Supporting Information

Boric acid as a precatalyst for BH$_3$-catalyzed hydroboration

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General experimental

The synthesis of aminoboranes derivatives 1-NR$_2$-2-BH$_2$-C$_6$H$_4$ (NR$_2$ = NMe$_2$, NEt$_2$ or piperidine) were done according to reported procedures$^{1,2}$ using standard Schlenk techniques. NMR spectra were recorded on Agilent Technologies NMR spectrometer at 500.00 MHz ($^1$H), 125.757 MHz
(13C), 160.46 MHz (11B) and 470.385 MHz (19F) or on Varian Inova NMR AS400 spectrometer, at 400.0 MHz (1H), 100.580 MHz (13C) and 376.29 (19F). 1H NMR and 13C{1H} NMR chemical shifts are referenced respectively to the residual hydrogen and carbon atoms in the deuterated solvents. 11B{1H} NMR calibration was performed using F3B•OEt2 as an external reference. 19F NMR was calibrated using CFCl3 as external standard. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. Deuterated-chloroform (CDCl3) was dried by distillation over P2O5. Mass spectrometry analyses were carried out on an Agilent 6210 LC Time of Flight Mass Spectrometer, using an electrospray ionization (ESI) method. Esters, carbonates, alkynes and all other chemicals bought from Sigma-Aldrich and were used without further purification. All solvents and boron reagents were used directly from the bottle, without additional purification steps. Microwave reactions were performed with a Monowave 400 from Anton Paar.

**Initial hydroboration tests with aminoboranes**

Reactions were performed in a J-Young NMR tube using 0.3 mmol of γ-caprolactone 1j and 0.6 mmol of HBpin under neat conditions at 80 °C for 16 h. To each of these reaction was added 10 mol % of either 1-piperidine-2-BH2-C6H4,1 1-NEt2-2-BH2-C6H4,1 1-NEt2-2-BH2-C6H4 or BH3•SMe2. The yield was determined by adding CDCl3 to the mixture and performing 1H NMR analysis using mesitylene as an internal standard.

**Procedure for the catalytic hydroboration of esters**

The ester (0.60 mmol, 1 equiv) and 435 µL (3.00 mmol, 5 equiv) of HBpin were dissolved in 2-methyltetrahydrofuran to give a total volume of 2.00 mL, then a catalytic amount of boric acid (3.71 mg, 0.06 mmol, 0.1 equiv) was introduced. All catalytic reactions were carried out using sealable microwave vials. The reaction mixture was subsequently heated at 200 °C for 1 h. Afterward, all volatiles were evaporated in a rotatory evaporator at 40 °C. The products and the internal standard were dissolved in CDCl3 and added to a cap-sealed NMR tube for characterization. To measure the NMR yield, 10 µl (0.072 mmol) of mesitylene was weighted and incorporated to the NMR solution.
NMR yield calculation

This is an example on the determination of the NMR yield from a $^1$H NMR (Figure S1) corresponding to entry 12 of Table 1. The hydroboration reaction was performed at 150 °C with 1a.

Inputted mesitylene: 8.9 mg (0.0724 mmol)
Inputted 1a: 132 mg (0.0627 mmol)
Maximum production of 2a: 0.125 mmol

2a CH$_2$ correction: 23.63/2 = 11.82
2a produced (vs STD): 11.82/9.00 x 0.0724 mmol = 0.095 mmol

2a NMR yield:

\[ \frac{0.095}{0.125} \times 100 \% = 76 \% \]

Figure S1 NMR analysis of entry 12 of Table 1 after the hydroboration catalysis at 150 °C.

Characterization of ester hydroboration products

Characterization data for the products of ester reduction are given below. Reported products were characterized by $^1$H, $^{11}$B{$^1$H}, and $^{13}$C{$^1$H} NMR and correspond to the values previously reported for these species.\(^3\,^4\)

1a Benzyl benzoate

\[
\begin{align*}
\text{Bpin} \\
\text{O} \\
\text{Ph}
\end{align*}
\]
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29-7.27 (m, 5H, PhCH$_2$OBpin), 4.88 (s, 2H, PhCH$_2$OBpin), 1.23 (s, 12H, PhCH$_2$OBpin).

$^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ 22.3 (PhCH$_2$OBpin).

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 139.2 (PhCH$_2$OBpin), 128.0 (PhCH$_2$OBpin), 126.7 (PhCH$_2$OBpin), 126.4 (PhCH$_2$OBpin), 82.7 (PhCH$_2$OBpin), 66.5 (PhCH$_2$OBpin), 24.7 (PhCH$_2$OBpin).

