Catalytic Asymmetric Synthesis Using Feedstocks

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Abstract

One of the major challenges facing organic synthesis in 21st century is the utilization of abundantly available carbon sources for fine chemical synthesis. The dual problems of activation of thermodynamically stable precursors and their stereoselective incorporation pose new challenges, solutions of which may have broader implications in homogeneous catalysis, and, at a practical level, how we synthesize/manufacture chemical intermediates.

This talk will provide a brief introduction to basics of asymmetric catalysis and a key reaction developed in our laboratories viz., asymmetric hydrovinylation reaction followed by applications of the asymmetric hydrovinylation reactions in synthesis. Substrates such as vinylarenes, cyclic and acyclic 1,3-dienes and strained alkenes undergo efficient heterodimerization with ethylene under catalysis by complexes of Ni, Co and Ru. Yields up to 99% can be realized for several of these substrates. Using chiral phospholanes, phosphinites and finely tuned phosphoramidites as ligands, enantioselectivities greater than 95% enantiomeric excess can be obtained for several substrates. Examples of how ligand tuning, properties of the counter ions and reaction conditions affect the yields and selectivities of these reactions will be illustrated. One major application of this chemistry is for the installation of an exocyclic stereocenter using a 1-vinylcycloalkene motif. These discoveries open expeditious routes to several biologically relevant classes of compounds including 2-arylpropionic acids, 1-arylethyl amines, steroid derivatives with uncommon D-ring side-chains, helioporins, pseudopterosins and analogs, and pyrrolidinoindolines such as physostigmine and phenserine, which contain all-carbon benzylic quaternary centers.

[Some leading references: (i) 'Hydrovinylation Reactions in Organic Synthesis', *Comprehensive Organic Synthesis*, *2nd edition*, Vol. 5, Oxford: Elsevier; 2014. pp. 1582-1620. DOI: 10.1016/B978-0-08-097742-3.00533-4. (ii) *Chem. Sci.* **2015**, *6*, 3994. DOI: 10.1039/c5sc00929d. (iii) *J. Am. Chem. Soc.* **2015**, 137, 14268. DOI: 10.1021/jacs.5b10364]

Biography

RajanBabu had his early education in India, at Kerala University and The Indian Institute of Technology (Madras) respectively. He obtained a Ph. D. degree from The Ohio State University working with Professor Harold Shechter, and was a postdoctoral fellow at Harvard University with the late Professor R. B. Woodward. He then joined the Research Staff of DuPont Central Research and Development becoming a Research Fellow in 1993. He returned to Ohio State as a Professor of Chemistry in 1995 and currently holds the Kimberly Chair. He has published over 150 publications in leading journals *including Science, J. Am. Chem. Soc., and Angew. Chem. Int. Ed.* and 13 US patents. His research interests are in New Methods for Stereoselective Synthesis, Green Chemistry, Enantioselective Catalysis, Multi-component Cyclization methods, Free Radical Chemistry, Natural Product Synthesis.