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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_3N 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 $CDCl_3$ δ_H = 7.27; CH_2Cl_2 in CD_2Cl_2 δ_H = 5.32) as internal standards and ^{13}C NMR using the centre line of $CDCl_3$ (δ_C = 77.0) or CD_2Cl_2 (δ_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_2O, ^{19}F to $CFCl_3$ and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(D_2O)_6^{3+}$). 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 $^{13}C\{^1H\}$ 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_3N (1.7 ml) in CH_2Cl_2 (10 ml) at 0 °C (pinacol, Et_3N and CH_2Cl_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_2Cl_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_2Py-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_2Py-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_3N (1.7 ml) in CH_2Cl_2 (10 ml) at 0 °C (pinacol, Et_3N and CH_2Cl_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_2Cl_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*.

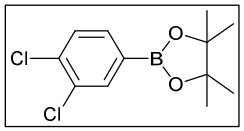
Borylation of 1,2-dichlorobenzene with DMTol-BCl_3/$AlCl_3$ in a 1 :2 ratio:

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

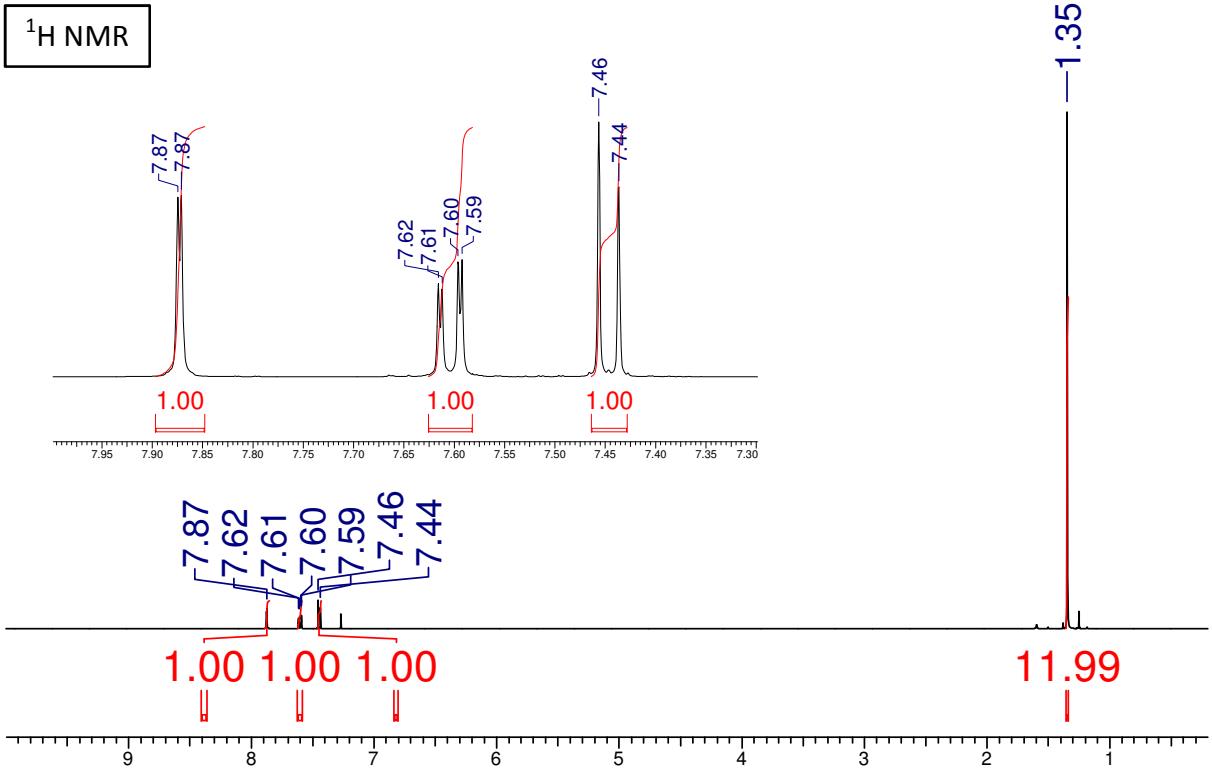
Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH_2Cl_2. The product was dried at 20 °C at $4x10^{-2}$ torr to remove DMTol giving 2-(3,4-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a pale yellow oil (173 mg, 80 %).

Elemental analysis Found: C, 52.40; H, 5.69. Calc. for $C_{12}H_{15}BCl_2O_2$: C, 52.80; H, 5.54.

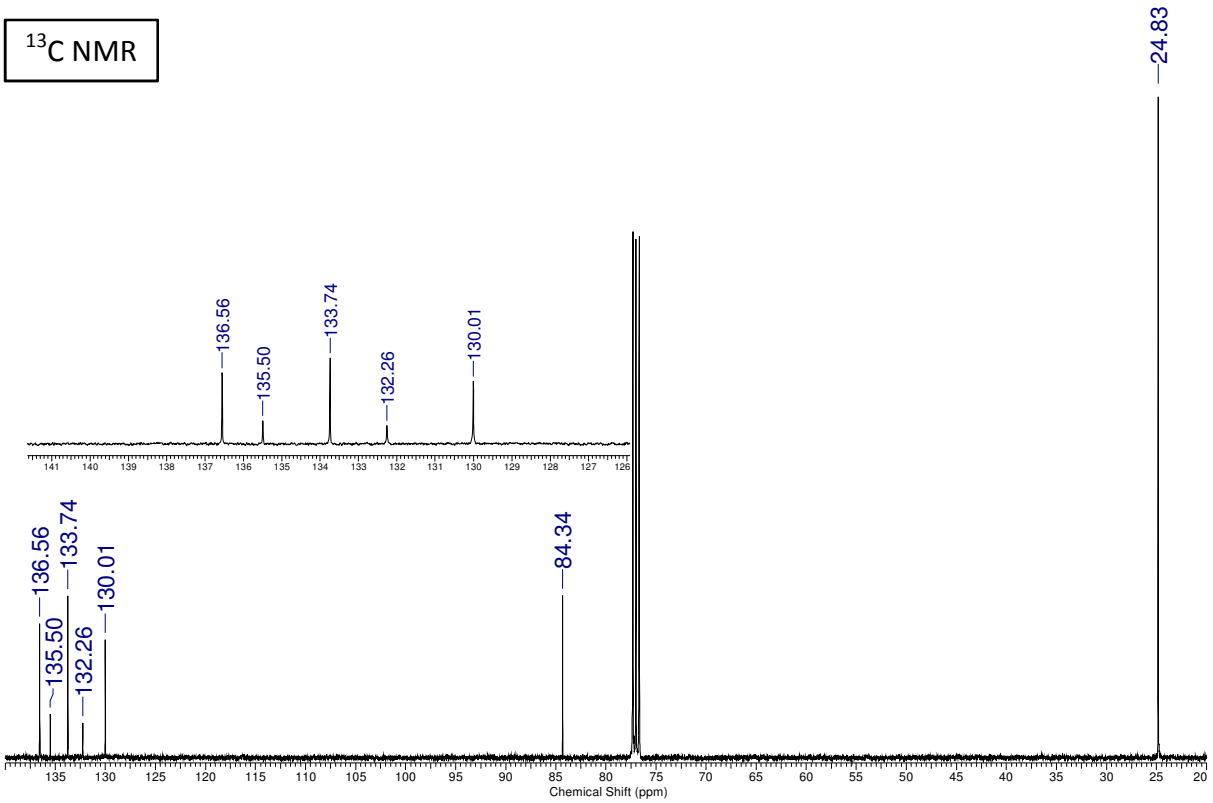
The ^1H and ^{13}C NMR data are identical to that previously reported.[2] Representative NMR spectra are shown below.



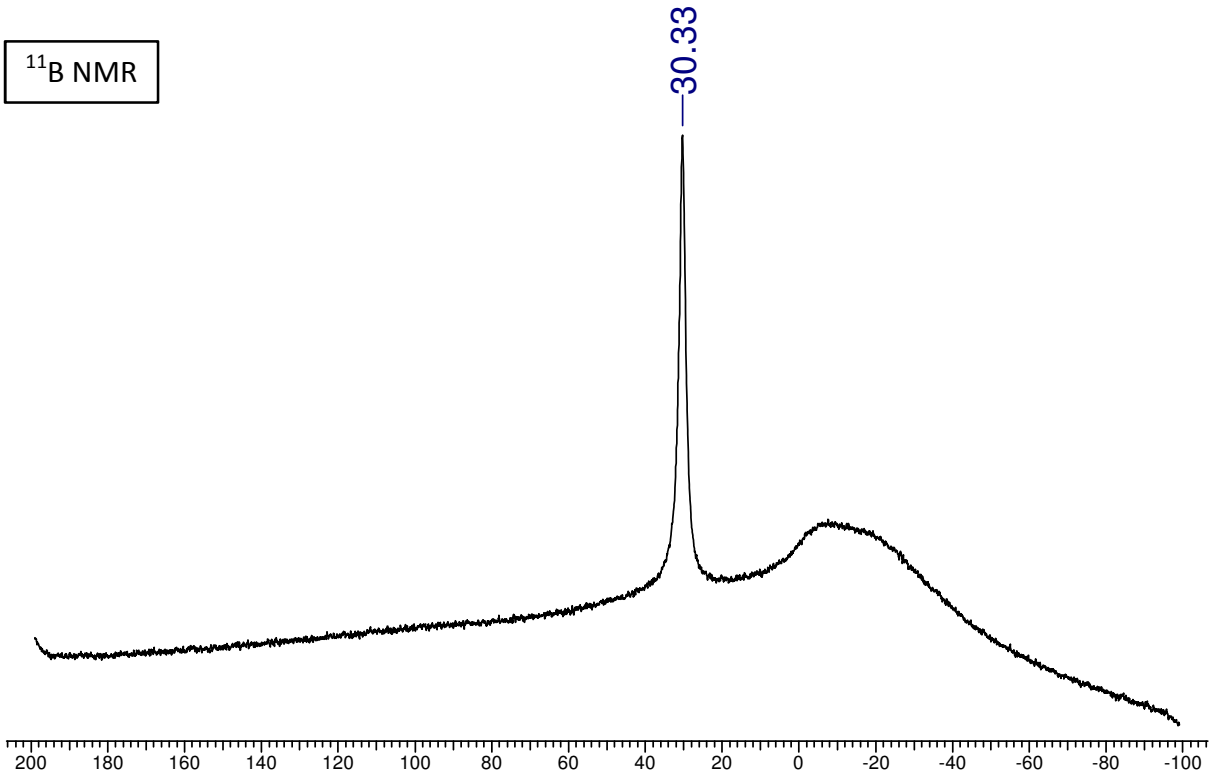
^1H NMR (400 MHz,$CDCl_3$) δ = 7.87 (d, *J* = 1.5 Hz, 1 H), 7.60 (dd, *J* = 1.5, 7.9 Hz, 1 H), 7.45 (d, *J* = 7.9 Hz, 1 H), 1.35 (s, 12 H).
$^{13}C\{^1H\}$ NMR (101MHz,$CDCl_3$) δ = 136.6, 135.5, 133.7, 132.3, 130.0, 84.3, 24.8.
^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.3.



^{13}C NMR



^{11}B NMR



Borylation of bromobenzene with DMTol-BCl_3/$AlCl_3$ in a 1 :2 ratio:

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

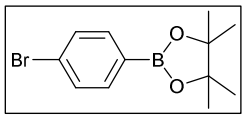
Purification: The crude product was absorbed on silica and purified by chromatography on silica gel (eluent hexane : CH_2Cl_2 1 :9 to hexane : CH_2Cl_2 = 2 : 8). The product was dried at 20 °C at $4x10^{-2}$ torr to remove residual DMTol giving 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 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 : CH_2Cl_2 1 : 9 to hexane : CH_2Cl_2 = 2 : 8). The product was dried at 20 °C at $4x10^{-2}$ torrto 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 $C_{12}H_{16}BBrO_2$: C, 50.94; H, 5.70.

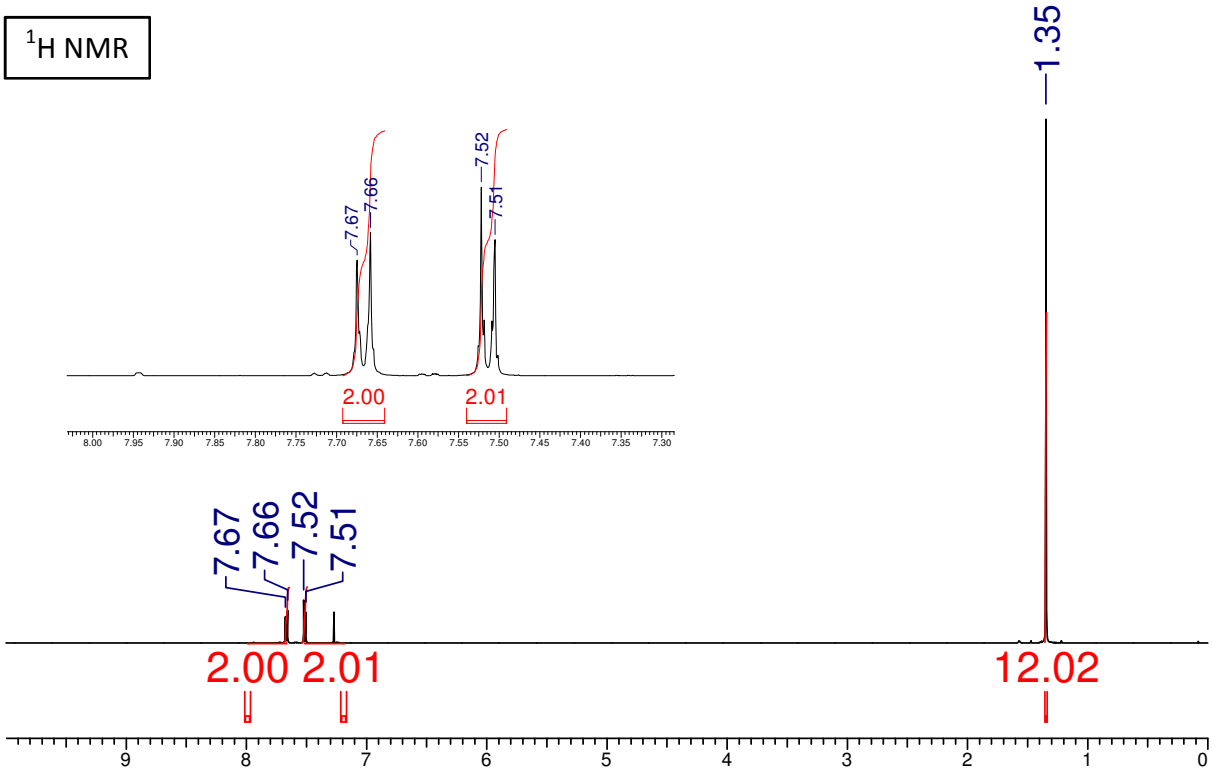
The NMR spectra are identical to that previously reported.[3] Representative spectra are shown below.

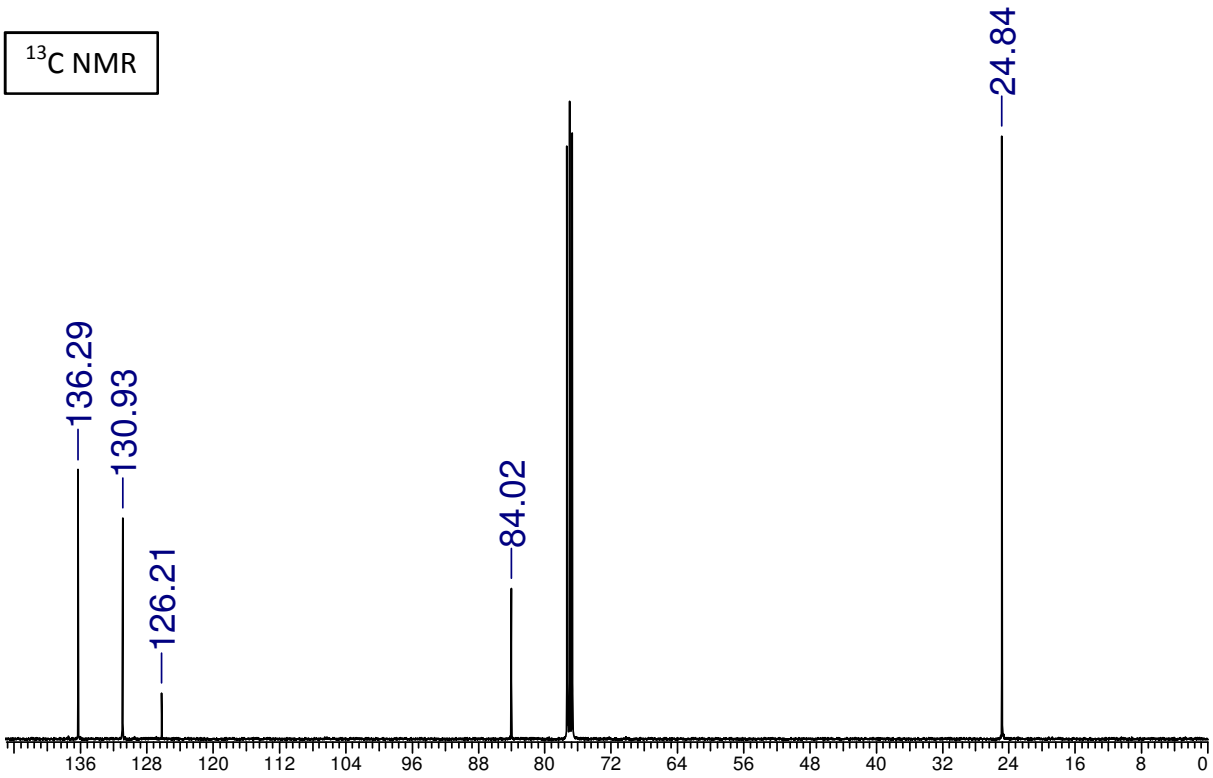


^{1}H NMR (400MHz,$CDCl_3$) δ = 7.67 (d, *J* = 8.2 Hz, 2 H), 7.51 (d, *J* = 8.2 Hz, 2 H), 1.35 (s, 12 H).

^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$) δ = 136.3, 130.9, 126.2, 84.0, 24.8.

^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.8.




^{13}C NMR
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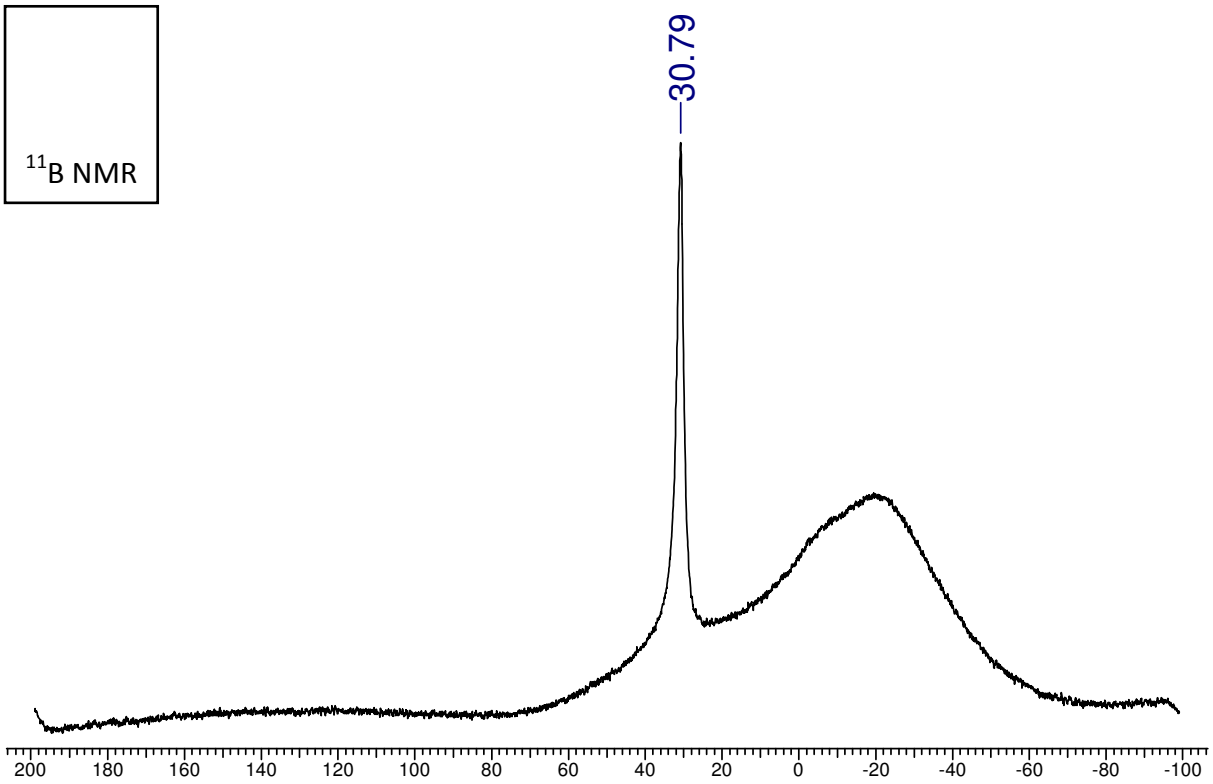
130.93
126.21
84.02
24.84
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

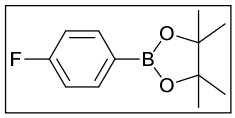

^{11}B NMR
30.79
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Borylation of fluorobenzene with DMTol-BCl_3/$AlCl_3$ in a 1 :2 ratio:

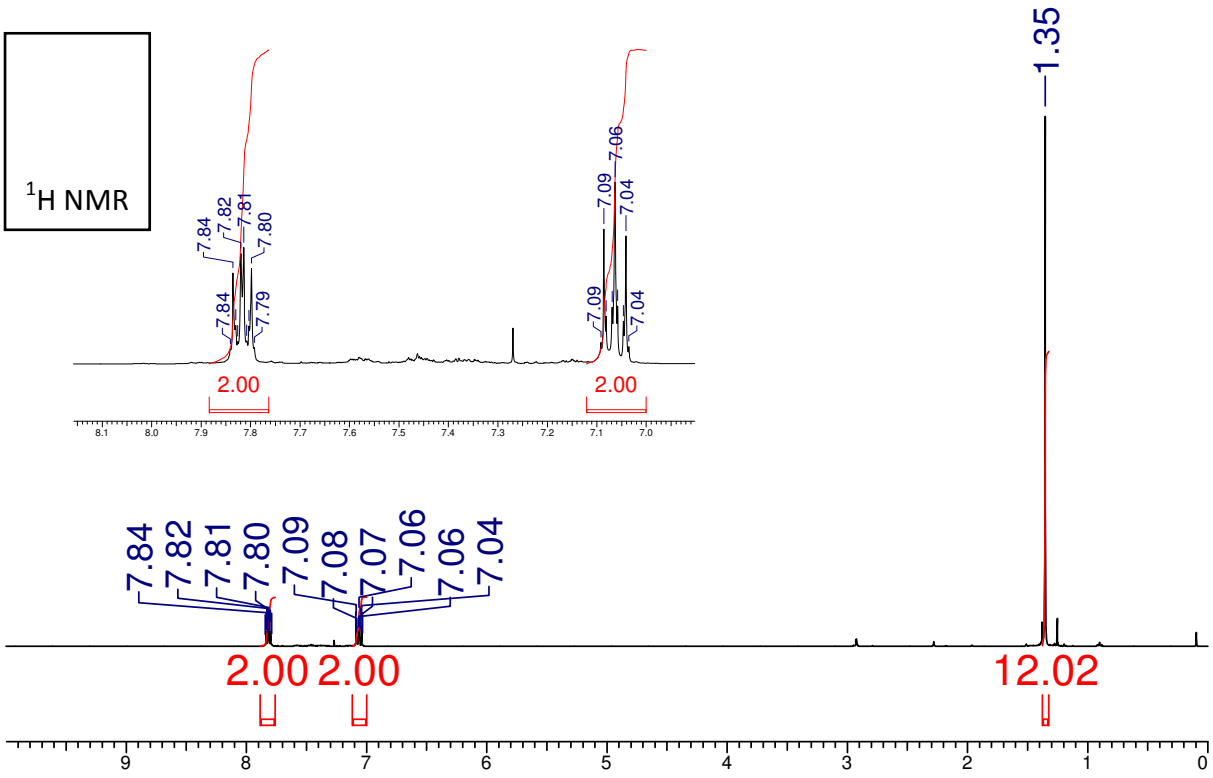
Following the general procedure A; Temperature: 100 °C; Reaction time: 2 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH_2Cl_2. The product was dried at 20 °C at $4x10^{-2}$ 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 %).

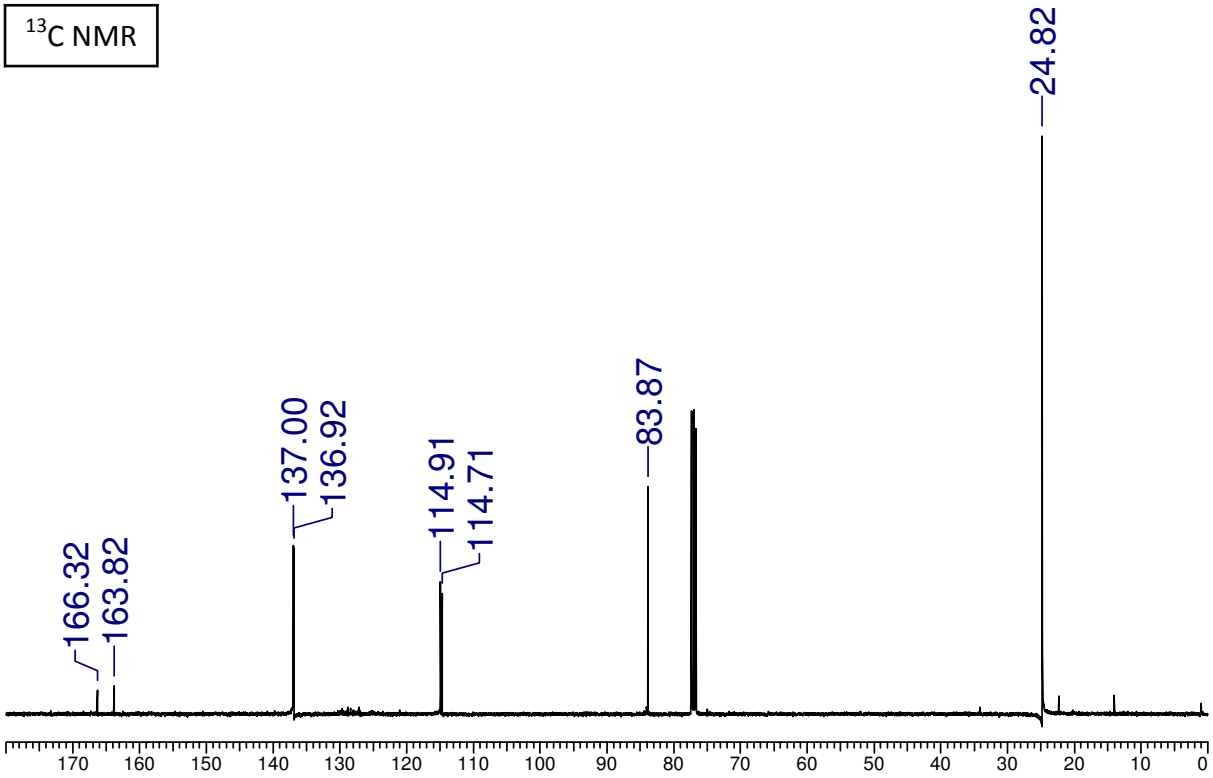
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported.[4] Representative spectra are shown below.



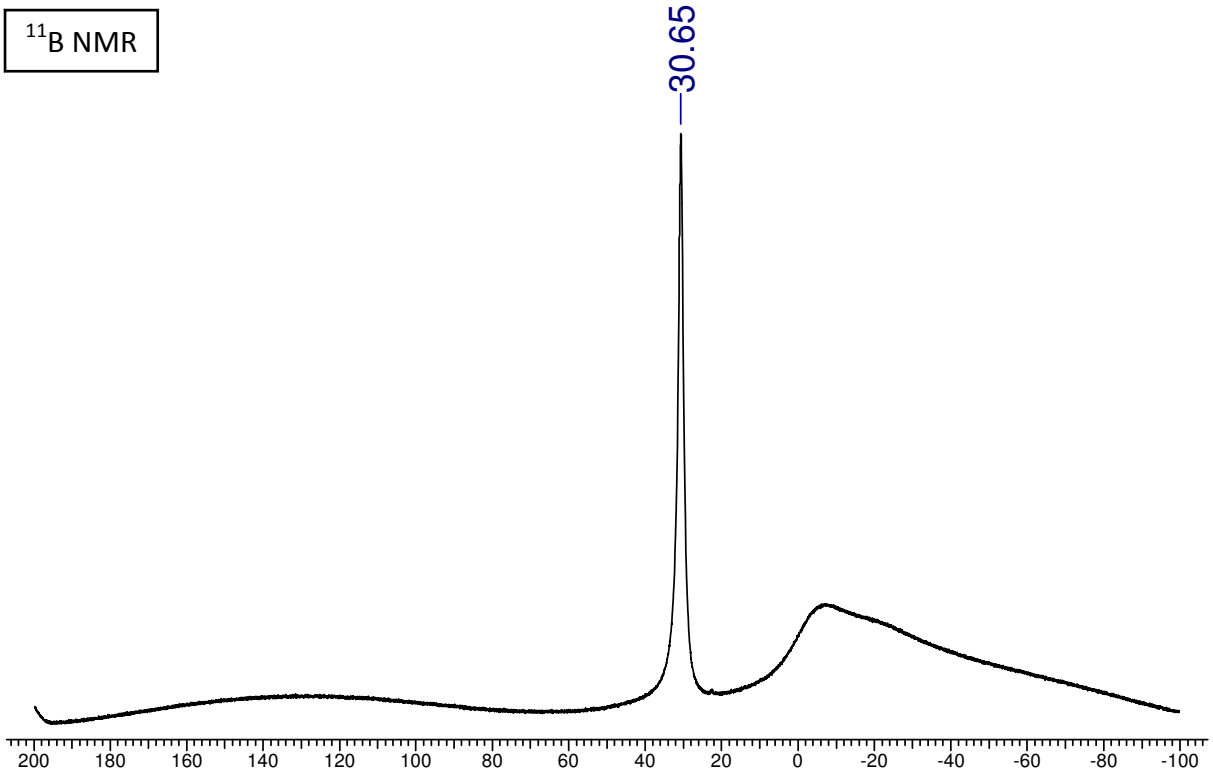
^{1}H NMR (400MHz,$CDCl_3$) δ = 7.82 (tdd, *J* = 2.2, 6.3, 8.6 Hz, 2 H), 7.06 (tdd, *J* = 2.2, 8.6, 9.2 Hz, 2 H), 1.35 (s, 12 H).
^{13}C NMR (101MHz,$CDCl_3$) δ = 165.1 (d, *J* = 251.0 Hz), 137.0 (d, *J* = 8.3 Hz), 114.8 (d, *J* = 220.3 Hz), 83.9, 24.8.
^{11}B NMR (128MHz,$CDCl_3$) δ = 30.6.
^{19}F NMR (376MHz,$CDCl_3$) δ = 108.4 (tt, *J* = 6.2, 9.2 Hz).



