SUPPORTING INFORMATION:

Aminoboranes via tandem iodination/dehydroiodination for one-pot borylation

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Experimental Section

Reaction optimization

Procedure for halogen and solvent study

In a 25 mL, round bottom flask, containing a stir bar, dimethylamine-borane (DMAB (1c)) (2 mmol, 1 eq.) was weighed. This was followed by addition of solvents (4 mL) detailed in Table 1 in the main text. After dissolution of the amine-borane, bromine or iodine (1-2 mmol, 0.5-1 eq.) were added portionwise at rt. After stirring for 5 min. at rt the reaction mixture was analyzed using $^{11}$B NMR spectroscopy.

Iodoborane synthesis procedure

In a 25 mL, round bottom flask, containing a stir bar, the amine-borane (2 mmol, 1 eq.) is weighed. This was followed by addition of dichloromethane (4 mL). After dissolution of the amine-borane, iodine (1 mmol, 0.5 eq.) was added portionwise at rt. After stirring for 5 min. at rt the reaction mixture was analyzed using $^{11}$B NMR spectroscopy.

Procedure for dehydrohalogenation study

The desired iodoborane-amine was prepared as described in the above synthesis. After complete formation of the iodoborane-amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylethylamine (2 mmol, 1 eq.) was added dropwise to the stirred reaction mixture at rt. After stirring for 5 min. at rt the reaction mixture was analyzed using $^{11}$B NMR spectroscopy, the results are summarized in the manuscript.

Procedure for study of the amine base

The desired iodoborane-amine was prepared as described in the above synthesis. After complete formation of the iodoborane-amine complex, as evidenced by a return to colorlessness of the reaction mixture, the amine (2 mmol, 1 eq.) was added dropwise to the stirred reaction mixture at rt. After stirring for 5 min. at rt the reaction mixture was analyzed using $^{11}$B NMR spectroscopy, the results are summarized in the manuscript.

General synthesis of aminoboranes

In a 25 mL, round bottom flask, containing a stir bar, the amine-borane (2 mmol, 1 eq.) is weighed. This was followed by addition of dichloromethane (4 mL). After dissolution of the amine-borane, iodine (1 mmol, 0.5 eq.) was added portionwise at rt. After complete formation of the iodoborane-amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylethylamine (2 mmol, 1 eq.) was added dropwise to the stirred reaction mixture at rt. After stirring for 5 min. at rt the reactions were complete.
Procedure for two flask boronate ester synthesis

1. a) I₂ 0.5 eq., DCM, r.t., 5 min. \( \text{Flask A} \)
   b) (i-Pr)₂NH 2eq., r.t., 5 min.

2. PdCl₂(dpbb) 5%, (i-Pr)₂NH 3eq., 4-iodoanisole, toluene, reflux, 16 h. \( \text{Flask B} \)

3. Et₂O, pinacol, r.t. 4 h.

Scheme S1. Reaction conditions for the 2-flask boronate ester synthesis

In a 25 mL, round bottom flask (Flask A), containing a stir bar, the amine-borane (2 mmol, 2 eq.) is weighed. This was followed by addition of dichloromethane (5 mL). After dissolution of the amine-borane, iodine (1 mmol, 1 eq.) was added portionwise at rt. After complete formation of the iodoborane-amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylamine (2 mmol, 2 eq.) was added to the stirred reaction mixture at rt. After stirring for 5 min. at rt the reactions were complete. In a second 25 mL, round bottom flask (Flask B), containing a stir bar, was weighed the arene substrate (1 mmol, 1 eq.) and PdCl₂(dppp) (0.05 mmol, 0.05 eq.). This was followed by addition of toluene (5 mL) and diisopropylamine (3 mmol, 3 eq.). The contents of Flask A were then transferred to Flask B using a cotton plugged cannula. An additional portion of dichloromethane (3 mL) was added to Flask A, which was also subsequently transferred to Flask B using the cannula. A reflux condenser was affixed to the flask and the mix was brought to reflux. After completion (~16 h) the reaction mixture was cooled to rt, then brought to 0 °C using an ice water bath. At 0 °C diethyl ether (3 mL) was added and the mixture, followed by pinacol (1.1 mmol, 1.1 eq.). The mixture was stirred for 4 h while being allowed to warm to rt. After completion, the reaction mixture was diluted with diethyl ether (10 mL) and the crude mixture was passed through a pad of silica gel contained in a fritted glass Büchner funnel and eluted with diethyl ether as necessary. The resulting filtrate was condensed by rotary evaporation following by drying in vacuo for 12 h.

