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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.

SYNFACTS Contributors: Paul Knochel, Thomas Klatt Synfacts 2014, 10(9), 0963 Published online: 18.08.2014 **DOI:** 10.1055/s-0034-1378966; **Reg-No.:** P09514SF

Metal-Mediated Synthesis

Key words

boron

aryllithium

cross-coupling

