

# Development of Iron Catalysts for Advanced Organic Synthesis

## Research Project Outline (From Oct. 2011 to Mar. 2017)

Development of highly efficient iron catalyst systems based on two concepts "ligand field control" and "reaction governed by the reaction media".

◎To develop the well-defined iron catalysts by controlling the "ligand-field" around the iron center

◎Establishment of the most suitable reaction media for iron catalysis which is achieved by the concept of the "reaction governed by the reaction media".

→The final goal of this project is development of highly active and selective iron catalysts, which should be recoverable from the reaction mixture and reusable. These are accomplished by two scientific fields, science of the element and process chemistry.

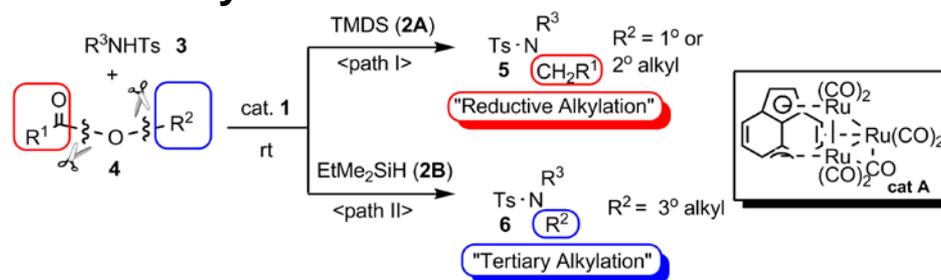
## Research Results (FY2011)

### ◆N-Alkylation Catalyzed by a Ruthenium Carbonyl Cluster

✓Carbon-nitrogen bond forming reactions by using esters as an alkyl source in the presence of hydrosilanes and a ruthenium catalyst (A) have been developed.

✓These N-alkylation reactions are useful for construction of naturally occurring azacyclic skeletons.

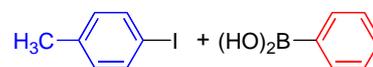
*Angew. Chem. Int. Ed.* 51, 5363 (2012).



### ◆Ultimate Streamline-Catalysis

✓A series of novel polymeric transition metal catalysts were prepared via self-assembly of a linear polymeric ligand with metal species in one step.

✓Cross-coupling reaction etc. were performed in water at a ppb-ppm mol level of the catalysts.



Novel Immobilization  
Catalysis at a ppb level  
Recyclable

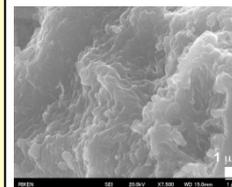
0.28 mol ppm Pd  
of new polymeric catalyst

$K_2CO_3$ ,  $H_2O$ , TBAF  
100 °C, 30 h



>99% yield

TON = 3,570,000  
TOF = 119,000 h<sup>-1</sup>



An example of the catalytic reaction and a microscopic image of the catalyst

*Angew. Chem. Int. Ed.* 50, 9437 (2011); *J. Am. Chem. Soc.* 134, 9285, (2012); *J. Am. Chem. Soc.* 134, 3190.