1b 4-Methyl phenyl benzoate

![4-Methyl phenyl benzoate structure]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29-7.27 (m, 5H, PhCH$_2$OBpin), 4.88 (s, 2H, PhCH$_2$OBpin), 1.21 (s, 12H, PhCH$_2$OBpin).

$^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ 21.1 (PhCH$_2$OBpin).

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 139.2 (PhCH$_2$OBpin), 128.2 (PhCH$_2$OBpin), 127.3 (PhCH$_2$OBpin), 126.6 (PhCH$_2$OBpin), 82.9 (PhCH$_2$OBpin), 66.5 (PhCH$_2$OBpin), 24.5 (PhCH$_2$OBpin).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.01 (d, $J = 7.9$ Hz, 2H, MePhOBpin), 6.93 (d, $J = 7.9$ Hz, 2H, MePhOBpin), 3.69 (s, 3H, MePhOBpin), 1.26 (s, 12H, MePhOBpin).

$^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ 21.1 (MePhOBpin).

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 151.2 (MePhOBpin), 132.1 (MePhOBpin), 129.6 (MePhOBpin), 119.1 (MePhOBpin), 83.2 (MePhOBpin), 55.0 (MePhOBpin), 24.5 (MePhOBpin).

1c Methyl benzoate
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29-7.28 (m, 5H, PhCH$_2$OBpin), 4.87 (s, 2H, PhCH$_2$OBpin), 3.55 (s, 3H, MeOBpin), 1.21 (s, 12H, PhCH$_2$OBpin), 1.20 (s, 12H, MeOBpin).

$^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.2 (PhCH$_2$OBpin/MeOBpin).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$): $\delta$ 128.1 (PhCH$_2$OBpin), 127.2 (PhCH$_2$OBpin), 126.8 (PhCH$_2$OBpin), 126.6 (PhCH$_2$OBpin), 82.9 (PhCH$_2$OBpin), 82.7 (MeOBpin), 66.5 (PhCH$_2$OBpin), 52.4 (MeOBpin), 24.5 (PhCH$_2$OBpin), 24.4 (MeOBpin).

1d Methyl 4-methyl benzoate

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20-7.18 (m, 2H, MePhCH$_2$OBpin), 7.10-7.08 (m, 2H, MePhCH$_2$OBpin), 4.84 (s, 2H, MePhCH$_2$OBpin), 3.56 (s, 3H, MeOBpin), 2.29 (s, 3H, MePhCH$_2$Bpin), 1.23 (s, 12H, MePhCH$_2$OBpin), 1.22 (s, 12H, MeOBpin).

$^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.2 (MePhCH$_2$OBpin/MeOBpin).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$): $\delta$ 136.7 (MePhCH$_2$OBpin), 136.2 (MePhCH$_2$OBpin), 128.8 (MePhCH$_2$OBpin), 126.7 (MePhCH$_2$OBpin), 82.8 (MePhCH$_2$OBpin), 82.6 (MeOBpin), 66.4 (MePhCH$_2$OBpin), 52.3 (MeOBpin), 24.4 (MePhCH$_2$OBpin), 24.4 (MeOBpin), 20.9 (MePhCH$_2$OBpin).

1e Methyl 4-fluoro benzoate
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.15-7.12 (m, 2H, FPhCH$_2$OBpin), 6.84-6.80 (m, 2H, FPhCH$_2$OBpin), 4.68 (s, 2H, FPhCH$_2$OBpin), 3.40 (s, 3H, MeOBpin), 1.07 (s, 12H, FPhCH$_2$OBpin), 1.06 (s, 12H, MeOBpin).

$^{11}$B$^{(1)}$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.1 (FPhCH$_2$OBpin/MeOBpin).

$^{13}$C$^{(1)}$H NMR (125 MHz, CDCl$_3$): $\delta$ 162.9 (FPhCH$_2$OBpin), 160.9 (FPhCH$_2$OBpin), 128.4 (FPhCH$_2$OBpin), 114.9 (d, FPhCH$_2$OBpin), 82.7 (FPhCH$_2$OBpin), 82.3 (MeOBpin), 65.7 (FPhCH$_2$OBpin), 52.1 (MeOBpin), 24.3 (MeOBpin), 24.2 (FPhCH$_2$OBpin).