Procedure for one-pot boronate ester synthesis

1. a) I₂ 0.5 eq., Toluene, r.t., 5 min.
   b) (i-Pr)₂NH 5eq., r.t., 5 min.

2. PdCl₂(dpbb) 5%, 4-iodoanisole, reflux, 16 h.

3. Et₂O, pinacol, r.t. 4 h.

Scheme S2. Reaction conditions for the one-pot boronate ester synthesis

In a 25 mL, round bottom flask, containing a stir bar, the amine-borane (2 mmol, 2 eq.) is weighed. This was followed by addition of toluene (5 mL). After dissolution of the amine-borane, iodine (1 mmol, 1 eq.) was added portionwise at rt. After complete formation of the iodoborane-amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylamine (5 mmol, 5 eq.) was added to the stirred reaction mixture at rt. After stirring for 5 min. at rt the reactions were complete. Then with stirring, the aryl halide substrate (1 mmol, 1 eq.) and PdCl₂(dpbb) (0.05 mmol, 0.05 eq.) were added to the reaction mixture at rt. A reflux condenser was affixed to the flask and the mix was brought to reflux. After completion (~12-16 h) the reaction
mixture was cooled to rt, then brought to 0 °C using an ice water bath. At 0 °C diethyl ether (3 mL) was added and the mixture, followed by pinacol (1.1 mmol, 1.1 eq.). The mixture was stirred for 4 h while being allowed to warm to rt. After completion, the reaction mixture was diluted with diethyl ether (10 mL) and the crude mixture was passed through a pad of silica gel contained in a fritted glass Büchner funnel and eluted with diethyl ether as necessary. The resulting filtrate was condensed by rotary evaporation following by drying in vacuo for 12 h.

Procedure for reaction monitoring experiment

The above procedure for the single flask boronate ester synthesis was followed. Aliquots of the solution were analyzed by $^{11}$B NMR at several points. The reaction was analyzed prior to iodine addition, after iodine addition but before amine addition, after amine addition, after refluxing for 16 h, and 4 h after pinacol addition.

Procedure for amine-borane study

The above procedure for the single flask boronate ester synthesis was followed using 4-iodoanisole as a substrate. The amine-borane used for each reaction is described in Table 4 in the main text.

Procedure for leaving group study

The above procedure for the single flask boronate ester synthesis was followed using 4-iodoanisole as a substrate. The arene substrate used for each reaction is described in Table 5 in the main text.

References:

1) Guerrand, H. D. S.; Vaultier, M.; Pinet, S.; Pucheault, M. Amine-Borane Complexes: Air- and Moisture-Stable Partners for Palladium-Catalyzed Borylation of Aryl Bromides and Chlorides. *Adv. Synth. Catal.* **2015**, *357*, 1167-1174.
NMR spectra of amine-boranes, amine-iodoborane, aminoboranes, and borate esters

Amine-borane spectra

\[ \text{NMR spectra of amine-boranes, amine-iodoborane, aminoboranes, and borate esters} \]

\[ \text{Amine-borane spectra} \]

\[ \text{1H NMR (300 MHz, Chloroform-}d\text{) Ethylamine-borane (1a)} \]

\[ \text{13C NMR (75 MHz, Chloroform-}d\text{) Ethylamine-borane (1a)} \]
$^{11}$B NMR (96 MHz, Chloroform-$d$) Ethylamine-borane (1a)

$^1$H NMR (300 MHz, Chloroform-$d$) Isopropylamine-borane (1b)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Isopropylamine-borane (1b)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Isopropylamine-borane (1b)
$^1$H NMR (300 MHz, Chloroform-$d$) dimethylamine-borane (Ic)

$^{13}$C NMR (75 MHz, Chloroform-$d$) dimethylamine-borane (Ic)
$^1$B NMR (96 MHz, Chloroform-d) dimethylamine-borane (1c)