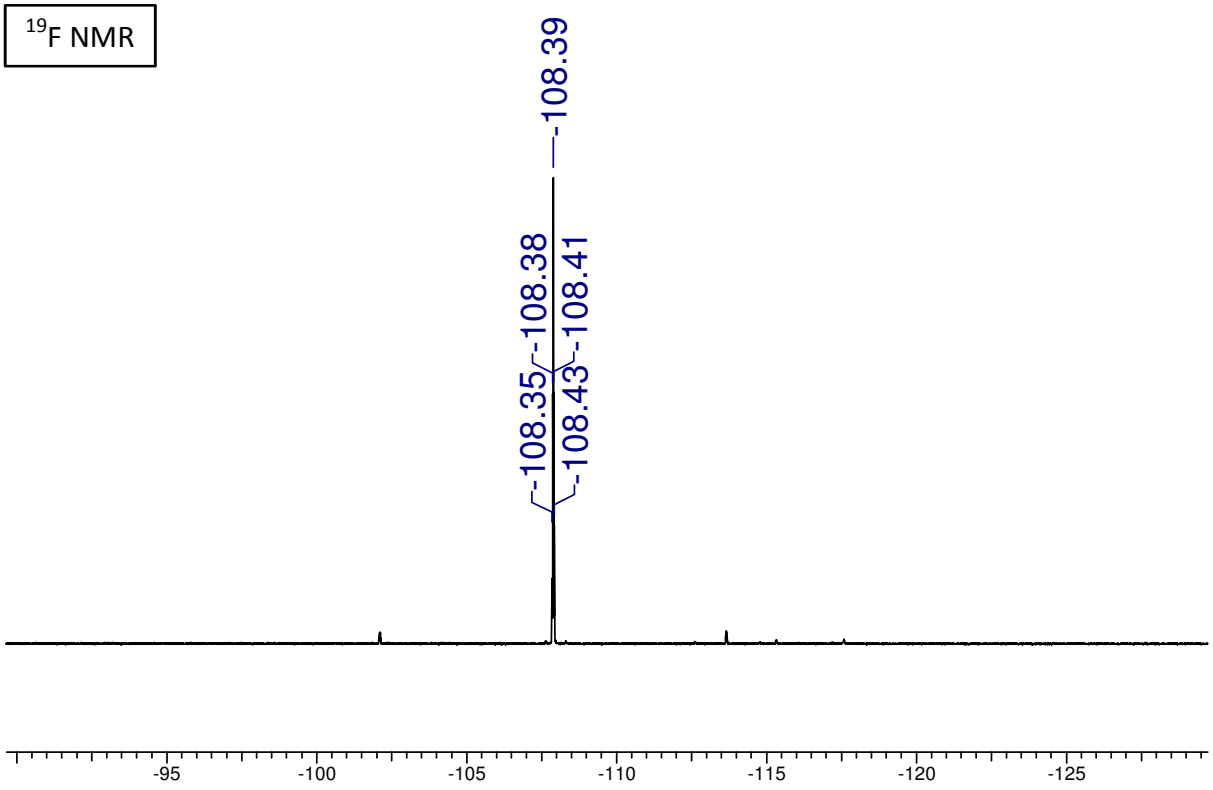
^{13}C NMR



^{11}B NMR



^{19}F NMR



Borylation of chlorobenzene with DMTol-BCl_3/$AlCl_3$ 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 CH_2Cl_2. 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

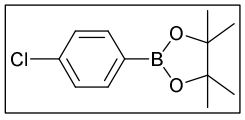
Following the general procedure A using 0.4 ml (5 equivalents) of chlorobenzene; Temperature: 100 °C; Reaction time: 7 hours.

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 $MgSO_4$. 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 $C_{12}H_{16}BClO_2$: C, 60.43; H, 6.76.

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

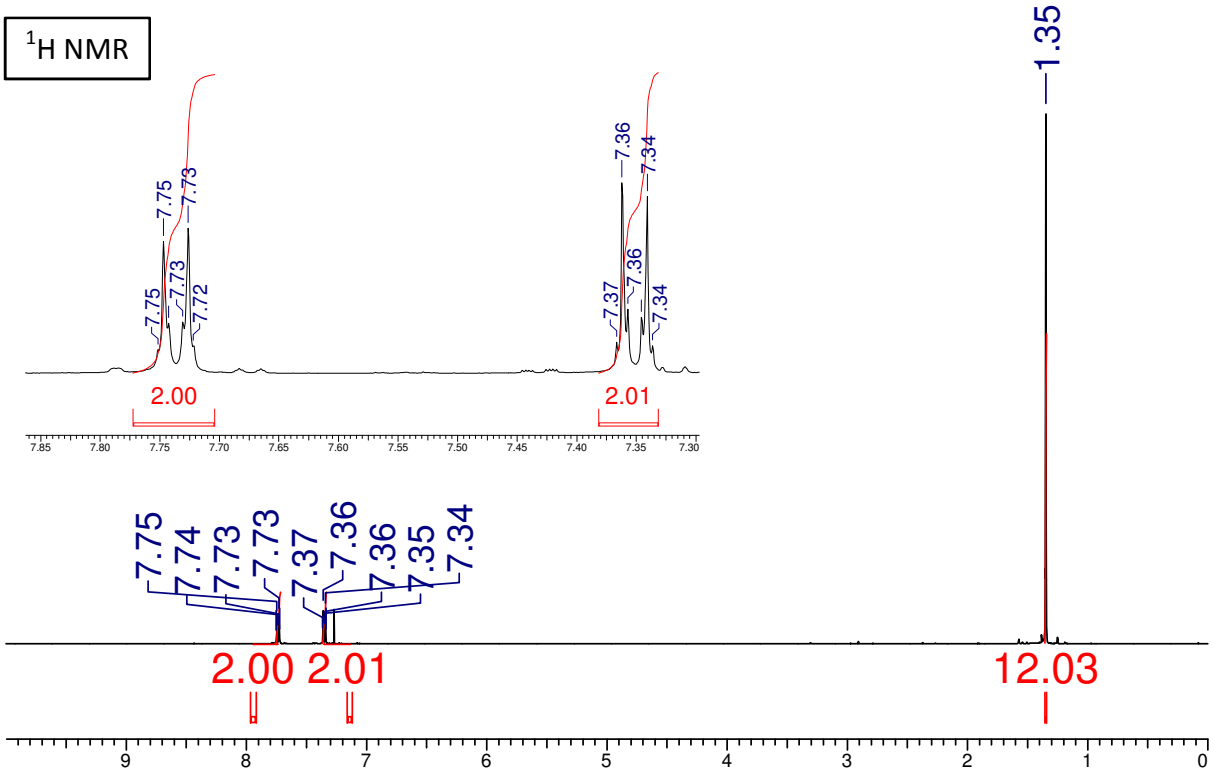
Selected NMR data for 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



^{1}H NMR (400 MHz,$CDCl_3$) 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).

$^{13}C\{^1H\}$ NMR (101MHz,$CDCl_3$) δ = 137.5, 136.1, 128.0, 84.0, 24.8.

^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.6.


1H NMR
7.75
7.73
7.72
7.36
7.34
7.37
2.00
2.01
1.35
7.75
7.74
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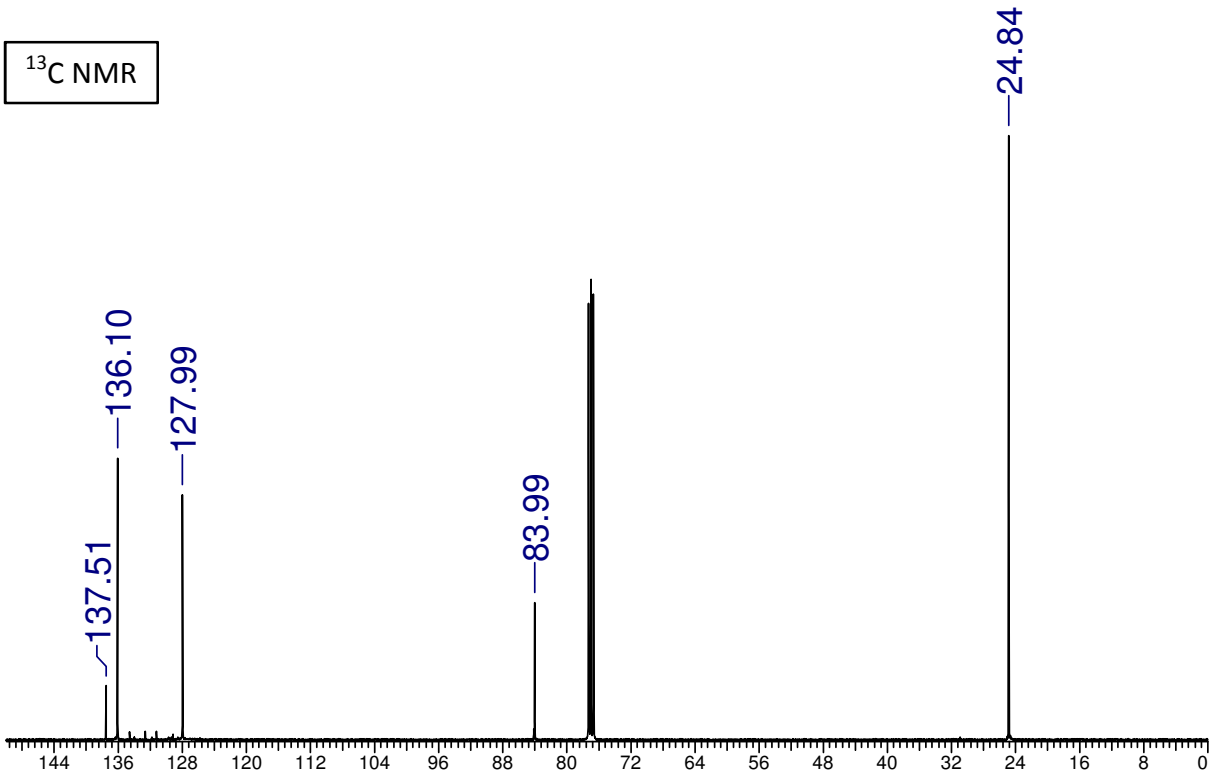
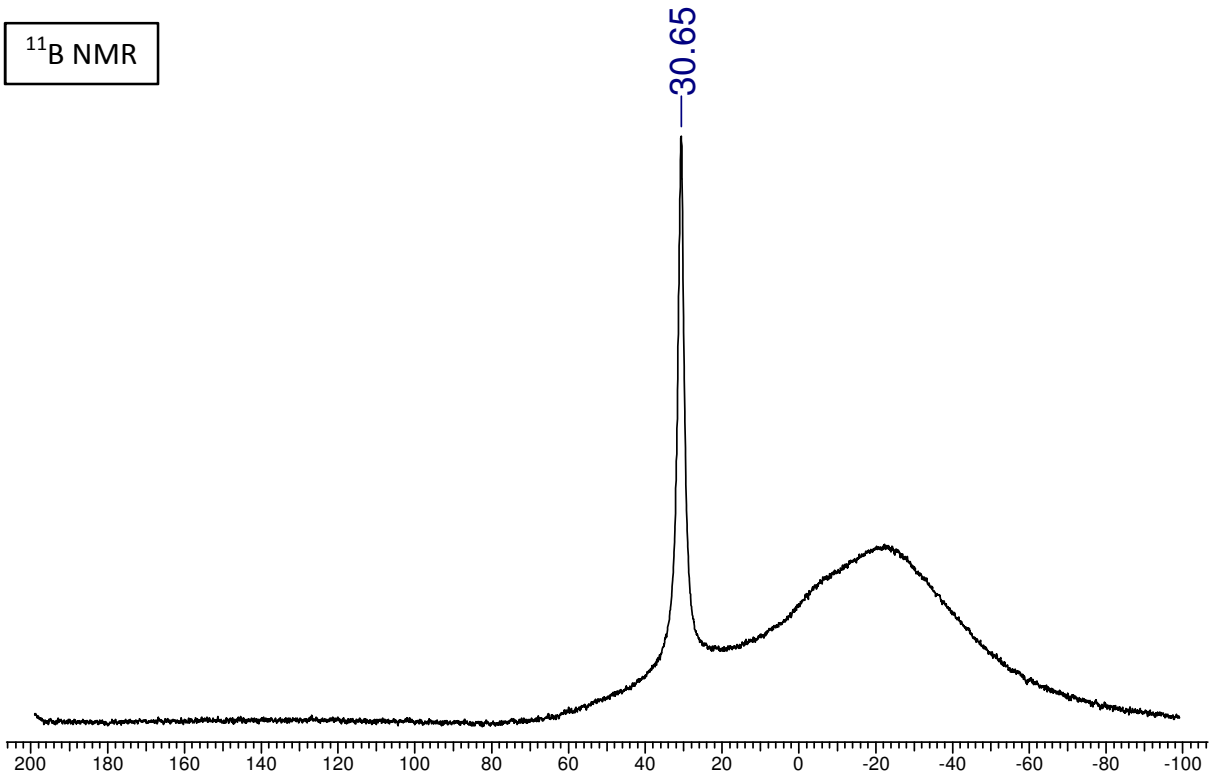
7.37
7.36
7.36
7.35
7.34
2.00 2.01
12.03


13C NMR
24.84
136.10
127.99
137.51
83.99


^{11}B NMR
30.65
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Borylation of 1-chloro-2-fluorobenzene

with DMTol-BCl_3/$AlCl_3$ 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 $MgSO_4$. Removal of volatiles at 20 °C at $4x10^{-2}$ 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_2Py-BCl_2][$AlCl_4$]/$AlCl_3$ in a 1 : 1 ratio:

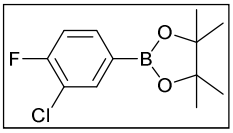
Following the general procedure B; Temperature: 140 °C; Reaction time: 41 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH_2Cl_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 $C_{12}H_{15}BClFO_2$: C, 56.19; H, 5.89.

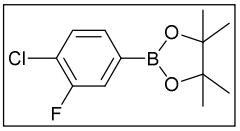
Representative NMR spectra are shown below.

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]

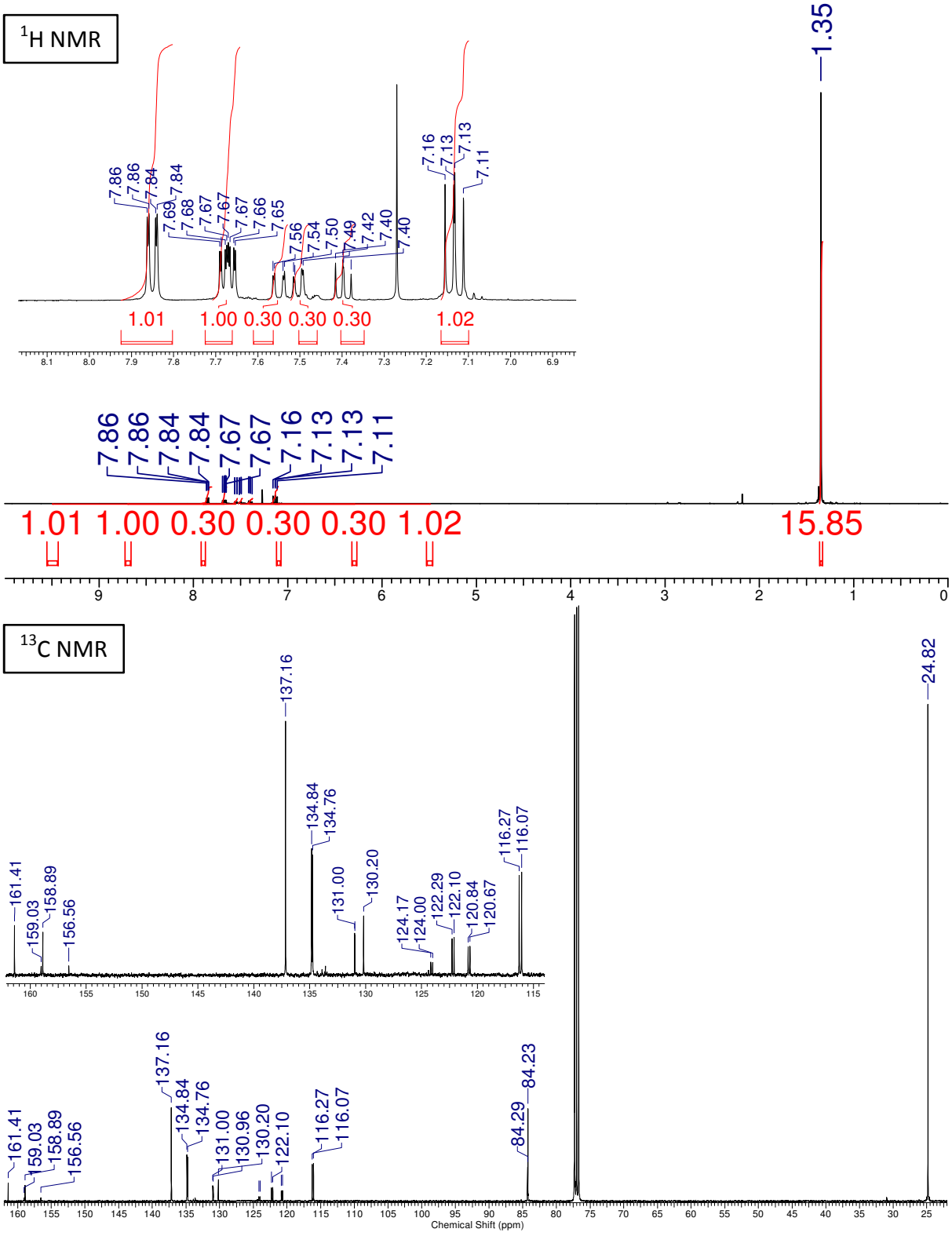


^{1}H NMR (400 MHz,$CDCl_3$)δ = 7.85 (dd, *J* = 1.5, 8.1 Hz, 1 H), 7.67 (ddd, *J* = 1.5, 5.2, 8.1 Hz, 1 H), 7.13 (dd, *J* = 8.2, 9.2 Hz, 1 H), 1.35 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 160.2 (d, *J* = 235.1 Hz), 137.2, 134.8 (d, *J* = 8.1 Hz), 120.8 (d, *J* = 16.9 Hz), 116.2 (d, *J* = 19.8 Hz), 84.2, 24.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ = 111.2 (dt, *J* = 5.1, 8.5 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.3.

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]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 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).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 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}F NMR (376 MHz, $CDCl_3$) δ = 111.2 (dd, *J* = 7.2, 9.2 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.3.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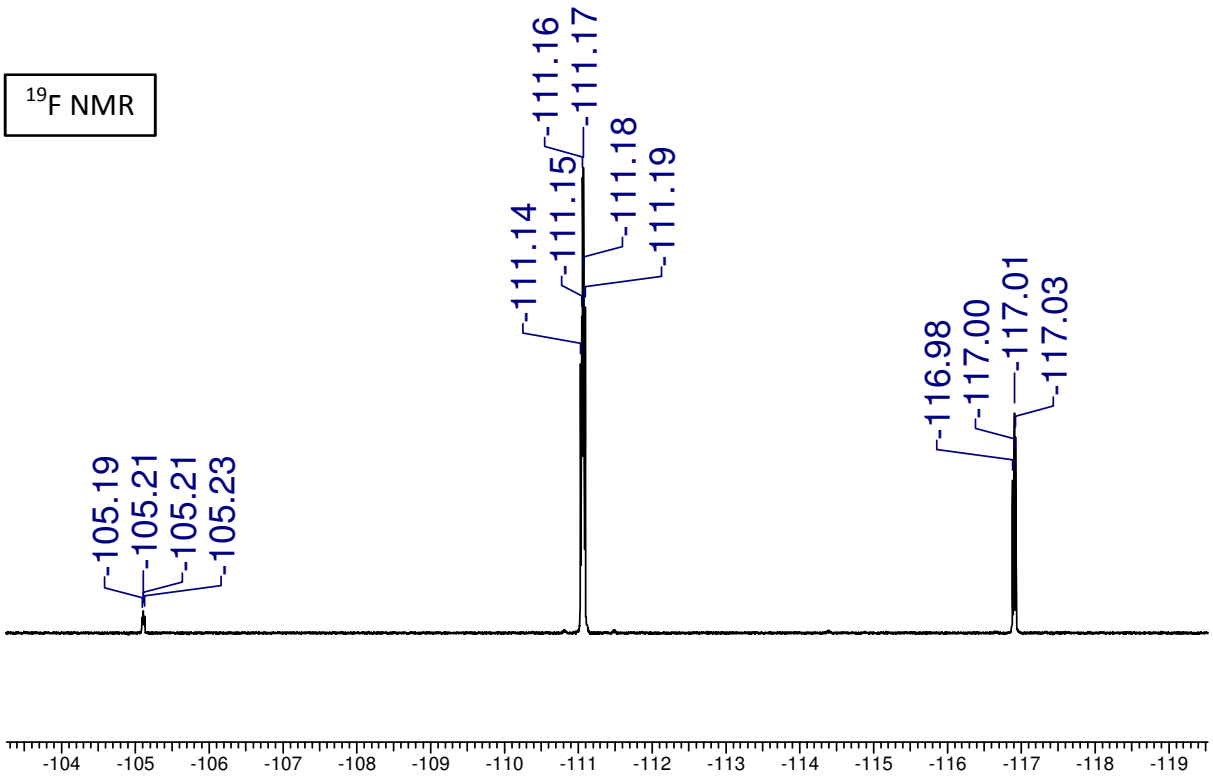
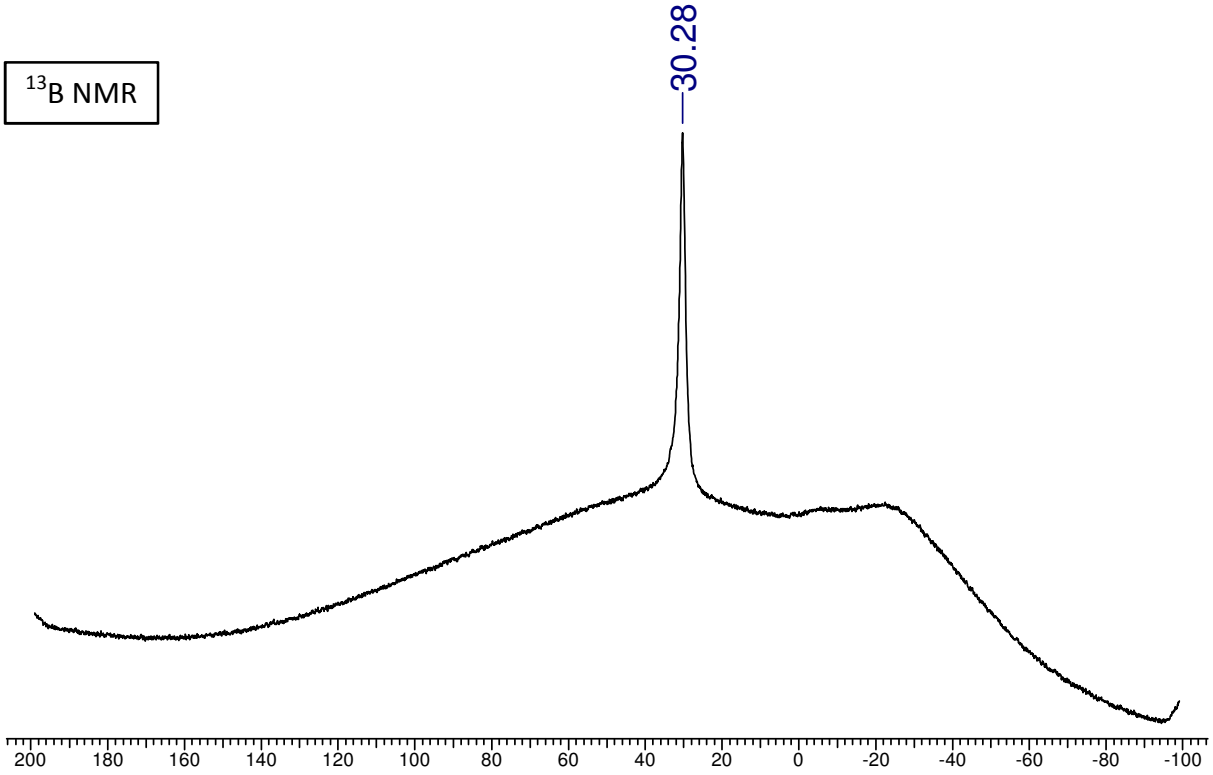
7.86
7.84
7.84
7.69
7.68
7.67
7.67
7.67
7.66
7.65
7.56
7.54
7.50
7.49
7.42
7.40
7.16
7.13
7.13
7.11
1.01
1.00
0.30
0.30
0.30
1.02
1.35
15.85
13C NMR
137.16
134.84
134.76
131.00
130.20
124.17
124.00
122.29
122.10
120.84
120.67
116.27
116.07
161.41
159.03
158.89
156.56
24.82
84.29
84.23
Chemical Shift (ppm)


19F NMR
-105.19
-105.21
-105.21
-105.23
-111.14
-111.15
-111.16
-111.17
-111.18
-111.19
-116.98
-117.00
-117.01
-117.03
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119


13B NMR
30.28
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Borylation of 1-bromo-2-fluorobenzene

with DMTol-BCl_3/$AlCl_3$ 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 CH_2Cl_2.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 %).

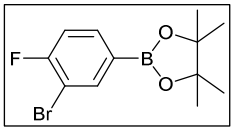
with [Cl_2Py-BCl_2][$AlCl_4$]/$AlCl_3$ in a 1 : 1 ratio:

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 : EtOAc3 : 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 isomeras pale yellow oil (189 mg, 78 %).