If Methyl 4-(dimethylamino) benzoate

![If Methyl 4-(dimethylamino) benzoate](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.97-6.95 (m, 2H, Me$_2$NPhCH$_2$OBpin), 6.60-6.59 (m, 2H, Me$_2$NPhCH$_2$OBpin), 3.53 (s, 3H, MeOBpin), 2.82 (s, 6H, Me$_2$NPhCH$_2$Bpin), 1.19 (s, 12H, Me$_2$NPhCH$_2$OBpin), 1.18 (s, 12H, MeOBpin).

$^{11}$B$^{(1)}$H NMR (128 MHz, CDCl$_3$): $\delta$ 21.1 (Me$_2$NPhCH$_2$OBpin/MeOBpin).

$^{13}$C$^{(1)}$H NMR (125 MHz, CDCl$_3$): $\delta$ 148.7 (Me$_2$NPhCH$_2$OBpin), 129.4 (Me$_2$NPhCH$_2$OBpin), 126.8 (Me$_2$NPhCH$_2$OBpin), 113.1 (Me$_2$NPhCH$_2$OBpin), 82.9 (Me$_2$NPhCH$_2$OBpin/MeOBpin), 67.2 (Me$_2$NPhCH$_2$OBpin), 52.3 (MeOBpin), 40.8 (Me$_2$NPhCH$_2$OBpin), 24.5 (Me$_2$NPhCH$_2$OBpin), 24.4 (MeOBpin).

Ig Methyl 4-nitro benzoate

![Ig Methyl 4-nitro benzoate](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.17-8.05 (m, 2H, NO$_2$PhCH$_2$OBpin), 7.40-7.39 (m, 2H, NO$_2$PhCH$_2$OBpin), 4.90 (s, 2H, NO$_2$PhCH$_2$OBpin), 3.45 (s, 3H, MeOBpin), 1.13 (s, 12H, NO$_2$PhCH$_2$OBpin), 1.12 (s, 12H, MeOBpin).
$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 21.0 (NO$_2$PhCH$_2$OBpin/MeOBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 146.5 (NO$_2$PhCH$_2$OBpin), 130.5 (NO$_2$PhCH$_2$OBpin), 126.7 (NO$_2$PhCH$_2$OBpin), 123.3 (NO$_2$PhCH$_2$OBpin), 83.8 (NO$_2$PhCH$_2$OBpin), 82.5 (MeOBpin), 65.3 (NO$_2$PhCH$_2$OBpin), 52.5 (MeOBpin), 24.7 (MeOBpin), 24.3 (NO$_2$PhCH$_2$OBpin).

Ih Ethyl 2-phenylacetate

![Ethyl 2-phenylacetate](image)

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.14-7.02 (m, 5H, PhCH$_2$CH$_2$OBpin), 4.02 (t, $J = 6.9$ Hz, 2H, PhCH$_2$CH$_2$OBpin), 3.90-3.85 (m, 2H, PhCH$_2$CH$_2$OBpin), 1.11 (s, 12H, PhCH$_2$CH$_2$OBpin).

$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.0 (PhCH$_2$OBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 138.3 (PhCH$_2$CH$_2$OBpin), 128.9 (PhCH$_2$CH$_2$OBpin), 128.1 (PhCH$_2$CH$_2$OBpin), 126.0 (PhCH$_2$CH$_2$OBpin), 82.3 (PhCH$_2$CH$_2$OBpin), 65.4 (PhCH$_2$CH$_2$OBpin), 37.0 (PhCH$_2$CH$_2$OBpin) 24.3 (PhCH$_2$CH$_2$OBpin).

![EtOBpin](image)

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.91 (q, $J = 7.0$ Hz, 2H, CH$_3$CH$_2$OBpin), 1.12 (s, 12H, EtOBpin) 1.08 (t, $J = 7.0$ Hz, 3H, CH$_3$CH$_2$OBpin).

$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.0 (EtOBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 82.7 (EtOBpin), 60.3 (CH$_3$CH$_2$OBpin), 24.4 (EtOBpin), 17.0 (CH$_3$CH$_2$OBpin).

Ii Ethyl acetate

![EtOBpin](image)

$^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.90 (q, $J = 7.0$ Hz 2H, CH$_3$CH$_2$OBpin), 1.19 (s, 12H, CH$_3$CH$_2$OBpin), 1.12 (t, $J = 7.0$ Hz, 3H, CH$_3$CH$_2$OBpin).
$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.0 (CH$_3$CH$_2$OBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 82.4 (CH$_3$CH$_2$OBpin), 60.5 (CH$_3$CH$_2$OBpin), 24.5 (CH$_3$CH$_2$OBpin), 17.1 (CH$_3$CH$_2$OBpin).

