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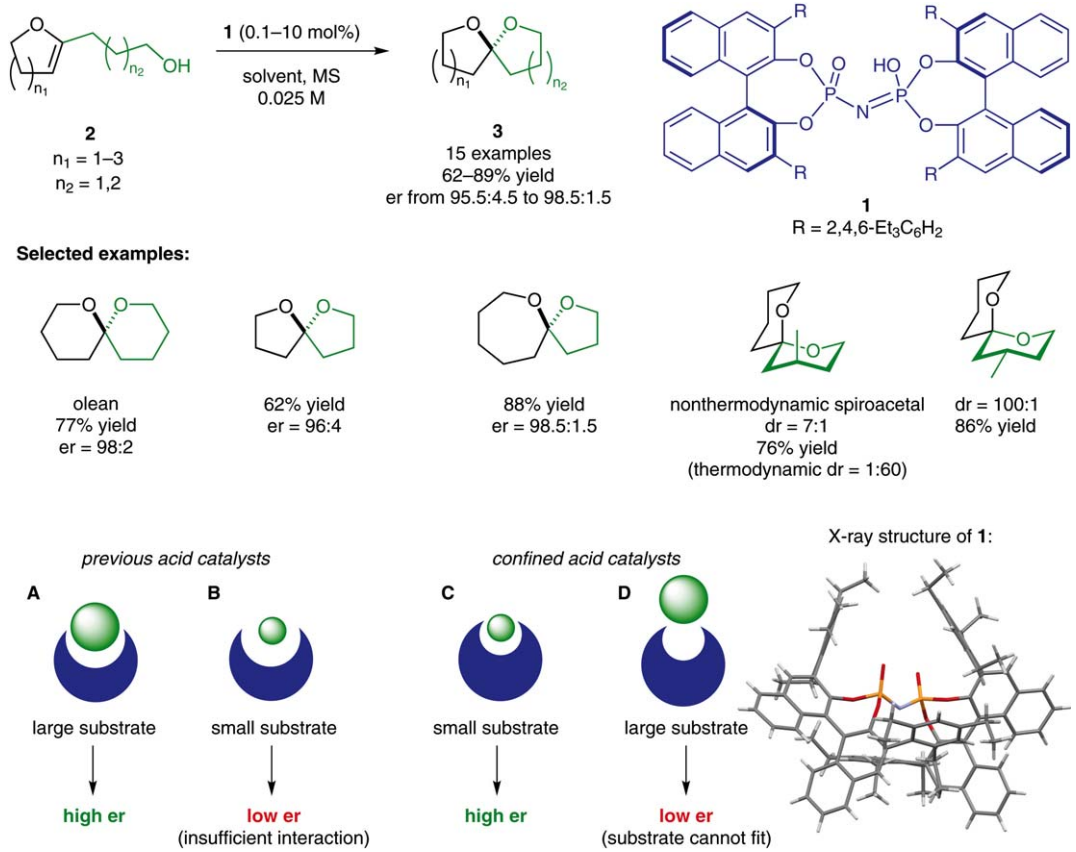
Asymmetric Spiroacetalization Catalysed by Confined Brønsted Acids
Nature **2012**, *483*, 315–319.

Category
Organo- and Biocatalysis

Key words
acetalization
confined Brønsted acids
spiroacetals

Confined Brønsted Acid Catalysis



Significance: Novel confined Brønsted acid catalysts based on a C_2-symmetric imidodiphosphoric acid motif were designed and synthesized. These catalysts possess an extremely sterically demanding chiral microenvironment. With catalyst **1**, an asymmetric spiroacetalization of hydroxyenol ethers **2** to give small spiroacetals **3** has been developed. The spiroacetalization also provides a catalyst-controlled access to nonthermodynamic as well as thermodynamic spiroacetals. Importantly, to access imidodiphosphoric acids **1**, only a single additional step is required compared to the corresponding phosphoric acids.

Comment: Despite numerous reports on Brønsted acid catalysis, particularly with phosphoric acids, reactions of small molecules still present a challenge. As shown schematically above, phosphoric acids typically give good results with relatively large substrates (**A**), while low enantioselectivity is obtained with small substrates due to insufficient interactions with the catalyst (**B**), and a resulting diversity of transition states that can be accommodated. In the case of confined acids, high enantioselectivity can be obtained with small substrates (**C**). In contrast, such catalysts may have difficulties in handling relatively large substrates, which may not fit into the catalytic cavity (**D**).

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Synfacts 2012, 8(6), 0671 Published online: 16.05.2012
DOI: 10.1055/s-0031-1291031; **Reg-No.:** B03912SF