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.