

## Supporting Information

### Ammonia-mediated, large-scale synthesis of ammonia borane

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#### Experimental Section

**General Information.** Unless otherwise noted, all manipulations were carried without inert atmosphere. The  $^{11}\text{B}$  NMR spectra were recorded using a Varian Inova-300 spectrometer (96 MHz) with a Nalorac quad probe and were referenced to  $\text{BF}_3 \cdot \text{OEt}_2$  (0.0 ppm) as an external standard. Tetrahydrofuran (THF, ACS grade containing 0.025% BHT) was purchased from Mallinckrodt chemicals. Sodium borohydride (powder, purity >99% by hydride estimation<sup>1</sup>) was purchased in bulk from Dow Chemical Co. (Rohm and Haas). Ammonium acetate (ACS reagent, Sigma-Aldrich), ammonium fluoride (98%, Sigma-Aldrich), ammonium bicarbonate (>99%, Sigma-Aldrich), ammonium chloride (ACS reagent, Mallinckrodt), ammonium formate (97%, Sigma-Aldrich), ammonium hydrogen fluoride (95%, Sigma-Aldrich), ammonium phosphate (>98.5%, Sigma-Aldrich), ammonium hydrogen sulfate (98%, Sigma-Aldrich), ammonium sulfate (ACS reagent, Mallinckrodt) and ammonium carbonate (ACS reagent, Sigma-Aldrich) were purchased from the respective commercial sources and were used as received.

#### **Caution:**

**Hydrogen** - Highly flammable.

**Ammonia** - Toxic, corrosive.

*All the reactions were carried out in a well-ventilated hood with the reaction vessel outlet directly leading into the hood exhaust due to the hazards associated with escaping ammonia and the liberation of large quantities of hydrogen.*

#### **General Procedure for the preparation of ammonia borane using sodium borohydride and ammonium salts (Table 1)**

Condensed liquid ammonia (2.5 mL) was transferred via cannula to reagent-grade THF (97.5 mL) contained in an indented 250 mL three-neck round bottom flask fitted with an overhead stirrer, stopper, and a cold finger. The flask was cooled in ice-water bath. Sodium borohydride (3.8 g, 100 mmol) and ammonium salt were transferred to the reaction flask after addition of ammonia.

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<sup>1</sup> H. C. Brown, *Organic Syntheses Via Boranes*, Wiley, New York, 1975, Chapter 9.

The mixture was stirred carefully at 0 °C and then at room temperature for desired period of time. Upon completion of the reaction, as monitored by <sup>11</sup>B NMR spectroscopy, THF (50 mL) was added to the reaction mixture, stirred for 30 min, filtered through celite, and washed with THF. The filtrate was concentrated under vacuum to obtain ammonia borane. The purity was determined by both <sup>11</sup>B NMR spectroscopy and hydride estimation (hydrolysis reaction).<sup>1</sup>

**Table 1:** Synthesis of AB: Examination of ammonium salts for the synthesis of AB in ammoniated THF.<sup>a</sup>

Entry	Ammonium salt	Ammonium salt equiv.	Reaction condition	Isolated Yield, %	Purity of AB (%) <sup>b</sup>
1	NH <sub>4</sub> OAc	2	0 °C, 2 h, rt 2 h	70	94
2	NH <sub>4</sub> F	2	0 °C, 2 h, rt 9 h	74	96
3	NH <sub>4</sub> HCO <sub>2</sub>	2	0 °C, 2 h, rt, 2.5 h	74	97
4	NH <sub>4</sub> Cl	2	0 °C, 2 h, rt, 2 h	71	98
5	NH <sub>4</sub> HCO <sub>3</sub>	2	0 °C, 2 h, rt 2 h	75	96
6	NH <sub>4</sub> HF <sub>2</sub>	2	0 °C 2 h, rt 3 h	73	95
7	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	1	0 °C 2 h, rt, >16 h	Incomplete	-
8	NH <sub>4</sub> HSO <sub>4</sub>	2	0 °C 2 h, rt 8 h	58	98
9	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1	0 °C, 4 h, rt 5 h	77	98
10	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	1	0 °C, 4 h, rt 6 h	76	97

<sup>a</sup>All the reaction were performed in THF containing 2.5% NH<sub>3</sub> and in 1 M concentration with respect to SBH. <sup>b</sup>Purity of the AB as determined by hydrogen estimation.

