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Enantiospecific sp^2 – sp^3 Coupling of Secondary and Tertiary Boronic Esters *Nature Chem.* **2014**, *6*, 584–589.

Stereospecific Coupling of Aromatics with Secondary and Tertiary Boronates

Significance: Aggarwal and co-workers report an effective, general method for coupling electronrich (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.

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Metal-Mediated Synthesis

Key words

boron

aryllithium

cross-coupling