1j γ-Caprolactone

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.92-3.84 (m, 1H), 3.79-3.74 (m, 2H), 1.60-1.29 (m, 6H), 1.19-1.17 (s, 24H), 0.83 (t, $J$ = 7.3 Hz, 3H).

$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 21.1 (CH$_3$CH$_2$CH(OBpin)(CH$_2$)$_3$OBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 82.5, 82.3, 75, 64.8, 31.8, 29.2, 27.4, 24.4, 9.6.

1k γ-Valerolactone

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.12-4.07 (m, 1H), 3.77-3.73 (m, 2H), 1.46-1.43 (m, 2H), 1.18-1.16 (s, 24H), 1.10 (d, $J$ = 6.1 Hz, 2H), 0.83-0.79 (m, 3H).

$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 21.0 (CH$_3$CH(OBpin)(CH$_2$)$_3$OBpin).

$^{13}$C$^{1}$H NMR (125 MHz, CDCl$_3$): $\delta$ 82.5, 82.3, 70.4, 64.6, 34.0, 27.4, 24.5, 24.4, 22.4.

1l δ-Valerolactone

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.88-3.59 (m, 6H, BpinO(CH$_2$)$_3$OBpin), 1.54-1.46 (m, 4H, BpinO(CH$_2$)$_3$OBpin), 1.18-1.16 (s, 24H, BpinO(CH$_2$)$_3$OBpin).

$^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.0 (BpinO(CH$_2$)$_3$OBpin).
Procedure for the catalytic hydroboration of carbonates

Carbonate substrates (0.60 mmol, 1 equiv) and 609 µL (4.2 mmol, 7 equiv) of HBpin were dissolved in 2-methyltetrahydrofuran to give a total volume of 2.00 mL, then a catalytic amount of boric acid (3.71 mg, 0.06 mmol, 0.1 equiv) was introduced. All catalytic reactions were carried out using sealable microwave vials. The reaction mixture was subsequently heated at 200 °C for 4 h. Afterward, all volatiles were evaporated in a rotatory evaporator at 40 °C. The products and the internal standard (mesitylene) were dissolved in CDCl₃ and added to a cap-sealed NMR tube, wrapped with parafilm for NMR characterization.

Characterization of carbonates hydroboration products

Characterization data for the products of carbonates reduction are given below. Reported products were characterized by ¹H, ¹¹B{¹H}, and ¹³C{¹H} NMR.

3a Ethylene carbonate

\[
\text{Bpin-CH}_2\text{-O-Bpin} \quad \text{O-Bpin}
\]

¹H NMR (500 MHz, CDCl₃): δ 3.86 (s, 4H, BpinOCH₂CH₂OBpin), 3.52 (s, 3H, MeOBpin), 1.19-1.18 (m, 36H, BpinO(CH₂)₂OBpin and MeOBpin).

¹¹B{¹H} NMR (128 MHz, CDCl₃): δ 22.2 (BpinO(CH₂)₂OBpin/MeOBpin).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 82.6 (BpinOCH₂CH₂OBpin), 82.5 (MeOBpin), 67.5 (BpinOCH₂CH₂OBpin), 64.9 (BpinOCH₂CH₂OBpin), 52.5 (MeOBpin), 24.7 (MeOBpin), 20.8 (BpinOCH₂CH₂OBpin).

3b Diethyl carbonate

\[
\text{O-Bpin} \quad \text{O-Bpin}
\]
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.89 (q, $J = 7.1$ Hz, 2H, CH$_3$CH$_2$OBpin), 3.59 (s, 3H, CH$_3$OBpin), 1.25 (s, 12H, MeOBpin), 1.24 (s, 12H, CH$_3$CH$_2$OBpin), 1.20 (t, $J = 7.1$ Hz, 3H, CH$_3$CH$_2$OBpin).

$^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta$ 22.0 (CH$_3$CH$_2$OBpin/MeOBpin).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$): $\delta$ 83.1 (MeOBpin), 82.5 (CH$_3$CH$_2$OBpin), 60.6 (CH$_3$CH$_2$OBpin), 52.6 (MeOBpin), 25.0 (MeOBpin), 24.5 (CH$_3$CH$_2$OBpin), 17.1 (CH$_3$CH$_2$OBpin).