Due to the low solubility of both NaBH<sub>4</sub> and ammonium salts in THF, the reactions are heterogeneous throughout its course. It was observed that scaling up the reactions with ammonium bicarbonate and ammonium carbonate led to frothing rendering stirring and filtration difficult.

**General Procedure for the optimization of reaction conditions with ammonium sulfate (Table 2)**

Condensed liquid ammonia was transferred via cannula to reagent-grade THF (97.5 mL) contained in an indented 250 mL three-neck round bottom flask fitted with an overhead stirrer, stopper, and a cold finger. The flask was cooled in ice-water bath. Sodium borohydride (3.8 g, 100 mmol) and ammonium salt were transferred to the reaction flask after addition of ammonia. The mixture was stirred carefully at 0 °C and then at room temperature for the desired period of time to complete the reaction, as monitored by <sup>11</sup>B NMR spectroscopy. In workup A, THF (50 mL) was added to the reaction mixture, whereas, in workup B, 1M ammoniated THF (50 mL) was added to the reaction mixture and stirred for 30 min, filtered through celite, and washed with THF. The filtrate was concentrated under vacuum to obtain ammonia borane. The purity was determined by both <sup>11</sup>B NMR spectroscopy and hydride estimation.

**Table 2: Synthesis of AB: Optimization of reaction condition with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.**

