【Grant-in-Aid for Scientific Research (S)】

Science and Engineering (Chemistry)

Title of Project : Development of Functional Organosuperbase Catalysts Enabling Molecular Recognition

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Research Project Number : 16H06354   Researcher Number : 50217428
Research Area : Synthetic chemistry
Keyword : Asymmetric synthesis, Organocatalyst, Selective synthesis, Catalyst design/reaction, Reaction field

【Purpose and Background of the Research】
The development of advanced molecular transformations with considering environmentally friendly system has become significantly important subject in synthetic organic chemistry, a fundamental and important research field for manufacturing. Brønsted bases have been extensively employed for activation of reactants having an acidic proton. Most of these bases are metal salts derived form alkaline metals or alkaline earth metals. Whereas organobases were commonly utilized as a reagent for molecular transformations, however applicable transformations have been quite limited because of these less basicity. In recent years, intensive interest has been devoted to the development of organosuperbases. However these metal salts and organosuperbases were utilized under equimolar conditions, little attention has been paid to the catalytic use of these fascinating molecules. We focused on the utilization of these organosuperbase as a catalyst and the development of functional organosuperbase catalysts enabling molecular recognition, namely chiral organosuperbases. The purpose of this research is that the design and synthesis of chiral organosuperbases and its application to develop stereoselective transformations.

【Research Methods】
It is well known that phosphazenes exhibit higher order basicity when conjugate system was introduced to the iminophosphorane unit via an imino functionality. In our research proposal, we design and synthesis of organosuperbases, which enable molecular recognition, and apply these organosuperbase catalysts to develop efficient enantioselective transformations. In order to introduce efficient recognition system and strong basicity to the catalyst molecules, we designed the following type of molecular frameworks. To make the catalyst molecule having C_2 symmetry, we introduced phosphazene or guanidine units to both ends of the iminophosphorane core. The other approach is the introduction of acidic functionality as a hydrogen bond donor site to the fundamental

organosuperbase framework resulting in the formation of bifunctional organosuperbase catalysts. We are planning to apply these organosuperbases to catalytic system which has never been established by using conventional organocatalysts. In addition, we also conduct the theoretical studies to elucidate the origin of the stereochemical outcome and catalytic cycles.

【Expected Research Achievements and Scientific Significance】
With the aim at initiating innovation to the industrial processes, we will establish unprecedent and remarkable catalytic activity, high selectivity, and construction of catalyst-recycling system.

【Publications Relevant to the Project】
· "Development of a Chiral Bis(guanidino)imino-phosphorane as an Uncharged Organosuperbase for the Enantioselective Amination of Ketones" T. Takeda, M. Terada, *J. Am. Chem. Soc.*, **2013**, *135*, 15306-15309.
· "Enantioselective Addition of a 2-Alkoxycarbonyl-1,3-dithiane to Imines Catalyzed by a Bis(guanidino) iminophosphorane Organosuper-base" A. Kondoh, M. Oishi, T. Takeda, M. Terada, *Angew. Chem. Int. Ed.*, **2015**, *54*, 15836-15839.
· "Construction of Vicinal Quaternary Stereogenic Centers by Enantioselective Direct Mannich-Type Reaction Using a Chiral Bis(guanidino) iminophosphorane Catalyst" T. Takeda, A. Kondoh, M. Terada, *Angew. Chem. Int. Ed.*, **2016**, *55*, 4734-4737.

【Term of Project】 FY2016-2020

【Budget Allocation】 143,500 Thousand Yen

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