

ORGANIC SEMINAR

Ni-catalyzed Enantioselective Carbene and Vinylidene Transfer Reactions and Their Synthetic Applications

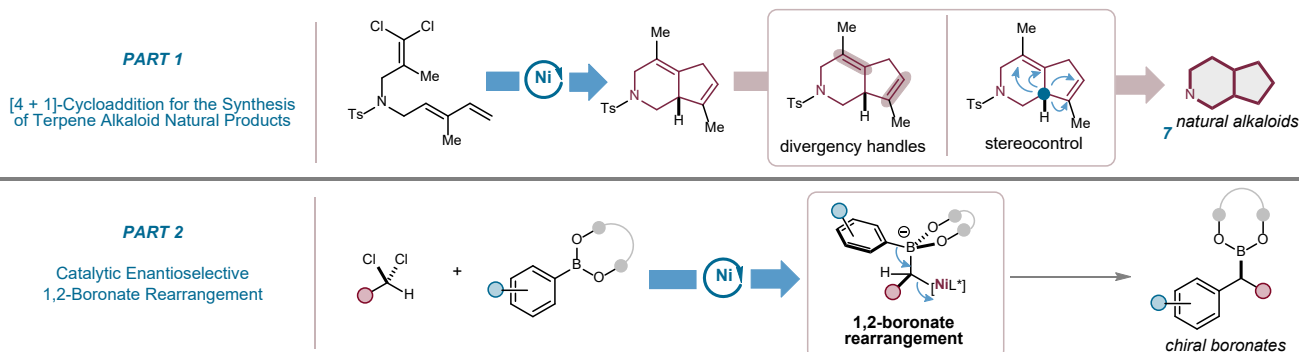
Wen Xiu

Graduate Student, Uyeda Group
Purdue University



First-row transition-metal catalyzed reductive carbene and vinylidene transfer reactions are emerging alternatives to traditional redox-neutral carbene transfer reactions based on diazo compounds. Our group has developed a Ni-catalyzed enantioselective [4 + 1]-cycloaddition between 1,1-dichloroalkenes and dienes. Using this method, we show that the entirety of a [4.3.0]-azabicyclic structure, a communal skeleton for iridoid alkaloids, can be constructed. This cycloadduct intermediate can then be diversified into 7 members of this natural product family by regioselective and stereoselective manipulation of the olefins generated. The asymmetric syntheses require only 8–11 chemical steps, most of which are the shortest syntheses to date.

gem-Dichloroalkanes can be activated by a nickel catalyst to generate a nucleophilic carbene species. A subsequent catalyst-controlled enantioselective addition to a boron compound generates a chiral boronate species. A stereospecific 1,2-boronate rearrangement then takes place to form highly valuable chiral boronates, which can be used in a variety of functional group transformation. This is the first example of catalytic enantioselective Matteson-type reaction without stoichiometric pyrophoric base.



Tuesday, November 26, 2024



4:30 pm



WTHR 104