3c Propylene carbonate

\[
\begin{align*}
\text{Bpin} & \quad \text{O} \quad \text{Bpin} \\
\text{O} & \quad \text{Bpin}
\end{align*}
\]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.18-4.14 (m, 1H), 3.85-3.74 (m, 2H), 3.48 (s, 3H, MeOBpin), 1.15-1.13 (m, 36H, BpinOCH$_2$CH(CH$_3$)OBpin and MeOBpin), 1.06 (d, $J = 6.0$ Hz, 3H).

$^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta$ 21.0 (BpinOCH$_2$CH(CH$_3$)OBpin and MOeBpin).

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$): $\delta$ 82.8, 82.4 (MeOBpin), 67.5, 52.4 (MeOBpin), 32.9, 24.4 (BpinOCH$_2$CH(CH$_3$)OBpin and MeOBpin), 20.8.

**Monitoring of the catalytic transformation**

A time study of the catalytic transformation was carried out for benzyl benzoate 1a using boric acid as catalyst by collecting 6 data points early in the reaction. A model reaction was first performed with 132 mg of 1a (0.60 mmol, 1 equiv), 435 µL (3.0 mmol, 5 equiv) of HBpin and 3.71 mg (0.06 mmol, 0.1 equiv) of boric acid. Three other reactions were done by doubling the amount of one of the reagents: a reaction with 264 mg of 1a (1.20 mmol, 2 equiv), another with 870 µL (6.00 mmol, 10 equiv) of HBpin and a fourth reaction with 7.42 mg (0.12 mmol, 0.2 equiv) of boric acid. Under these conditions, the reaction can be approximated as a zeroth order with respect to the substrate concentrations. The consumption of 1a was measured by $^1$H NMR with the area of the peak (CH$_2$; 5.37 ppm) relative to a mesitylene internal standard. The reactions were done at 120 °C using Monowave 400. Orders for HBpin and benzyl benzoate were approximated by doubling the concentration of the corresponding reagent. The order for catalyst was approximated from the rates of reduction at 2 different catalyst loadings (10-20%). The rates (r)
were measured as the slope of the line for consumption of benzylbenzoate ([1a]/[1a]₀) over time (t).

\[
\frac{[1a]}{[1a]₀} = rt
\]

**Stoichiometric studies**

Reactions a-d described in **Scheme 3** were performed following a model reaction in a J-Young NMR tube using 0.3 mmol of benzyl benzoate 1a, 0.9 mmol of HBpin under neat conditions at 80 °C for 16 h.

a) Reactions with and without 10 mol% of boric acid afforded NMR yields of 80 % and 10 %. ¹¹B NMR of the catalyzed shows a small quadruplet at -13.2 ppm (\(J = 96\) Hz) as seen in **Figure S2**. The catalyzed reaction performed in a closed J-Young tube in CDCl₃ shows a singlet at 4.6 ppm characteristic for molecular hydrogen.

**Figure S2.** ¹¹B{¹H} NMR and ¹¹B NMR (inlet) of the catalyzed reaction shown in **Scheme 3a**.
b) No transformation was observed for the reaction between 1 equiv of benzyl benzoate 1a and 1 equiv of boric acid under the same conditions than a).

c) The reaction between 1 equiv of HBpin and 1 equiv of BH$_3$•SMe$_2$ produces a little amount of multiple small singlets in $^{11}$B{H} NMR. In $^{11}$B NMR it is possible to see a multiplet at -13.2 ppm corresponding to the speculated adduct (Figure S3).

![Figure S3. $^{11}$B NMR of reaction c.](image)

The reaction between 12 equiv of HBpin and 1 equiv of BO$_3$H$_3$ produces the speculated adduct, (Bpin)$_2$O and an unidentified compound in $^{11}$B NMR (Figure S4).
The reaction between benzyl benzoate 1a and 1 equiv of BH$_3$•SMe$_2$ was monitored. After 16h, four products are present by $^{11}$B NMR: BH$_3$•SMe$_2$, benzyl borate 4, bis(phenylmethyl) boronate 5 and the adduct observed in e) at -13.2 ppm (Figure S5). Heating the mixture after adding 2 equiv of HBpin produces the benzylOBpin 2a and regenerates BH$_3$•SMe$_2$ overtime.

