

Highly Efficient Catalytic Synthesis of Nitrogen-Containing Compounds

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As a part of our continuing studies on development of atom-economical synthetic methodologies, we will present efficient catalytic syntheses of nitrogen-containing compounds. For the catalytic synthesis of nitrogen-containing compounds, appropriate catalyst design to prevent product inhibition is important. The oral presentation consists of three parts: 1) Synthesis of chiral β -amino- α -hydroxy ketones and β -amino- α -hydroxy acids via direct catalytic asymmetric Mannich-type reactions using chiral Et_2Zn and $\text{In}(\text{O}-i\text{Pr})_3/\text{linked-BINOL}$ complexes: In the Zn-catalyzed Mannich-type reaction, catalyst loading was successfully reduced to as little as 0.01 mol %, still giving product in high yield and high ee (98% ee). Property of *N*-acylpyrrole as a monodentate and activated ester equivalent donor played a key role in Indium-catalyzed reaction. 2) Synthesis of chiral β -amino acids and chiral aziridines via catalytic asymmetric *aza*-Michael reaction using chiral rare earth metal complexes: Y-Li-BINOL complex and Dy-Li-BINOL complex were effective for the *aza*-Michael reaction. α,β -Unsaturated *N*-acylpyrroles were used as ester equivalent acceptors in the reaction. chiral β -amino acids were obtained in up to 94% ee. 3) Bismuth-catalyzed intermolecular hydroamination of dienes and amides to afford allylic amines in good yield: Catalyst loading was successfully reduced to 0.5 mol % without any problems. Reaction proceeded through proximity-effect-control mechanism realized by Bismuth catalyst. Counter anion exchange from OTf^- to PF_6^- was crucial for promoting the reaction effectively. In all three topics, the reactions proceed in highly atom-economical manner with the aid of catalytic amount of metal complexes.