

Iridium Catalyzed Hydrosilane-Directed ortho-Borylation

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A direct route to aryl boronic esters has been developed that occurs by metal catalyzed functionalization of aromatic C-H bonds with bis(pinacolato)diboron (B_2pin_2). The most efficient catalyst for this transformation is generated from the combination of 4,4'-di-*tert*-butylbipyridine (dtbpy) and $[Ir(cod)Cl]_2$. In general, the regioselectivity of the catalytic borylation of arenes is governed by steric factors; functionalization occurs at the least hindered position of the arene ring. We now describe a strategy to overcome this bias that makes use of a new substituent for ortho-functionalization. We show that arenes containing hydrosilyl substituents undergo ortho-borylation. This transformation is amenable to a one-pot directed borylation of free phenols and mono-protected anilines to form amino- and alkoxy-substituted organoboron derivatives.