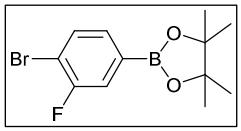
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (albeit containing two major isomers). Representative NMR spectra are shown below. Isomers were identified by comparison to the known related chloro isomers (see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

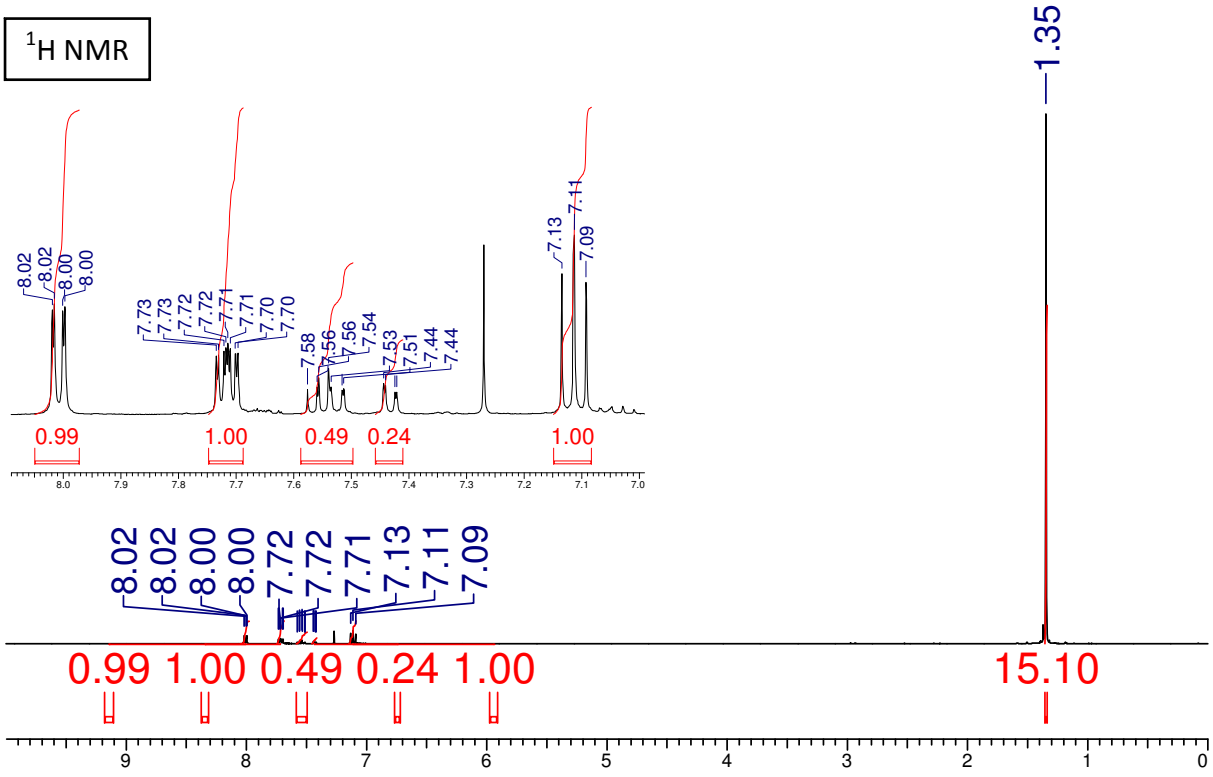


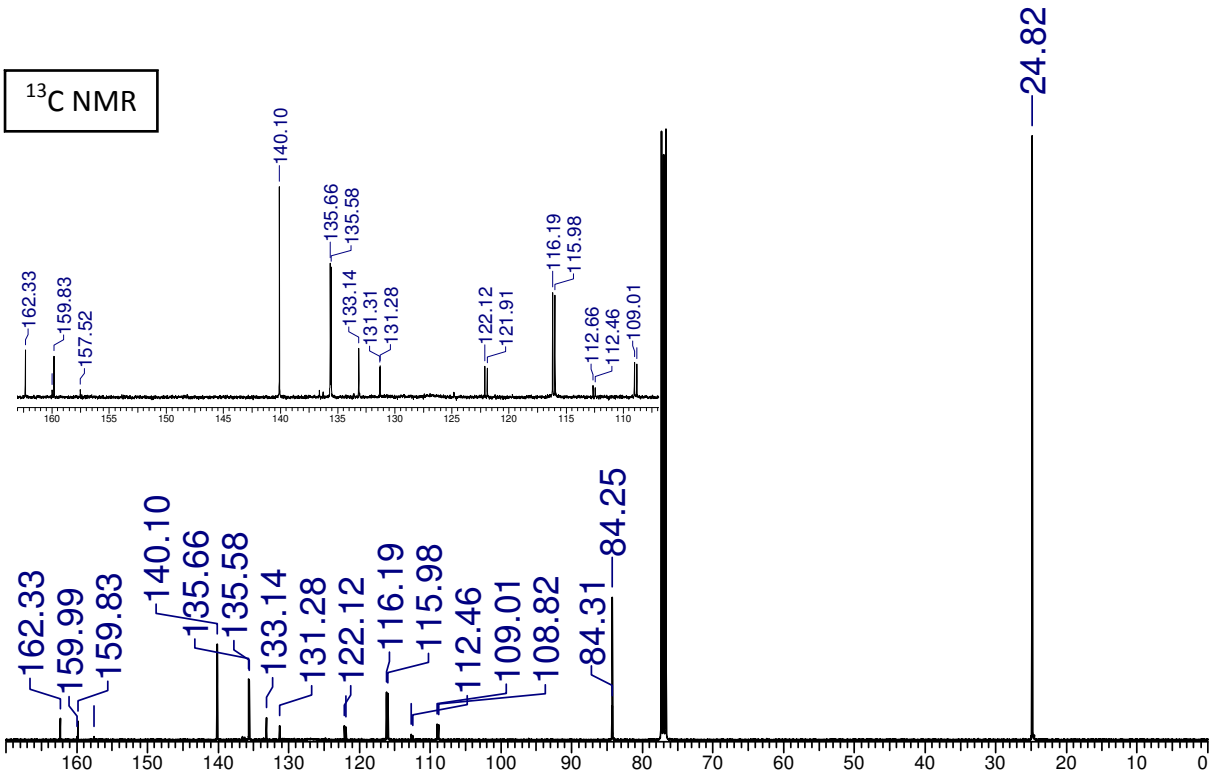
^{1}H NMR (400MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 1.5, 7.3 Hz, 1 H), 7.72 (ddd, *J* = 1.6, 5.3, 8.2 Hz, 1 H), 7.11 (dd, *J* = 8.2, 8.8 Hz, 1 H), 1.35 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 161.1 (d, *J* = 251.6 Hz), 140.1, 135.6 (d, *J* = 8.1 Hz), 116.1 (d, *J* = 21.3 Hz), 108.9 (d, *J* = 19.8 Hz), 84.2, 24.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -102.9 (ddd, *J*=5.3, 7.3, 8.8 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.1.

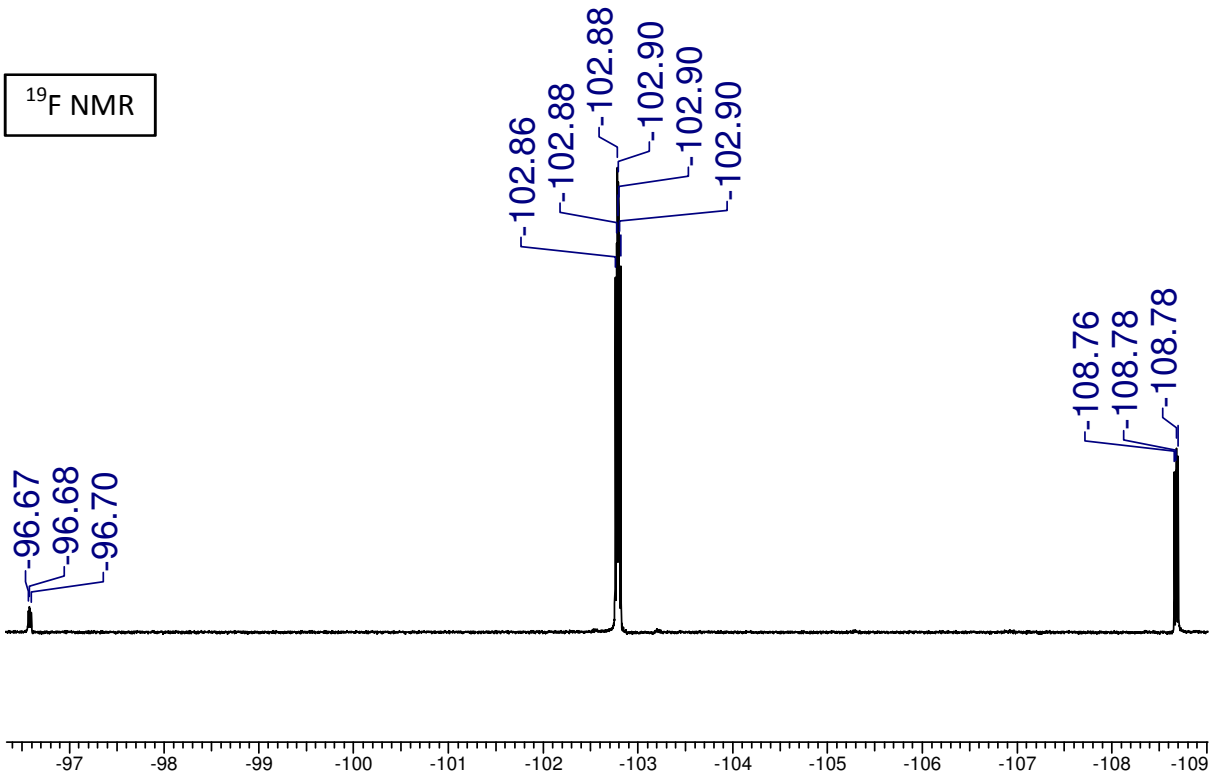
Selected NMR data for 2-(4-bromo-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 - 7.50 (m, 2 H), 7.43 (dd, *J* = 1.5, 7.8 Hz, 1 H), 1.35 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -108.78 (dd, *J* = 6.8, 8.9 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.1.


1H NMR
8.02
8.02
8.00
8.00
7.73
7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.58
7.56
7.56
7.54
7.53
7.51
7.44
7.44
7.13
7.11
7.09
0.99
1.00
0.49
0.24
1.00
1.35
15.10


13C NMR
162.33
159.83
157.52
140.10
135.66
135.58
133.14
131.31
131.28
122.12
121.91
116.19
115.98
112.66
112.46
109.01
24.82
162.33
159.99
159.83
140.10
135.66
135.58
133.14
131.28
122.12
116.19
115.98
112.46
109.01
108.82
84.31
84.25


19F NMR
-96.67
-96.68
-96.70
-102.86
-102.88
-102.88
-102.90
-102.90
-102.90
-108.76
-108.78
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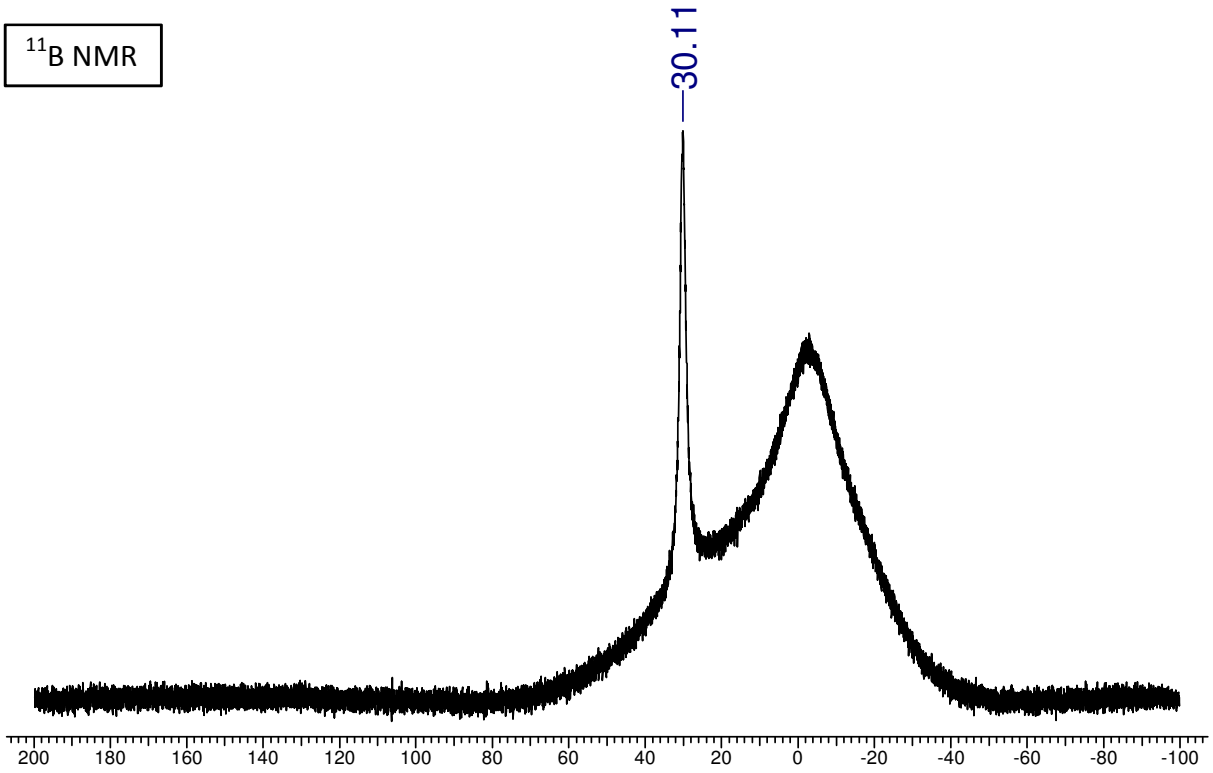
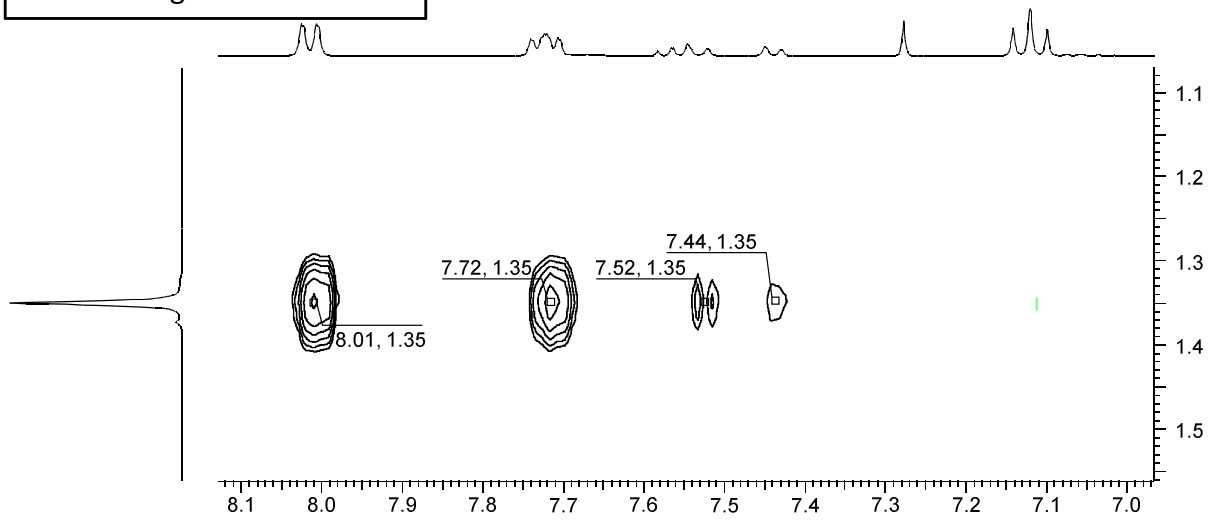
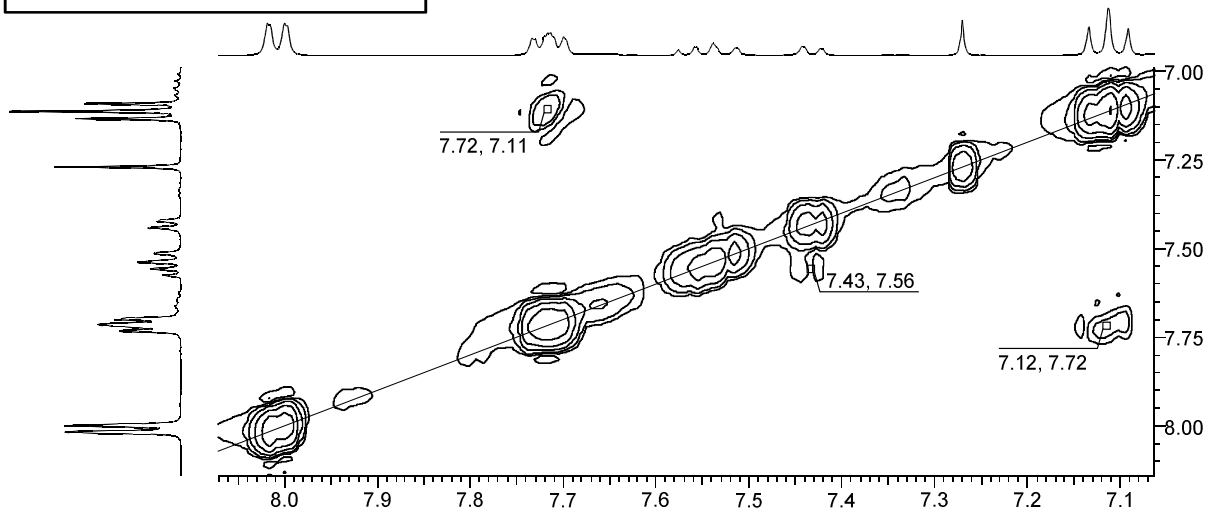
-103
-104
-105
-106
-107
-108
-109


11B NMR
30.11
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

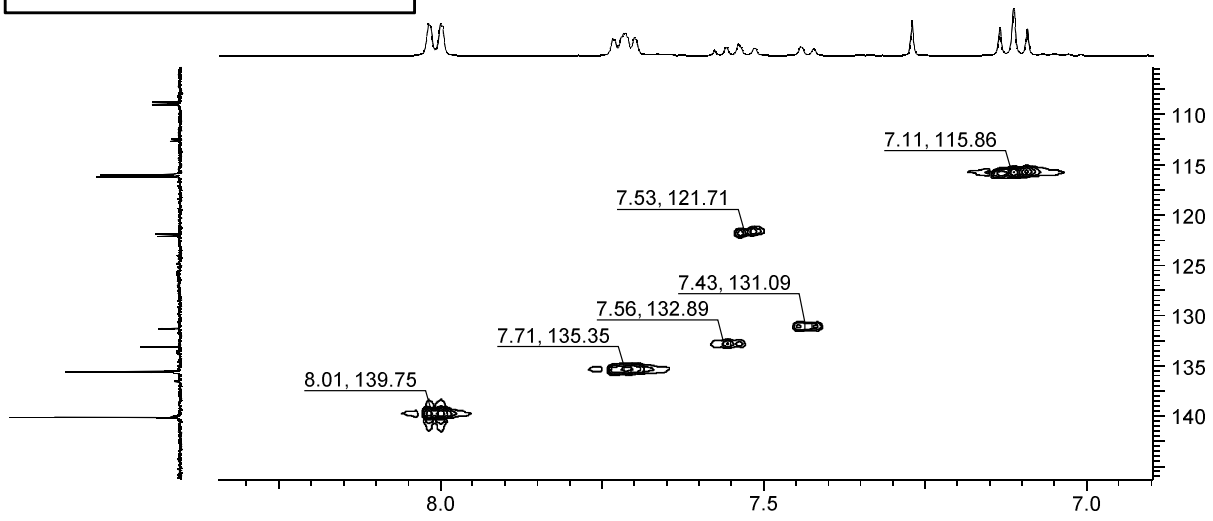
Selected region of the NOESY



Selected region of the NOESY



Selected region of the HBQC

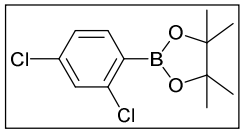


Borylation of 1,3-dichlorobenzene with DMTol-BCl_3/$AlCl_3$ in a 1 : 2 ratio:

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 CH_2Cl_2. 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 %).

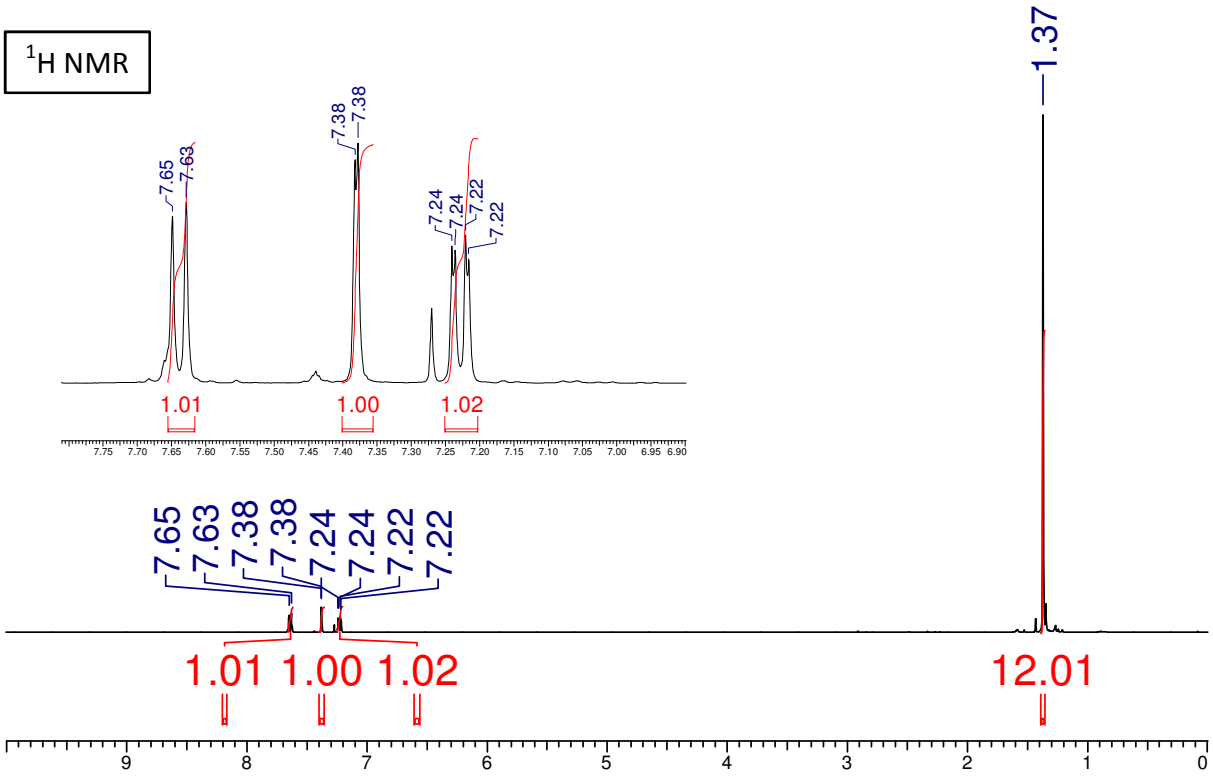
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported.[7] Representative NMR spectra are shown below.



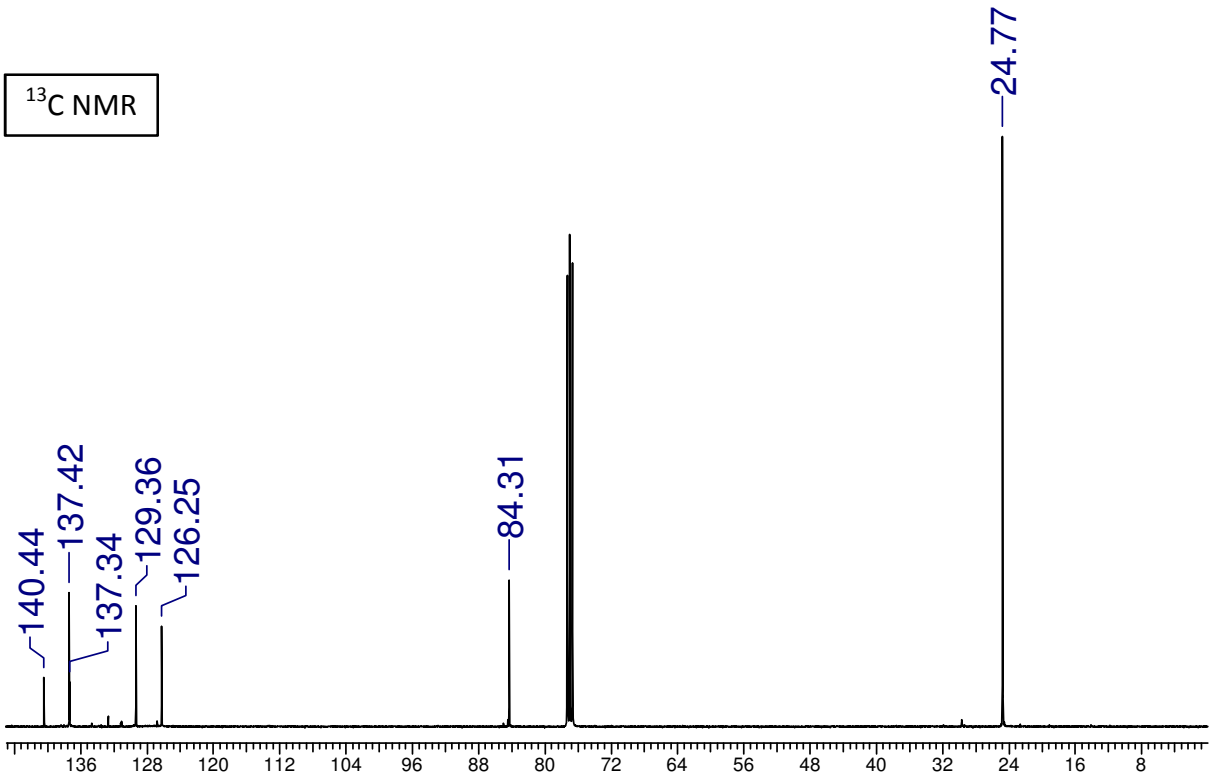
^{1}H NMR (400MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 1.8 Hz, 1 H), 7.15 (dd, *J* = 1.8, 8.0 Hz, 1 H), 1.29 (s, 12 H).

^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) δ = 140.4, 137.4, 137.3, 129.4, 126.2, 84.3, 24.8.

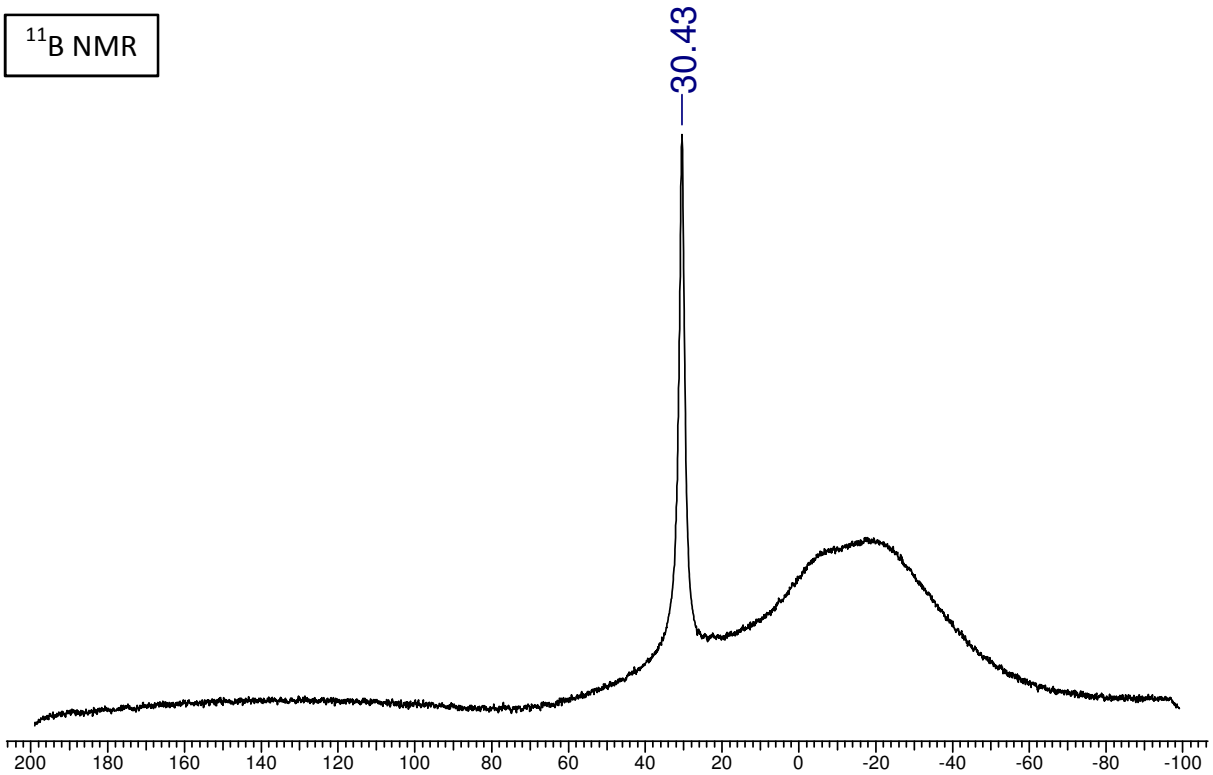
^{11}B NMR (128MHz, $CDCl_3$) δ = 30.4.



^{13}C NMR



^{11}B NMR

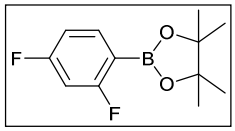


Borylation of 1,3-difluorobenzene with DMTol-BCl_3/$AlCl_3$ in a 1 : 2 ratio:

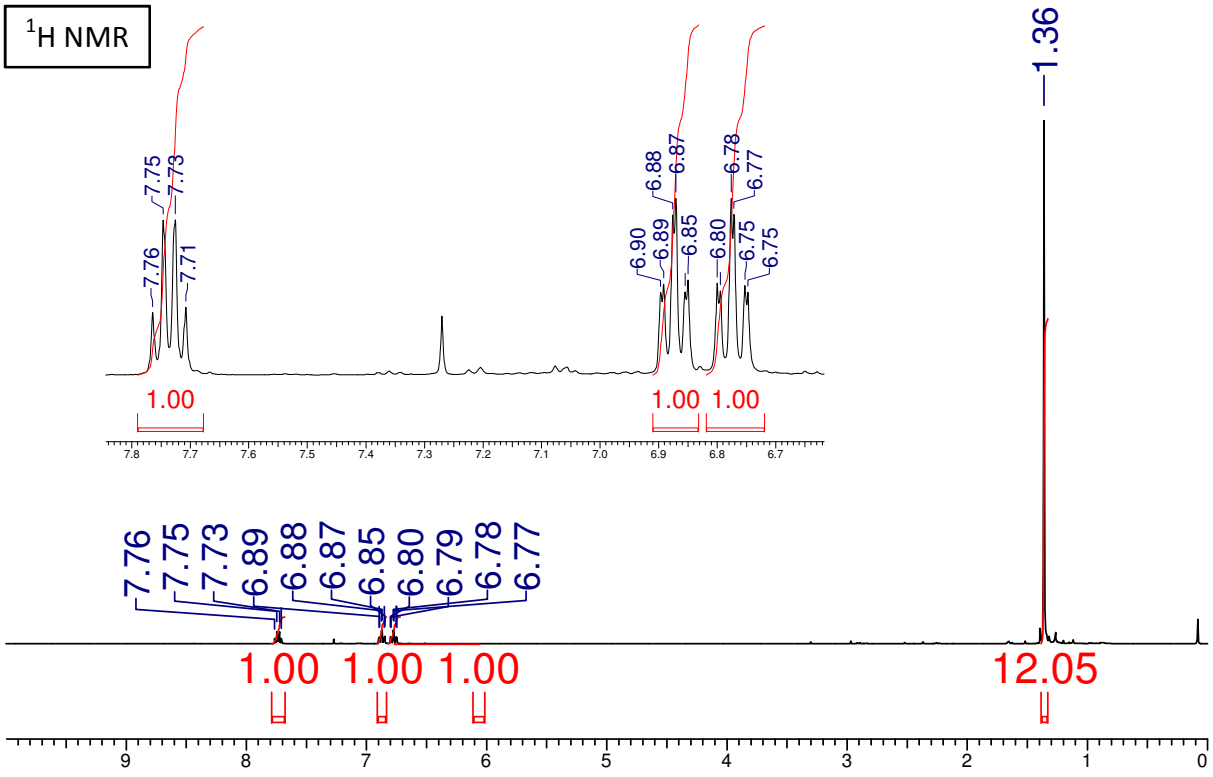
Following the general procedure A; Temperature: 140 °C; Reaction time: 17 hours.

