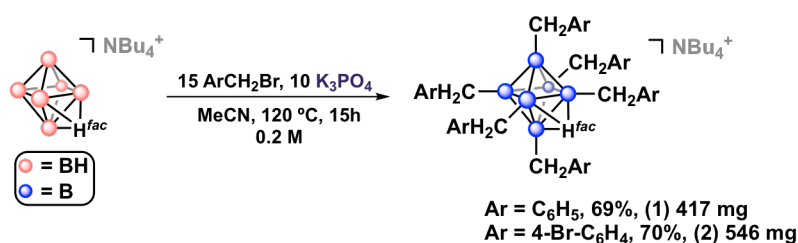


1. PRF #56562-DNI3.
2. Metal-Free Nucleophilic Borylation Chemistry Using Boron Cluster Reagents
3. Alexander M. Spokoyny, UCLA.

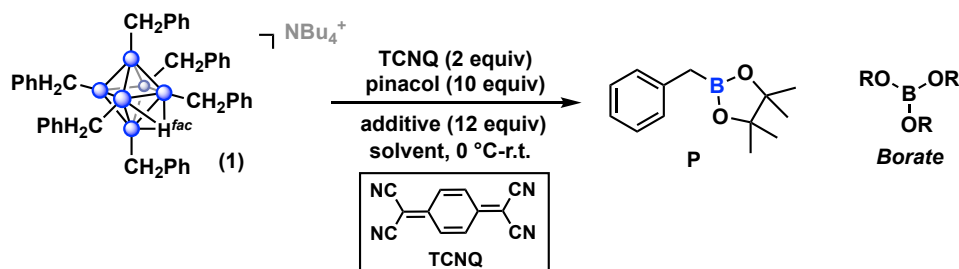
Previously, we have reported the first synthesis of perbenzylated hexaborate dianion under microwave conditions. A more scalable reaction procedure without using a microwave is needed in order to further investigate the degradation of this persubstituted cluster to generate organoboron compounds. By screening various solvent/base combinations, we identified that MeCN/K<sub>3</sub>PO<sub>4</sub> could achieve full conversion and produce products in 70% yield after one crystallization on half-gram scale (Scheme 1).



**Scheme 1.** Perbenzylation of hexaborate dianion under heating condition.

Previously, the cyclic voltammogram (CV) of perbenzylated product **1** which lacks a reductive peak below 500 mV/s scan rate has suggested the irreversible degradation could be achieved in the presence of external oxidants. Different types of oxidants were tested in the presence of pinacol as trapping reagent to stabilize decomposed organoboron species derived from **1**. By using I<sub>2</sub>, TCNQ (tetracyanoquinodimethane) and TCNE (tetracyanoethylene), we successfully observed the formation of the benzyl boronic acid pinacol ester from <sup>1</sup>H and <sup>11</sup>B NMR, and optimization of degradation conditions was carried out using TCNQ as the choice of oxidant (Table 1). MgSO<sub>4</sub> proved to be the optimal additive providing the best product/borate ratio and isolated yield by using THF as the solvent (Entry 2, Table 1). We also tested a two-step sequence under optimized condition without purifying the persubstituted boron cluster, and 31% overall isolated yield was obtained. This is comparable to stepwise sequence to generate degradation product.