$^1$H NMR (300 MHz, Chloroform-d) Diethylamine-borane (1d)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Diethylamine-borane (1d)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Diethylamine-borane (1d)
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$\text{BH}_3$

\[ \text{N} \]

\[ \text{H} \]

$\text{H NMR (300 MHz, Chloroform-}$d$)$ Dipropylamine-borane (1e)

$\text{BH}_3$

\[ \text{N} \]

\[ \text{H} \]

$\text{C NMR (75 MHz, Chloroform-}$d$)$ Dipropylamine-borane (1e)
$^{11}$B NMR (96 MHz, Chloroform-$d$) Dipropylamine-borane (1e)

$^1$H NMR (300 MHz, Chloroform-$d$) Diisopropylamine-borane (1f)
$^{13}\text{C NMR (75 MHz, Chloroform-}d\text{)}$ Diisopropylamine-borane (1f)

$^{11}\text{B NMR (96 MHz, Chloroform-}d\text{)}$ Diisopropylamine-borane (1f)
$^{1}H$ NMR (300 MHz, Chloroform-$d$) Dibutylamine-borane (1g)

$^{13}C$ NMR (75 MHz, Chloroform-$d$) Dibutylamine-borane (1g)
$^1$H NMR (300 MHz, Chloroform-$d$) Diisobutylamine-borane (1h)

$^1$H NMR (300 MHz, Chloroform-$d$) Diisobutylamine-borane (1h)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Diisobutylamine-borane (1h)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Diisobutylamine-borane (1h)
$^1$H NMR (300 MHz, Chloroform-$d$) Dipentylamine-borane (Ii)

$^{13}$C NMR (75 MHz, Chloroform-$d$) Dipentylamine-borane (Ii)
$^{11}$B NMR (96 MHz, Chloroform-$d$) Dipentylamine-borane (1i)

$^1$H NMR (300 MHz, Chloroform-$d$) Dicyclohexylamine-borane (1j)
$^{13}$C NMR (75 MHz, Chloroform-d) Dicyclohexylamine-borane (1j)

$^{11}$B NMR (96 MHz, Chloroform-d) Dicyclohexylamine-borane (1j)
$^{1}H$ NMR (300 MHz, Chloroform-$d$) Piperidine-borane (1k)

$^{13}C$ NMR (75 MHz, Chloroform-$d$) Piperidine-borane (1k)
$^8$^1^B$ NMR (96 MHz, Chloroform-$d$) Piperidine-borane (I$^k$)

$^1^H$ NMR (300 MHz, Chloroform-$d$) 2,6-Dimethylpiperidine-borane (II)
$^{13}$C NMR (75 MHz, Chloroform-$d$) 2,6-Dimethylpiperidine-borane (I)

$^{11}$B NMR (96 MHz, Chloroform-$d$) 2,6-Dimethylpiperidine-borane (II)
$^{1}$H NMR (300 MHz, Chloroform-$d$) 2,2,6,6-Tetramethylpiperidine-borane (1m)

$^{13}$C NMR (75 MHz, Chloroform-$d$) 2,2,6,6-Tetramethylpiperidine-borane (1m)
$^{11}$B NMR (96 MHz, Chloroform-$d$) 2,2,6,6-Tetramethylpiperidine-borane (1m)

$^1$H NMR (300 MHz, Chloroform-$d$) Morpholine-borane (1n)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Morpholine-borane (In)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Morpholine-borane (In)
\( ^1H \text{NMR (300 MHz, Chloroform-}d) \text{ Azepane-borane (1o)} \)

\( ^{13}C \text{NMR (75 MHz, Chloroform-}d) \text{ Azepane-borane (1o)} \)
$^{11}$B NMR (96 MHz, Chloroform-$d$) Azepane-borane (1o)

$^1$H NMR (300 MHz, Chloroform-$d$) Pyrrolidine-borane (1p)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Pyrrolidine-borane (1p)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Pyrrolidine-borane (1p)
$^{1}$H NMR (300 MHz, Chloroform-$d$) Dibenzylamine-borane (1q)

$^{13}$C NMR (75 MHz, Chloroform-$d$) Dibenzylamine-borane (1q)
$^11$B NMR (96 MHz, Chloroform-$d$) Dibenzylamine-borane (1q)

$^1$H NMR (300 MHz, Chloroform-$d$) Triethylamine-borane (1r)
$^{13}$C NMR (75 MHz, Chloroform-$d$) Triethylamine-borane ($1r$)