Purification: The crude material was absorbed on silica, filtered through a plug of silica gel and the plug washed with CH_2Cl_2.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 %).

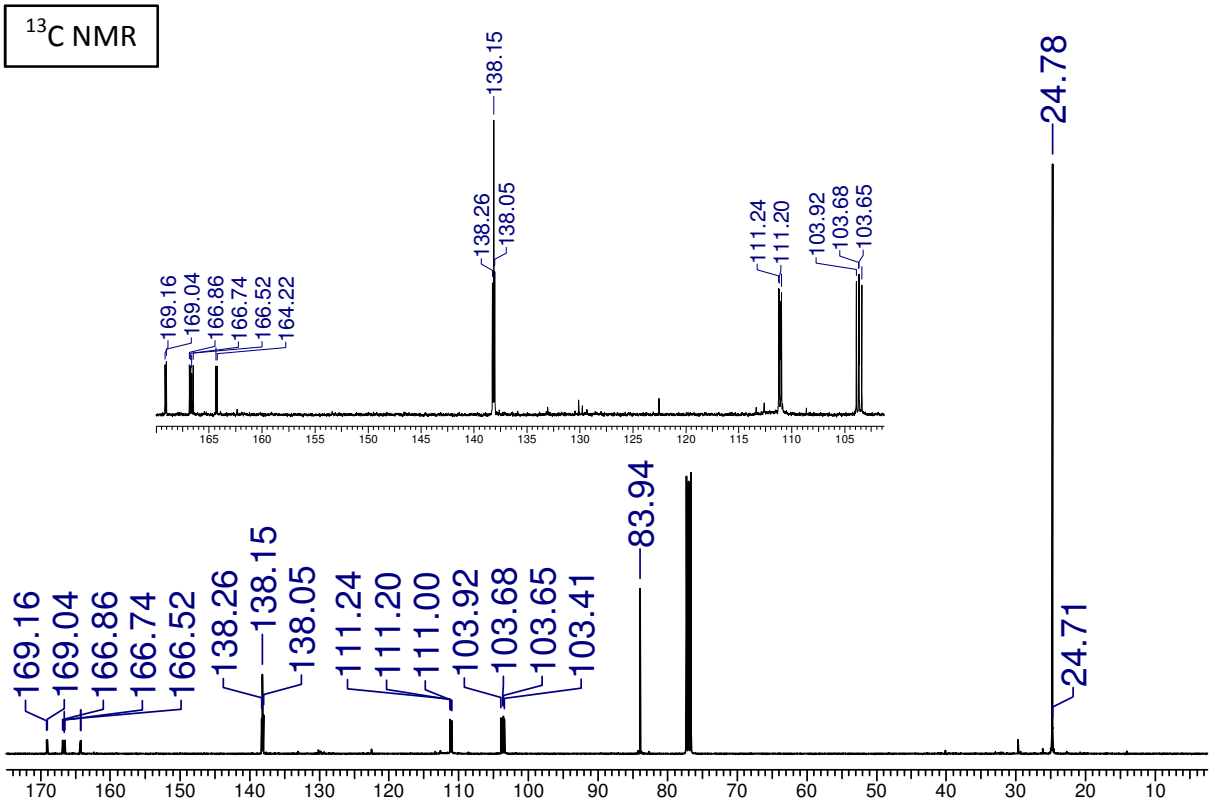
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure. The NMR spectra are identical to that previously reported.[8] Representative NMR spectra are shown below.



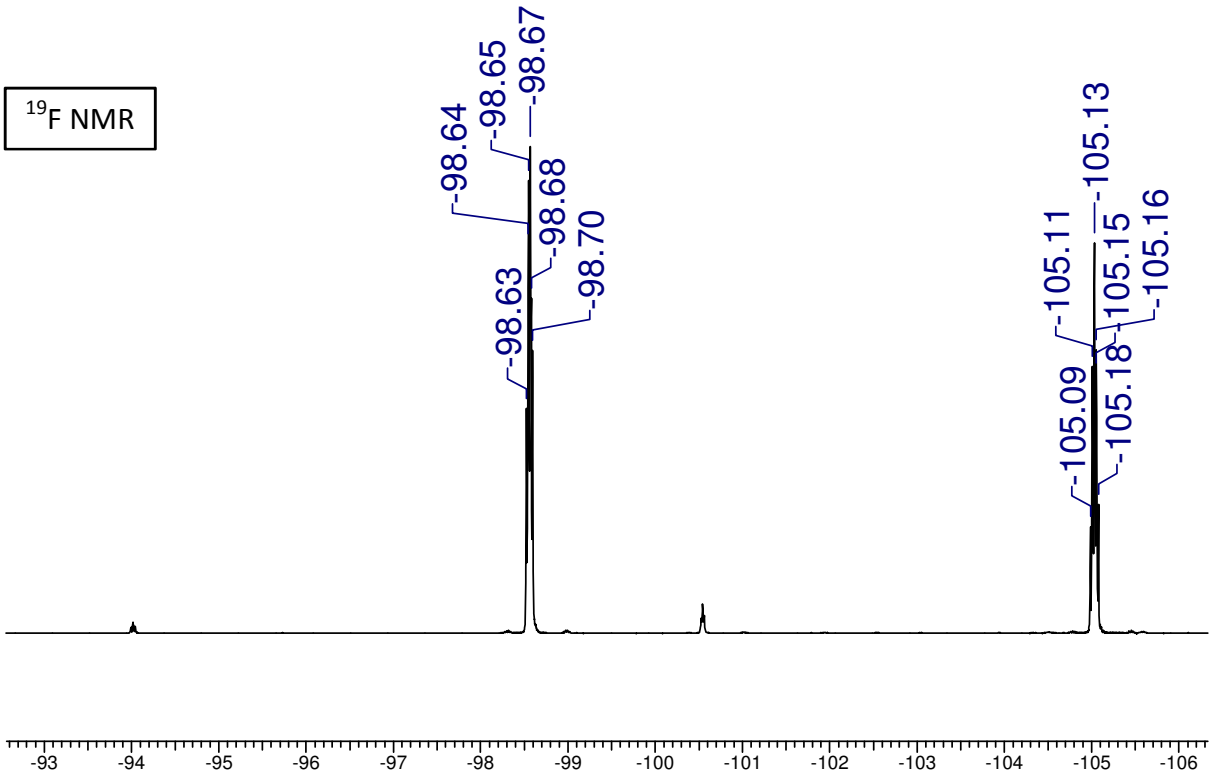
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (q, *J* = 7.3 Hz, 1 H), 6.87 (dt, *J* = 2.1, 8.3 Hz, 1 H), 6.77 (dt, *J* = 2.1, 9.5 Hz, 1 H), 1.36 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 167.8 (dd, *J* = 11.7, 253.8 Hz), 165.5 (dd, *J* = 12.5, 253.1 Hz), 138.2 (t, *J* = 10.3 Hz), 111.1(dd, *J* = 3.7, 20.2 Hz), 103.7 (dd, *J* = 24.2, 27.9 Hz), 83.9, 24.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -98.7 (dt, *J*=7.2, 10.0 Hz), -105.1 (tt, *J*=9.5, 8.3 Hz).
^{11}B NMR (128 MHz,$CDCl_3$) δ = 29.9.

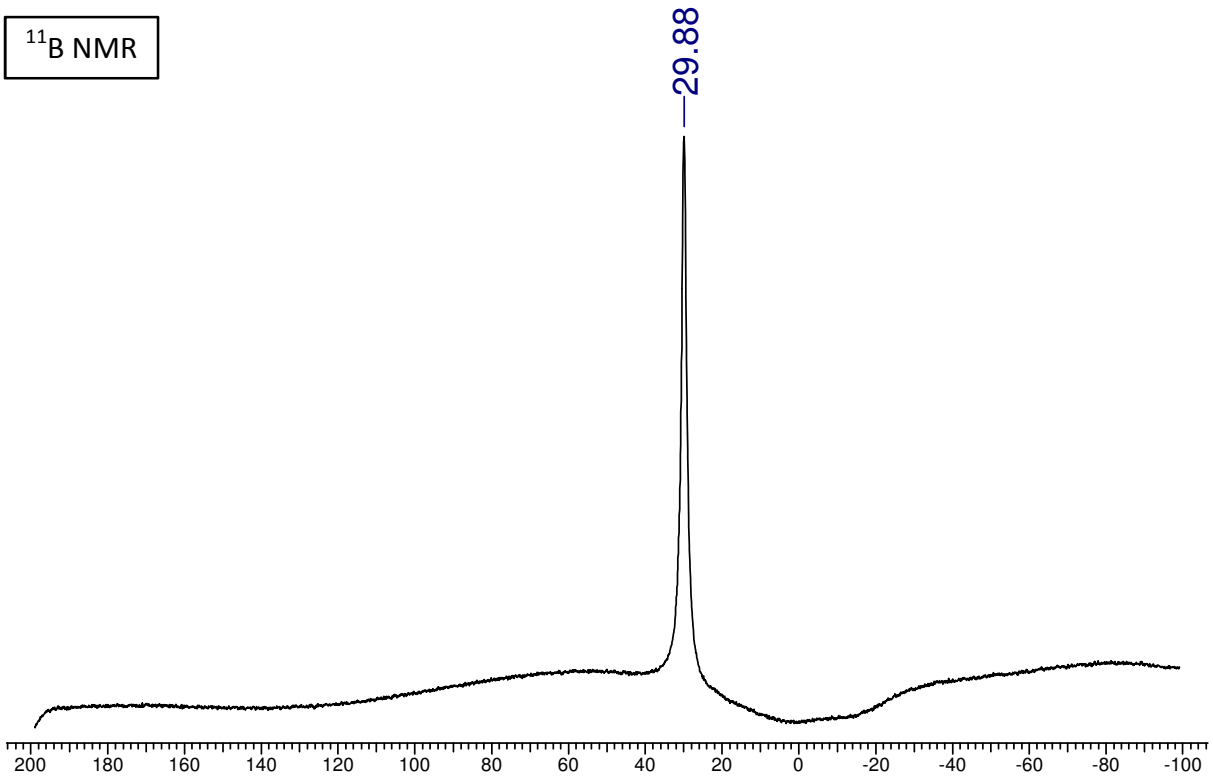


^{13}C NMR



^{19}F NMR




^{11}B NMR
29.88
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

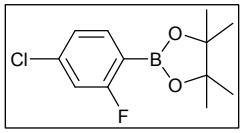
Borylation of 1-chloro-3-fluorobenzene:

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

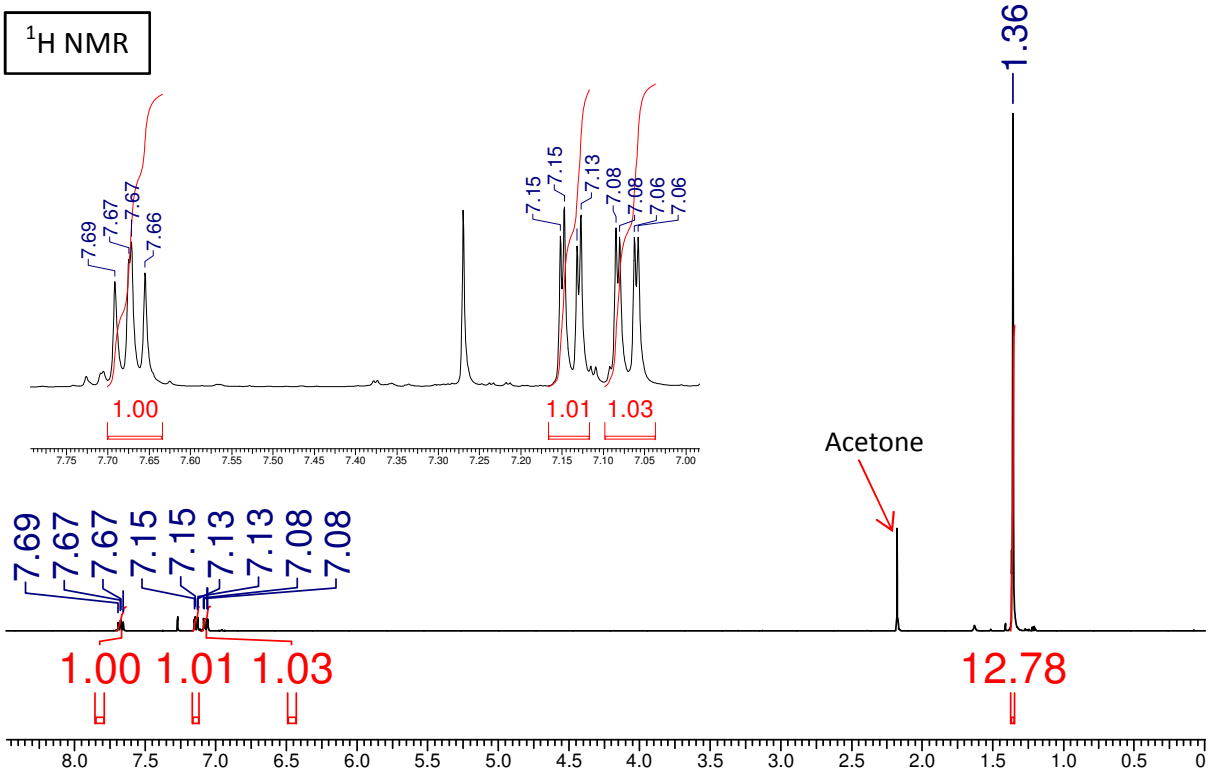
Purification: The crude material was filtered through a plug of silica gel and the plug washed with CH_2Cl_2. The product was dried at 20 °C at $4x10^{-2}$ torr to remove DMTol giving 2-(4-chloro-2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with less than 5 % of another isomer as a colourless solid (131 mg, 64 %).

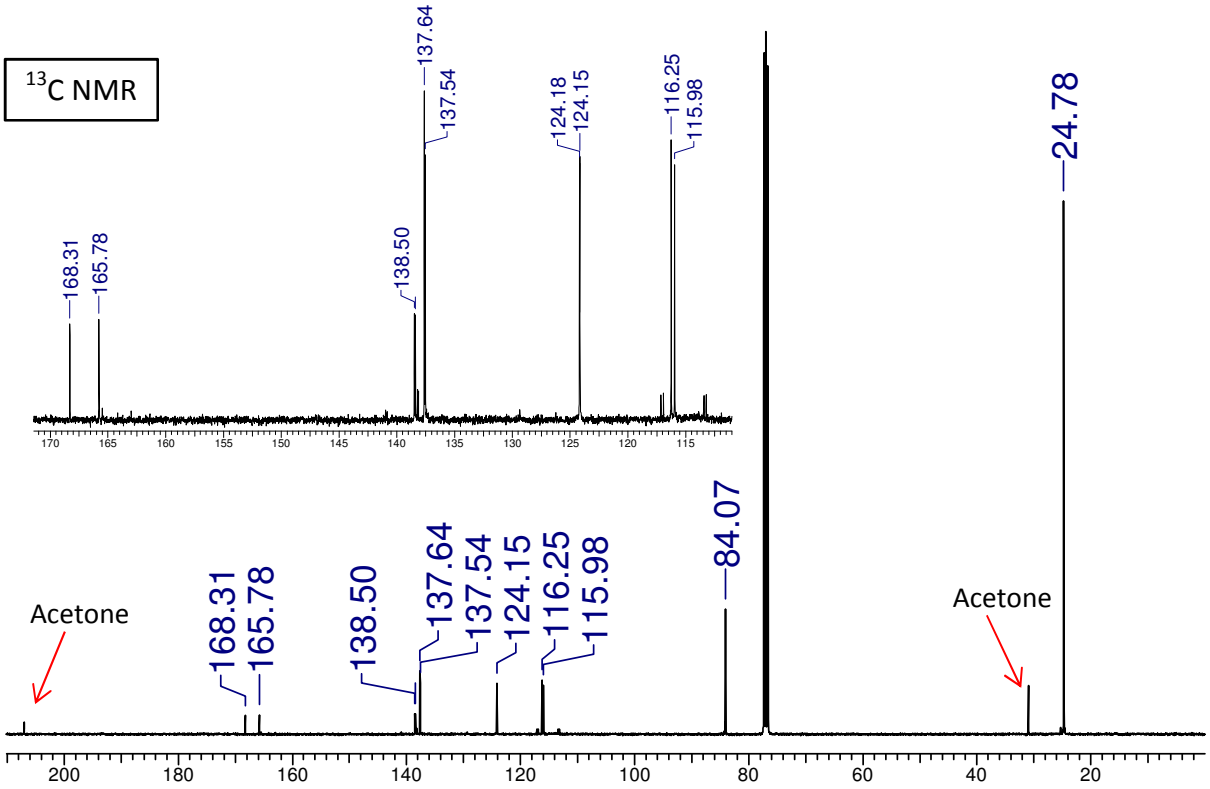
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (with only visible impurity due to a minor isomer). HRMS (APCI) Found: 257.0896. Calc. for $C_{12}H_{15}BClFO_2$ ($M + H^+$): 257.0918.

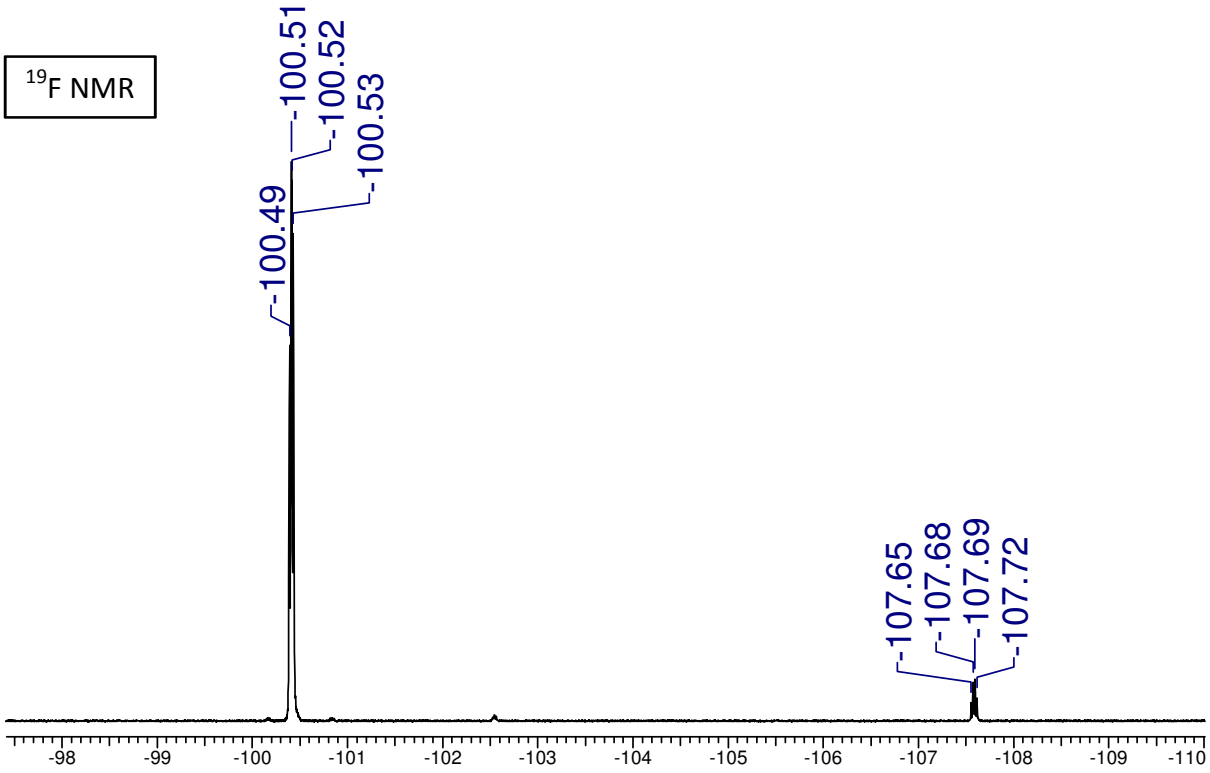
Product characterised by combined NMR spectroscopy / X-ray diffraction studies. Representative NMR spectra are shown below.

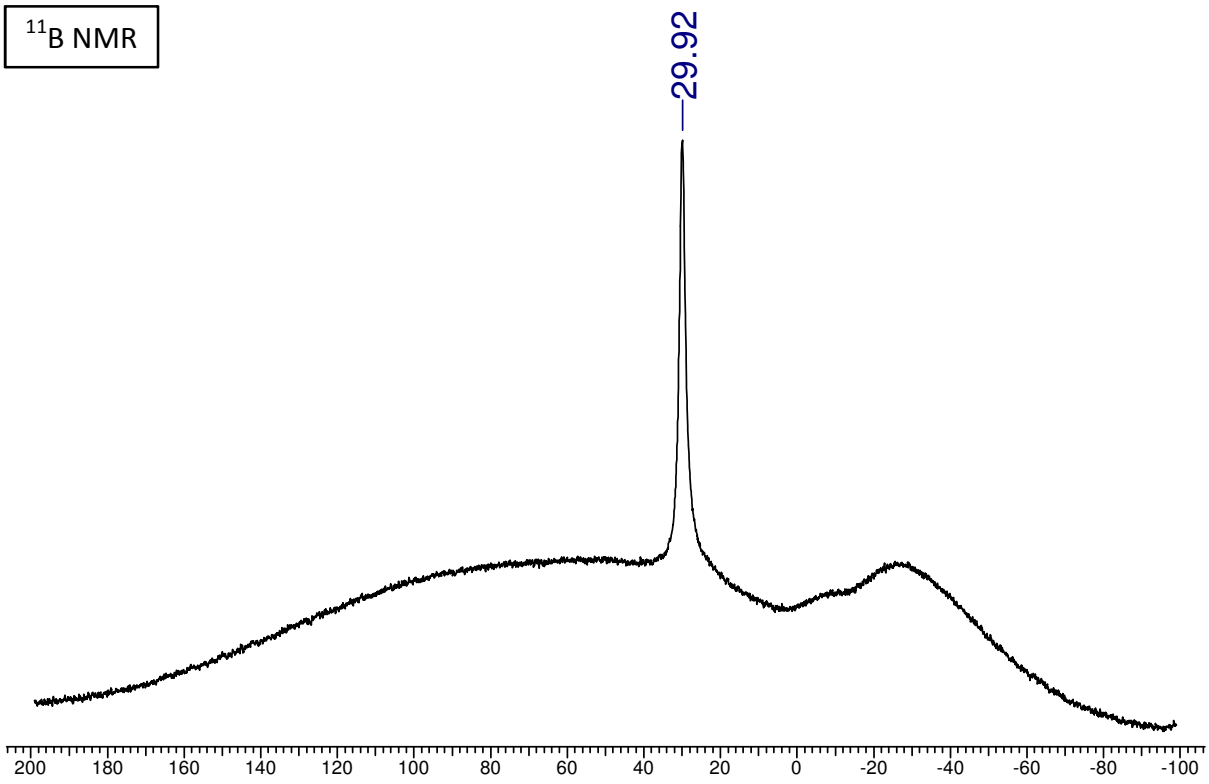


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (dd, *J* = 6.7, 7.9 Hz, 1 H), 7.14 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.07 (dd, *J* = 1.8, 9.0 Hz, 1 H), 1.36 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 167.0 (d, *J* = 254.6 Hz), 138.4 (d, *J* = 10.3 Hz), 137.6 (d, *J* = 9.5 Hz), 124.2 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 27.1 Hz), 84.1, 24.8.
^{19}F NMR (376MHz,$CDCl_3$) δ = -100.5 (dd, *J* = 6.6, 9.0 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 29.9.




13C NMR
168.31
165.78
138.50
137.64
137.54
124.18
124.15
116.25
115.98
24.78
Acetone
84.07
Acetone


19F NMR
-100.51
-100.52
-100.53
-100.49
-107.65
-107.68
-107.69
-107.72


^{11}B NMR
29.92
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Borylation of 1-bromo-3-fluorobenzene:

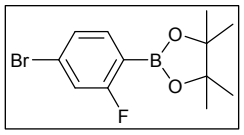
Following the general procedure A; Temperature: 140 °C; Reaction time: 48 hours.

Purification: The crude material was dissolved in 30 ml of hexane/CH_2Cl_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 %).

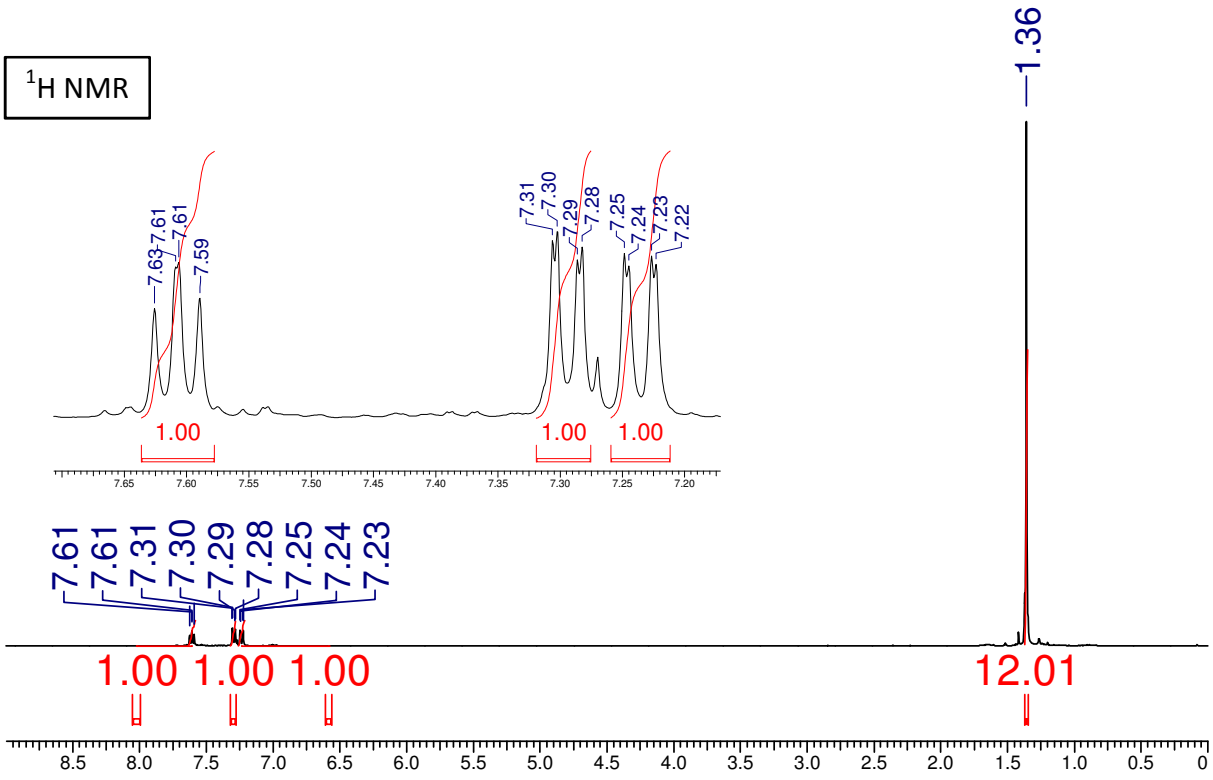
Elemental analysis Found: C, 49.17; H, 4.97. Calc. for $C_{12}H_{15}BBrFO_2$: C, 47.89; H, 5.02.

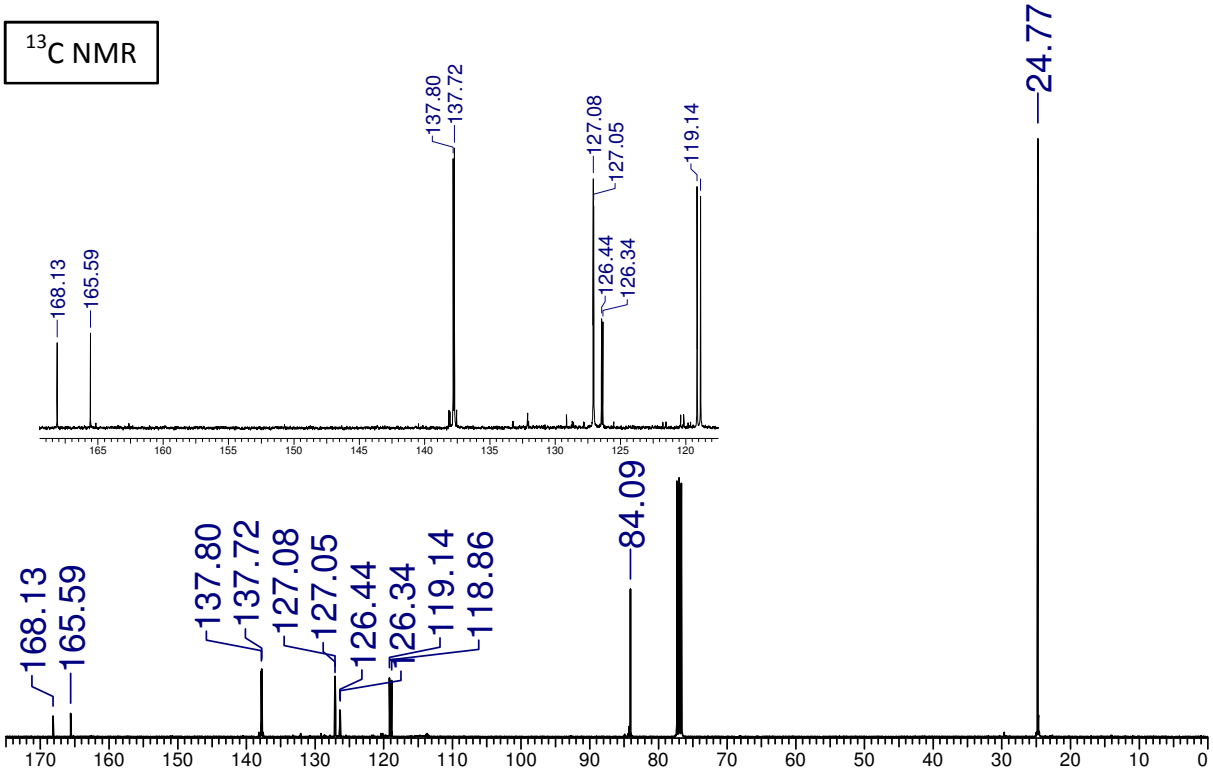
HRMS (APCI) Found: 301.0395. Calc. for $C_{12}H_{15}BBrFO_2$ ($M + H^+$): 301.0413.

