

An Economical and Readily Accessible Preparation of *o,o*-Disubstituted Arylboronates through Palladium-Catalyzed Borylation of Bromoarenes

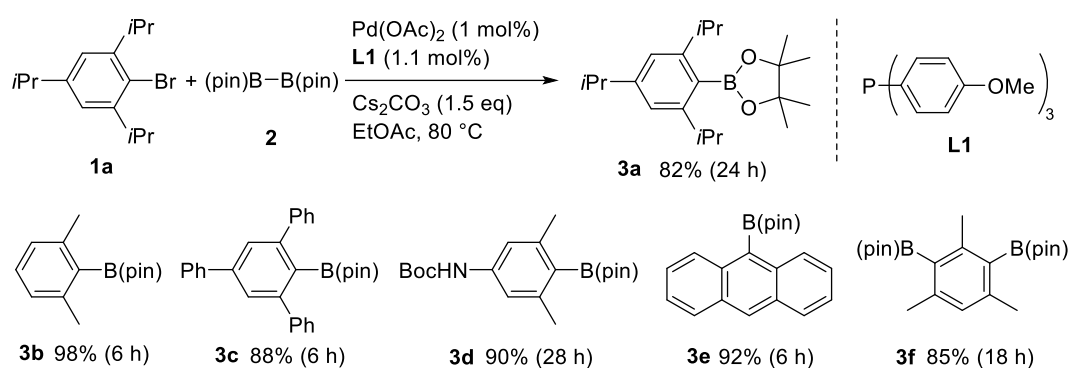
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Palladium-catalyzed borylation of haloarenes **1** with diboron **2** is a good and widely-used method for preparing arylboronates. However, the borylation of highly congested bromoarenes, such as **1a**, have required an expensive and limitedly available catalyst to produce the arylboronate **3a** in high yields.¹⁾ In this presentation, we will disclose a readily available and cost effective catalyst for the synthesis of various *o,o*-disubstituted boronates.²⁾

A mixture of 2,4,6-tri(isopropyl)phenyl bromide (**1a**), **2**, and Cs₂CO₃ in EtOAc was heated at 80 °C in the presence of Pd(OAc)₂–tris(*p*-methoxyphenyl)phosphine (**L1**) catalyst, giving the desired product **3a** in 82% yield. In the reaction, the efficient C–B bond formation is affected by choice of the base as well as the phosphine ligand. The optimized reaction condition is applicable to preparation of a broad range of *o,o*-disubstituted arylboronates. The sterically-demanding borylation was compatible with some reactive functional groups, *e.g.* cyano, carboxylate, carbamate. With the Pd(OAc)₂–**L1** catalyst, 9-bromoanthracene (**1e**) was transformed into anthraceneboronate **3e** in high yields. Furthermore, the present method was applicable to the double borylation of dibromobenzenes.



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