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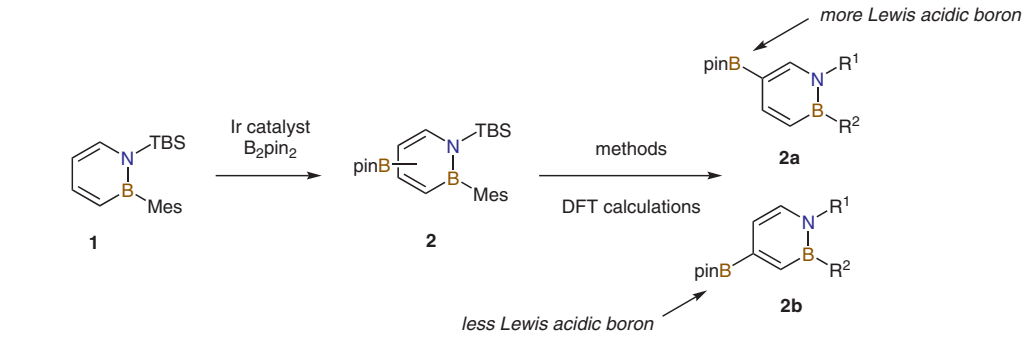
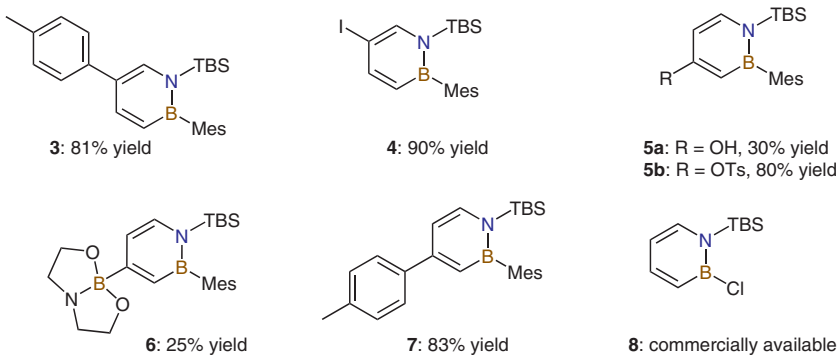
1,2-Azaborine's Distinct Electronic Structure Unlocks Two New Regioisomeric Building Blocks via Resolution
J. Am. Chem. Soc. **2019**, *141*, 9072–9078.

Synthesis of Two Azaborine Building Blocks



Selected products/commercially available starting material:



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*-butyl(dimethyl)silyl]-2-chloro-1,2-dihydro-1,2-azaborinine (**8**) become commercially available.

Review: Z. X. Giustra, S.-Y. Liu *J. Am. Chem. Soc.* **2018**, *140*, 1184–1194.

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.

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Category
Synthesis of Heterocycles

Key words
isosterism
azaborines
iridium catalysis