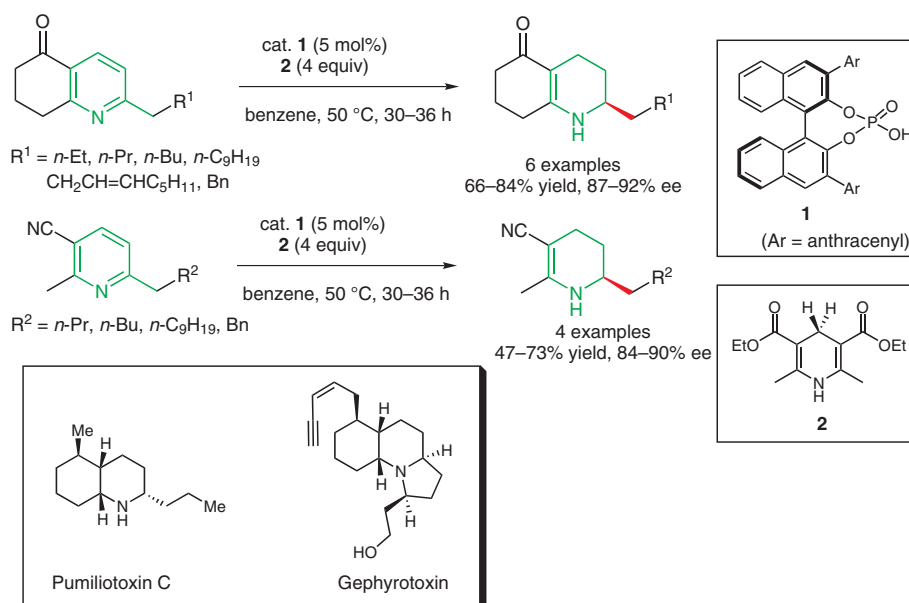


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Organocatalytic Enantioselective Reduction of Pyridines

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Enantioselective Reduction of Pyridines via Brønsted Acid Catalysis



Significance: An organocatalytic enantioselective reduction of 2-substituted simple and fused pyridines is reported. The reaction is designed to undergo catalytic protonation by Brønsted acid **1**, followed by reduction by hydride transfer from the Hantzsch dihydropyridine **2**. The hexahydroquinolinone and tetrahydropyridine products are formed in moderate to good yields with good enantioselectivities. The scope of the reaction was modestly investigated.

Comment: The chiral piperidine moiety is prevalent in the large class of piperidine plant and animal natural products, for example the dendrobatid alkaloid pumiliotoxin C, a noncompetitive blocker of nicotinic receptors (see book and review below). A previous synthesis of hexahydroquinolinones involves a multistep process and use of stoichiometric amounts of a chiral auxiliary (H. M. Sklenicka et al. *J. Am. Chem. Soc.* **2002**, *124*, 10435). The present methodology establishes the first direct and efficient organocatalytic route for the synthesis of such compounds.

Book: J. W. Daly, H. M. Garraffo, T. F. Spande In *Alkaloids: Chemical and Biological Perspectives*, Vol. 13; S. W. Pelletier, Ed.; Pergamon: New York, **1999**, 1-161.

Review: J. W. Daly, T. F. Spande, H. M. Garraffo *J. Nat. Prod.* **2005**, *68*, 1556.

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