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Catalytic, Transition Metal-Free Semireduction of Propiolamide Derivatives: Scope and Mechanistic Investigation

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We report a transition-metal-free trans-selective semireduction of alkynes with pinacolborane and catalytic potassium tert-butoxide. A variety of 3-substituted primary and secondary propiolamides, including an analog of FK866, a potent nicotinamide mononucleotide adenyltransferase (NMNAT) inhibitor, are reduced to the corresponding (E)-3-substituted acrylamide derivatives in up to 99% yield with >99:1 E/Z selectivity. Mechanistic studies suggest that an activated Lewis acid–base complex transfers a hydride to the α-carbon followed by rapid protonation in a trans fashion.

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