

Catalytic, Enantioselective Thiooxyfunctionalization of Alkenes

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Catalytic, enantioselective, vicinal thiooxyfunctionalization of alkenes has been accomplished with the chiral, BINAM-P(V)-selenophosphoramidate Lewis base **1**. Activation of S(II)-electrophile **2** by the catalyst (in combination with a Brønsted acid) generates a chiral sulfenylating agent that reacts with olefins to form enantioenriched, vicinally-disubstituted products including 2,3-disubstituted tetrahydropyrans and tetrahydrofurans as well as their benzo-fused counterparts. The reaction proceeds by the enantioselective construction of a thiiranium ion that is stereospecifically captured by an oxygen nucleophile either intra- or intermolecularly. High enantioselectivity is observed for *trans*-alkene substrates. The configurational stability of the intermediate thiiranium ions under the experimental conditions is demonstrated. For stabilized thiiranium ions, capture is reversible, and thermodynamic equilibration between *endo* and *exo* capture products is observed. Kinetic studies show that the reaction is first order in substrate, first order in catalyst and zeroth order in electrophile. A buffering effect of the nucleophile leads to a complicated order for the acid component.