Figure S5. $^{11}$B NMR of reaction d.
Procedure for the catalytic hydroboration of alkynes

Alkyne substrates (0.32 mmol, 1 equiv) and HBpin (75.0 µL; 0.52 mmol, 1.6 equiv) were dissolved in CDCl$_3$ with a total volume of 0.4 mL in a J-Young tube. A catalytic amount of boric acid (2.0 mg, 0.03 mmol, 0.1 equiv) and 5 µL of mesitylene as internal standard were added to the tube. The reaction mixture was subsequently heated at 60 ºC for 48 h. NMR yields were calculated using $^1$H NMR spectroscopy.$^6$

7 (E)-4,4,5,5-Tetramethyl-2-(phenyl-1-enyl)-1,3,2-dioxaborolane

![Image of the compound](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.52–7.47 (m, 2 H), 7.41 (d, $J = 18.4$ Hz, 1 H), 7.36–7.27 (m, 3 H), 6.18 (d, $J = 18.4$ Hz, 1 H), 1.32 (s, 12 H).

$^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): $\delta$ 29.0.

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta$ 149.6, 137.6, 129.0, 128.7, 127.2, 116.4 (br, C-B), 83.5, 25.0.

9 Methyl 4-[(E)-2-(4,4,5,5-tetramethyl-2-yl)ethenyl]benzoate-1,3,2-dioxaborolane

![Image of the compound](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.11–7.90 (m, 2 H), 7.55–7.52 (m, 2 H), 7.41 (d, $J = 18.3$ Hz, 1 H), 6.22 (d, $J = 18.2$ Hz, 1 H), 3.83 (s, 3 H), 1.26 (s, 12 H).

$^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): $\delta$ 28.1.

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta$ 166.6, 148.0, 141.6, 130.1, 129.8, 126.8, 119.5 (br, C-B), 83.4, 52.0, 24.8.
Computational details

All calculations were performed on the full structures of the reported compounds using the Gaussian 16 suite of programs. The ωB97XD functional was used in combination with the 6-31+G** basis set for all atoms. All geometry optimizations were carried out without any symmetry constraints. The transition states were located and confirmed by frequency calculations (single imaginary frequency). Similarly, the stationary points were characterized as minima (no imaginary frequency). The energies were then refined by single point calculations to include solvent effect using the SMD solvation model with the experimental solvent (tetrahydrofuran) at the same level of theory. All structures with their associated free enthalpy and Gibbs free energies as well as their Cartesian coordinates are fully detailed in the following section.

Cartesian coordinates

**BO₃H₃**

![BO₃H₃ Structure]

**Sum of electronic and thermal Enthalpies**: -252.384419

**Sum of electronic and thermal Free Energies**: -252.416814

|   | B  | O  | H  |
|---|----|----|----|
| B | 0.54026 | 0.15505 | -0.02899 |
| O | -0.07106 | 1.34692 | -0.31710 |
| H | -1.02777 | 1.34871 | -0.28556 |

|   | H  |
|---|----|
| H | 1.90171 | 0.13840 | -0.07011 |

**H₂**

![H₂ Structure]

**Sum of electronic and thermal Enthalpies**: -1.161066

**Sum of electronic and thermal Free Energies**: -1.175857

|   | H  | H  |
|---|----|----|
| H | -0.16970 | 0.54471 | 0.02916 |
| H | -0.91220 | 0.54471 | 0.02916 |

**HBpin**
Sum of electronic and thermal Enthalpies= -411.583431
Sum of electronic and thermal Free Energies= -411.626594

C  -0.86461  0.50266  -0.05325  
B  -0.08027  2.62859  -0.10750  
H  -0.08036  3.81612  -0.15807  
O  -1.15954  1.86367  -0.44994  
C  -1.53290  0.28436  1.30523  
H  -2.60219  0.48872  1.20813  
H  -1.40589  -0.74570  1.65066  
H  -1.12616  0.95997  2.06306  
C  -1.45374  -0.44912  -1.08410  

(Bpin)$_2$O

Sum of electronic and thermal Enthalpies= -897.303677
Sum of electronic and thermal Free Energies= -897.370417

O  0.15961  0.28873  0.09593  
C  -2.31971  2.83424  0.30023  
C  -1.08254  3.51165  0.99505  
C  3.50852  -0.78681  -0.44798  
C  3.31076  0.28559  -1.58079  
O  2.15589  -1.01661  -0.00148  
O  3.50852  -0.97004  -1.14890  
C  0.00277  2.64716  0.59759  
O  -1.92170  1.44843  0.24447  
B  -0.55169  1.42905  0.29078  
B  1.43669  0.10402  -0.32782  
C  -3.62393  2.94279  1.07637  
C  -3.90103  3.99320  1.21399  
H  -4.42401  2.44788  0.51960  
H  -3.54840  2.46699  2.05551  
C  -1.15414  3.46842  2.52246  
H  -0.18518  3.77034  2.92839  
H  -1.98877  4.15033  2.90551  
H  -1.37436  2.45937  2.88291  
C  -0.78323  4.92715  0.52405  
H  -1.63373  5.58610  0.72777  