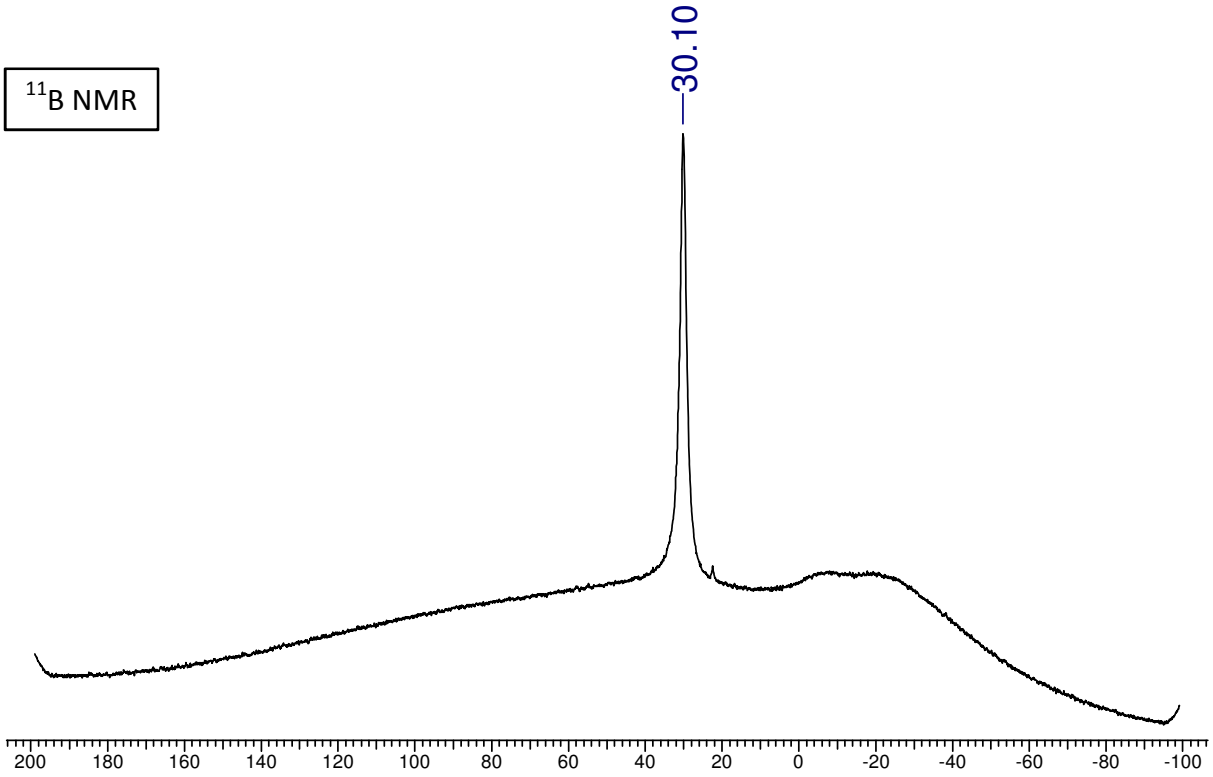
Product characterised by combined NMR spectroscopy / X-ray diffraction studies. Representative NMR spectra are shown below.



^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.61 (dd, *J* = 6.8, 7.8 Hz, 1 H), 7.29 (dd, *J* = 1.5, 7.8 Hz, 1 H), 7.24 (dd, *J* = 1.5, 8.8 Hz, 5 H), 1.36 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$) δ = 166.9 (d, *J* = 256.0 Hz), 137.8 (d, *J* = 8.8 Hz), 127.1(d, *J* = 3.7 Hz), 126.4(d, *J* = 10.3 Hz), 119.0(d, *J* = 27.9 Hz), 84.1, 24.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -100.2 (dd, *J* = 6.8, 8.8 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.1.




13C NMR
168.13
165.59
137.80
137.72
127.08
127.05
126.44
126.34
119.14
118.86
84.09
24.77


11B NMR
30.10

Borylation 2-fluorotoluene

with DMTol-BCl_3/$AlCl_3$ 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/CH_2Cl_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 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 %)

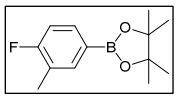
with [Cl_2Py-BCl_2][$AlCl_4$]/$AlCl_3$ in a 1 : 1 ratio:

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 CH_2Cl_2. 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 %).

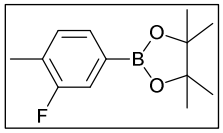
A satisfactory elemental analysis was not obtained for this compound despite the NMR spectra (see below) indicating that it is highly pure (albeit as a mixture of two isomers).

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.

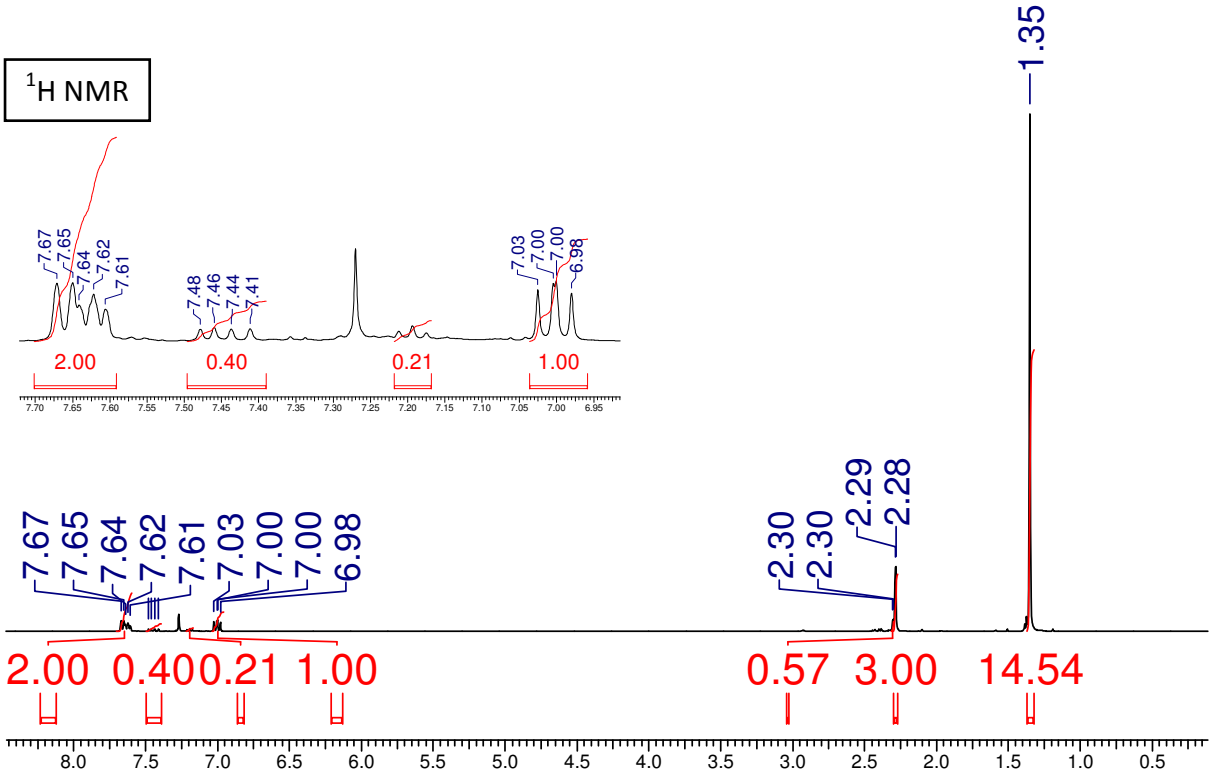


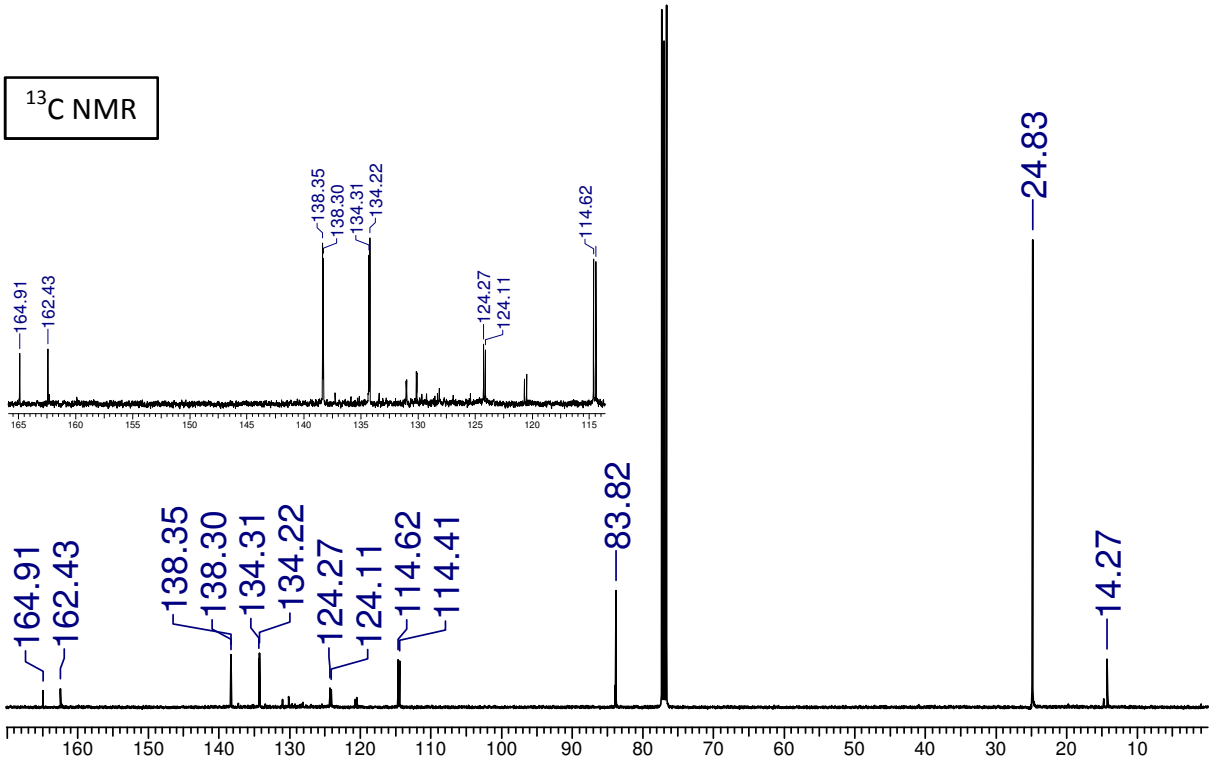
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 - 7.51 (m, 2 H), 6.92 (dd, *J* = 8.2, 10.0 Hz, 1 H), 2.20 (d, *J* = 1.8 Hz, 3 H), 1.26 (s, 12 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.7 (d, *J* = 163.7 Hz), 138.3 (d, *J* = 5.1 Hz), 134.3 (d, *J* = 8.8 Hz), 124.2 (d, *J* = 16.1 Hz), 114.5 (d, *J* = 21.3 Hz), 83.8, 24.8, 14.3 (d, *J* = 3.7 Hz)
^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.9 (m).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.7.

Selected NMR data for 2-(3-fluoro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:
The ^{1}H NMR data is identical to that previously reported.[9]

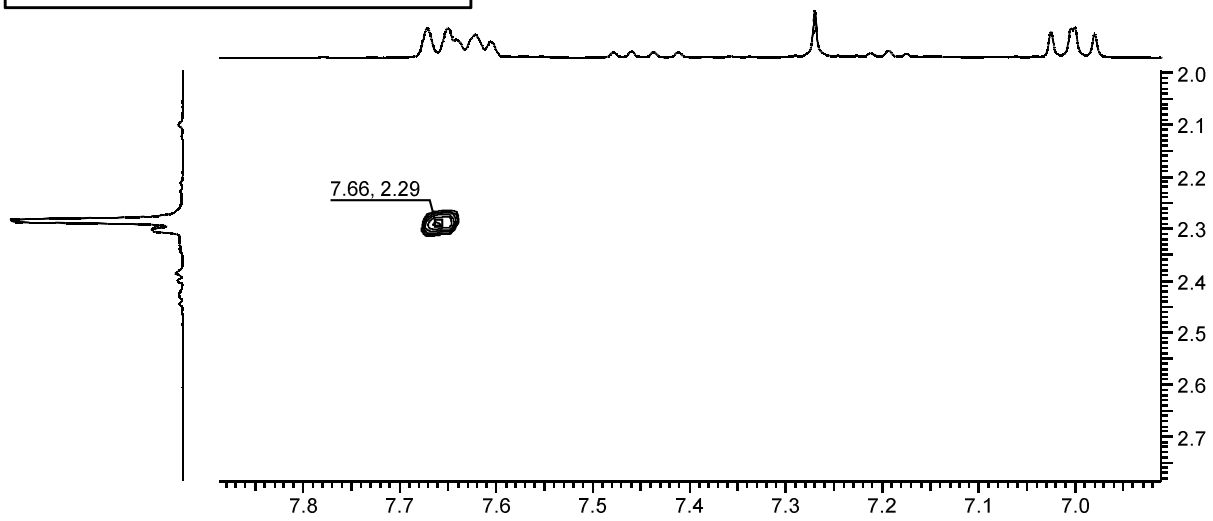


^{1}H NMR (400MHz, $CDCl_3$) δ = 7.41 - 7.30 (m, 2 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 2.22 (d, *J* = 1.8 Hz, 3 H),1.26 (s, 12 H).
^{19}F NMR (376MHz, $CDCl_3$) δ = -119.0 (qdd, *J* = 1.7, 7.8, 10.0 Hz).
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.7.

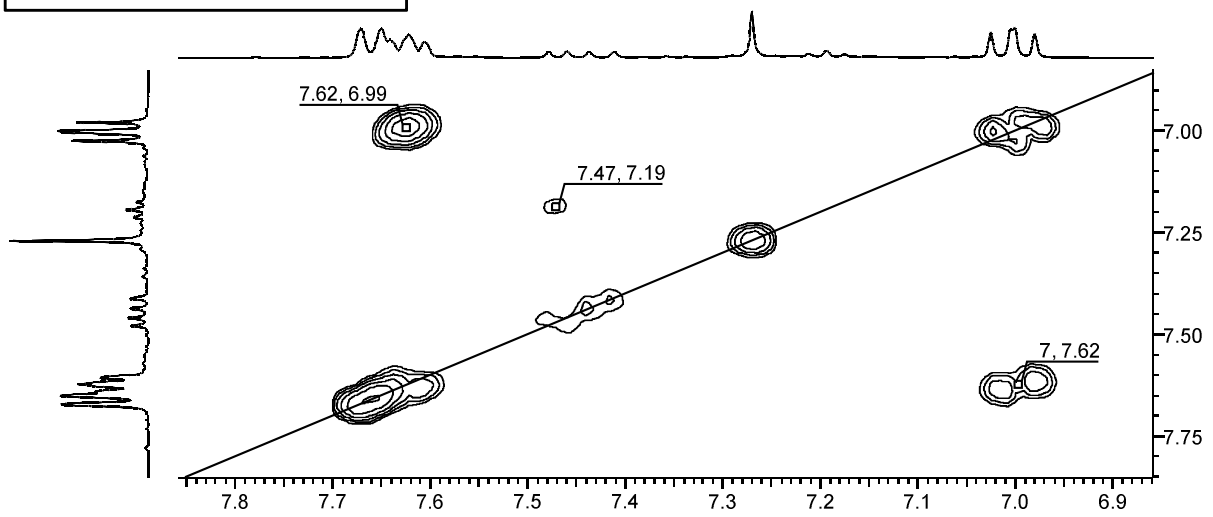

1H NMR
7.67
7.65
7.64
7.62
7.61
7.48
7.46
7.44
7.41
7.03
7.00
7.00
6.98
2.00
0.40
0.21
1.00
1.35
2.30
2.30
2.29
2.28
0.57
3.00
14.54


13C NMR
164.91
162.43
138.35
138.30
134.31
134.22
124.27
124.11
114.62
114.41
83.82
24.83
14.27

Selected region of the NOESY



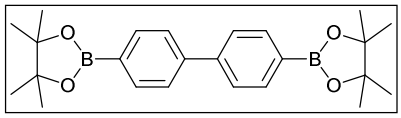
Selected region of the COSY



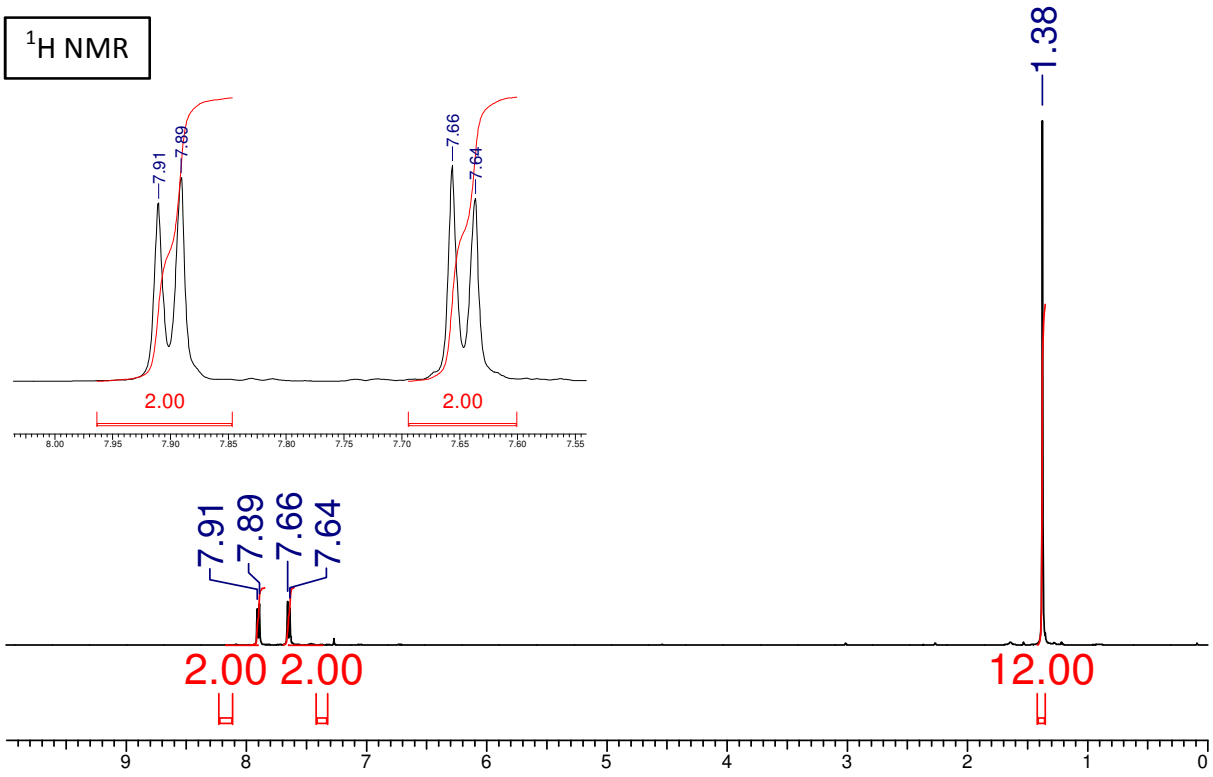
Borylation of biphenyl with DMTol-BCl_3/$AlCl_3$ in a 1 : 2 ratio:

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), 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 Et_3N (1.7 ml) in CH_2Cl_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_2Cl_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 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 : CH_2Cl_2 2 : 8 to CH_2Cl_2) giving 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl as colourless solid (59 mg, 56 %).

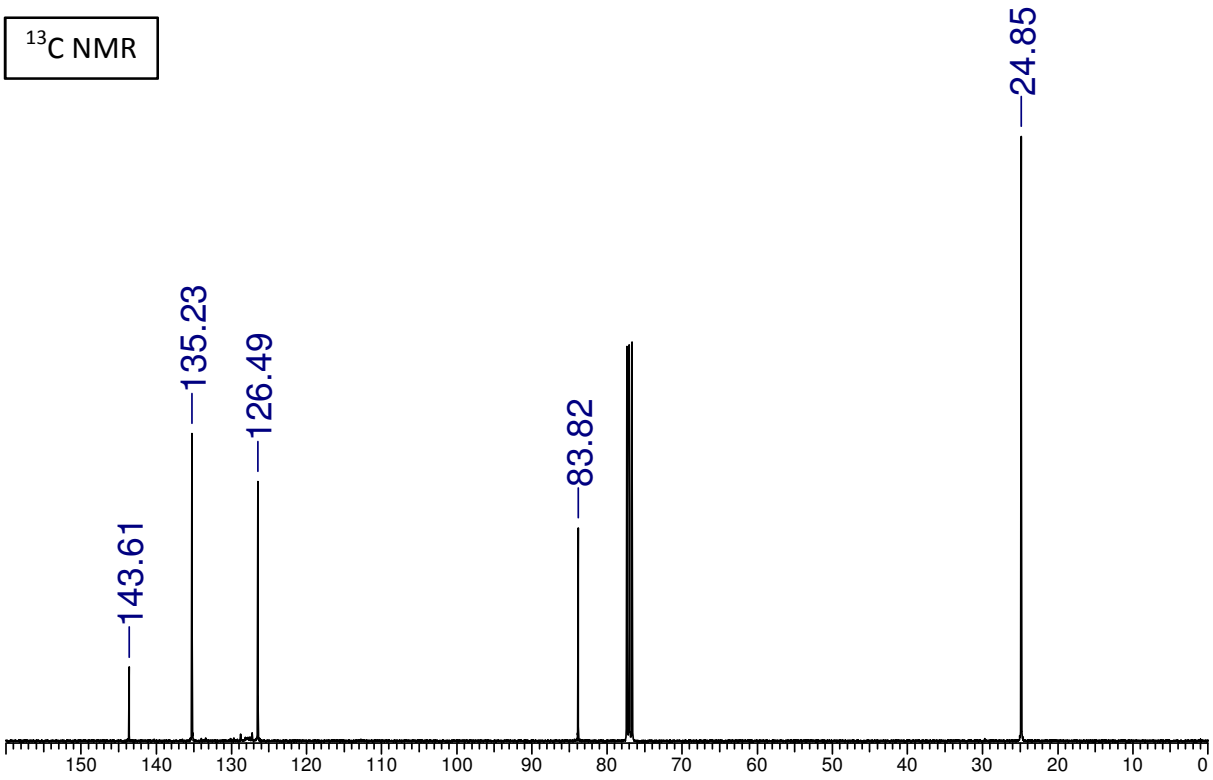
The NMR spectra are identical to that previously reported.[10] Representative NMR spectra are shown below.



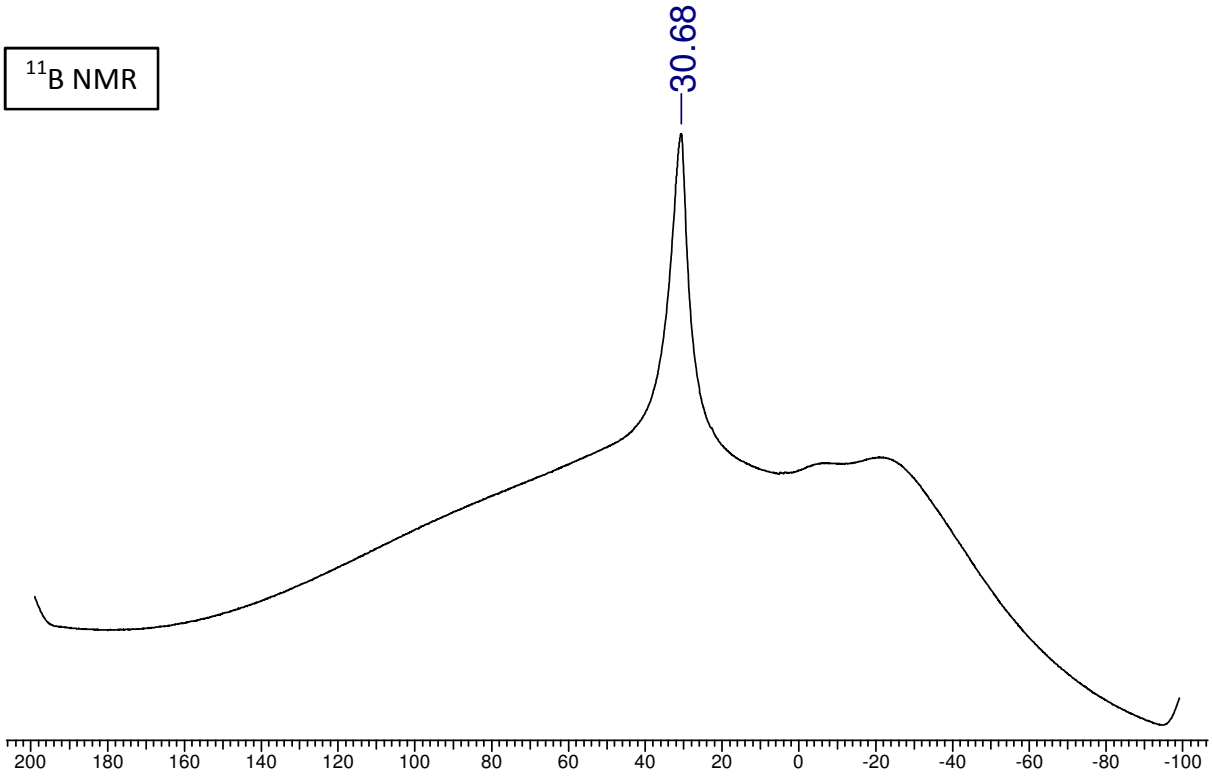
^{1}H NMR (400MHz, $CDCl_3$) δ = 7.90 (d, *J* = 7.8 Hz, 4 H), 7.65 (d, *J* = 8.0 Hz, 4 H), 1.38 (s, 24 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 143.6, 135.2, 126.5, 83.8, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.7.



^{13}C NMR



^{11}B NMR



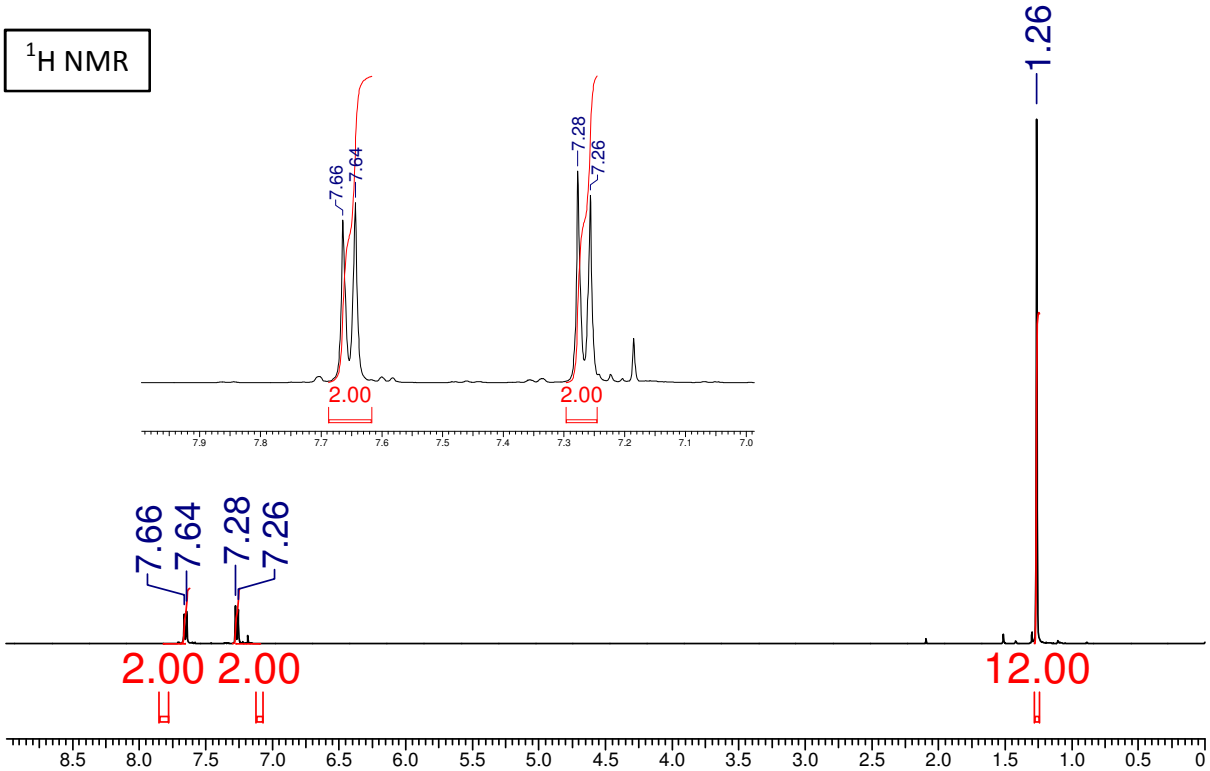
Large scale borylation outside glovebox

An additional 0.5 equivalents of $AlCl_3$ / amine are used in these reactions due to reaction with protic impurities (e.g., H_2O) in the unpurified solvent/reagent generating ammonium[$AlCl_4$]

Borylation of chlorobenzene with DMTol-BCl_3/DMTol/$AlCl_3$ in a 1 : 0.5 : 2.5 ratio:

An oven dried 100 ml Schlenk tube fitted with a J. Youngs valve was flushed with N_2 and charged with $AlCl_3$ (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-BCl_3 (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 Et_3N (45 ml) in CH_2Cl_2 (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 CH_2Cl_2 (2 × 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 × 300 ml) the extracts were combined and the volume reduced to *ca.* 200 ml. The solution was washed with HCl (6 N, 200 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-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 %).

