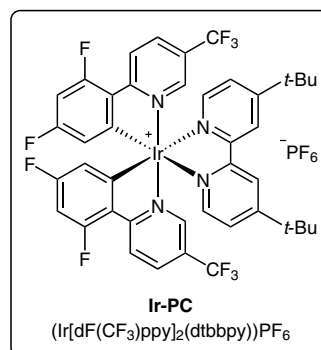
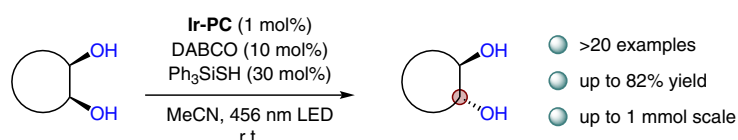
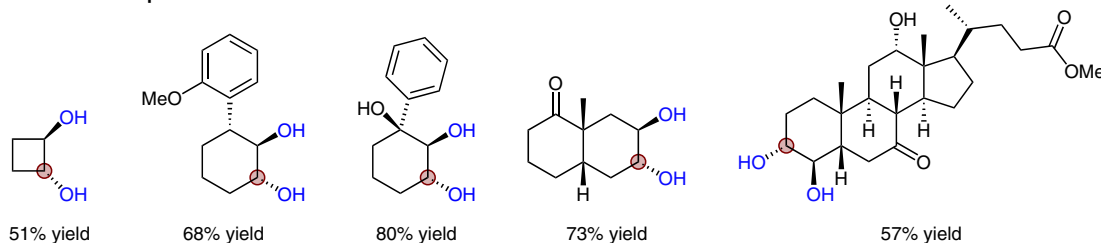


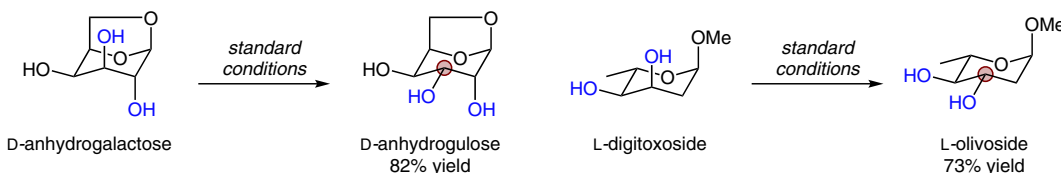
Thermodynamic Control Enables *trans*-Selective Isomerization of Vicinal Diols via Iridium Photocatalysis



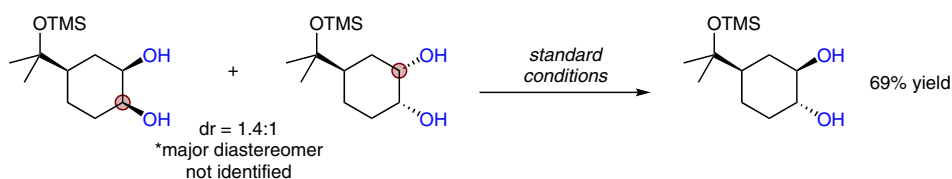
Selected examples:



Carbohydrate-derived examples:



Example from mixture of *cis*-diols:



Significance: The Wendlandt group reports a selective catalytic isomerization of *cis*-1,2-diols to *trans*-diequatorial-1,2-diols via photoredox catalysis. The use of Ph₃SiSH was found to be essential, as the nature of the silanethiol catalyst influenced the product distribution of the two isomers. The reaction was amenable to a variety of 1,2-diols and as well as mixtures of diastereomers, giving a single product isomer.

Comment: A series of mechanistic experiments revealed that, under the optimal conditions, the H-atom abstraction and donation steps were mediated by the Ph₃SiSH catalyst. The amine additive served as a base, not as a H-atom abstractor. The authors conclude that since the H-atom abstraction process is reversible, the equilibrium ratio represents the thermodynamic product distribution of the isomers.