$^{11}$B NMR (96 MHz, Chloroform-$d$) Triethylamine-borane ($1r$)
Amine-iodoborane spectra

11B NMR (96 MHz, Dichloromethane) Ethylamine-iodoborane (2a)

11B NMR (96 MHz, Dichloromethane) Isopropylamine-iodoborane (2b)
$^{11}$B NMR (96 MHz, Dichloromethane) Dimethylamine-iodoborane (2c)

$^{11}$B NMR (96 MHz, Dichloromethane) Diethylamine-iodoborane (2d)
$^{11}$B NMR (96 MHz, Dichloromethane) Dipropylamine-iodoborane (2e)

$^{11}$B NMR (96 MHz, Dichloromethane) Diisopropylamine-iodoborane (2f)
$^{11}\text{B} \text{NMR (96 MHz, Dichloromethane) Diisopropylamine-chloroborane (2f-Cl)}$

$^{11}\text{B} \text{NMR (96 MHz, Dichloromethane) Dibutylamine-iodoborane (2g)}$
$^{11}\text{B NMR (96 MHz, Dichloromethane) Diisobutylamine-iodoborane (2h)}$ 

$^{11}\text{B NMR (96 MHz, Dichloromethane) Dipentylamine-iodoborane (2i)}$
$^{11}$B NMR (96 MHz, Dichloromethane) Dicyclohexylamine-iodoborane (2j)

$^{11}$B NMR (96 MHz, Dichloromethane) Piperidine-iodoborane (2k)
$^{11}\text{B NMR (96 MHz, Dichloromethane) 2,6-Dimethylpiperidine-iodoborane (2l)}$

$^{11}\text{B NMR (96 MHz, Dichloromethane) 2,2,6,6-Tetramethylpiperidine-iodoborane (2m)}$
$^{11}$B NMR (96 MHz, Dichloromethane) Morpholine-iodoborane (2n)

$^{11}$B NMR (96 MHz, Dichloromethane) Azepane-iodoborane (2o)
$^{11}$B NMR (96 MHz, Dichloromethane) Pyrrolidine-iodoborane (2p)

$^{11}$B NMR (96 MHz, Dichloromethane) Dibenzyamine-iodoborane (2q)
$^{11}$B NMR (96 MHz, Dichloromethane) Triethylamine-iodoborane (2r)

Aminoborane spectra

$^{11}$B NMR (96 MHz, Dichloromethane) Ethylaminoborane (3a)
$^{11}$B NMR (96 MHz, Dichloromethane) Isopropylaminoborane (3b)

$^{11}$B NMR (96 MHz, Dichloromethane) Dimethylaminoborane (3c)
$^{11}\text{B} \text{ NMR (96 MHz, Dichloromethane) Diethylaminoborane (3d)}$

$^{11}\text{B} \text{ NMR (96 MHz, Dichloromethane) Dipropylaminoborane (3e)}$
$^\text{11}B$ NMR (96 MHz, Dichloromethane) Diisopropylaminoborane (3f)

$^\text{11}B$ NMR (96 MHz, Dichloromethane) Dibutylaminoborane (3g)
$^{11}$B NMR (96 MHz, Dichloromethane) Diisobutylaminoborane ($3h$)

$^{11}$B NMR (96 MHz, Dichloromethane) Dipentylaminoborane ($3i$)
$^{11}$B NMR (96 MHz, Dichloromethane) Dicyclohexylaminoborane (3j)

$^{11}$B NMR (96 MHz, Dichloromethane) Piperidinoborane (3k)
$^{11}$B NMR (96 MHz, Dichloromethane) 2,6-Dimethylpiperidinoborane (3l)

$^{11}$B NMR (96 MHz, Dichloromethane) 2,2,6,6-Tetramethylpiperidinoborane (3m)
$^{11}$B NMR (96 MHz, Dichloromethane) Morpholinoborane (3n)

$^{11}$B NMR (96 MHz, Dichloromethane) Azepanoborane (3o)
$^{11}$B NMR (96 MHz, Dichloromethane) Pyrrolidinoborane (3p)