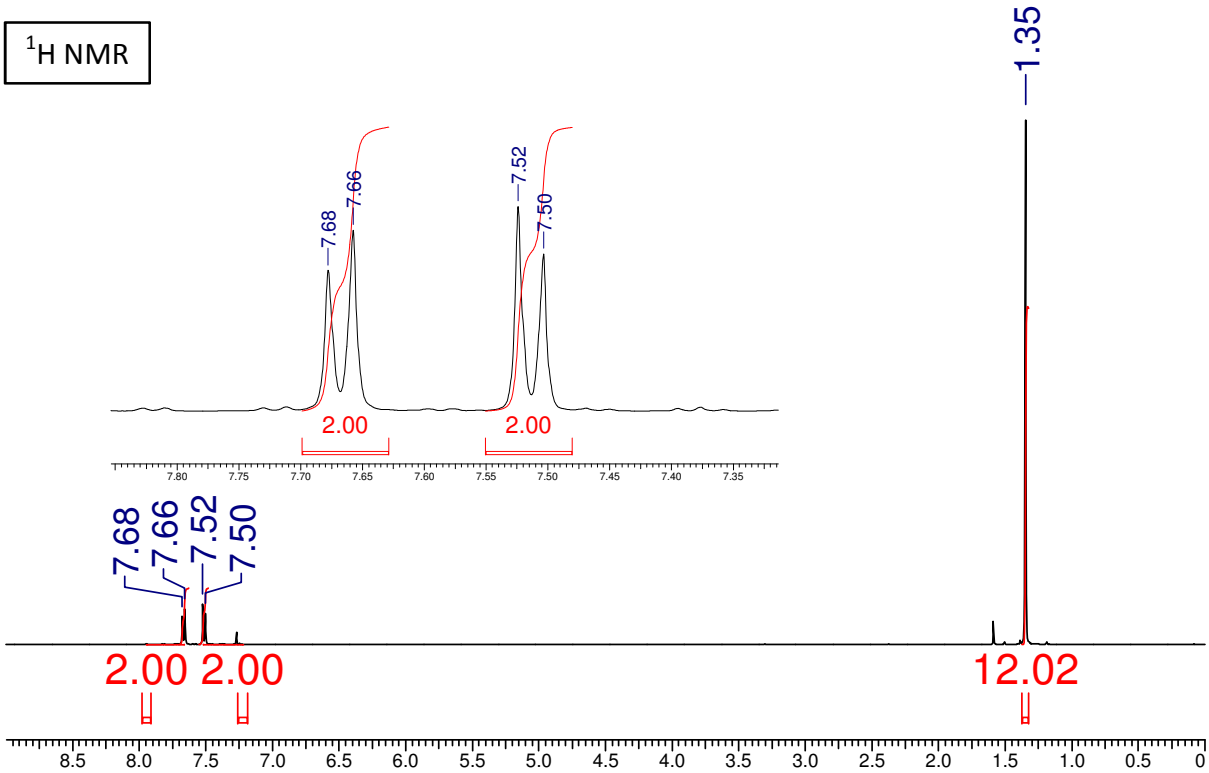
Representative ^{1}H NMR spectra are shown below.



Borylation of bromobenzene with DMTol/BCl_3/$AlCl_3$ 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_3N (25 ml) in CH_2Cl_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_2Cl_2 (2 × 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 × 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.

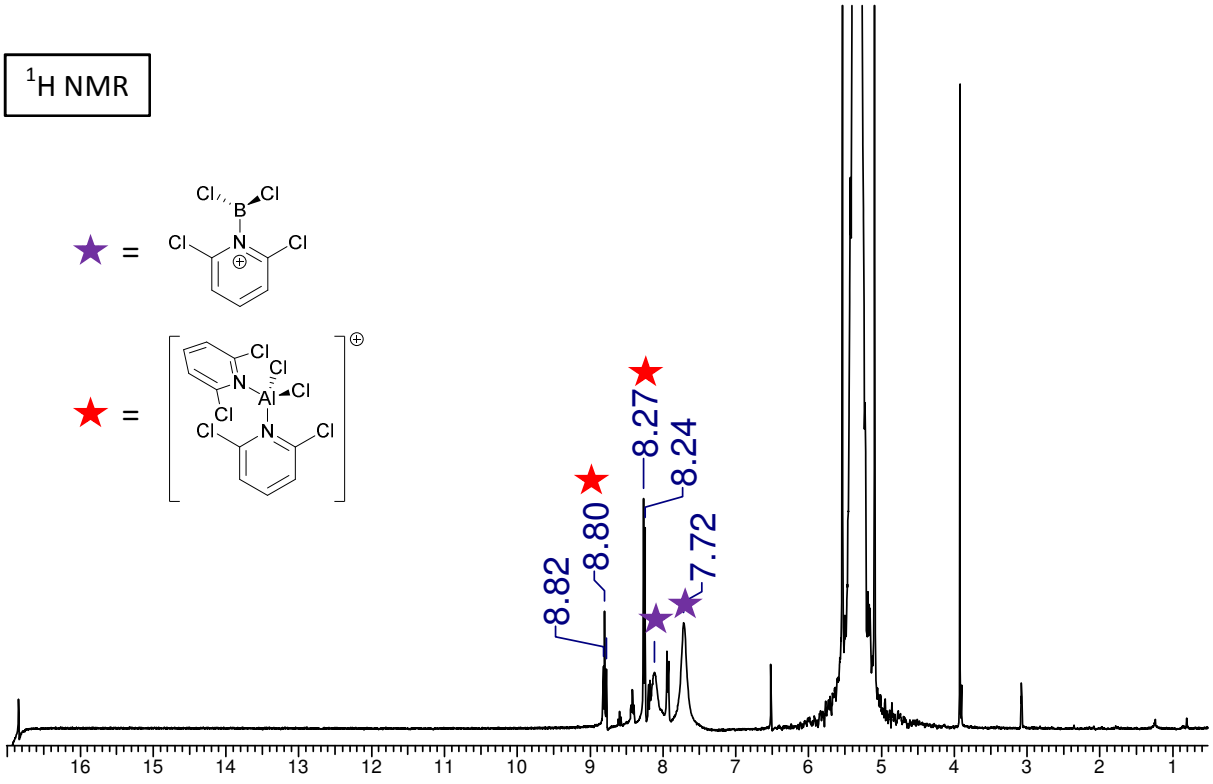


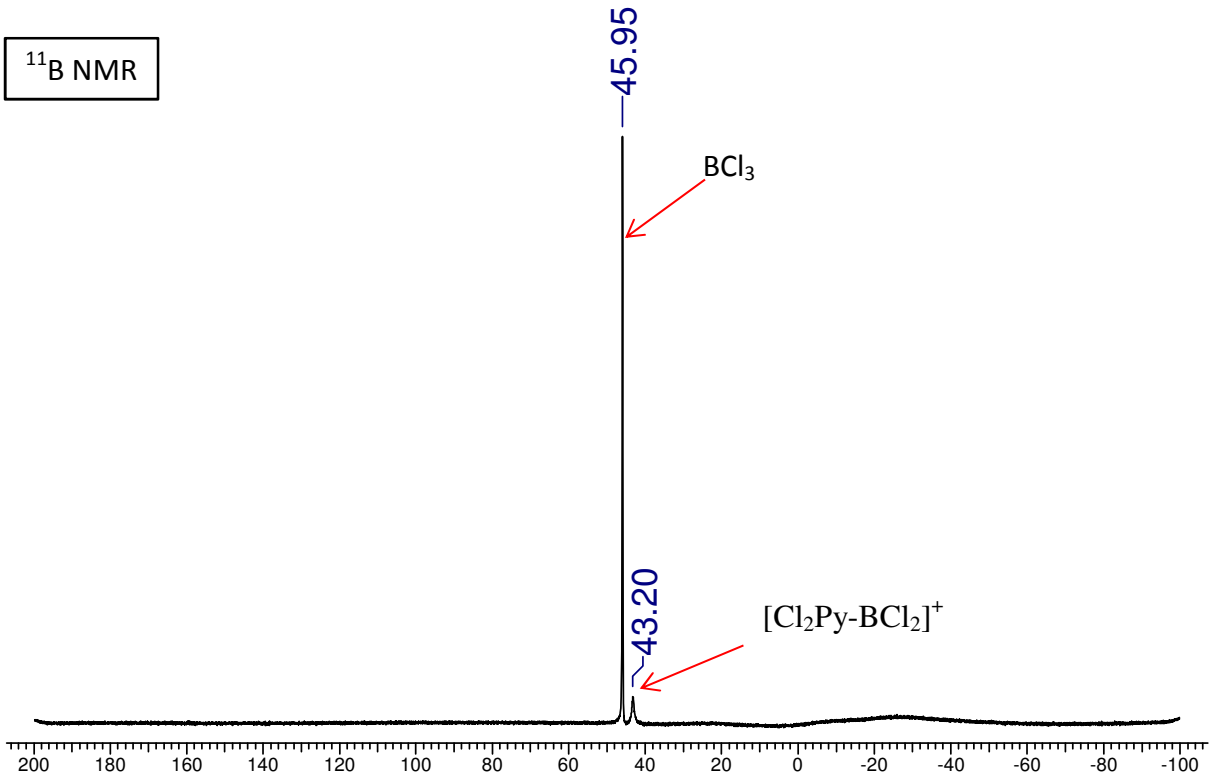
Synthesis of $[Cl_2Py\text{-}BCl_2][AlCl_4]$:

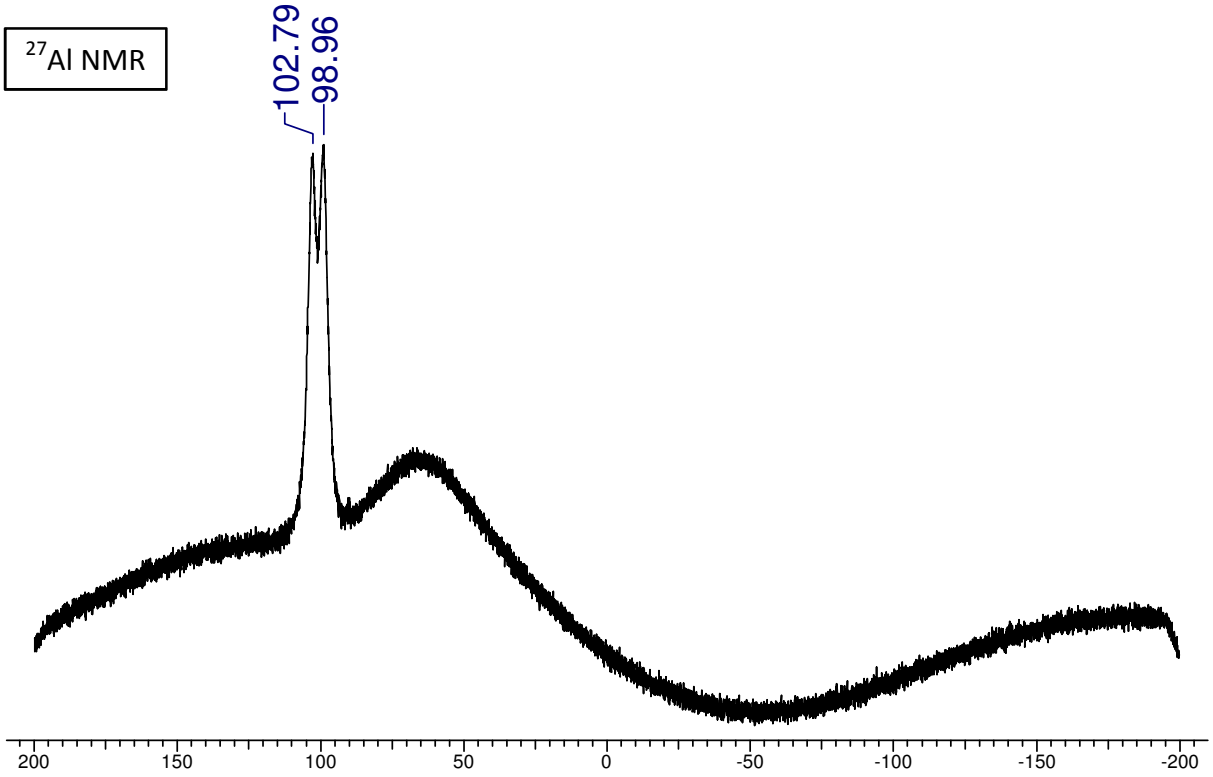
In the glove box, an oven dried Schlenk tube was charged with 2,6-dichloropyridine (1.480 g, 10.0 mmol) and $AlCl_3$ (1.333 g, 10.0 mmol). The Schlenk tube was removed from glovebox and BCl_3 (1.0 M in CH_2Cl_2, 11 ml , 11.0 mmol) was added, under inert atmosphere, to the solid mixture and stirred for 10 min. The precipitated product was decanted, washed with anhydrous CH_2Cl_2 (2 mL) and dried at 20 °C at $4x10^{-2}$ torr for 2 h to give $[Cl_2Py\text{-}BCl_2][AlCl_4]$ (2.3 g, 58 %) as colourless solid.

Elemental analysis Found: C, 15.14; H, 0.81; N, 3.66. Calc. for $C_5H_3AlBCl_8N$: C, 15.07; H, 0.76; N, 3.52.

Dissolution of 50 mg of solid in 0.8 ml of CH_2Cl_2 showed that $[Cl_2Py\text{-}BCl_2][AlCl_4]$ is in equilibrium with BCl_3 and $[(Cl_2Py)_2AlCl_2][AlCl_4]$. NMR spectra were recorded using a DMSO-d_6 capillary as lock solvent.

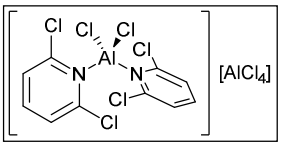



^{11}B NMR
45.95
BCl_3
43.20
$[Cl_2Py\text{-}BCl_2]^+$
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100


^{27}Al NMR
102.79
98.96
200 150 100 50 0 -50 -100 -150 -200

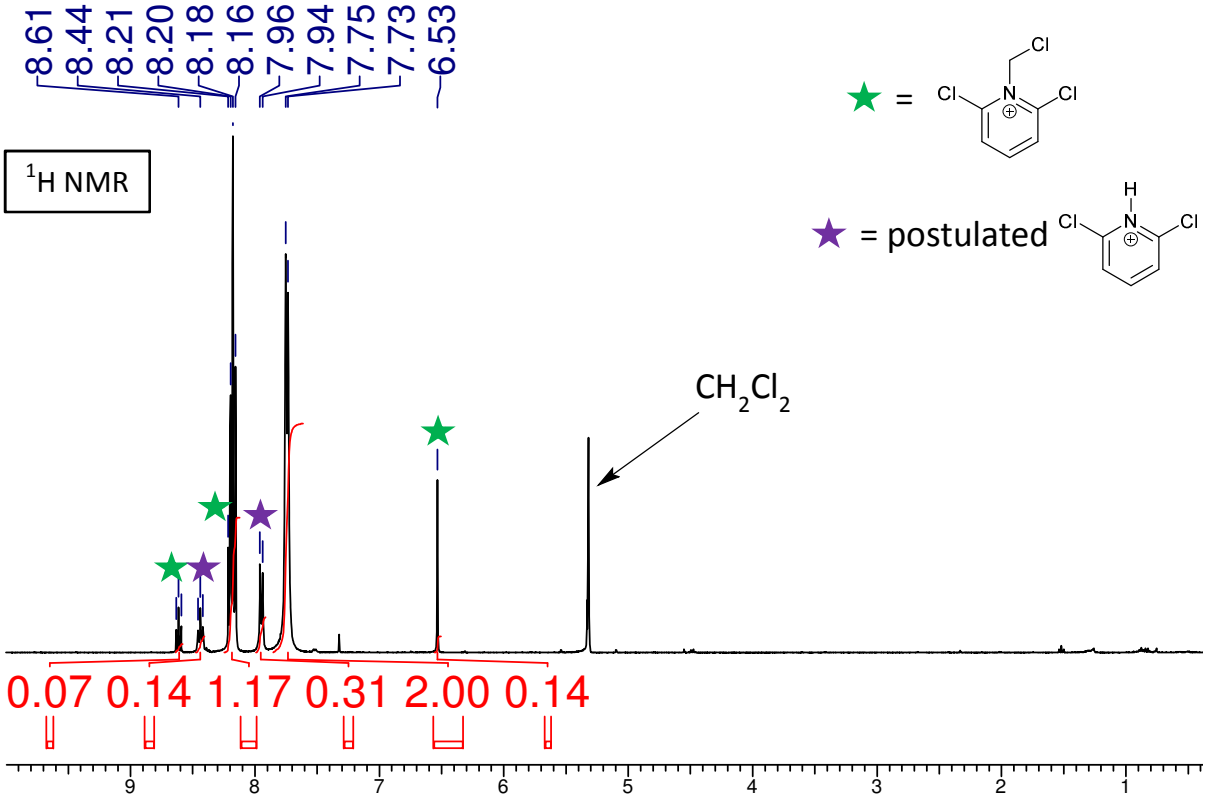
Synthesis of $[(Cl_2Py)_2AlCl_2][AlCl_4]$:

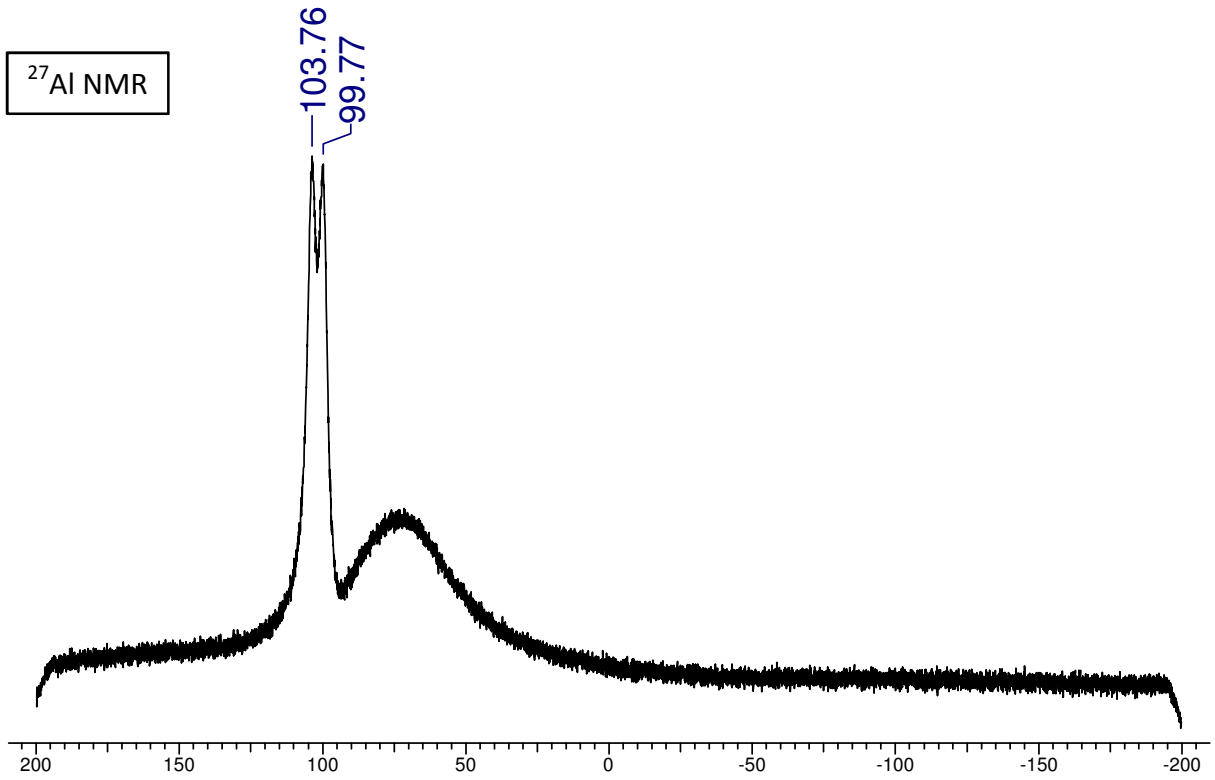
In the glove box, an oven dried Schlenk tube was charged with 2,6-dichloropyridine (148mg, 1.0mmol) and $AlCl_3$ (133 g, 1.0 mmol). The Schlenk tube was removed from glovebox and CH_2Cl_2 (5 ml) was added to the solid mixture and the reaction mixture stirred for 1 hour. Then the solution was filtered with a filter cannula and layered with pentane and stored at -20 °C. After the slow diffusion of pentane / CH_2Cl_2 finished colourless crystals suitable for X-ray analysis were obtained. The solution was removed and the crystals dried in vacuo yielding $[(Cl_2Py)_2AlCl_2][AlCl_4]$ as colourless solid (236 mg, 84 %). The product was contaminated with ~7 % of $[Cl_2Py\text{-}CH_2Cl][AlCl_4]$ (from solvent activation) and ~15 % of another species assigned as $[Cl_2Py\text{-}H][AlCl_4]$ frustrating attempts to obtain accurate elemental analysis.



^{1}H NMR (400 MHz ,CD_2Cl_2) δ = 8.18 (t, *J* = 8.1 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 2 H).

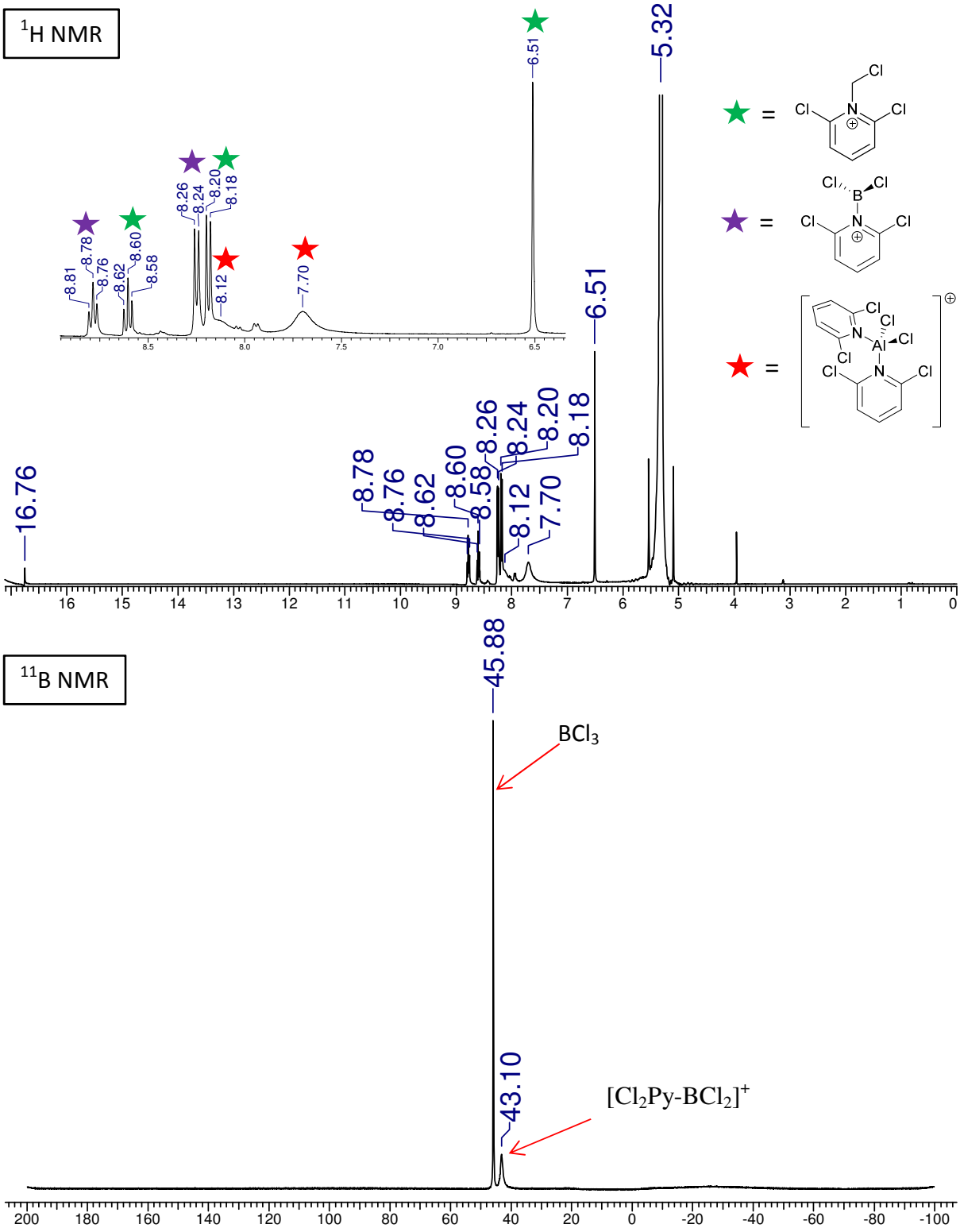
^{27}Al NMR (104 MHz, CD_2Cl_2) δ = 103.8, 99.8.

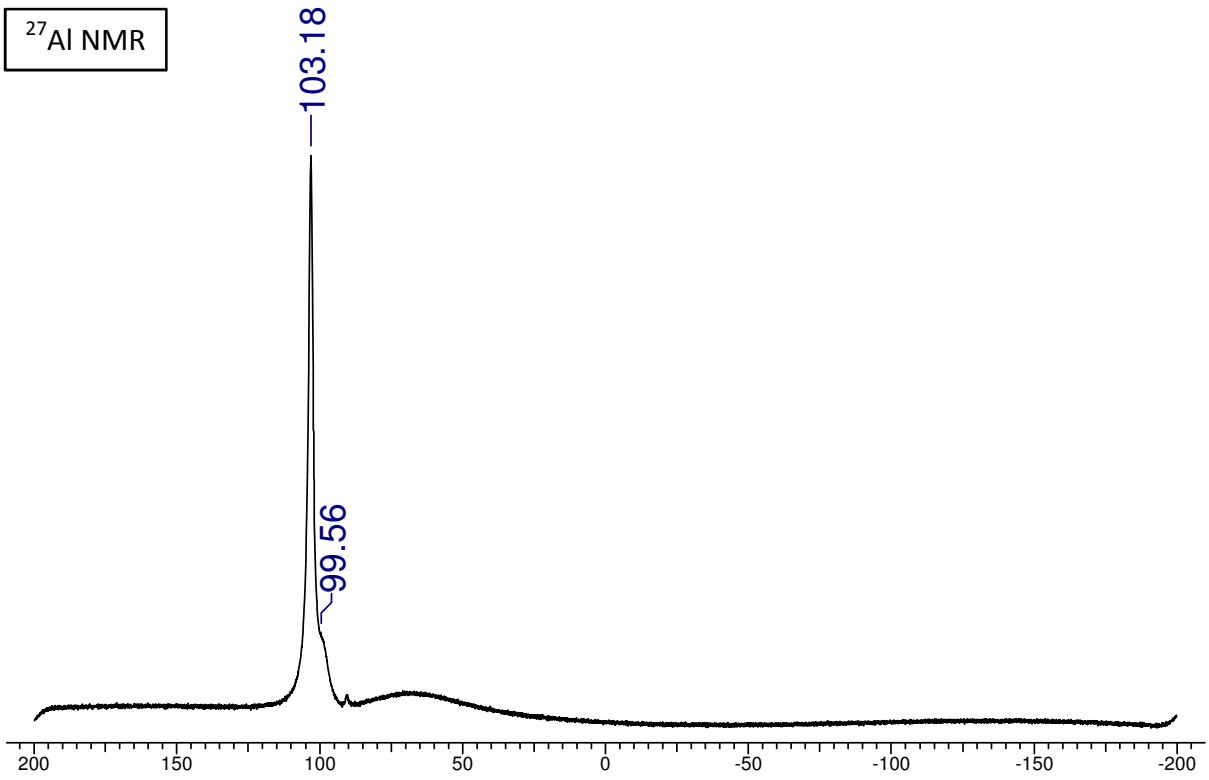



27Al NMR
103.76
99.77
200
150
100
50
0
-50
-100
-150
-200

Equimolar combination of Cl_2Py, BCl_3 and $AlCl_3$ in CH_2Cl_2:

In the glove box, an oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary was charged with $AlCl_3$ (67 mg, 0.50 mmol). The NMR tube was removed from the glovebox and under inert atmosphere anhydrous CH_2Cl_2 (0.5 ml), 2,6-dichloropyridine (74 mg, 0.50 mmol) and BCl_3 (1 M in CH_2Cl_2, 0.5 ml, 0.50 mmol) were added. The NMR tube was shaken until all $AlCl_3$ dissolved.

