

Cluster Preface: Development and Applications of Novel Ligands/Catalysts and Mechanistic Studies on Catalysis

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Zhipeng Zhang (left) received his B.S. degree from Shandong University (China) in 2004, and his Ph.D. degree from the Shanghai Institute of Organic Chemistry (SIOC) in 2010 under the supervision of Professor Kuiling Ding. In 2011, he began his postdoctoral studies with Professor Benjamin List at the Max Planck Institute for Coal Research in Mülheim an der Ruhr, Germany. After three years of research on asymmetric organocatalysis, he joined the group of Professor Jin-Quan Yu at The Scripps Research Institute in La Jolla, California as a postdoctoral research associate in 2014. He subsequently worked at the Genomics Institute of the Novartis Research Foundation (GNF) from 2016, before he began his independent career as a professor at the East China University of Science and Technology (ECUST) in 2017. His current research interests include asymmetric catalysis and synthetic methodology, focusing on the design and development of novel chiral ligands and catalysts.

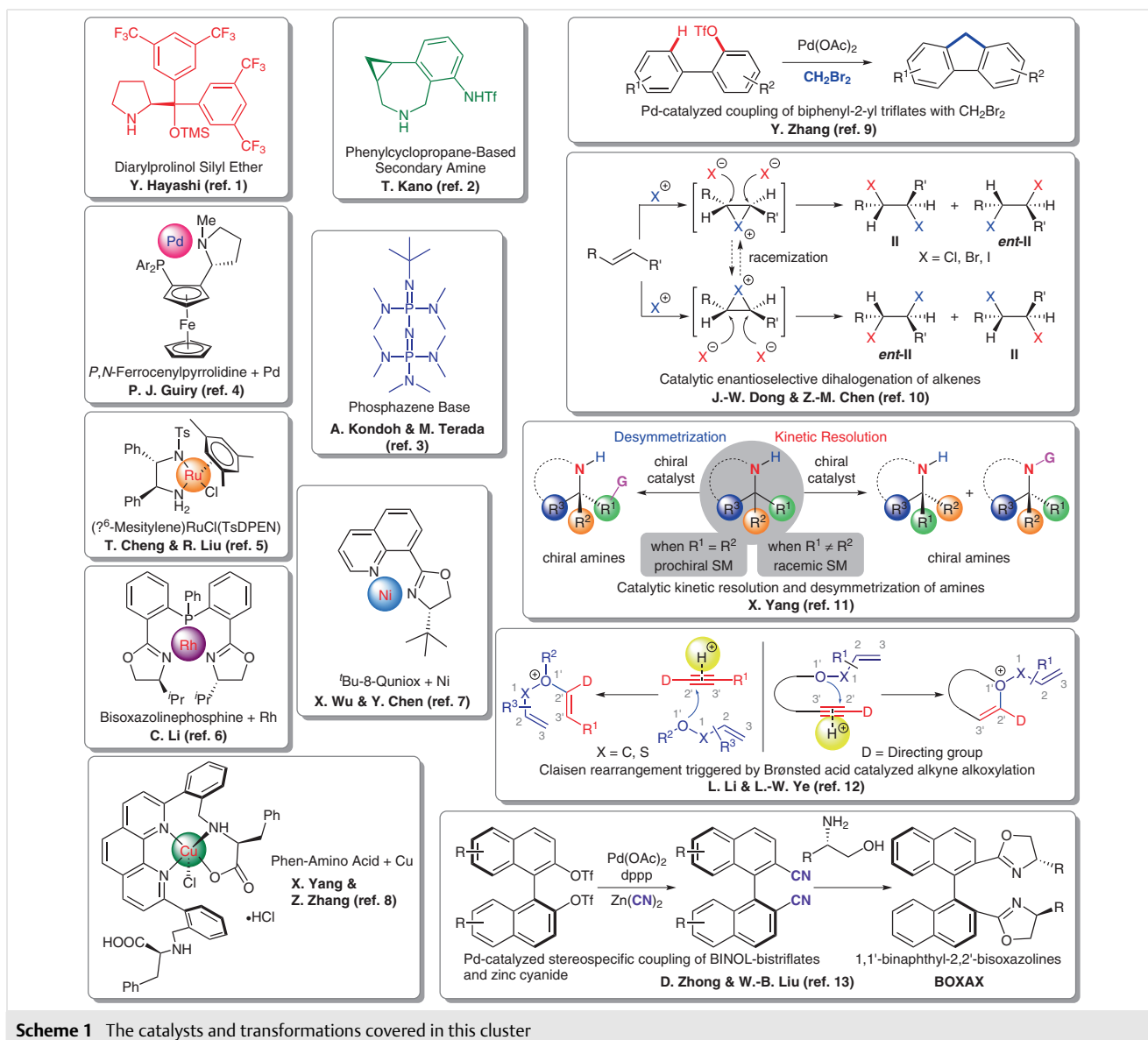
Baoguo Zhao (right) received his B.S. degree from Wuhan University in 1996, his M.S. degree from Nanjing University under the supervision of Professor Jianhua Xu in 2002, and his Ph.D. degree from the Shanghai Institute of Organic Chemistry (SIOC) under the supervision of Professor Kuiling Ding in 2006. He subsequently worked with Professor Yian Shi for five years as a postdoctoral fellow at the Department of Chemistry of Colorado State University. In 2011, he joined Shanghai Normal University at the Department of Chemistry as a full professor. His current research interests are in the area of biomimetic asymmetric catalysis, including the development of bioinspired chiral catalysts and synthetic methodologies.

