Stereospecific Coupling of Aromatics with Secondary and Tertiary Boronates

**Significance:** Aggarwal and co-workers report an effective, general method for coupling electron-rich (hetero)aromatics with enantioenriched secondary and tertiary boronic esters. The reaction involves the initial formation of a boronate complex followed by activation of the electron-rich aromatic by NBS, which triggers a stereospecific 1,2-migration and subsequent elimination–rearomatization.

**Comment:** The methodology uses simple, readily available reagents and proceeds without transition metals. Broad scope with respect to the boronic ester and the electron-rich aromatic was illustrated, and the reactions proceeded with complete stereospecificity.

**Selected examples:**

- **93% yield**
  - er = 93:7

- **68% yield**
  - er = 93:7

- **74% yield**
  - er = 93:7

- **76% yield**
  - er > 99:1

- **85% yield**
  - er = 96:4

- **86% yield**
  - er = 98:2

- **83% yield**
  - er = 98:2

- **63% yield**
  - er > 99:1