Studies on Catalytic Asymmetric Hydrogenation of Fused Carbocyclic Arenes

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論　文　内　容　の　要　旨

The asymmetric hydrogenation of heteroarenes is one of the most straightforward ways to synthesize enantio-enriched heterocycles. As compare to heteroarenes, asymmetric hydrogenation of carbocyclic arenes is less explored because the substrates are highly stabilized with their own aromaticity. Nevertheless, Glorius group firstly reported the asymmetric hydrogenation of carbocycles in quinoxalines with a chiral carbene–ruthenium catalyst. In the following years, our group continuously reported the hydrogenation of naphthalenes, as well as quinoline carbocycles, with high enantioselectivities by using PhTRAP–ruthenium catalyst.

In this thesis, the first example of catalytic asymmetric chemoselective hydrogenation of isoquinoline carbocycles was described. It was found that the hydrogenation of isoquinolines selectively took place on their carbocycles by using the chiral *trans*-chelation bisphosphine PhTRAP–ruthenium complex. The heterocyclic moiety of the isoquinoline remained intact during the reduction of the carbocycle, although the pyridine ring is commonly more reactive than the dearomatization of benzene moiety. The bite angle of the chelate bisphosphine ligand PhTRAP is vital to achieve this unique chemoselectivity. The PhTRAP–ruthenium catalyst allowed the selective formation of 5,6,7,8-tetrahydroisoquinolines as major products. Various 5- and 8-substituted isoquinoline carbocycles were exclusively reduced to give the corresponding 5,6,7,8-tetrahydroisoquinolines in high yields, while the hydrogenations of 6- and 7-substituted isoquinolines proceed with moderate to high chemoselectivities. Furthermore, the hydrogenation also proceeded through enantioselective fashion, yielding the desired optically active 5,6,7,8-tetrahydroisoquinolines with moderate to good enantioselectivities. The mechanism of this hydrogenation was investigated with deuteration experiments. As a result, the deuteration indicated that the four hydrogen atoms were incorporated into the isoquinoline carbocycle with all *cis*-manner one another.