Substrate Directed ortho-C-H Borylation of Benzylic Amines

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Metal-catalyzed borylation reactions have received significant attention over the past several decades due to the versatility of the C–B bond in organic synthesis. Complex synthetic targets can be accessed by incorporating boron substituents into organic frameworks. Iridium-catalyzed ortho-borylation of benzylic amines will be described, where the catalysts have been modified using diamine ligands to direct the C–H borylation event to the ortho position of the benzylic amine. This directing effect is in opposition to the inherent selectivity of substituted arenes and results in access to valuable substrates that are precursors to known glucose sensors. The acidic N–H bond of the diamine ligand was expected to be responsible for selective ortho C–H borylation through hydrogen bonding between the amine substrate and the acidic ligand-based N–H bond. Recent experiments suggest that the amine coordinates to the Ir catalyst to promote the directing effect. The C–H borylation products have been isolated by addition of KHF₂, to provide the corresponding trifluoroborate salt in good yields.

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