

Rapid, Secondary B-Alkyl Suzuki-Miyaura Cross-Coupling of Alpha-Oxygen Boronic Esters

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The Suzuki-Miyaura Cross-Coupling (SMCC) is well-regarded as a premier method for the construction of C(sp²)-C(sp²) bonds; however, progress toward the stereospecific C(sp²)-C(sp³) variant remains underdeveloped. Despite extensive precedence for Ni- and Pd-catalyzed cross-couplings using 2° aliphatic nucleophiles, 2° α-oxygen cross-coupling has been scarcely reported with palladium catalysis. Additionally, Ni-catalyzed α-oxygen cross-couplings are limited by reactive radical intermediates. Thus, a general, stereospecific, two-electron cross-coupling method would be valuable for the construction of functionalized, stereodefined cyclic ether and alcohol moieties. In this work, we describe a rapid, 2° B-alkyl SMCC, enabling the cross-coupling of a variety of aryl and vinyl bromides with α-oxygen tetramethyl *N*-methyliminodiacetic acid (TIDA) boronates. Crucial to the success of this method is the use of TIDA boronates, which are activated *in-situ* by the organic soluble base, potassium trimethylsilylanolate (TMSOK). Utilizing these conditions, cross-coupled products were rapidly obtained in under one hour with moderate to great yields.

