

# Supporting Information:

## Synthesis, Purification, and Analysis of the

### Weakly-Coordinating Anion $\text{BAr}_4^{\text{F}-}$

David Qiu

*Department of Chemistry, University of Illinois at Urbana-Champaign, 505 S Matthews  
Avenue, Urbana, IL, 61801*

E-mail: davidlq2@illinois.edu

## Contents

<b>1</b>	<b>General Information</b>	<b>S-2</b>
<b>2</b>	<b>Materials and Methods</b>	<b>S-2</b>
2.1	Synthesis of $\text{NaBAr}_4^{\text{F}}$ . . . . .	S-2
2.2	Purification of $\text{NaBAr}_4^{\text{F}}$ . . . . .	S-3
<b>3</b>	<b>Analysis of <math>\text{NaBAr}_4^{\text{F}}</math></b>	<b>S-4</b>
	<b>References</b>	<b>S-6</b>

## 1 General Considerations

A 60 MHz Nanalysis NMReady-60PRO tabletop NMR instrument coupled with a STC-1000 digital temperature controller was used to record all  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR spec-

tra. NMR spectra were taken in DMSO-d<sub>6</sub> sourced from Cambridge Isotope Laboratories, Inc. Activated carbon charcoal and benzene was sourced from EMD Millipore. Sodium sulfate was sourced from Alfa Aesar. Mg and NaBF<sub>4</sub> were sourced from Sigma-Aldrich. BrC<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub> was sourced from Oakwood Chemicals. 1,2-dibromoethane and diethyl ether were sourced from Fisher Chemicals. Air and moisture-free experimental conditions were achieved with a Schlenk line following standard procedure unless specified otherwise.

## 2 Materials and Methods

### 2.1 Synthesis of NaBAr<sub>4</sub><sup>F</sup>

To a 500 mL three-necked round-bottom flask was added 1.17 g (48.1 mmol) of magnesium turnings, 0.813 g (7.40 mmol) NaBF<sub>4</sub>, and a stir bar. A reflux condenser, an addition funnel, and a rubber septum secured with copper wire were fit on each neck. The apparatus was attached to the Schlenk line, and was vacuumed and refilled with nitrogen three times. Using an airtight syringe, 75 mL of diethyl ether was added to the flask, followed by 0.57 mL (6.7 mmol) of 1,2-dibromoethane added similarly. The mixture was then heated on a heating mantle attached to a 40 V Variac until the solution began to bubble softly and turn a cloudy gray, signaling the initiation of the magnesium turnings.

Upon initiation, the heating mantle was removed from contact with the system, and the solution was allowed to continue stirring until the reflux ceased. While the flask cooled, 7.15 mL (41.5 mmol) of BrC<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub> was mixed with 50 mL of diethyl ether and injected into the separate, closed addition funnel. While the solution inside the flask was warm, but no longer refluxing, the addition funnel's stopcock was turned slightly to allow the dropwise addition of the BrC<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub> solution over the course of 30 minutes. The flask solution gradually darkened into a caramel brown, indicative of successful BA<sub>4</sub><sup>F-</sup> synthesis.

Upon complete addition of the BrC<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub> solution, the reaction mixture was

then refluxed again for 30 minutes on a heating mantle attached to a 40 V Variac. Afterwards, the solution was allowed to cool to room temperature, and the experimental apparatus was disassembled quickly to minimize exposure of the  $\text{NaBAr}_4^{\text{F}}$  solution to ambient conditions. The round-bottom flask containing the newly-synthesized  $\text{NaBAr}_4^{\text{F}}$  solution was sealed with glass stoppers, and stored at room temperature for a week.

## 2.2 Purification of $\text{NaBAr}_4^{\text{F}}$

The  $\text{NaBAr}_4^{\text{F}}$  solution was transferred into a 1 L separatory funnel, and washed with 50 mL of diethyl ether and 100 mL of brine, followed by a second washing with 100 mL of DI water. The organic  $\text{NaBAr}_4^{\text{F}}$  solution was collected into a 500 mL Erlenmeyer flask, was dried with 27 g of sodium sulfate, and was de-colored with 2 g of activated carbon charcoal. The solution was mixed vigorously for five minutes, and was filtered through a Buchner funnel into a 500 mL three-necked round-bottom flask. The side necks were sealed with rubber septa and copper wire, and the  $\text{NaBAr}_4^{\text{F}}$  solution was dried with a rotary evaporator to yield a thick, dark-brown oil.