H  -1.17392  -1.48241  -0.85384  
H  -2.54442  -0.37827  -1.06689  
C  1.37260  0.17267  -1.31552  
H  2.44190  0.38461  -1.23644  
H  1.24552  -0.88312  -1.57174  
C  0.96564  0.78107  -2.12818  
C  1.01435  -1.40382  0.98595  
H  2.38446  -0.28511  1.10454  
H  0.95421  -0.03033  2.11261  

H  0.08678  5.31564  1.06008  
H  -0.86290  4.95509  -0.54427  
C  -2.52492  3.29995  -1.14266  
H  -3.26286  2.64979  -1.61947  
H  -2.89174  4.32976  -1.18168  
H  -1.59592  3.23815  -1.71705  
C  3.00476  -0.33331  -2.94580  
H  3.88752  -0.82047  -3.36998  
H  2.19875  -1.06978  -2.87789  
H  2.68452  0.45911  -3.62724  
C  4.44045  1.29723  -1.70496  
H  5.38311  0.79141  -1.93860  
H  4.21808  1.99764  -2.51438  
H  4.56619  1.87115  -0.78549  
H  4.10473  -2.10567  -0.91726  
H  5.09858  -1.94465  -1.34784  
H  4.20608  -2.78524  -0.06697  
H  3.47146  -2.58869  -1.66324  
C  4.29190  -0.25179  0.75244  
H  3.88465  0.70198  1.10068  
H  4.21560  -0.97256  1.57053
**B₂H₆**

![B₂H₆ molecule]

**Sum of electronic and thermal Enthalpies= -53.204311**

**Sum of electronic and thermal Free Energies= -53.231966**

|     | H  | 5.34927 | -0.11208 | 0.50942 |
|-----|----|---------|----------|---------|
| B   | -2.46886 | 1.57400 | 0.18012  |          |
| H   | -1.36492 | 1.23119 | 0.81203  |          |
| H   | -2.24595 | 2.52887 | -0.49806 |          |
| H   | -2.98190 | 0.59420 | -0.26490 |          |
| B   | -2.46886 | 1.57400 | 0.18012  |          |
| H   | -1.36492 | 1.23119 | 0.81203  |          |
| H   | -2.24595 | 2.52887 | -0.49806 |          |
| H   | -2.98190 | 0.59420 | -0.26490 |          |

**HB(OBenzyl)₂ (5)**

![HB(OBenzyl)₂ molecule]

**Sum of electronic and thermal Enthalpies= -717.450462**

**Sum of electronic and thermal Free Energies= -717.501094**

|     | H  | 5.34927 | -0.11208 | 0.50942 |
|-----|----|---------|----------|---------|
| H   | -1.45257 | -0.05582 | 0.40930  |          |
| O   | -0.80176 | 1.91616 | 1.23741  |          |
| O   | 0.68162  | 0.54067 | 0.11373  |          |
| C   | -2.10461 | 2.26825 | 1.66063  |          |
| H   | -1.99585 | 2.76137 | 2.63264  |          |
| H   | -2.71795 | 1.37900 | 1.80909  |          |
| C   | 1.03396  | -0.68959 | -0.48835 |          |
| H   | 0.15075  | -1.17071 | -0.92827 |          |
| H   | 1.72502  | -0.45268 | -1.30447 |          |
| C   | -2.79539 | 3.20059 | 0.68887  |          |
| C   | -2.07905 | 3.90880 | -0.27565 |          |
| C   | -4.17809 | 3.38092 | 0.77899  |          |
| C   | -2.73770 | 4.78445 | -1.13791 |          |
| H   | -1.00545 | 3.77034 | -0.34894 |          |
| C   | -4.83528 | 4.25826 | -0.07834 |          |

