## Lewis Base-catalyzed Enantioselective Sulfenocyclization of Polyenes

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The application of Lewis base catalysis in organic synthesis is a topic of continued interest in our laboratories. The paradigm of using Lewis bases to activate Lewis acids by enhancing their electrophilicity has been utilized for sulfenofunctionalization of a wide range of unactivated olefins. The asymmetric variant using a chiral Lewis base proceeds via enantioselective generation of a thiiranium ion and affords complex products with a high degree of stereochemical control. We envisioned employing chiral Lewis base catalysis for the sulfenocyclization of simple linear achiral polyenes to quickly access highly complex polycyclic molecules containing several stereogenic centers. After screening conditions, hexafluoroisopropanol (HFIP) was determined to be an excellent solvent for this catalytic, enantioselective polyene cyclization. In addition to providing the desired polycyclic products in good yields, the low $pK_a$ of HFIP also obviates the usual need for stoichiometric amounts of strong acid additives in sulfenofunctionalization reactions. A wide range of electron-neutral to electron-rich homogeranylarenes successfully cyclized to the tricyclic products with consistently good yields (63-79%) and high enantiomeric ratios (>90:10). Additionally, *ortho*-geranylphenols cyclize under the same conditions, with the phenolic oxygen atom serving as the terminal nucleophile, with similar yields and enantioselectivities. Advantages of this method include (1) low catalyst loadings, (2) complete cyclizations, (3) simple, non-engineered substrates, and (4) installation of a useful functional handle introduced by the initiation event. The resulting thioether moiety may be easily cleaved or otherwise transformed to install carbon and oxygen functionality at this position, which has helped us achieve concise, enantioselective syntheses of two natural products, ferruginol and hinokiol.