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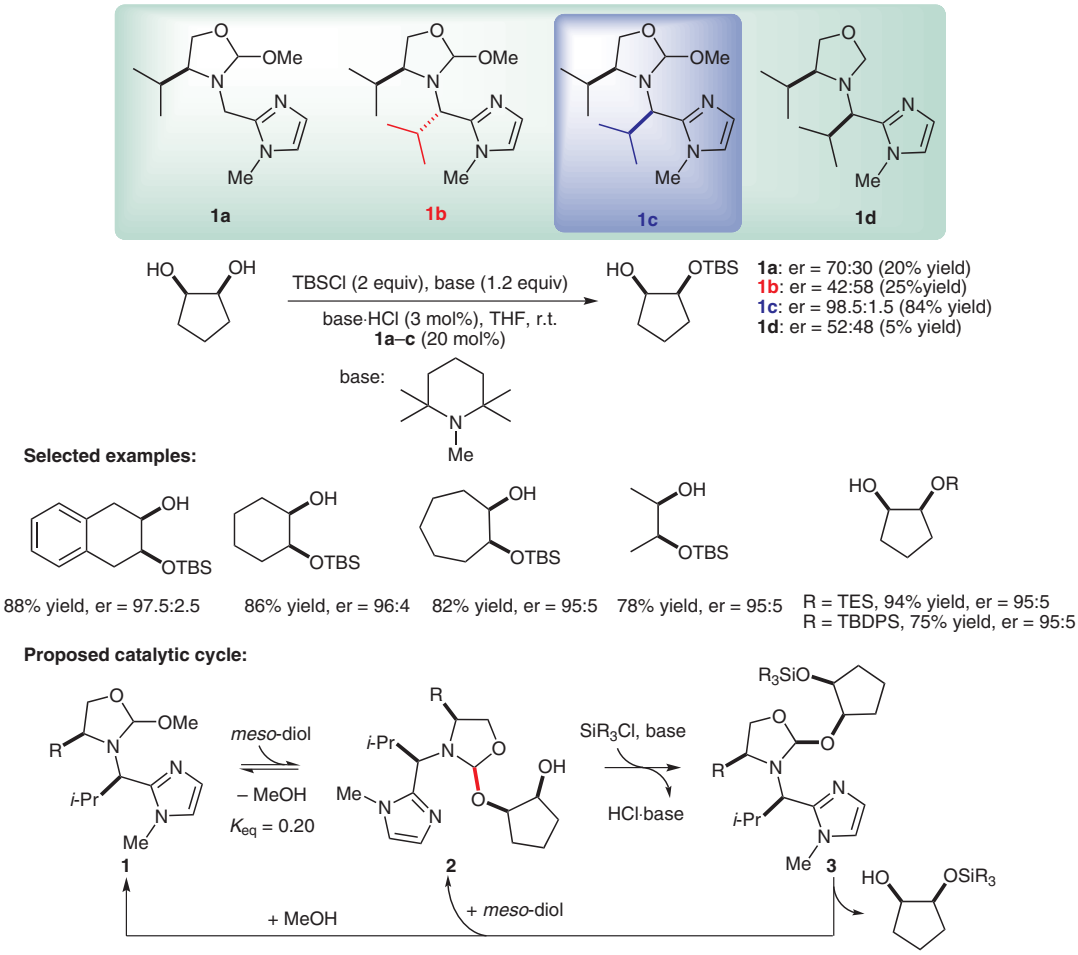
Scaffolding Catalysts: Highly Enantioselective Desymmetrization Reactions
Angew. Chem. Int. Ed. **2011**, DOI: 10.1002/anie.201103470.

Desymmetrization of *meso*-Diols via Covalent Substrate Binding Catalysis



Significance: The desymmetrization of *meso*-diols is a highly useful asymmetric transformation since it can provide synthetically valuable intermediates with theoretically quantitative yields. The authors utilized catalysts **1** as a substrate-binding module as well as a silyl chloride activator. High enantioselectivity was obtained for cyclic and acyclic *meso*-diols (er up to 97.5:2.5). Also, the substituent adjacent to the imidazole group affects the enantioselectivity dramatically and displays strong match/mismatch effects on the enantioselectivity.

Comment: The presented method features a highly elegant substrate activation mode. As a part of the proposed catalytic cycle, the authors detected a reversible covalent bond equilibrium between catalyst and diol adduct **2** (K_{eq} = 0.20). Also, from the X-ray crystal structure obtained with 4-bromobenzyl alcohol and **1c**, the configuration of adduct **2** was assigned as depicted in the Scheme (highlighted in red), although the observed diastereomeric ratio of **2** was low (dr = 60:40). Further detailed investigations on the catalytic intermediates (**2** or **3**) are anticipated.

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Synfacts 2011, 9, 1013-1013 Published online: 19.08.2011
DOI: 10.1055/s-0030-1260922; **Reg-No.:** B08711SF