Key words ligands, catalysts, transition-metal, organocatalyst, chemoselectivity, regioselectivity, stereoselectivity, enantioselectivity

A catalyst is a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change of the reaction. It can be an enzyme, a metal complex, or an organic molecule. As compared to enzymes, chemical catalysts, including transition-metal catalysts (usually derived from ligands and transition metals) and organocatalysts, are much smaller, more diverse, and easier to modify, and consequently they have been utilized in a tre-

mendous number of applications in organic chemistry. Ligands/catalysts, especially chiral examples, have played a crucial role in modern synthetic chemistry, enabling chemists to develop numerous new transformations with excellent control of the chemo-, regio-, stereo-, and/or enantioselectivities. During recent decades, a large variety of ligands/catalysts have been developed, greatly enlarging the toolbox of chemists for organic synthesis, and a huge number of challenging transformations have been realized with the assistance of such catalysts. In this SYNLETT cluster, we are delighted to present and discuss several novel catalysts and interesting transformations that have been developed in recent years (Scheme 1).

The highly enantioselective Michael reaction of malononitrile and α,β -unsaturated aldehydes catalyzed by a chiral diarylprolinol silyl ether has been developed (Y. Hayashi).¹ The design and synthesis of novel phenylcyclopropane-based secondary amine catalysts and their applications in asymmetric reactions have been summarized in this cluster (T. Kano).² A phosphazene base catalyst has been utilized to catalyze the addition reaction of allyl sulfones possessing a diethoxyphosphoryloxy group with α,β -unsaturated ketones (A. Kondoh & M. Terada).³ Novel *P,N*-ferrocenylpyrrolidine-containing-ligands have been synthesized and applied in Pd-catalyzed allylic alkylations (P. J. Guiry).⁴ The mechanochemical asymmetric transfer hydrogenation of diketones to provide chiral 1,3-diol derivatives with exceptionally high enantioselectivities has been developed in the presence of a chiral ruthenium complex under solvent-free conditions (T. Cheng & R. Liu).⁵ A rhodium-catalyzed regio- and enantioselective direct allylation of methyl ketones was realized by using a bisoxazolinephosphine ligand (C. Li).⁶ 8-Quinolinyloxazoline ligands have been utilized in the Ni-catalyzed asymmetric reductive carbamoyl-alkylation of carbamoyl chloride tethered styrenes with unactivated alkyl iodides, providing access to valuable chiral oxindoles



with excellent enantioselectivities (X. Wu & Y. Chen).⁷ In addition, a novel class of chiral C_2 -symmetric multidentate ligands have been designed and developed by merging the 1,10-phenanthroline unit with various chiral amino acids (X. Yang & Z. Zhang).⁸

Pd-catalyzed coupling of biphenyl-2-yl triflates with CH_2Br_2 for the construction of fluorenes has been developed, which involved forming two $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bonds in one step (Y. Zhang).⁹ Recent advances in the catalytic enantioselective dihalogenation of alkenes have been summarized (J.-W. Dong & Z.-M. Chen).¹⁰ The development of kinetic resolution and desymmetrization of amines through nonenzymatic asymmetric catalytic approaches in the last two decades has also been systematically summarized in

this cluster (X. Yang).¹¹ Recent progress on the Brønsted acid catalyzed intramolecular and intermolecular alkyne alkoxylation/Claisen rearrangement has been discussed (L. Li & L.-W. Ye).¹² Additionally, a Pd-catalyzed stereospecific coupling of BINOL-bistriflates and zinc cyanide and its application in the synthesis of 1,1'-binaphthyl-2,2'-bisoxazolines (BOXAX) has been reported (D. Zhong & W.-B. Liu).¹³

We are extremely grateful to all the distinguished scientists who have contributed to this SYNLETT cluster. The catalysts and transformations reported in this cluster are limited examples but are highly inspiring for further development. A successful catalyst may result in many reactions with excellent selectivities, and it is thus important to continue to pursue new powerful catalysts in the area of syn-

thetic chemistry. We strongly believe that with the development of synthetic chemistry, more and more novel catalysts and new transformations will be developed in the future.

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October 2022

Conflict of Interest

The authors declare no conflict of interest.

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