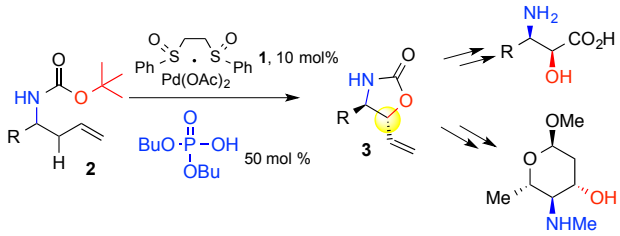
N-Boc Amines to Oxazolidinones via Pd(II)/Bis-sulfoxide / Brønsted Acid Co-catalyzed Allylic C-H Oxidation

Thomas J. Osberger and M. Christina White

A Pd(II)/bis-sulfoxide/Brønsted acid catalyzed allylic C—H oxidation reaction for the synthesis of *anti*-oxazolidinones from simple *N*-Boc amines is reported. A range of oxazolidinones are furnished in good yields (avg. 63%) and excellent diastereoselectivities (avg. 15:1) to furnish products with different regiochemistry from those previously obtained using allylic C—H amination reactions. We present applications of this method to the synthesis of hydroxyamino acids, individually and as a late-state strategy for the formation of amino alcohol motifs in peptide settings, as well as the synthesis of a biologically relevant amino sugar. This process marks the first use of an aprotic, non-acidic nucleophile in a Pd(II) / sulfoxide catalyzed allylic C-H oxidation. Mechanistic studies suggest the role of the phosphoric acid is to furnish a Pd(II)bis-sulfoxide phosphate catalyst that promotes allylic C—H cleavage and π-allylPd functionalization with a weak oxygen nucleophile, and to promote catalyst regeneration.



Streptomonomicin: a Hydrophobic Lasso Peptide Antibiotic from the Halophilic Bacterium *Streptomonospora alba*

Jonathan I. Tietz and Douglas A. Mitchell

Increasing rates of antibiotic resistance and the burden of natural product rediscovery necessitate the development of strategies to accelerate secondary metabolite discovery. One such strategy is to investigate "neglected" organisms: those without sequenced genomes or characterized metabolism. Herein we report the characterization of streptomonomicin, the first natural product isolated from the neglected halophilic bacterial genus *Streptomonospora*. Streptomonomicin is an unusually hydrophobic peptide that forms a lasso structure wherein a C-terminal tail is threaded through an N-terminal ring, endowing conformational restraints to the molecule. Bacteria resistant to streptomonomicin harbor mutations to WalR, a two-component signaling response regulator involved in cell wall metabolism, and exhibit striking phenotypic defects. Complete genome sequencing of *Streptomonospora alba* indicates that its growing genus has prolific and diverse biosynthetic potential.