Synthesis of Two Azaborine Building Blocks

**Significance:** The search for heterocycles with novel properties is a continuing research endeavor. The azaborine ring system is emerging in compounds of material science and medicinal chemistry interest but is in the early stages of development (see Review below). In fact, only recently has 1-[tert-butyldimethylsilyl]-2-chloro-1,2-dihydro-1,2-azaborinine (8) become commercially available.


**Comment:** The current article describes the synthesis of the C–H borylation products 2 from dihydroazaborinine 1, and the isolation and subsequent reactivity profiles of 2a and 2b. The separation of the mixture of 2a and 2b by using physical methods was unsuccessful. However, careful consideration of the electronic structures of each isomer pointed to 2b as being prone to oxidation to 5a, thereby permitting the isolation of 2a. In addition, the compound 2a was found to be more reactive to protodeborylation, thereby permitting the isolation of 2b from a mixture of 2a and 2b. The reactions of 2a and 2b to give compounds 3–7 were demonstrated.

---

**Methods:**
- Selective oxidation
- Selective protodeborylation
- Selective transesterification (accomplished utilizing unique electronic structural differences for differentiation)

**Selected products/commercially available starting material:**

- 3: 81% yield
- 4: 90% yield
- 5a: R = OH, 30% yield
- 5b: R = OTs, 80% yield
- 6: 25% yield
- 7: 83% yield
- 8: commercially available