University of Minnesota
Driven to Discover℠

Department of Chemistry

Seminar

9:45 a.m. Tuesday, December 16, 2014 • 331 Smith Hall

Post-Doctoral Research Associate

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Enantioselective Carbon-Carbon Bond Formation via Nucleophilic and Electrophilic Allylation

Abstract

Enantioselective carbonyl addition using allylmetal reagents is an important transformation to synthesize acyclic molecules with contiguous stereocenters. Compared to the vast majority of conventional carbonyl allylation methods that produce homoallylic alcohols with a terminal olefin unit, allylation with enantioenriched, bifunctional allylboron reagents represents an important advance in allylmetal chemistry. Allylborations of aldehydes with these reagents provide enantioenriched homoallylic alcohols with a functionalized olefin unit that enables subsequent C-C bond-forming reaction without functional group transformation. However, enantioselective synthesis of such reagents has been challenging and remains underdeveloped. The first part of the talk will focus on the development and synthetic applications of enantioenriched, bifunctional allylboron reagents. We have developed a convenient method to generate a variety of enantioenriched, bifunctional allylboron reagents using asymmetric allene hydroboration. The synthetic applications of these reagents are demonstrated by the total synthesis of several polyketide natural products.

Iridium-catalyzed asymmetric allylic substitution is a useful method to access enantioenriched molecules with high branched selectivity. Compared to the well-developed asymmetric allylation utilizing heteroatom nucleophiles, carbon nucleophiles that have been studied for this transformation are largely limited to stabilized enolates. The second part of the talk will focus on the development of Ir-catalyzed asymmetric allylic substitutions using unstabilized enolates as the nucleophiles. These methods are highly useful in the preparation of natural products and pharmaceutical agents as demonstrated by the syntheses of TEI-9826 and Toviaz.

Host: Christopher Douglas
Refreshments will be served prior to the seminar.