



CHEMISTRY SEMINAR 291

Take a CA_HB Direct to Chiral Boronic Esters, But Don't Interrupt?

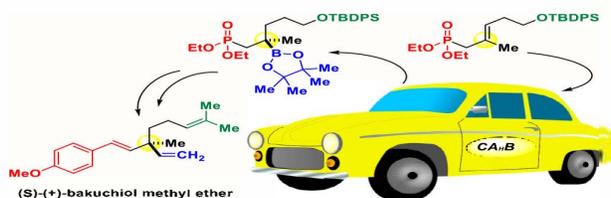
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Time: 3:00 PM
Location: COB 267

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ABSTRACT

Catalytic Asymmetric Hydroboration (CAHB) has been around for a long time, and many outstanding research groups have contributed to developing this (fiendishly complex) catalyzed counterpart of the classic stoichiometric reaction. Now, as new methods rapidly evolve using chiral secondary and tertiary boronic esters for stereospecific carbon-carbon bond construction, the development of new catalyst systems and the exploration of new substrates for CAHB are enjoying renewed interest. Recent work in the Takacs group has focused on developing CAHBs, mostly rhodium-catalyzed CAHBs, of substrates capable of two-point binding to the metal center and leading to functionalized chiral boronic esters. The nature of the alkene substitution pattern plays a key role in the observed regioselectivity and sense of pi-facial discrimination. The observation of unusual Markovnikov regioselectivity leading to chiral tertiary boronic esters is among the important recent advances in the research. For example, we recently published a simple, in situ-generated, chiral rhodium catalyst for which methylidene and trisubstituted alkene substrates form chiral tertiary boronic esters (up to 87% yield and 96:4 enantiomer ratio (er)) via oxime-directed CAHB. Subsequent C-C coupling is used to form a quaternary all carbon stereocenter, while other transformations lead to chiral diols, O-substituted hydroxylamines, and isoxazolines. Similarly, phosphonate-derived CAHB affords new, bifunctional chiral tertiary boronic ester synthons suitable for further elaboration. Recently, it has been discovered that H₂ will “hitch a ride” on the CAHB catalyst interrupting hydroboration to arrive at efficient Catalytic Asymmetric Hydrogenation (CAH) of tetrasubstituted alkenes.



BIO:

Dr. Takacs received his bachelor's degree from Rutgers University (1976) where he carried out undergraduate research under the direction of Dr. Paul Hudrlik and his doctorate from Caltech (1981) where he studied under Dr. David A. Evans. After postdoctoral studies under Dr. Albert Eschenmoser at ETH-Zurich (1981-82), he was appointed Assistant Professor of Chemistry at the University of Utah (1982). He moved to the University of Nebraska-Lincoln in 1988 where he is currently Charles J. Mach University Professor in Chemistry. Dr. Takacs received the UNL College of Arts and Science Outstanding Research and Creative Achievement Award in the Sciences, served as Chemistry Department Chair (2007-2013) and is currently the Director of the interdisciplinary Nebraska Center for Integrated Studies of Biomolecular Communication (2016-present). Along with numerous undergraduate coworkers, more than 65 graduate students and postdocs have trained in the Takacs labs.