**Table 1.** Optimization of degradation reaction conditions for **1**.



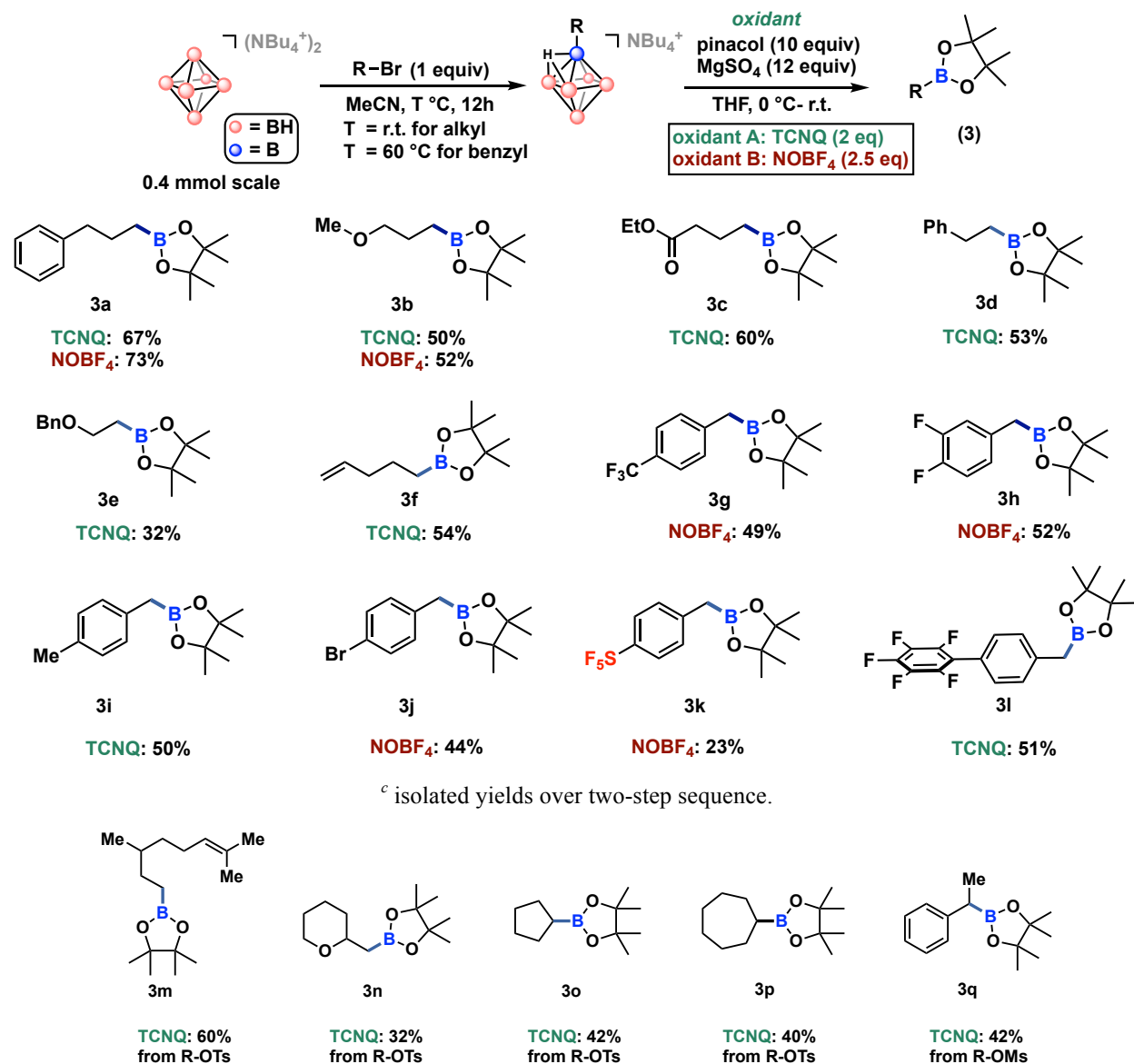
Entry	Solvent	Additive	Product/Borate ratio <sup>a</sup>	Yield <sup>b</sup> (%)
1	MeCN	MgSO <sub>4</sub>	30/1	42
2	THF	MgSO <sub>4</sub>	35/1	47
3	THF	K <sub>2</sub> CO <sub>3</sub>	1/3	N/A
4	MeCN	Et <sub>3</sub> N	--	--
5	THF	Et <sub>3</sub> N	--	--
6	THF	K <sub>3</sub> PO <sub>4</sub>	--	--
7	THF	DMSO	25/1	44

0.1 mmol scale reaction of purified cluster **1** was used for each reaction. <sup>a</sup> ratio determined by <sup>11</sup>B NMR. <sup>b</sup> Isolated yields.

Under modified conditions, high conversions were obtained for primary alkyl bromides (including benzyl bromides and unactivated alkyl bromides) in substitution step. For the degradation step, NOBF<sub>4</sub> was applied as

oxidant in the case of electrophiles bearing electron deficient groups (Table 2). For unactivated substrates, such as those containing ester group (**3c**), benzyl ether (**3e**) and terminal alkene (**3f**) were proved to be compatible under standard reaction conditions.

**Table 2.** Substrate scope of primary alkyl bromide electrophiles<sup>c</sup>.



<sup>c</sup> isolated yields over two-step sequence.

**Scheme 2.** Substrate scope of primary and secondary alkyl pseudo halides containing C-O bonds.

We also tested primary and secondary alkyl electrophiles bearing OTs and OMs leaving groups under elevated temperatures using excess of hexaborate dianion. The corresponding boronic esters could be obtained with moderate yields after the two-step procedure. This transformation has showcased a rare C-O bond cleavage/C-B bond forming reaction in the absence of any transition metal catalysts. For substitution step, two sets of experiments were carried out to determine if the reaction between the hexaborate dianion and electrophiles follows the general S<sub>N</sub>2 pattern. First, (bromomethyl) cyclopropane as radical probe was subjected to two-step reaction sequence. No cyclopropane ring-opening product could be observed from <sup>1</sup>H NMR after degradation, this suggested that a radical pathway is unlikely.

We are currently evaluating chiral electrophiles and main group species to ascertain whether the scope of this transformation can be expanded further.