# **Plenary Lecture**

57th Annual Convention of Chemists (ACC) - Indian Chemical Society (ICS)
Recent Trends in Chemical Sciences (RTCS 2020)

# Stereoselective Functionalization of Unsaturated Hydrocarbons via Pericyclic Reactions

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### Abstract:

The Tambar Group is interested in developing catalytic stereoselective reactions for the functionalization of unsaturated hydrocarbons. We have developed a catalytic enantioselective allylic amination of unactivated alkenes via a [2,3]-rearrangement. In this method, a diimidosulfur reagent serves as the source of nitrogen, and it reacts selectively with terminal alkenes through a hetero-ene reaction. The resulting ene adduct undergoes a Pd-catalyzed enantioselective [2,3]-rearrangement to generate chiral amines in high enantiomeric excess. Based on this chemistry, we have developed a copper-catalyzed enantioselective allylic alkylation of unactivated alkenes to generate internal alkenes with high regioselectivity and Eselectivity. We have also discovered regioselective and diastereoselective aminoarylations and aminothiolations of 1,3-dienes. These results represent a general strategy for functionalizing unsaturated hydrocarbons with aromatic, aliphatic, and vinyl Grignard reagents. As an extension of our approach to the catalytic allylic functionalization of unactivated terminal alkenes, we recently pursued the more challenging problem of catalytic asymmetric allylic functionalization of *internal* alkenes. We have developed an enantioselective, regioselective, and E/Z selective allylic oxidation of unactivated internal alkenes via a catalytic asymmetric hetero-ene reaction with an imido-sulfur oxidant.

### Figure:

$$\begin{array}{c} \text{CF}_{3} \\ \text{Enantioselective} \\ \text{Catalysis} \\ \text{Me} \\ \text{OS}_{N=S} \\ \text{Me} \\ \text{Pericyclic Reactions} \\ \end{array}$$

## **References and Notes:**

- 1. Sharique, M.; Tambar. U. K. J. Am. Chem. Soc. 2019, 141, 17305-17313.
- 2. Bayeh, L.; Le, P. Q.; Tambar, U. K. Nature 2017, 546, 196-200.
- 3. Bao, H.; Bayeh, L.; Tambar, U. K. Angew. Chem. Int. Ed. 2014, 53, 1664-1668.
- 4. Bao, H.; Tambar, U. K. J. Am. Chem. Soc. 2012, 134, 18495-18498.

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## **Bio-Sketch of Speaker**

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Uttam K. Tambar moved from India to the United States in 1982. He received his A.B. degree from Harvard University in 2000 and his Ph.D. from the California Institute of Technology in 2006 with Professor Brian Stoltz. After he completed his NIH Postdoctoral Fellowship at Columbia University with Professor James Leighton in 2009, he began his independent research career at UT Southwestern Medical Center in Dallas. He is currently an Associate Professor in the Biochemistry Department and a W. W. Caruth, Jr. Scholar in Biomedical Research. The Tambar lab is interested in asymmetric catalysis, natural product synthesis, and medicinal chemistry.

Dr. Tambar is interested in developing new strategies and concepts in synthetic chemistry to address challenging problems in biomedical research. In addition to making fundamental advances in chemistry, he will take advantage of the unique opportunities for collaborative research at UT Southwestern.

## **Research Interests**

- Development of new chemical reactions
- Discovery of small molecule drugs
- Synthesis of complex biologically active natural products

## **Educational Background**

Undergraduate School Harvard University (2000), Chemistry

Graduate School
California Inst of Technology (2006), Organic Chemistry
(Advisor: Professor Brian Stoltz)

Post-doctoral Postdoctoral Fellowship at Columbia University (Advisor: Professor James Leighton)

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#### Awards & Honors:

Welch Foundation Norman Hackerman Award In Chemical Research (2019)

Dallas Tiki Week Home Bartender Tiki Cocktail Winner (2019)

Chair of the Chemistry and Cancer Program, Harold C. Simmons Comprehensive Cancer Center (2018-present)

Sloan Foundation Research Fellowship (2013)

NSF Faculty Early Career Development (CAREER) Award (2012)

Thieme Chemistry Journal Award (2012)

Novartis Award Lecturer at Boston University (2012)

Member of the Harold C. Simmons Comprehensive Cancer Center (2009-present)

W.W. Caruth, Jr. Endowed Scholar in Biomedical Research (2009-present)

NIH Ruth L. Kirschstein NRSA Postdoctoral Fellow (2006-2009)

2008 Stereochemistry GRC Chair's Award for Exceptional Accomplishments in Organic Chemistry

American Chemical Society Travel Grant from Division of Medicinal Chemistry (2008)

National Defense Science and Engineering Graduate Fellow (2001-2004)

John Harvard Scholar (1997, 1998, 1999)

Institute of Chemistry and Cell Biology Grant for Undergraduate Research (1999)

Howard Hughes Medical Institute Grant for Undergraduate Research (1998)

Harvard College Research Program Award (1998, 1999, 2000)