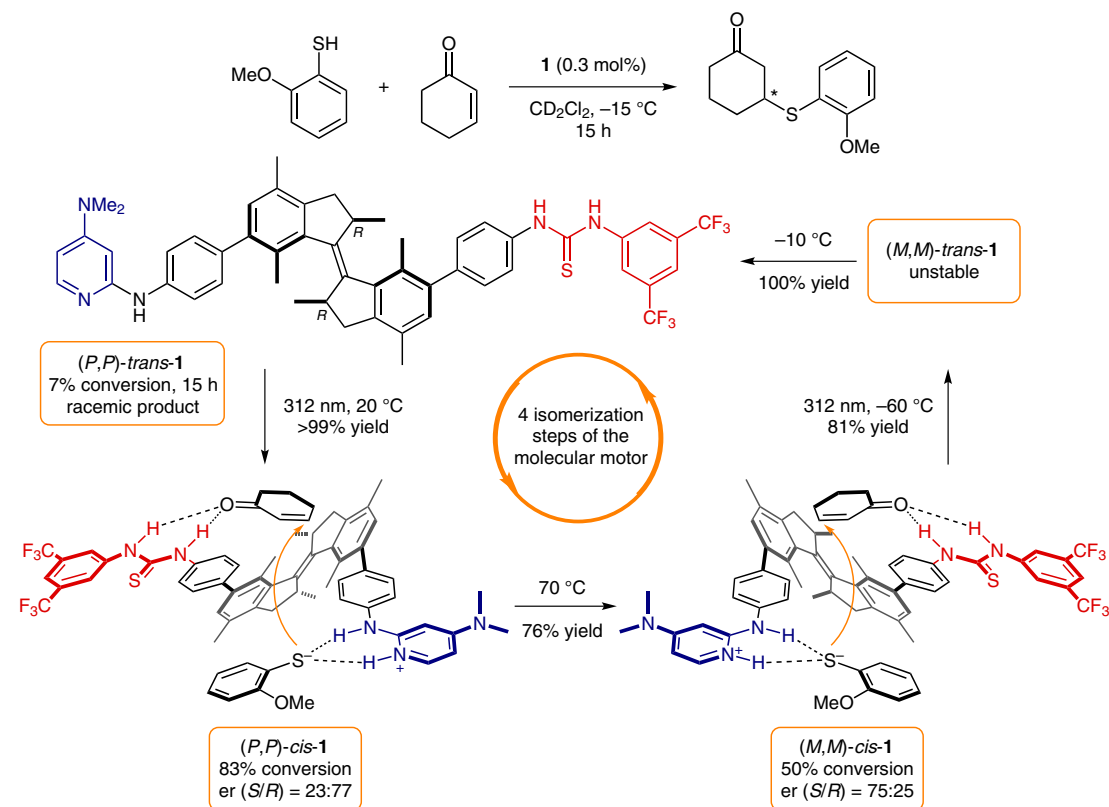


Control of Reaction Enantioselectivity with a Molecular Motor Switch



Significance: Wang and Feringa describe the use of molecular motor **1** as a chiral switchable organocatalyst. Molecular motor **1** decorated with Brønsted acidic thiourea and Brønsted basic DMAP groups can be driven through an unidirectional rotatory cycle with a series of two photoisomerizations and two thermal isomerizations. The rotation of the molecular motor provides the means to control the relative orientations of the two catalytic moieties. It was demonstrated that different preformed isomers of the molecular motor enable the switching of the enantioselectivity of the addition of *o*-methoxythiophenol to cyclohexanone. The (*R*)- and (*S*)-enriched or racemic products can be obtained depending on the rotational state of the catalyst.

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Comment: The Feringa group has previously demonstrated that the chiral crowded alkene moiety in **1** is capable of performing a unidirectional motion through a series of four isomerizations (*Org. Biomol. Chem.* **2008**, *6*, 507). In the current paper, three distinct isomers of alkene **1** demonstrated different enantioselectivities for a well-established sulfa-Michael reaction (for example, see: N. K. Rana, S. Selvakumar, V. K. Singh *J. Org. Chem.* **2010**, *75*, 2089). However, full rotation of the ‘molecular motor’ could not be achieved in situ. Three isomers of the alkene had to be pre-prepared and only the ‘switching on’ step [(*P,P*)-*trans-1* to (*P,P*)-*cis-1*] was demonstrated to be compatible with sulfa-Michael reaction conditions. Although an interesting catalyst design is presented, its true potential has yet to be revealed.