**TS-m**
Sum of electronic and thermal Enthalpies= -1129.012615
Sum of electronic and thermal Free Energies= -1129.08859

B  -0.02465  -1.72524  -2.16730  O  0.11733  -1.29355  -0.78334
H   0.58629  -1.11259  -2.99443  O  -0.40703  -3.02061  -2.34647
C   0.15892  -2.28935  0.26599  C  -0.14723  -3.70279  -3.56709
H  -0.68258  -2.97442  0.15265  H  -0.00073  -2.97684  -4.37581
H  -1.40678  -0.80854  -2.22512  H  -1.03462  -4.29848  -3.79810
B  -1.27451  -0.40129  -1.03746  C  1.06575  -4.59166  -3.43404
O  -1.05181  0.97927  -0.95808  C  2.34615  -4.03117  -3.42506
O  -2.23744  -0.81753  -0.09868  C  0.93013  -5.97222  -3.29329
C  -1.65404  1.42838  0.26265  C  3.46961  -4.83730  -3.28327
C  -2.79605  0.37125  0.48009  H  2.46173  -2.95471  -3.52267
C  -2.14508  2.85756  0.06888  C  2.05489  -6.78498  -3.15536
C  -0.58969  1.39943  1.36491  H  -0.06201  -6.41656  -3.29362
C  -3.13254  0.09385  1.93936  C  3.32604  -6.21820  -3.15236
C  -4.07203  0.70973  -0.29588  H  4.45786  -4.38883  -3.26984
H  -2.70845  3.19517  0.94563  H  1.93649  -7.89353  -3.05207
H  -1.28934  3.52501  -0.06593  H  4.20343  -6.84862  -3.04463
H  -2.78136  2.94176  -0.81370  C  1.47631  -3.01503  0.23645
H  -0.26487  1.99892  1.04030  C  1.51284  -4.40581  0.14111
H  -0.96984  1.81284  2.30415  C  2.67617  -2.30339  0.31578
H  -0.23373  0.38345  1.55446  C  2.72998  -5.08187  0.14686
H  -3.47280  1.00803  2.43758  H  0.58442  -4.96071  0.04282
H  -3.93527  -0.64651  1.99786  C  3.89415  -2.97654  0.30899
H  -2.26930  -0.29935  2.48026  H  2.65115  -1.21865  0.37489
H  -4.73938  -0.15575  -0.26509  H  3.92209  -4.36843  0.23096
H  -4.59469  1.56752  0.13836  H  2.74599  -6.16326  0.05971
H  -3.84739  0.92943  -1.34352  H  4.82182  -2.41564  0.36917
H  0.02812  -1.73161  1.19466  H  4.87204  -4.89415  0.22482

H2BOBenzyl (10)

Sum of electronic and thermal Enthalpies= -372.01281
Sum of electronic and thermal Free Energies= -372.053661

B  -2.34294  1.36785  -0.13700  O  -1.43019  0.73149  0.62069
H  -2.49479  2.55786  -0.02740  C  -0.58425  1.43658  1.53402
H  -2.98120  0.69773  -0.89460  H  -1.03840  2.40135  1.78745

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BenzylOBpin (2a)

Sum of electronic and thermal Enthalpies= -757.013318
Sum of electronic and thermal Free Energies= -757.0727

TS-d

Sum of electronic and thermal Enthalpies= -744.022363
Sum of electronic and thermal Free Energies= -744.083866
|     | X1   | Y1   | Z1   |     | X2   | Y2   | Z2   |
|-----|------|------|------|-----|------|------|------|
| C   | 2.18561 | -3.17636 | -0.05400 | C   | -0.66019 | 3.13933 | -2.05304 |
| C   | 1.96227 | -4.51224 | -0.38927 | C   | -0.41860 | 3.87910 | -3.21433 |
| C   | 3.49738 | -2.69458 | -0.01300 | C   | -1.16918 | 3.78608 | -0.92883 |
| C   | 3.03232 | -5.35807 | -0.67749 | C   | -0.68534 | 5.24364 | -3.25300 |
| H   | 0.94525 | -4.89335 | -0.42755 | H   | -0.01820 | 3.38310 | -4.09592 |
| C   | 4.56675 | -3.53478 | -0.30427 | C   | -1.43565 | 5.15489 | -0.96691 |
| H   | 3.67607 | -1.65376 | 0.24290  | H   | -1.35093 | 3.21394 | -0.02591 |
| C   | 4.33537 | -4.86992 | -0.63622 | C   | -1.19636 | 5.88728 | -2.12589 |
| H   | 2.84672 | -6.39604 | -0.93516 | H   | -0.49332 | 5.80579 | -4.16178 |
| H   | 5.58155 | -3.15100 | -0.26958 | H   | -1.83135 | 5.64856 | -0.08445 |
| H   | 5.16991 | -5.52679 | -0.86066 | H   | -1.40427 | 6.95236 | -2.15306 |
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