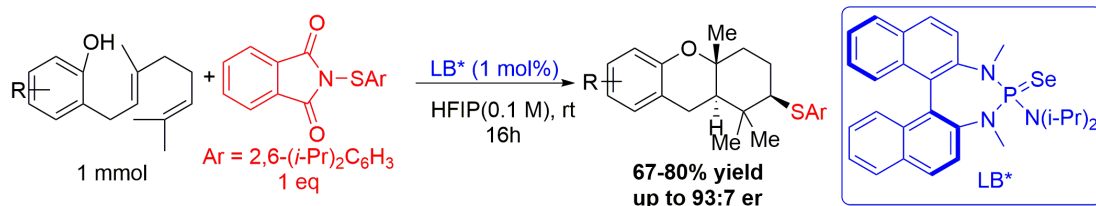


Chiral Lewis Base Catalyzed Thiiranium-ion-induced Polyene Cyclization

Zhonglin Tao and Scott E. Denmark

Polyene cyclization has proven to be one of the most straightforward methods to construct diverse polycyclic skeletons, such as steroids and terpenoidal natural products. Inspired by Nature, synthetic chemists have developed approaches to realize such transformations. Most importantly, catalytic, enantioselective polyene cyclization reactions have attracted lot of attention. Nevertheless, there are some drawbacks to these reports, such as low functional group compatibilities due to strong acid conditions or low manipulation ability of the cyclized products. Here we describe a thiiranium ion-induced polyene cyclization with a selenophosphoramidate catalyst under mild conditions. Both homogeranylbenzenes and geranylphenols are compatible substrates, delivering the cyclized products in good yields with high enantioselectivities. Several manipulations of the thioether are also described, showing the diversity of polyene cyclization products which may be accessed.



Metal Organic Nanoparticles for Intracellular Catalysis

Edzna S. Garcia and Steven C. Zimmerman

Intracellular transition metal catalysis is a relatively new area of research. In recent years intracellular metal catalysis has been used for the modification of biomolecules and the uncaging of molecules. Thus, we may envision that these biorthogonal metal catalyzed reactions open the possibility for targeted intracellular drug synthesis if the required precursors and catalyst are selectively delivered to a specific site. Recently, our group reported a metal organic nanoparticle (MONP) containing copper which showed efficient catalytic activity for alkyne-azide click chemistry in aqueous solution. Also, this Cu-MONP was shown to enter cells and perform intracellular click reactions. We are working on expanding this novel approach using other metals for intracellular catalysis under mild conditions. For example, Pd-MONPs for the Suzuki-Miyaura and Sonogashira cross-coupling reactions and Ru-MONPs for uncaging reactions are being developed.