

COOPERATIVE CATALYST: SYNERGY BETWEEN TRANSITION METAL AND HYDROGEN-BONDING. Sukwon Hong, Department of Chemistry, University of Florida, P.O.Box 117200, Gainesville, FL 32611-7200

Simultaneous, cooperative activation of two reaction partners has emerged as a powerful strategy in asymmetric catalysis. Novel chiral salen-cobalt catalysts capable of self-assembly through 2-pyridone/aminopyridine hydrogen bonding interaction were developed. Compared to the corresponding monomeric salen-cobalt catalyst, this self-assembling catalyst displayed significant rate acceleration (48-fold) as well as higher enantioselectivity (96% ee vs 55% ee) in asymmetric nitroaldol (Henry) reactions. As a second example, bis-urea functionalized salen-Co(III) complexes were developed for hydrolytic kinetic resolution of epoxides. Significant rate acceleration was observed at low catalyst loading (0.05 mol%) for this bimetallic transformation, which could be attributed to the self-assembly of catalysts through urea-urea hydrogen bonding. These bis-urea-Co(salen) catalysts also proved to be excellent for asymmetric nitroaldol (Henry) reaction. Broad substrate scope, good yield, excellent enantioselectivity, and high anti-diastereoselectivity were observed for asymmetric Henry reactions with nitroethane. Interestingly, an alternative monometallic (first-order) mechanism involving synergistic activation by urea (H-bond) and the cobalt (Lewis acid), is suggested based on preliminary mechanistic studies.