Catalytic Enantioselective Thiofunctionalization of Olefins

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Catalytic enantioselective vicinal thiofunctionalization of alkenes has been accomplished with the chiral BINAM-P(V)-selenophosphoramide Lewis base **1**. Activation of S(II)-electrophile **2** by the catalyst generates a chiral sulfenylating agent that reacts with olefins to form enantioenriched, vicinally disubstituted products including 2,3-disubstituted pyrans and furans. The reaction proceeds via the enantioselective construction of thiiranium ions that are stereospecifically captured by a heteroatomic nucleophile either intra- or intermolecularly.