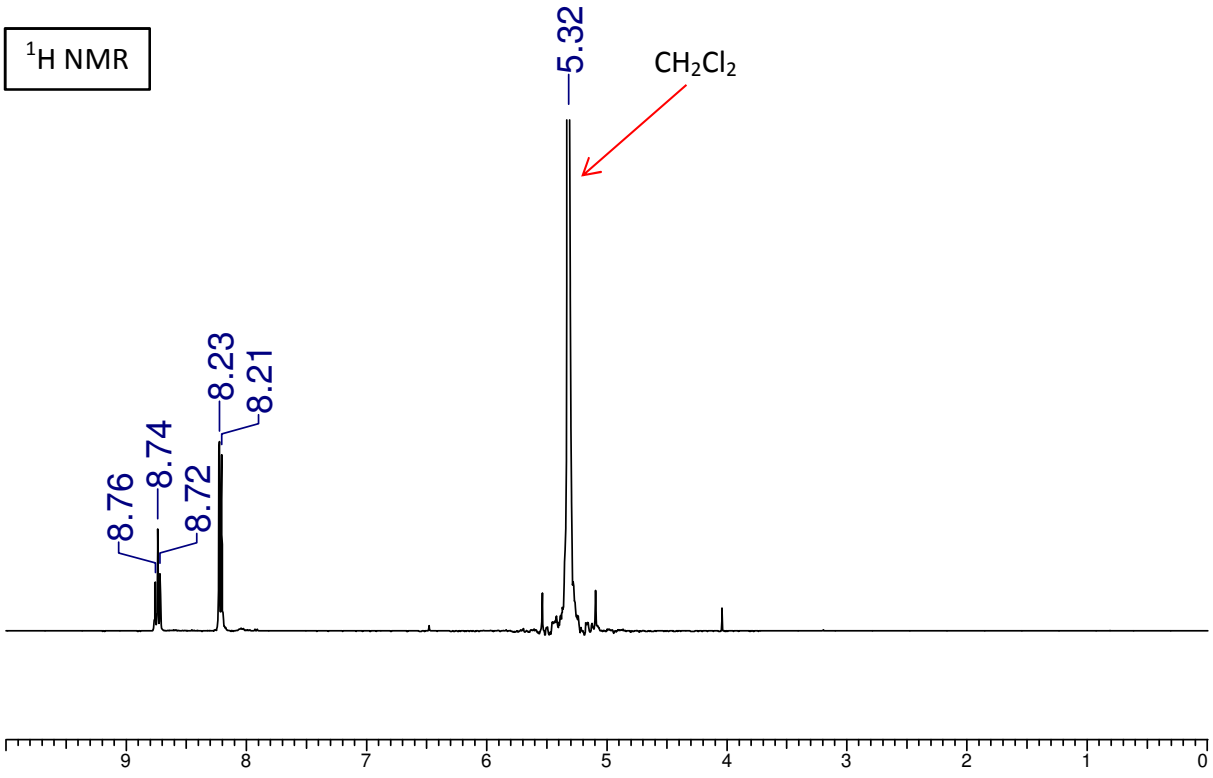


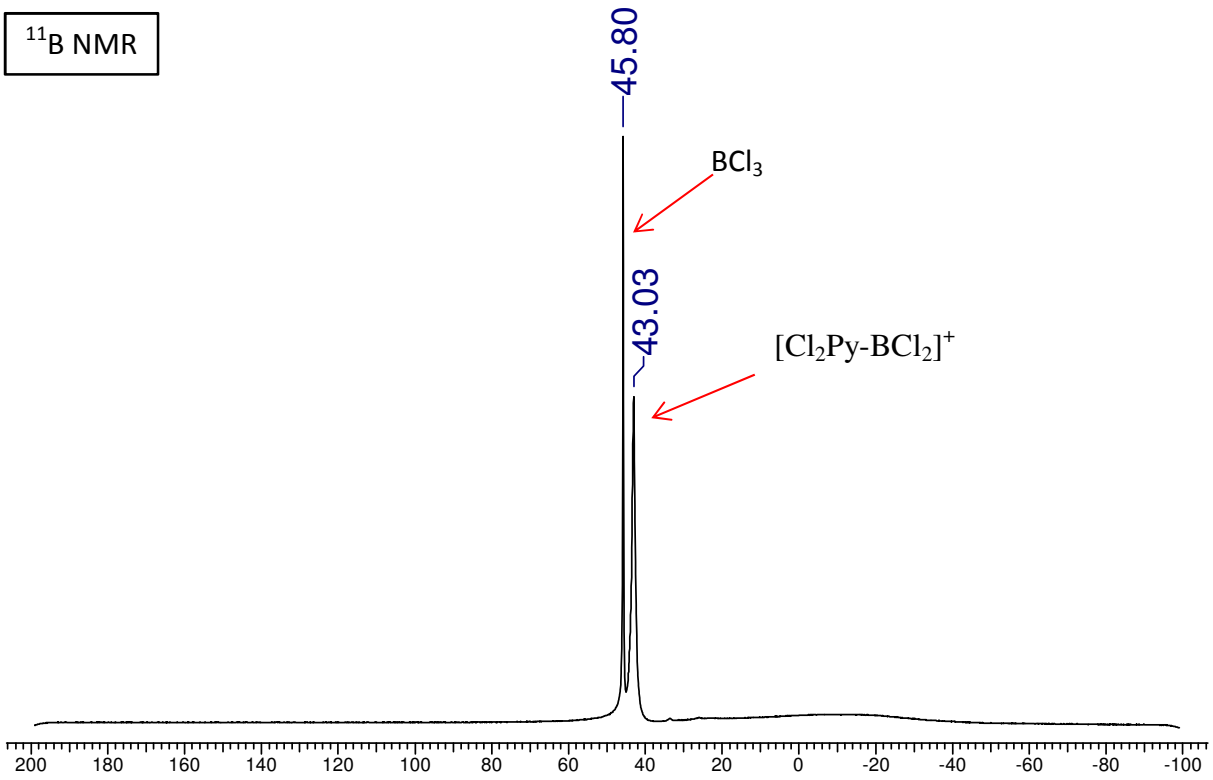

^{27}Al NMR
103.18
99.56
200
150
100
50
0
-50
-100
-150
-200

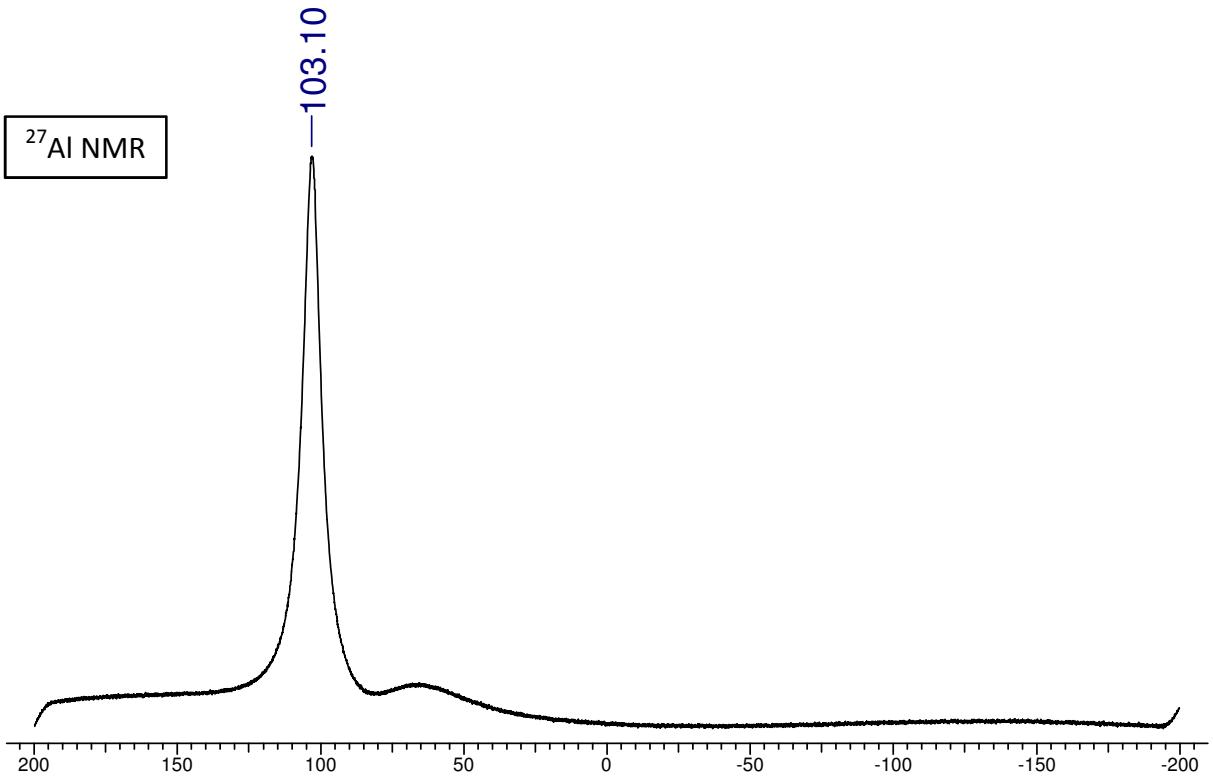
Synthesis of $[Cl_2Py\text{-}BCl_2][Al_2Cl_7]$

An oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary, under inert atmosphere, was charged with 2,6-dichloropyridine (111 mg, 0.75mmol) and BCl_3(1 M in CH_2Cl_2, 0.9 ml, 0.90 mmol). The NMR tube was sealed, transferred in the glovebox and powdered $AlCl_3$ (200 mg, 1.50mmol) was added to the mixture. The NMR tube was shaken until all $AlCl_3$ dissolved. Repeated attempts to generate crystalline material from this reaction mixture failed.

^{1}H NMR (400 MHz, CH_2Cl_2 with DMSO-d_6 capillary) δ = 8.74 (t, J = 8.3 Hz, 2 H), 8.22 (d, J = 8.3 Hz, 4 H).
^{11}B NMR (128 MHz, CH_2Cl_2 with DMSO-d_6 capillary) δ = 43.0, 45.8 (free BCl_3).
^{27}Al NMR (104 MHz, CH_2Cl_2 with DMSO-d_6 capillary) δ = 103.8, 99.8.




^{11}B NMR
45.80
BCl_3
43.03
$[Cl_2Py\text{-}BCl_2]^+$
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100


^{27}Al NMR
103.10
200 150 100 50 0 -50 -100 -150 -200

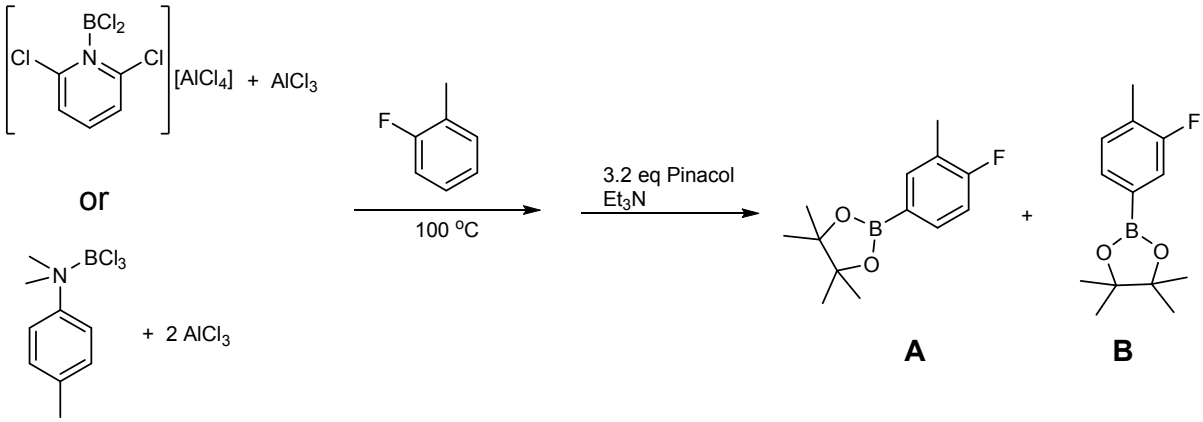
Borylation of 2-fluorotoluene with DMTol-BCl_3/$AlCl_3$ monitored at different times:

In the glovebox, an oven dried 5 ml Schlenk tube fitted with a J. Youngs valve was charged with DMTol-BCl_3 (505 mg, 2.0 mmol), $AlCl_3$ (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 Et_3N (1 ml) in CH_2Cl_2 (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 CH_2Cl_2 (5 ml), passed through a plug of silica gel and the plug washed with CH_2Cl_2. After removal of volatiles at 20 °C at $4x10^{-2}$ torr, a sample for GC was prepared.

Borylation of 2-fluorotoluene with [Cl_2Py-BCl_2][$AlCl_4$]/$AlCl_3$ at different times:

In the glove box, an oven dried 5 ml Schlenk tube fitted with a J. Youngs valve was charged with [Cl_2Py-BCl_2][$AlCl_4$] (797 mg, 2.0 mmol), $AlCl_3$ (267 mg, 2.0 mmol) and 4 ml of fluorotoluene. The ampule 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 Et_3N (1 ml) in CH_2Cl_2 (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 CH_2Cl_2(5 ml), passed through a plug of silica gel and the plug washed with CH_2Cl_2. 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.



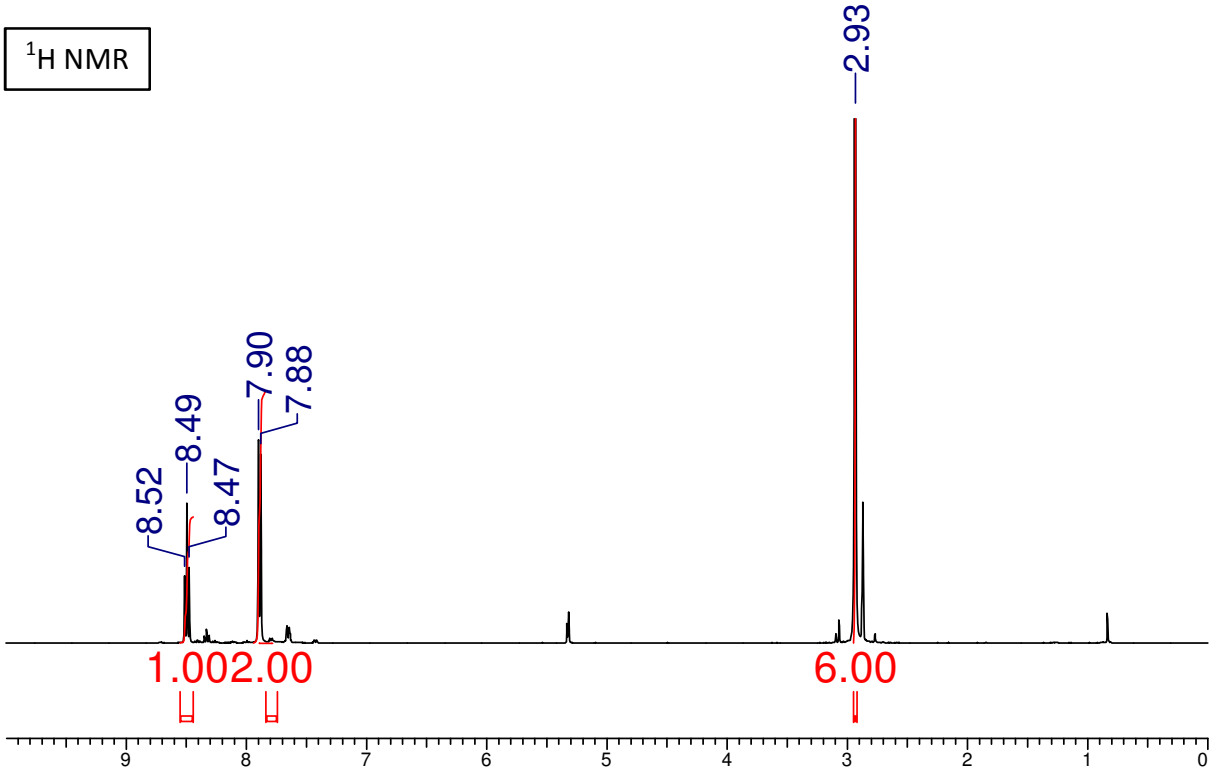
	$[Cl_2Py\text{-}BCl_2][AlCl_4]/AlCl_3$			$DMTol\text{-}BCl_3/AlCl_3$		
Time	**A**	**B**	**Ratio A/B**	**A**	**B**	**Ratio A/B**
10 min	92.74	7.26	12.77	85.95	14.05	6.12
30 min	92.39	7.61	12.14	84.93	15.07	5.64
1 h	91.03	8.97	10.15	83.86	16.04	5.23
5 h	87.02	12.98	6.70	77.64	22.36	3.47
25 h	76.96	23.04	3.34	68.84	31.16	2.21
3 d	68.77	31.23	2.20	64.47	35.48	1.82
7 d	63.6	36.4	1.74	63.08	36.87	1.71

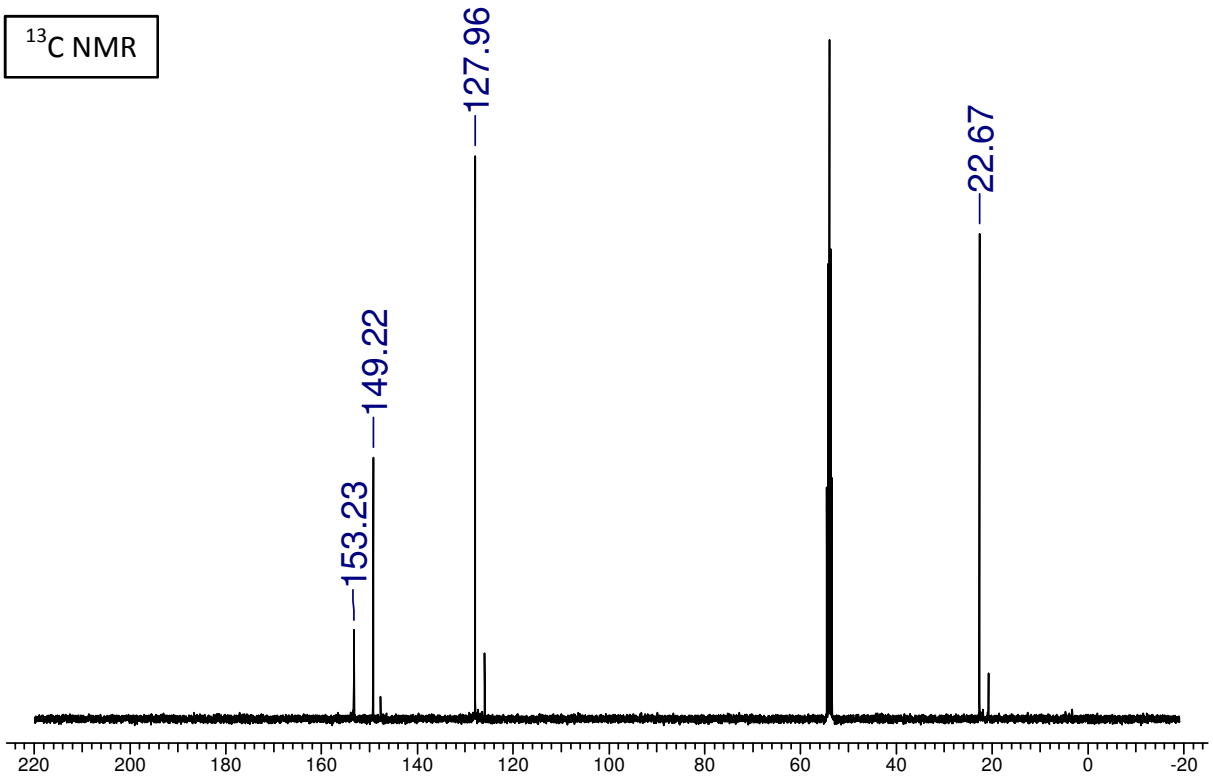
Synthesis [Cl_2B(2,6-lutidine)][$AlCl_4$]:

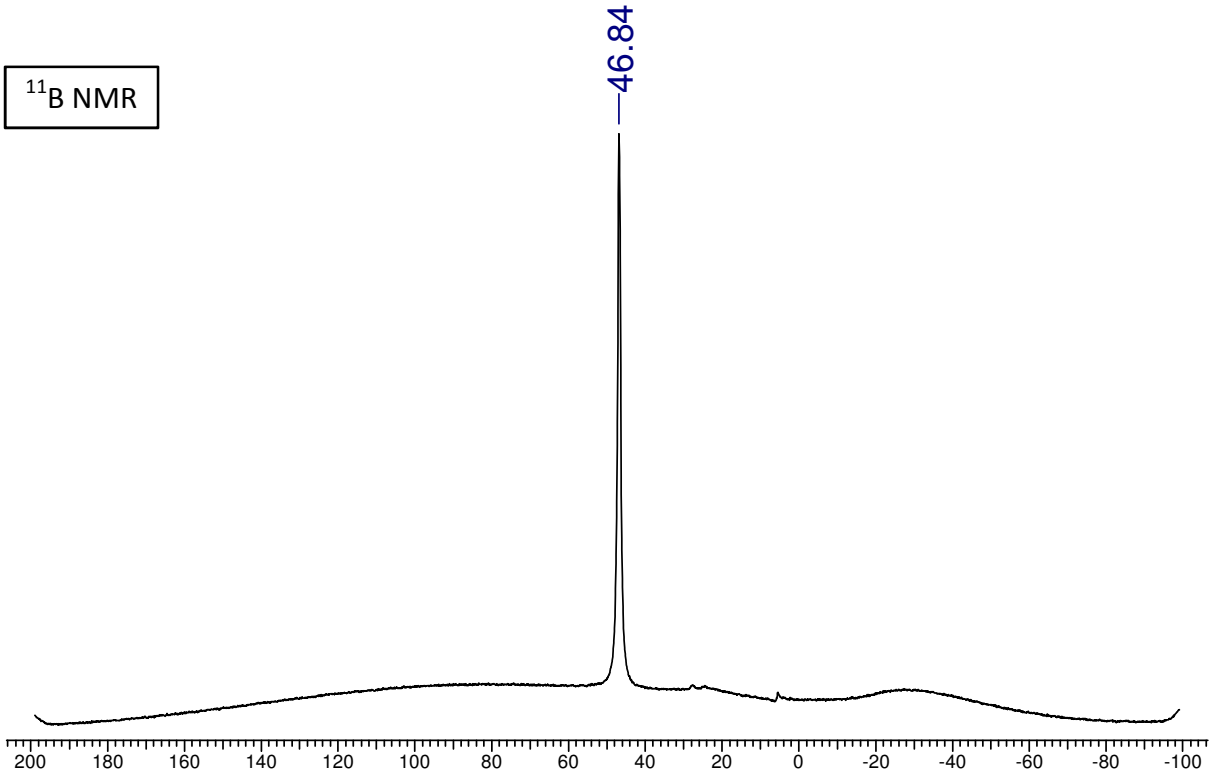
An oven dried Schlenk tube, under inert atmosphere, was charged with a solution of BCl_3 (1 M in CH_2Cl_2, 12 ml, 12.0 mmol) and the solution was cooled at 0 °C. 2,6-Lutidine (1 ml, 8.6 mmol) was added dropwise over 15 minutes. The reaction mixture was warmed to room temperature and stirred for 1 hour. 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 $AlCl_3$ (1.15 g, 8.6 mmol). The former Schlenk tube was washed with anhydrous CH_2Cl_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 CH_2Cl_2 finished the solution was removed and the solid dried *in vacuo* yielding [Cl_2B(2,6-lutidine)][$AlCl_4$] with ~ 5% of [2,6-lutidine-H][$AlCl_4$] as pale brown solid (2.94 g, 96 %).
Elemental analysis Found: C, 23.62; H, 2.50; N, 3.97. Calc. for $C_7H_9AlBCl_6N$: C, 15.07; H, 0.76; N, 3.52.

The NMR data are identical to that previously reported.[1]

^{1}H NMR (CD_2Cl_2) δ = 8.49 (t, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 2.93 (s, 6 H).
^{13}C{^{1}H} NMR (CD_2Cl_2) δ = 153.2, 149.2, 128.0, 22.7.
^{11}B NMR (CD_2Cl_2) δ = 46.8.

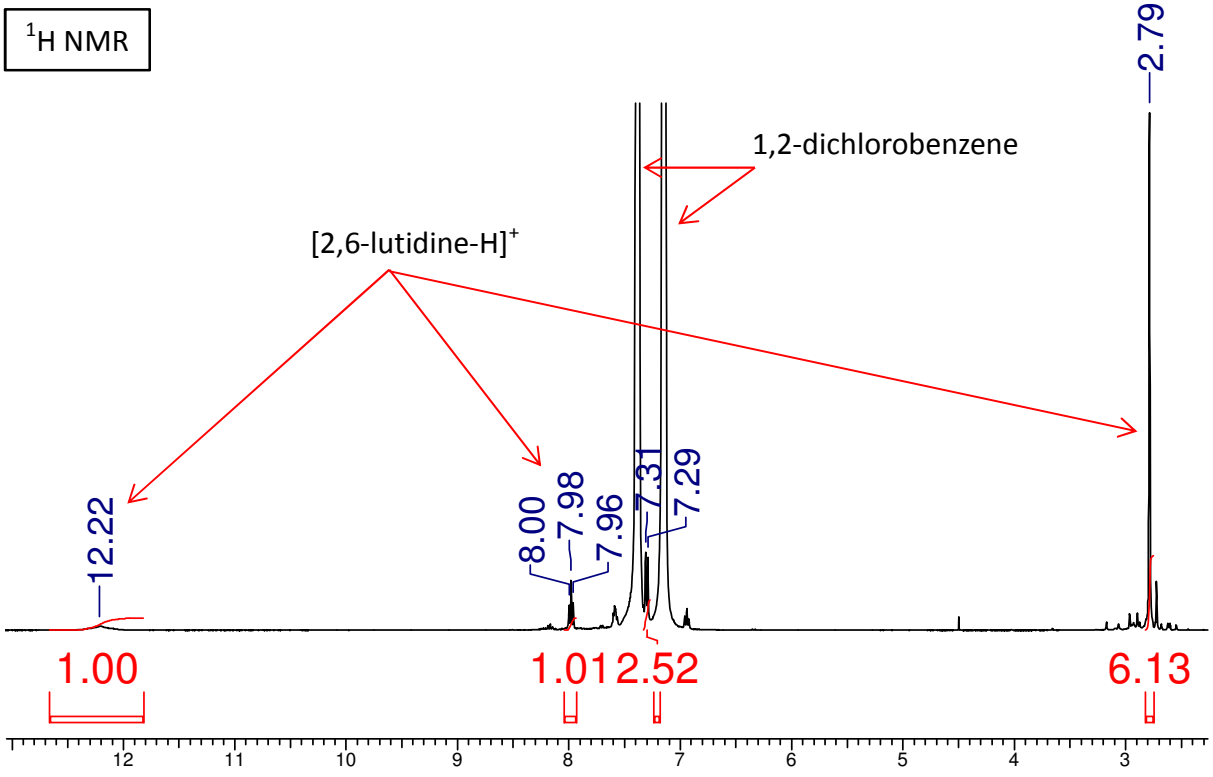


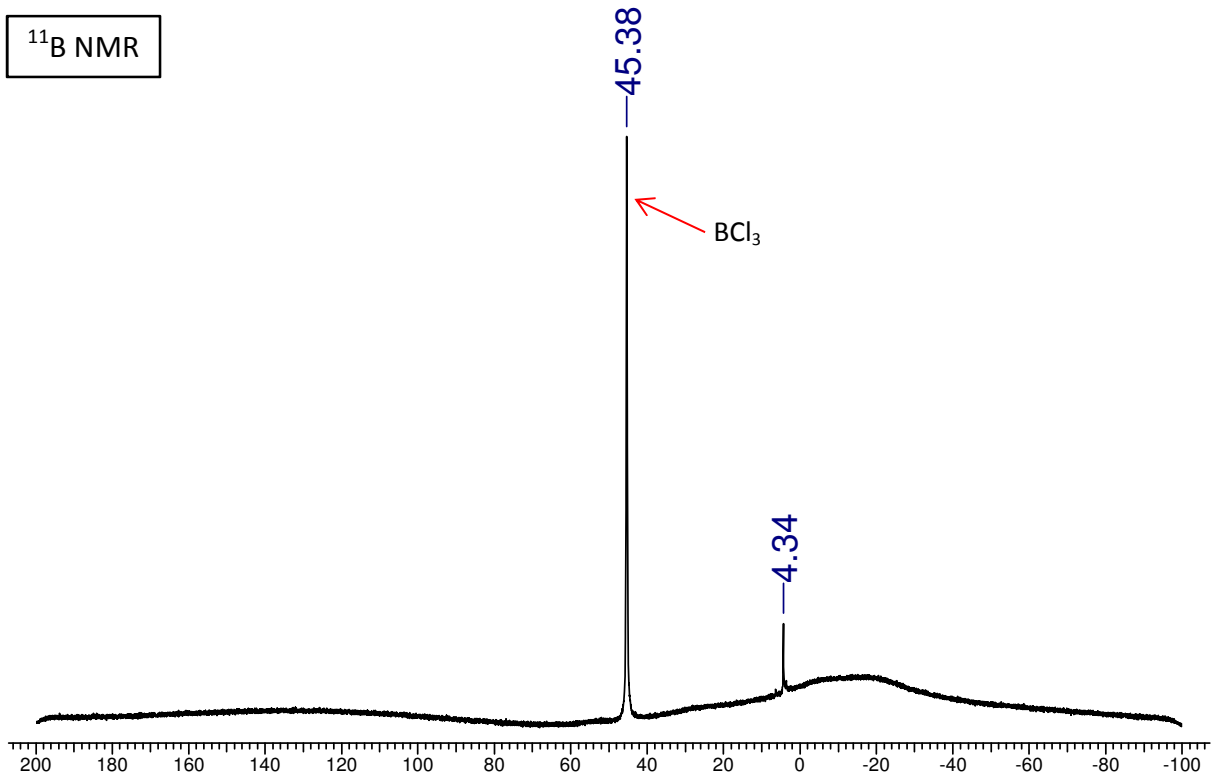

13C NMR
127.96
22.67
149.22
153.23
220
200
180
160
140
120
100
80
60
40
20
0
-20


11B NMR
46.84
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Attempt to borylate 1,2-dichlorobenzene with [2,6-lutidine-BCl_2][$AlCl_4$]:

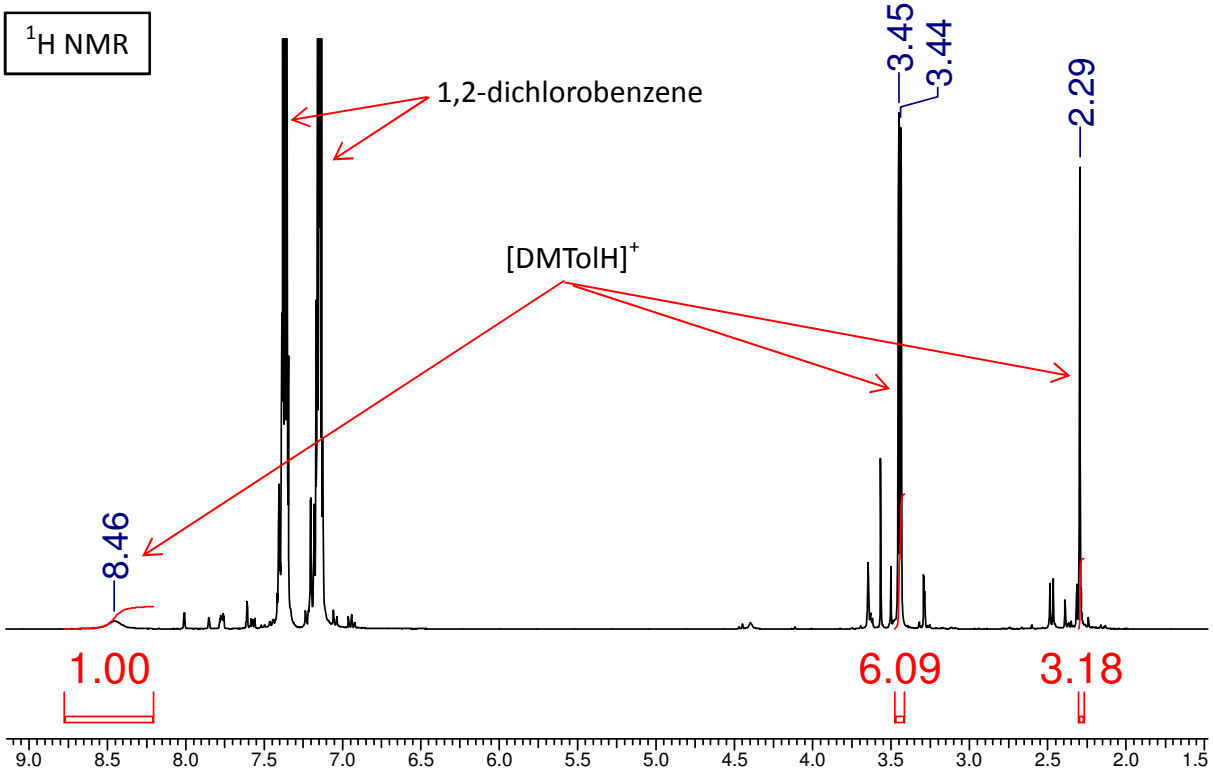
In the glove box, an oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary was charged with [2,6-lutidine-BCl_2][$AlCl_4$] (80 mg, 0.22 mmol) and anhydrous 1,2-dichlorobenzene (0.8 ml). The NMR tube was sealed, removed from the glovebox and heated at 140 °C. The NMR tube was occasionally shaken and the reaction was monitored by NMR spectroscopy. After 21 hours, the ^{11}B NMR spectrum showed no arene borylation although ^{1}H NMR spectrum showed that almost all 2,6-lutidine was protonated.



