °C for 14 hours. All further manipulations were performed without using Schlenk line techniques and dried solvents. The volatiles were removed in vacuo and the product was purified by chromatography on silica gel (eluent hexane:CH$_2$Cl$_2$ from 8:2 to 10:0). The product was dried at 20 °C at 4x10$^{-2}$ torr to remove DMTol giving 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as pale yellow oil (172 mg, 71%).
Borylation of bromobenzene with Et₃N-BCl₃ and AlCl₃ in a 1 : 2 ratio:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d₆ capillary was charged with Et₃N-BCl₃ (200 mg, 0.91 mmol), AlCl₃ (244 mg, 1.82 mmol) and anhydrous bromobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and the reaction mixture was heated with initial shaking to ensure complete dissolution of solids. Periodically the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. After 14 hours at 100 °C, multinuclear NMR spectra showed the formation of benzene and only small amounts of borylated product. The temperature was increased at 140 °C. After 5 hours, the mixture was cooled at room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (375 mg, 3.17 mmol) and Et₃N (1.0 ml) in CH₂Cl₂ (10 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH₂Cl₂ (2 × 2 ml) the mixture was stirred at 20 °C for 14 hours. All further manipulations were performed without using Schlenk line techniques and dried solvents. The volatiles were removed in vacuo and the crude mixture was absorbed on silica and purified by chromatography on silica gel (eluent hexane : CH₂Cl₂ 1 : 9 to hexane : CH₂Cl₂ 5 : 5). 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in 0.8 : 1 : 1.5 ratio.

\[ ^1H \text{NMR of the reaction mixture after 14 hours at 100 °C} \]
Borylation of bromobenzene with [2,6-lutidine-BCl$_2$][AlCl$_4$] and AlCl$_3$ in a 1 : 1 ratio:

In the glove box, an oven dried J. Young’s NMR tube fitted with a DMSO-d$_6$ capillary was charged with [2,6-lutidine-BCl$_2$][AlCl$_4$] (283 mg, 0.79 mmol), powdered AlCl$_3$ (106 mg, 0.79 mmol) and anhydrous bromobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and the reaction mixture was heated at 140 °C with initial shaking to ensure complete dissolution of solids. Periodically the sample was removed from the oil bath and borylation progress was monitored by NMR spectroscopy. NMR spectra showed the formation of benzene. After 5 hours, the mixture was cooled to room temperature and transferred via cannula under a positive pressure of nitrogen to a mixture of pinacol (375 mg, 3.17 mmol) and anhydrous Et$_3$N (1.7 ml) in anhydrous CH$_2$Cl$_2$ (10 ml) at 0 °C, with care taken not to allow any significant rise in reaction temperature (CAUTION EXOTHERMIC REACTION!). After washing the NMR tube with CH$_2$Cl$_2$ (2 × 2 ml) the mixture was stirred at 20 °C for 1 hour. The volatiles were removed in vacuo and the resulting solid was suspended in hexane (100 mL) and the solids removed by filtration through celite, upon washing with further hexane (2 × 150 ml) the extracts were combined and the volatiles removed in vacuo. The crude material was then passed through a plug of silica gel and the plug washed with CH$_2$Cl$_2$. The product was dried at 20 °C at 4x10$^{-2}$ torr giving a mixture of 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 1 : 5 ratio along with a trace of and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane as pale yellow oil.

\[ ^1H \text{ NMR of the reaction mixture after 5 hours at 140 °C} \]
Preparation of 2-bromobenzyl-1,3,2-benzodioxaborole for GC comparison:

In a round bottom flask pinacol (59 mg, 0.50 mmol) and MgSO$_4$ (1 g) were added to a stirred suspension of the respective bromobenzylboronic acid (100 mg, 0.50 mmol) in toluene (15 ml). The reaction mixture was stirred for 24 h at 20 °C. Then the solid was removed by filtration and the volatiles removed in-vacuo to afford the clean product.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

Isolated as colourless solid (134 mg, 95 %).
The NMR data are identical to that previously reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.67 (d, $J = 8.2$ Hz, 2 H), 7.51 (d, $J = 8.2$ Hz, 2 H), 1.35 (s, 12 H).
$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 136.3, 130.9, 126.2, 84.0, 24.8.
$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = 30.8.

2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

Isolated as colourless solid (130 mg, 92 %).
The NMR data are identical to that previously reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.94 (s, $J = 1.0$ Hz, 1 H), 7.72 (td, $J = 1.0$, 7.5 Hz, 1 H), 7.59 (qd, $J = 1.0$, 8.0 Hz, 1 H), 7.25 (dd, $J = 7.5$, 8.0 Hz, 1 H), 1.35 (s, 12 H).
$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 137.5, 134.2, 133.1, 129.5, 122.4, 84.1, 24.8.
$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = 30.4.

2-(2-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

Isolated as colourless oil (128 mg, 91 %).
The NMR data are identical to that previously reported.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62 (dd, $J = 1.8$, 7.3 Hz, 1 H), 7.54 (dd, $J = 0.9$, 7.7 Hz, 1 H), 7.34 - 7.21 (m, 1 H), 1.39 (s, 12 H).
$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 136.3, 132.6, 131.8, 128.0, 126.3, 84.3, 24.8.
$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ = 30.8.
## Crystallographic Details of [Cl₂Py·BCl₂][AlCl₄]

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Crystallographic Details of [(Cl₂Py)₂AlCl₃][AlCl₄]

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Crystallographic Details of 2-(4-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

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Crystallographic Details of 2-(4-bromo-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

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