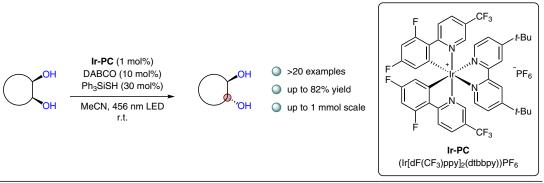
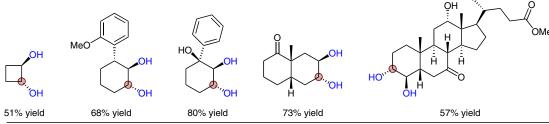
Y.-A. ZHANG, X. GU, A. E. WENDLANDT* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, USA)

A Change from Kinetic to Thermodynamic Control Enables *trans*-Selective Stereochemical Editing of Vicinal Diols *J. Am. Chem. Soc.* **2022**, *144*, 599–605, DOI: 10.1021/jacs.1c11902.

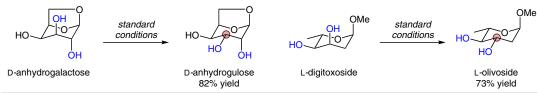
Thermodynamic Control Enables *trans*-Selective Isomerization of Vicinal Diols via Iridium Photocatalysis



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-diequitorial-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.

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Category

Metals in Synthesis

Key words

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thermodynamic control

trans selectivity

