

論文内容の要旨

Development of Organic Reactions in Water Utilizing Innovative Reaction Environments

(革新的反応場を活用した水中での有機反応の開発)

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Introduction

Water is the most abundant liquid in the earth and it plays an important role in nurturing all the creatures. In chemistry, water, as one of solvents, is known to be safe, benign, environmentally friendly, and inexpensive compared with organic solvents. Organic reactions in water have been investigated because enzymatic reactions are carried out in water, and because unique reactivity and selectivity that are not observed in organic solvents have been found in aqueous media. On the other hand, chemists have devoted their efforts toward efficient catalysis. In particular, catalytic reactions in water have been regarded to be attractive from a viewpoint of green sustainable chemistry. Despite its usability and uniqueness, water has been rarely employed as a reaction medium due to two major obstacles. First, many catalysts may be decomposed or deactivated in water. Second, most organic substances are insoluble in water, resulting in aggregation and unfavorable side reactions in some cases.

On the other hand, catalysts occupied a pivotal position in most of biochemical and chemical processes. An ideal catalysis is considered to possess three major factors: 1. A choice of green solvent such as water to satisfy requirements of green sustainable chemistry; 2. A dispersed and stable environment with an exquisite assemblage of all components in water that inhibits self-aggregation of organic materials; and 3. A tunable electrochemical property that produces higher reactivity and selectivity.

Here I report my efforts on constructing innovative reaction environment to overcome the disadvantages of using water as solvent, and to satisfy the requests of efficient catalysis.

1. Utilization of Insoluble Cu(II) Salts as Catalysts

Cu(II)-catalyzed enantioselective boron and silicon conjugate additions to α,β -unsaturated carbonyl compounds and $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds in water were developed. In boron conjugate addition reactions, substrate scope were further expanded with three optimized catalyst conditions: 1. Heterogeneous $\text{Cu}(\text{OH})_2$ system, 2. Heterogeneous $\text{Cu}(\text{OH})_2 + \text{AcOH}$ system, and 3. Homogeneous $\text{Cu}(\text{OAc})_2$ system. By

choosing the suitable catalysts for each substrate, the corresponding products were obtained in good yields with excellent enantioselectivities, including both α,β -unsaturated imines and nitriles bearing either electron-donating or -withdrawing groups. In silicon conjugate addition reactions, chiral Cu(II) complexes with fixed coordination geometry from Cu(II) salts and chiral 2,2'-bipyridine **L** were prepared. After examining several

conditions, it was found that acicular purplish crystals obtained from $\text{Cu}(\text{acac})_2$ and **L** could promote the Michael addition reaction of $\text{PhMe}_2\text{SiB}(\text{pin})$ toward chalcone in water in excellent yield with high enantioselectivity. The scope of the reaction was examined under the optimized reaction conditions. Various chalcone derivatives reacted smoothly with $\text{PhMe}_2\text{SiB}(\text{pin})$ to afford the desired products in high yields with high enantioselectivities. The silyl group could be transferred to a crowded position to generate a quaternary carbon center bearing a C–Si bond. Cyclic ketones were also applicable without significant loss of enantioselectivity. Similarly, nitroolefins, acyclic α,β -unsaturated esters, lactones, and nitriles were also reacted with $\text{PhMe}_2\text{SiB}(\text{pin})$ in a highly stereoselective manner. It is noted that in both borylation and silylation reactions, δ -addition products were obtained exclusively when cyclic $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds were employed. The catalyst was also

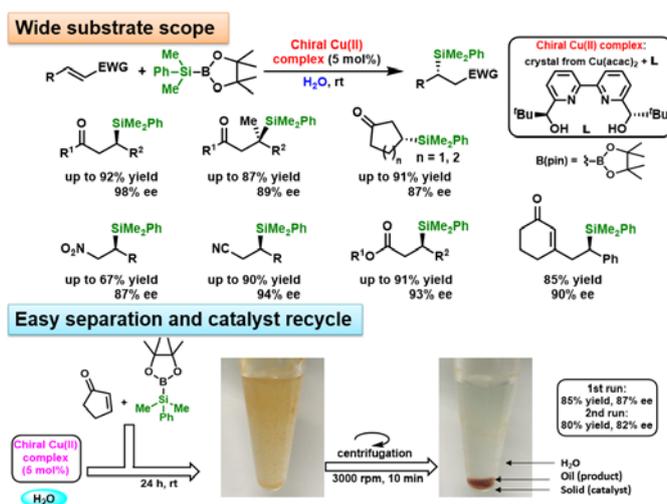


Figure 1. Cu(II)-catalyzed enantioselective silicon conjugate additions

applicable to a gram-scale reaction without any loss of enantioselectivity. Catalyst reusability was also evaluated in the reaction of cyclopentenone with $\text{PhMe}_2\text{SiB}(\text{pin})$. It was found that after the completion of the reaction, the separation of the product from the crude mixture and catalyst reuse were achieved through centrifugation (Figure. 1).

These results exhibited that the solubilities of neither catalysts nor reactants were necessary toward high yield and enantioselectivity. The approach is also in line with the concepts of green sustainable chemistry because it leads to reduction in the amount of organic solvents used and is amenable to catalyst recovery and reuse.

2. Asymmetric Lewis Acid –Single-walled Carbon Nanotube Integrated Catalysts

5年以内に雑誌等で刊行予定のため非公開

3. Development of New Light-induced Catalysts and Its Application toward Hydration Reactions in Water

5年以内に雑誌等で刊行予定のため非公開

Conclusion

During my PhD course, several new catalysts were designed. These discoveries, improvement of various Lewis acid catalysts and their applications to several reactions are believed to open new opportunities in the development of designed catalysis in water.