$^{11}$B NMR (96 MHz, Dichloromethane) Dibenzylaminoborane (3q)
\[^{11}\text{B NMR (96 MHz, Dichloromethane) Triethylamine-iodoborane (2r) + } N,N-\text{diisopropylethylamine}\]

\[\text{Borate ester spectra}\]

\[^{1}\text{H NMR (300 MHz, CDCl}_3-\text{d) 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)}\]
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)
$^{1}H$ NMR (300 MHz, CDCl$_3$-d)
2-(4-Ethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

$^{13}C$ NMR (75 MHz, CDCl$_3$-d)
2-(4-Ethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)
2-(4-Ethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

$^1$H NMR (300 MHz, CDCl$_3$-d)
2-(4-Methoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)

2-(4-Methoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)

2-(4-Methoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)
$^{1}H$ NMR (300 MHz, CDCl$_3$-d)
2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

$^{13}C$ NMR (75 MHz, CDCl$_3$-d)
2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)
2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

$^1$H NMR (300 MHz, CDCl$_3$-d)
2-(2,3-Dihydrobenzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
2-(2,3-Dihydrobenzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
2-(2,3-Dihydrobenzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)
$^1$H NMR (300 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (4f)

$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (4f)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (4f)

$^1$H NMR (300 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (4g)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane ($4g$)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane ($4g$)
\(\text{\(^1\)H NMR (300 MHz, CDCl}_3\text{-}d\)}

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (4h)

\(\text{\(^{13}\)C NMR (75 MHz, CDCl}_3\text{-}d\)}

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (4h)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (4h)

$^1$H NMR (300 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (4i)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (4i)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (4i)
$^1$H NMR (300 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (4j)

$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (4j)
$^{11}B$ NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (4j)

$^1$H NMR (300 MHz, CDCl$_3$-d)
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)
$^{1}$H NMR (300 MHz, CDCl$_3$-d)
2-(3,5-Di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)

$^{13}$C NMR (75 MHz, CDCl$_3$-d)
2-(3,5-Di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)

2-(3,5-Di-tert-butyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)

$^1$H NMR (300 MHz, CDCl$_3$-d)

4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4m)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4m)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4m)
$^1$H NMR (300 MHz, CDCl$_3$-d)
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (4n)

$^{13}$C NMR (75 MHz, CDCl$_3$-d)
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (4n)
$^{11}$B NMR (96 MHz, CDCl$_3$-$d$)
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (4n)

$^1$H NMR (300 MHz, CDCl$_3$-$d$)
$N,N$-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4o)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
$N,N$-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4o)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
$N,N$-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4o)
$^{1}H$ NMR (300 MHz, CDCl$_3$-d)
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4p)

$^{13}C$ NMR (75 MHz, CDCl$_3$-d)
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4p)
$^1$B NMR (96 MHz, CDCl$_3$-d)
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4p)

$^1$H NMR (300 MHz, CDCl$_3$-d)
2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4q)
$^{13}$C NMR (75 MHz, CDCl$_3$-d)
2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4q)

$^{11}$B NMR (96 MHz, CDCl$_3$-d)
2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4q)
$^1$H NMR (300 MHz, CDCl$_3$-d)
2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)

$^{13}$C NMR (75 MHz, CDCl$_3$-d)
2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)
$^{11}$B NMR (96 MHz, CDCl$_3$-$d$)

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)

$^{19}$F NMR (282 MHz, CDCl$_3$-$d$)

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4r)
\[ \text{H NMR (300 MHz, CDCl}_3\text{-d)} \]

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (4s)

\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl}_3\text{-d)} \]

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (4s)
$^{11}$B NMR (96 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (4s)

$^{19}$F NMR (282 MHz, CDCl$_3$-d)
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (4s)
Boronic acid and Ammonium salt spectra

$^1$H NMR (300 MHz, CDCl$_3$-d) (4-Methoxyphenyl)boronic acid

$^{13}$C NMR (75 MHz, CDCl$_3$-d) (4-Methoxyphenyl)boronic acid
$^{11}$B NMR (96 MHz, CDCl$_3$-d) (4-Methoxyphenyl)boronic acid

$^1$H NMR (300 MHz, CDCl$_3$-d) Diisopropylammonium chloride
\(^{13}\text{C} \text{NMR} (75 \text{ MHz}, \text{CDCl}_3-d) \) Diisopropylammonium chloride