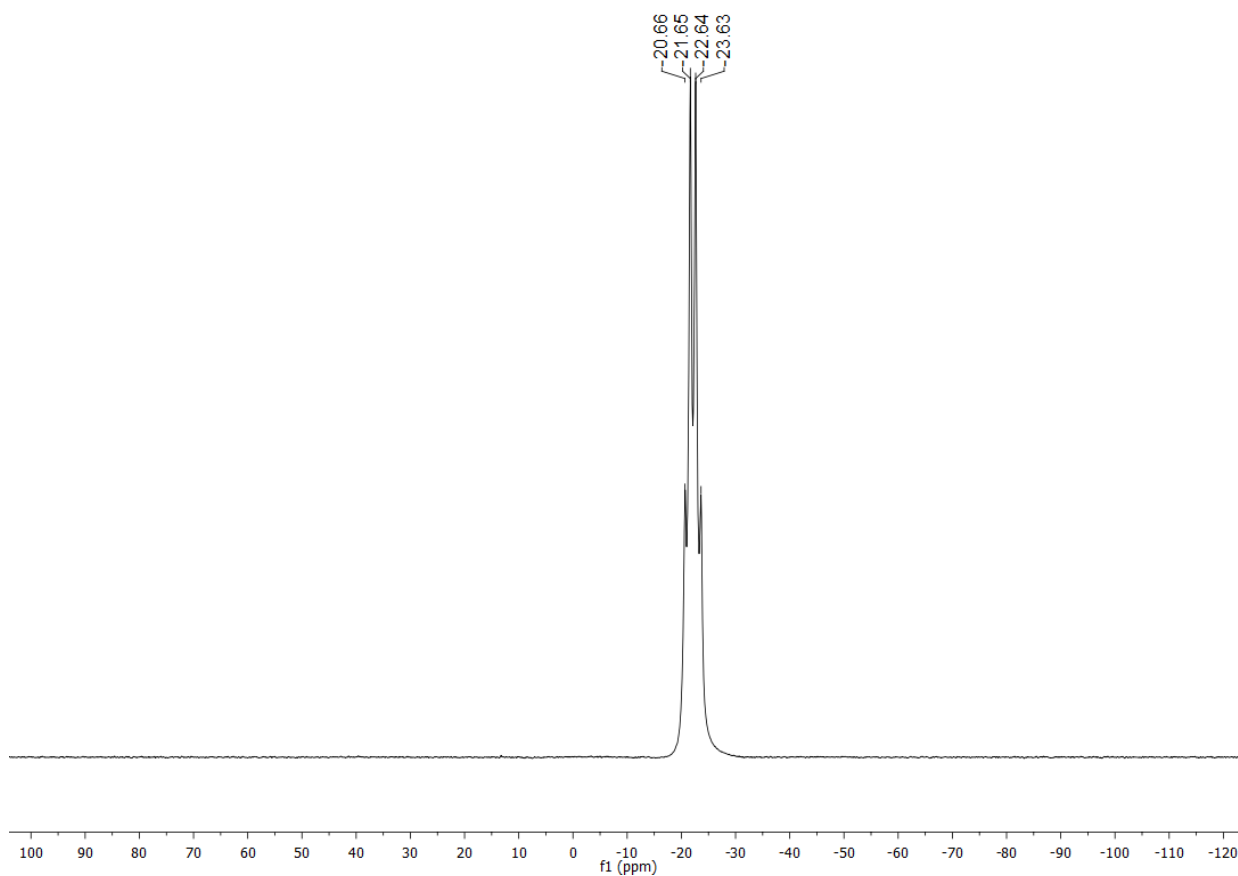
entry	Molarity <sup>a</sup>	% NH <sub>3</sub>	Reaction condition	Workup <sup>b</sup>	Yield <sup>c</sup>
1	1	2.5	0 °C, 4 h, rt, 5 h	A	77%
2	1	2.5	0 °C, 4 h, rt, 5 h	B	87%
3	1	2.5	rt, 15 h	B	70%
<b>4</b>	<b>1</b>	<b>5</b>	<b>0 °C, 2 h, rt, 8 h</b>	<b>B</b>	<b>92%</b>
5	1.5	5	0°C, 2 h, rt, 10 h	B	69%
6	2	5	0°C, 2 h, rt, 18 h	B	43%
7	2	10	0°C, 2 h, rt, 13 h	A	80%

<sup>a</sup>Molarity of SBH or ammonium salt in THF containing NH<sub>3</sub>. <sup>b</sup>A: No addition of ammoniated THF prior to isolation. B: Additional 1 M solution of NH<sub>3</sub> in THF was added to the reaction mixture prior to isolation. <sup>c</sup>Isolated yield.

**Optimized large-scale preparation of AB:**

Condensed liquid ammonia (500 mL) was transferred via cannula to 10 L reagent-grade THF contained in an indented 22 L three-neck round bottom flask fitted with an overhead stirrer, stopper, and a cold finger. The flask was cooled in ice-water bath. Sodium borohydride (378.3 g, 10 mol) and powdered ammonium sulfate (1.32 Kg, 10 mol) were transferred to the reaction flask after addition of ammonia. The mixture was stirred carefully for 2 h at 0 °C and then at room temperature for 8 h. Upon completion of the reaction, as monitored by <sup>11</sup>B NMR spectroscopy, 1

*M* ammoniated THF solution (5 L) was added to the reaction mixture, stirred for 30 min, filtered through celite, and washed with THF. The filtrate was concentrated under vacuum to obtain ammonia borane (283.9 g, 92%) at ~98% chemical purity, as was determined by both  $^{11}\text{B}$  NMR spectroscopy (Figure 1) ( $64\text{ MHz}$ ,  $\delta -22.1\text{ ppm}$  (q)) and hydride analysis.<sup>1</sup> Most of the solvent THF was recovered and re-used.



**Figure 1.**  $^{11}\text{B}$  NMR spectrum of AB prepared in THF (1M) containing 2.5%  $\text{NH}_3$ .