A standard Dean-Stark apparatus was then assembled with the  $\text{NaBAr}_4^{\text{F}}$  flask, and was connected to the Schlenk line under an inert nitrogen atmosphere. 100 mL of benzene was injected into the flask, and the solution was heated until 75 mL of organic and aqueous solvent had been removed. The  $\text{NaBAr}_4^{\text{F}}$  solution was dried again using a rotary evaporator, unfortunately yielding a thick, dark-brown  $\text{NaBAr}_4^{\text{F}}$  slurry which failed to dry under 10 minutes of vacuum on the Schlenk line.

The purified  $\text{NaBAr}_4^{\text{F}}$  sample was then weighed, and a small sample was saved for NMR analysis. The measured yield of this reaction was 6.825 g (104% yield), which is likely inaccurate due to the residual solvent unable to be removed from the system.

### 3 Analysis of NaBAr<sub>4</sub><sup>F</sup>

Unfortunately, the NMR instrument had a severe software malfunction near the end of the last experimental period, and NMR data was unable to be obtained for the NaBAr<sub>4</sub><sup>F</sup> sample. Sample <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra of NaBAr<sub>4</sub><sup>F</sup> in deuterated acetone collected via a 400 MHz Bruker NMR instrument were provided by the TAs and analyzed.

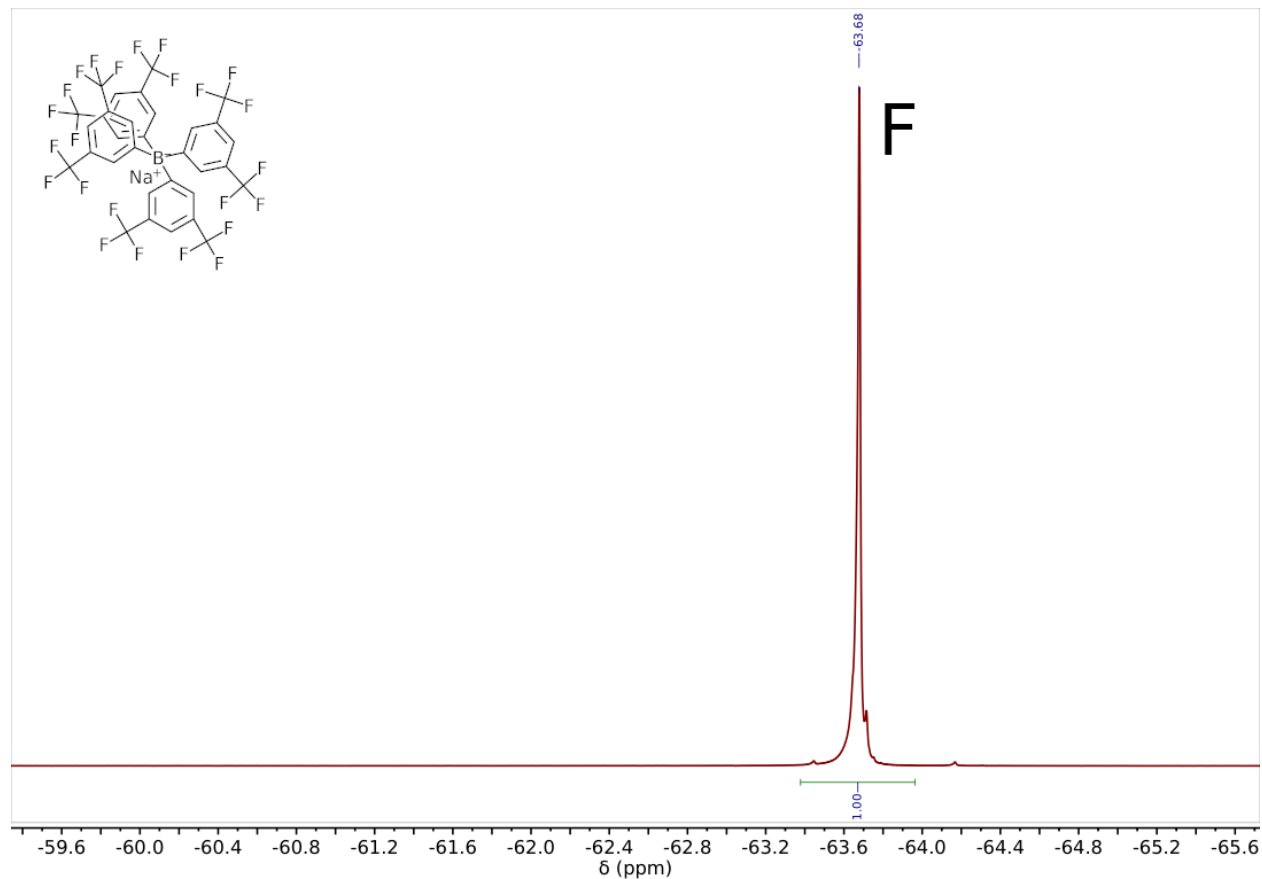


Figure S1: Provided <sup>19</sup>F NMR spectra of NaBAr<sub>4</sub><sup>F</sup>.

