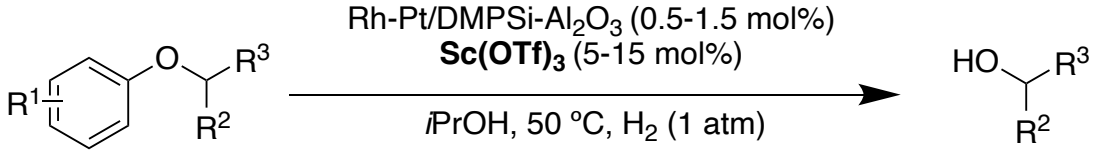
Development of Reductive Cleavage of Aryl Ethers Using Cooperative Catalytic Systems of Heterogeneous Metal Nanoparticles and Lewis Acids

(School of Science, The Univ. of Tokyo) ○ Hiroyuki MIYAMURA, Shū KOBAYASHI
Keywords: Heterogeneous Catalyst; Metal Nanoparticle; Lewis Acid; Cooperative Catalysis; Ether Cleavage

We have developed Rh-Pt bimetallic nanoparticles immobilized on a composite support of polydimethylsilane and alumina (Rh-Pt/DMPSi-Al_2O_3) as highly active catalysts for arene hydrogenation.[1] It was also found that a significant rate acceleration occurred by cooperative catalytic systems of Rh-Pt/DMPSi-Al_2O_3 and Lewis acids compared to the case without use of Lewis acids, and that sterically hindered substrates could be hydrogenated under mild conditions.[2]

In this study, we found that aryl alkyl ethers gave the corresponding aliphatic alcohols under reductive conditions using the cooperative catalytic systems. The reaction proceeded under very mild conditions; 50 ºC and atmospheric hydrogen. Interestingly, aryl alkyl ethers containing bulkier aryl groups gave high selectivity toward reductive cleavage. Wide scope of alkyl groups in the ether was demonstrated under the optimized reaction conditions. We also investigated mechanistic studies and obtained insight about intermediates during the reductive cleavage reactions. To the best of our knowledge, this is unpreceded general reductive cleavage of aryl alkyl ethers to afford the corresponding aliphatic alcohols in high yields. We opened new methods to use aryl ethers as robust protecting groups, which can be deprotected catalytically under very mild conditions.



1) Miyamura, H. Kobayashi, S. *et al. J. Am. Chem. Soc.* **2018**, *140*, 11325.
2) Miyamura, H. Kobayashi, S. *submitted.*