

## New Dimension of Acid and Base Catalysis

Shū Kobayashi

*Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku,  
Tokyo 113-0033 Japan.*

Email: shu\_kobayashi@chem.s.u-tokyo.ac.jp; Fax: +81-3-5684-0634

Catalytic asymmetric 1,4-addition and [3+2] cycloaddition reactions using chiral calcium complexes prepared from calcium isopropoxide and chiral bisoxazoline ligands have been developed. Glycine Schiff bases reacted with acrylic esters to afford 1,4-addition products, glutamic acid derivatives, in high yields with high enantioselectivities. During the investigation of the 1,4-addition reactions, we unexpectedly found that a [3+2] cycloaddition occurred in the reactions with crotonate derivatives affording substituted pyrrolidine derivatives in high yields with high enantioselectivities. Based on this finding, we investigated asymmetric [3+2] cycloadditions, and it was revealed that several kinds of optically active substituted pyrrolidine derivatives containing contiguous stereogenic tertiary and quaternary carbon centers were obtained with high diastereo- and enantioselectivities. NMR spectroscopic analysis and observation of non-amplification of enantioselectivity in non-linear effect experiments suggested that a monomeric calcium complex with an anionic ligand was formed. A stepwise mechanism of the [3+2] cycloaddition, consisting of 1,4-addition and successive intramolecular Mannich-type reaction was suggested. Furthermore, modification of the Schiff base structure resulted in a modification of the reaction course from a [3+2] cycloaddition to a 1,4-addition affording 3-substituted glutamic acid derivatives with high diastereo- and enantioselectivities.

