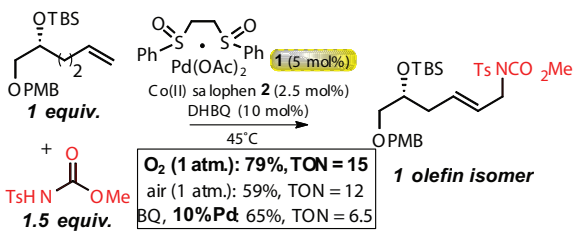
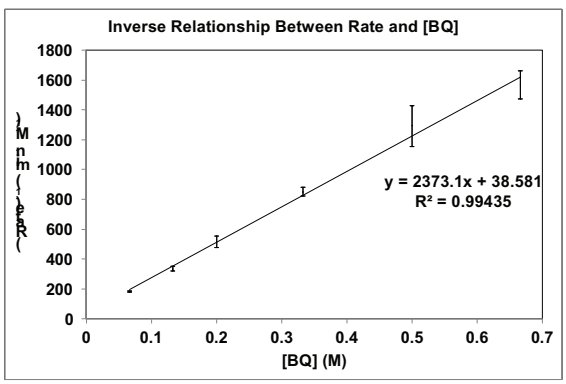
## Aerobic Linear Allylic C-H Amination: Overcoming Benzoquinone Inhibition

Christopher Pattillo, Iulia Strambeanu, Pilar Callerja, Nicolaas Vermeulen, Tomokazu Mizuno and M. Christina White

A Pd(II)-catalyzed linear allylic C—H amination reaction is reported which employs molecular oxygen as the stoichiometric oxidant. This reaction allows for the allylic amination of a variety of terminal olefins using only 2.5-5 mol% of Pd(II) catalyst under mild conditions of temperature and O2 pressure. The elimination of benzoquinone as the stoichiometric oxidant has resulted in an efficient reaction affording higher or comparable yields of aminated product as compared to previous systems operating at higher Pd(II) catalyst loadings (10 mol%) and elevated concentrations of BQ. Experiments aimed at understanding this effect have revealed an inhibitory effect of BQ on both overall reaction yields and the rate of product formation. Kinetic experiments have demonstrated that an increase in concentration of benzoquinone leads to a progressive decrease in reaction rate. At elevated concentrations, BQ may bind to Pd(II) in a manner that competes with coordination of the bis-sulfoxide ligand, which is required for C—H cleavage and productive reactivity.




## RiPPs Bioengineering Results in a New Class of Hybrid Natural Products

Nidhi Kakkar and Wilfred A. van der Donk

Ribosomally synthesized and post-translationally modified peptides (RiPPs) are a rapidly expanding class of natural products. Despite covering highly diverse sequences, structural and functional spaces, these natural products share a common feature in their biosynthetic pathways: the N-terminal part of the precursor peptide guides the biosynthetic enzymes towards the residues of the C-terminus that undergo modifications. These modifications bestow on the peptide higher proteolytic stability and bioactivities against a range of pathogens. Utilizing this simplistic biosynthetic platform and the recent advances in identifying the sequence requirements for precursor peptide recognition, we developed a strategy to bring together biosynthetic enzymes from different RIPP biosynthetic pathways, which don't act together in nature, and created a new class of hybrid natural products that further pushes the structural diversity of the RIPPs universe and can potentially result in better and/or unique bioactivities.