The NMR interpretation is as follows. <sup>19</sup>F NMR:  $\delta$  63.68 (s, 24 F). <sup>1</sup>H NMR:  $\delta$  7.68 (d, 8 H), 7.68 (d, 4 H). The NMR spectra and their interpretation are in excellent agreement with those of existing literature.<sup>S1</sup>

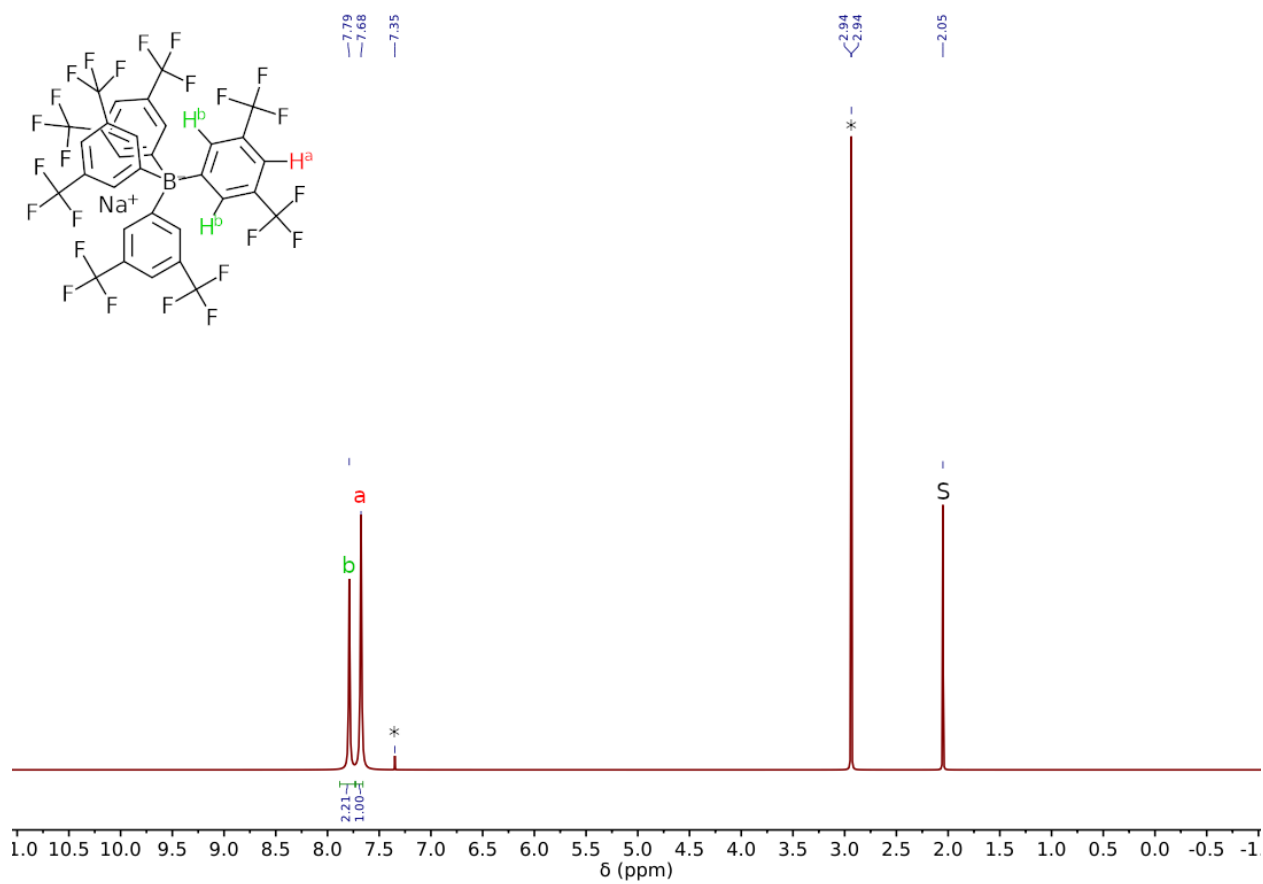


Figure S2: Provided  $^1\text{H}$  NMR spectra of  $\text{NaBAR}_4^{\text{F}}$ . “S” denotes residual non-deuterated acetone present in the solvent, and “\*” denotes an unidentified impurity.

## References

- (S1) Yakelis, N. A.; Bergman, R. G. Sodium Tetrakis [(3, 5-trifluoromethyl) phenyl] borate (NaBArF<sub>24</sub>): Safe Preparation, Standardized Purification, and Analysis of Hydration. *Organometallics* **2005**, *24*, 3579.