

Cyanation of Arenes via Ir-Catalyzed C–H Borylation

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A method to conduct the one-pot meta cyanation of arenes by iridium-catalyzed C–H borylation and copper-mediated cyanation of the resulting pinacol arylboronate esters is reported. This methodology relies on new $\text{Cu}(\text{NO}_3)_2$ -mediated cyanation of pinacol arylboronate esters, and conditions for this new transformation are reported. Conditions for the copper-mediated cyanation of arylboronic acids are also described. By the resulting sequence of borylation and cyanation, 1,3-disubstituted and 1,2,3-trisubstituted arenes and heteroarenes containing halide, ketone, ester, amide, and protected alcohol functionalities are converted to the corresponding meta-substituted aryl nitriles in 51–67% yield. The utility of this methodology is demonstrated through the conversion of a protected 2,6-disubstituted phenol to 4-cyano-2,6-dimethylphenol, which is an intermediate in the synthesis of the pharmaceutical etravirine.