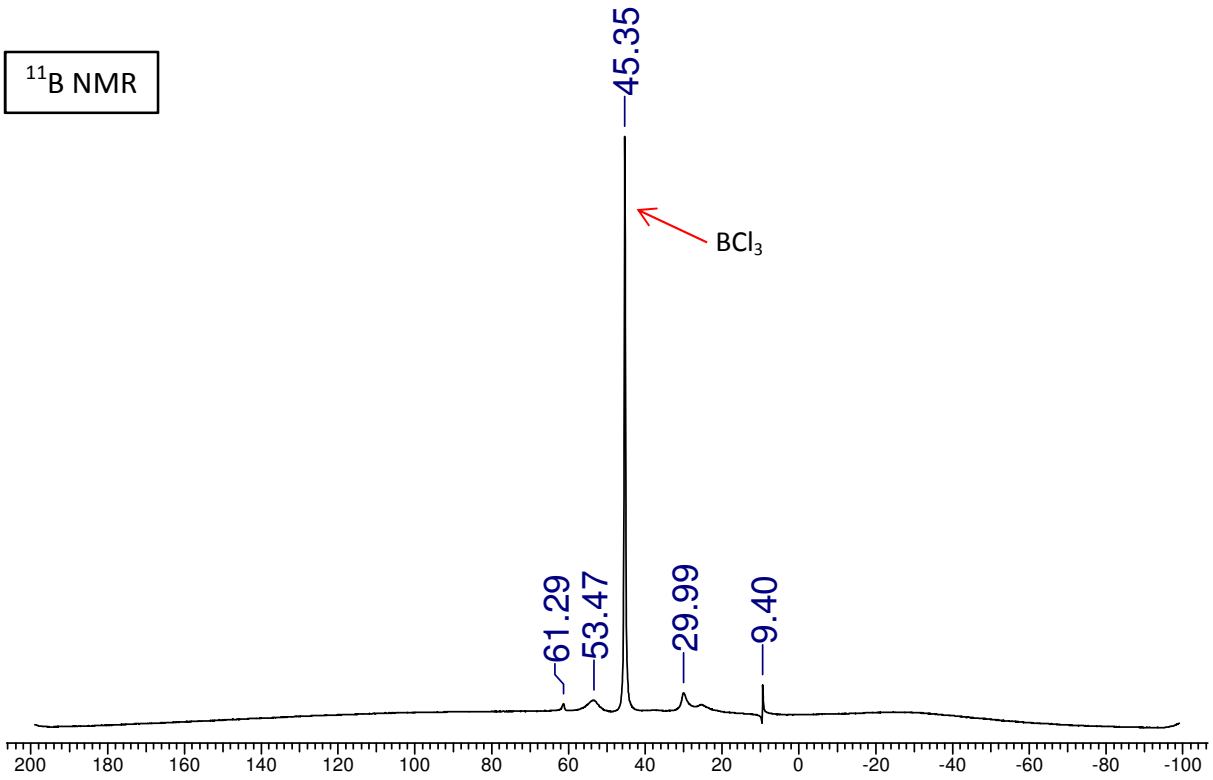

^{11}B NMR
45.38
BCl$_3$
4.34
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

Attempt to borylate1,2-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.

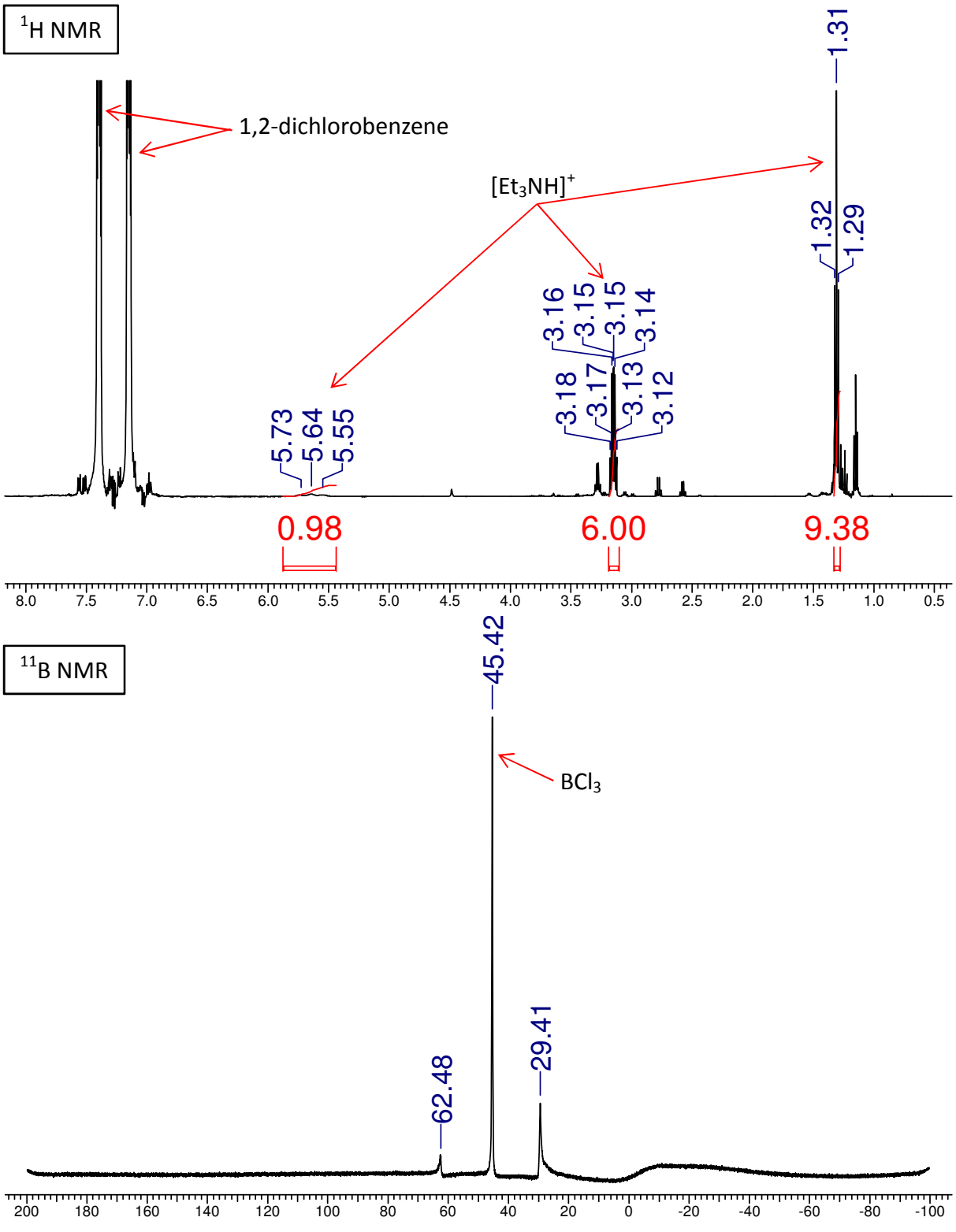


^{11}B NMR


45.35
BCl3
61.29
53.47
29.99
9.40
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

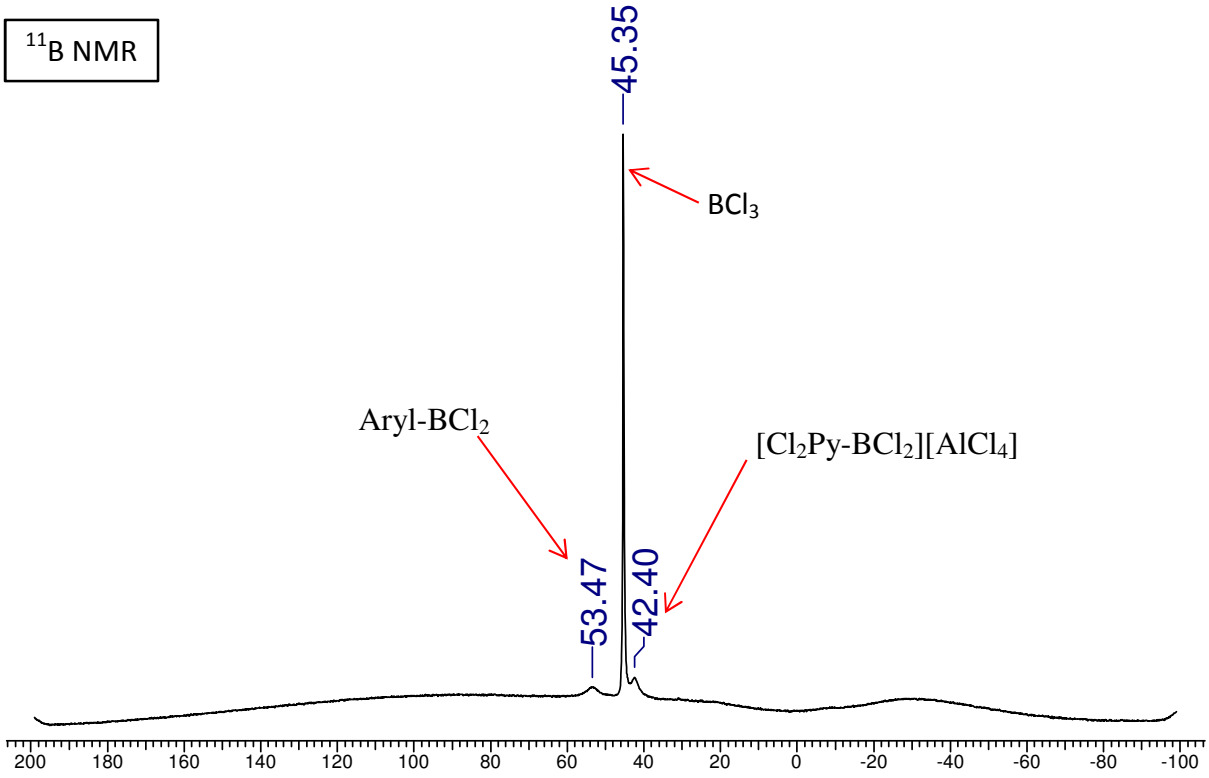
Attempt to borylate 1,2-dichlorobenzene with the mixture of Et_3N-BCl_3 and $AlCl_3$:

In the glove box, an oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary was charged with Et_3N-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_3N was protonated.



Attempt to borylate 1,2-dichlorobenzene with $[Cl_2Py\text{-}BCl_2][AlCl_4]$:

In the glove box, an oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary was charged with $[Cl_2Py\text{-}BCl_2][AlCl_4]$ (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.

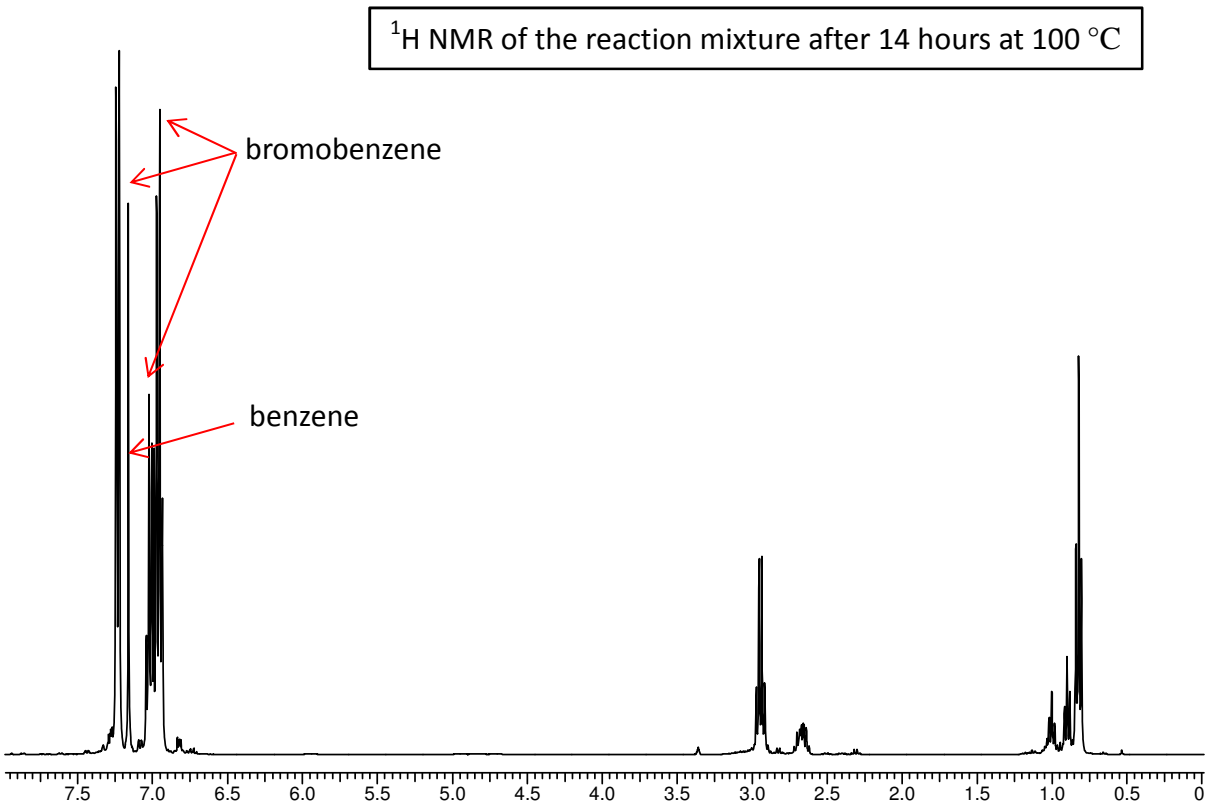


Borylation of 1,2-dichlorobenzene with 2,6-lutidine-BCl_3/$AlCl_3$ in a 1 : 2 ratio:

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_3N (2 ml) in CH_2Cl_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_2Cl_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 product was purified by chromatography on silica gel (eluent hexane:CH_2Cl_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%).

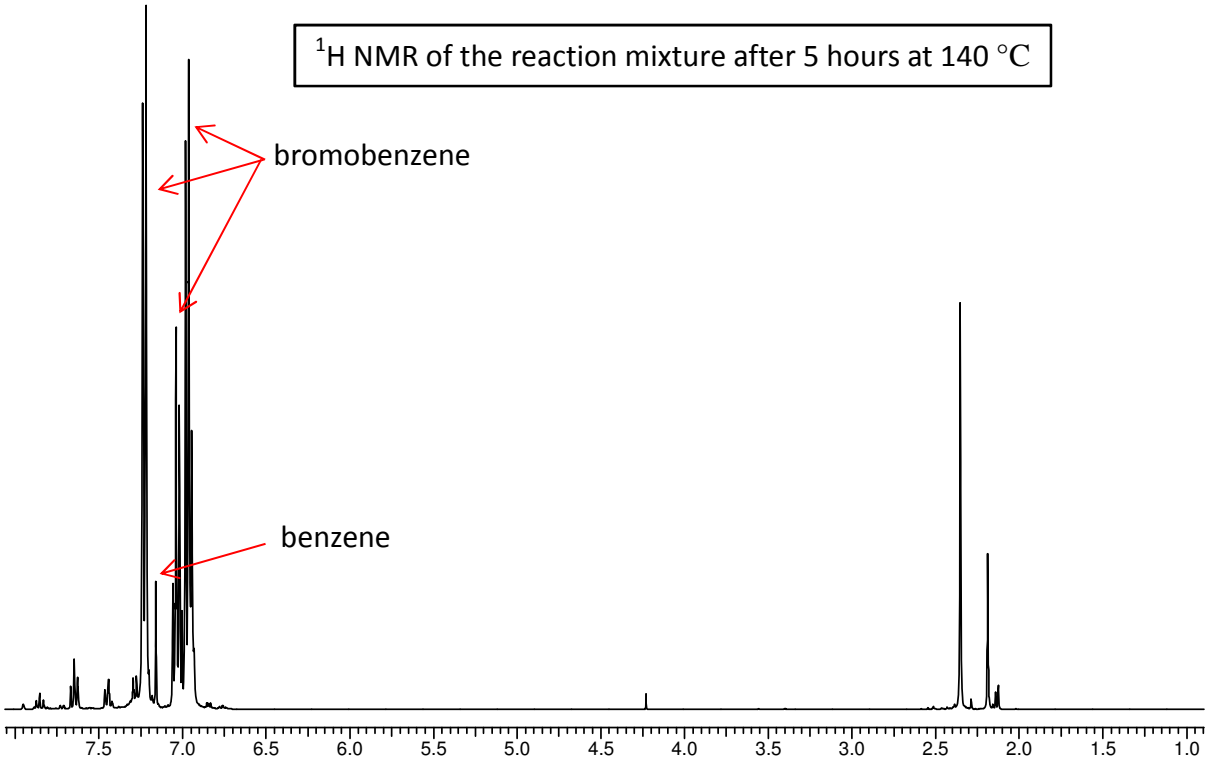
Borylation of bromobenzene with Et_3N-BCl_3 and $AlCl_3$ in a 1 : 2 ratio:

In the glove box, an oven dried J. Young's NMR tube fitted with a DMSO-d_6 capillary was charged with Et_3N-BCl_3 (200 mg, 0.91mmol), $AlCl_3$ (244 mg, 1.82mmol) 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 Et_3N (1.0 ml) in CH_2Cl_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_2Cl_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 crude mixture was absorbed on silica and purified by chromatography on silica gel (eluent hexane : CH_2Cl_2 1 : 9 to hexane : CH_2Cl_2 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.



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_3N (1.7 ml) in anhydrous CH_2Cl_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_2Cl_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_2Cl_2. The product was dried at 20 °Cat $4x10^{-2}$ 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.



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.[3]
^{1}H NMR (400MHz,$CDCl_3$) δ = 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,$CDCl_3$) δ = 136.3, 130.9, 126.2, 84.0, 24.8.
^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.8.

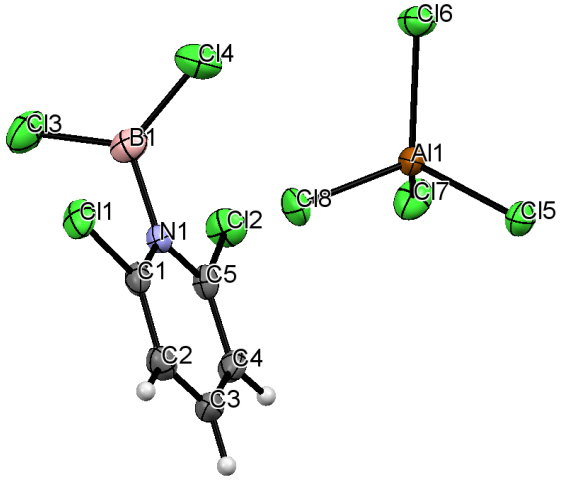
2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

Isolated as colourless solid (130 mg, 92 %).
The NMR data are identical to that previously reported.[11]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 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 (101MHz,$CDCl_3$) δ = 137.5, 134.2, 133.1, 129.5, 122.4, 84.1, 24.8.
^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.4.

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

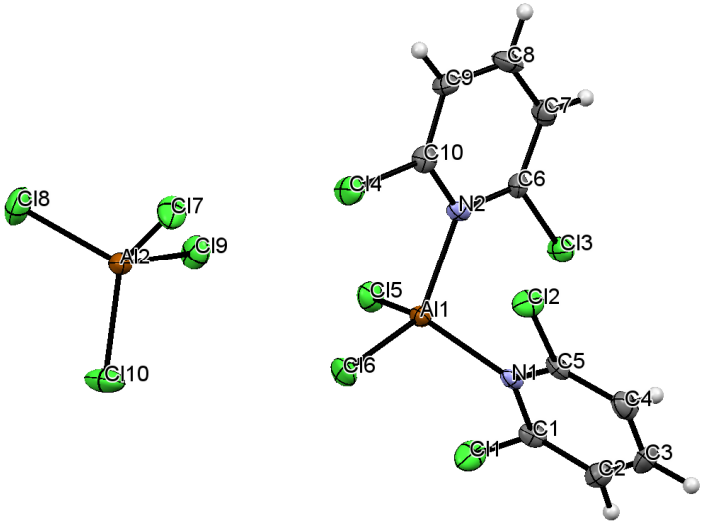
Isolated as colourless oil (128 mg, 91 %).
The NMR data are identical to that previously reported.[12]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 1.8, 7.3 Hz, 1 H), 7.54 (dd, *J* = 0.9, 7.7 Hz, 1 H), 7.34 - 7.21 (m, 1 H), 1.39 (s, 12 H).
$^{13}C\{^{1}H\}$ NMR (101MHz,$CDCl_3$) δ = 136.3, 132.6, 131.8, 128.0, 126.3, 84.3, 24.8.
^{11}B NMR (128 MHz,$CDCl_3$) δ = 30.8.

Crystallographic Details of $[Cl_2Py\text{-}BCl_2][AlCl_4]$



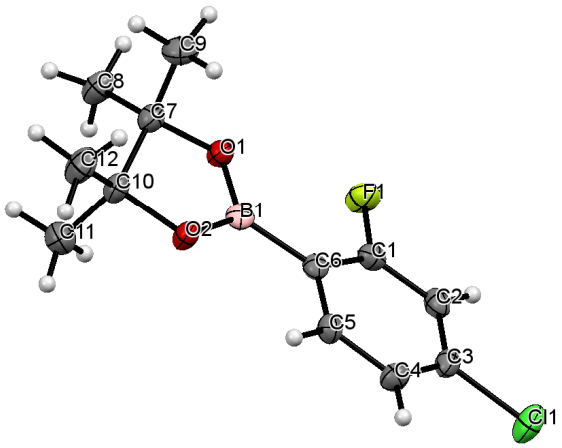
Empirical formula	$C_5H_3AlBCl_8N$
Formula weight	398.47
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.2646(4)
b/Å	13.5445(8)
c/Å	14.7907(7)
α/°	90
β/°	97.625(5)
γ/°	90
Volume/Å^3	1442.46(13)
Z	4
ρ_{calc}mg/mm^3	1.835
m/mm^{-1}	1.591
F(000)	776.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
2Θ range for data collection	5.964 to 50.686°
Index ranges	$-4 \leq h \leq 8$, $-16 \leq k \leq 8$, $-17 \leq l \leq 17$
Reflections collected	5221
Independent reflections	2607[R(int) = 0.0306]
Data/restraints/parameters	2607/0/145
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0883
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.0932
Largest diff. peak/hole / e Å^{-3}	0.50/-0.46

Crystallographic Details of $[(Cl_2Py)_2AlCl_2][AlCl_4]$



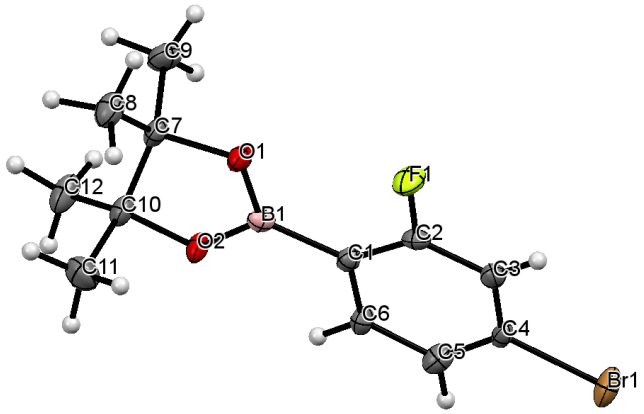
Empirical formula	$C_{10}H_6Al_2Cl_{10}N_2$
Formula weight	562.63
Temperature/K	150.03(12)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.1166(5)
b/Å	11.5660(8)
c/Å	25.5436(18)
α/°	90
β/°	91.390(5)
γ/°	90
Volume/Å^3	2101.9(2)
Z	4
ρ_{calc}mg/mm^3	1.778
m/mm^{-1}	1.407
F(000)	1104.0
Crystal size/mm^3	0.5 × 0.2 × 0.05
2Θ range for data collection	6.382 to 51.98°
Index ranges	$-8 \leq h \leq 6$, $-12 \leq k \leq 14$, $-31 \leq l \leq 18$
Reflections collected	6536
Independent reflections	4115[R(int) = 0.0456]
Data/restraints/parameters	4115/0/217
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0637, wR_2 = 0.0960
Final R indexes [all data]	R_1 = 0.1039, wR_2 = 0.1118
Largest diff. peak/hole / e Å^{-3}	0.57/-0.53

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



Empirical formula	$C_{12}H_{15}BClFO_2$
Formula weight	256.50
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.8661(7)
b/Å	7.5020(4)
c/Å	12.4291(8)
α/°	90
β/°	92.422(5)
γ/°	90
Volume/Å^3	1291.77(12)
Z	4
ρ_{calc}mg/mm^3	1.319
m/mm^{-1}	0.294
F(000)	536.0
Crystal size/mm^3	0.6 × 0.2 × 0.05
2Θ range for data collection	6.562 to 57.722°
Index ranges	$-17 \leq h \leq 17$, $-5 \leq k \leq 10$, $-16 \leq l \leq 7$
Reflections collected	5252
Independent reflections	2898[R(int) = 0.0343]
Data/restraints/parameters	2898/0/158
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1038
Final R indexes [all data]	R_1 = 0.0837, wR_2 = 0.1230
Largest diff. peak/hole / e Å^{-3}	0.30/-0.31

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



Empirical formula	$C_{12}H_{15}BBrFO_2$
Formula weight	300.96
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.8821(8)
b/Å	7.6711(4)
c/Å	12.4528(6)
α/°	90
β/°	92.002(5)
γ/°	90
Volume/Å^3	1325.30(12)
Z	4
ρ_{calc}mg/mm^3	1.508
m/mm^{-1}	3.100
F(000)	608.0
Crystal size/mm^3	0.6 × 0.4 × 0.2
2Θ range for data collection	6.848 to 57.73°
Index ranges	$-16 \leq h \leq 18$, $-10 \leq k \leq 10$, $-16 \leq l \leq 16$
Reflections collected	5945
Independent reflections	3024[R(int) = 0.0432]
Data/restraints/parameters	3024/0/158
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	$R_1 = 0.0523$, $wR_2 = 0.0995$
Final R indexes [all data]	$R_1 = 0.0747$, $wR_2 = 0.1105$
Largest diff. peak/hole / e Å^{-3}	0.77/-0.77

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