

Development and Application of Transition Metal-Catalyzed Asymmetric Reactions Based on a Novel Function of Diaminophosphine Oxides as Ligands

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From a functional point of view, a value of enantiomeric excess is the simplest index for evaluating the ability of chiral ligands. However, from a practical point of view, air-stable, inexpensive, and easily accessible ligands are highly desirable. We have developed a new class of chiral phosphorus ligands, amino acid-derived P-chirogenic diaminophosphine oxides: DIAPHOXs. These air-stable pentavalent phosphorus compounds are activated to trivalent diamidophosphite species in situ by *N,O*-bis(trimethylsilyl)acetamide (BSA)-induced tautomerization, and function as the chiral ligands. Pd- and Ir-DIAPHOX catalyst systems were successfully applied to the following asymmetric reactions. 1) Pd-catalyzed enantioselective synthesis of quaternary carbon centers through asymmetric allylic substitutions using prochiral nucleophiles. 2) Highly enantioselective synthesis of nitrogen-containing chiral compounds through asymmetric allylic substitution with various amines and nitromethane as nucleophiles. 3) Ir-catalyzed asymmetric allylic amination and alkylation. In addition, we succeeded in enantioselective syntheses of biologically active compounds using the developed catalytic asymmetric reactions.