Borylation of Dialkyl Ethers via Cleavage of Inert Etheric C–O Bonds Enabled by Unsupported Nanoporous Gold Catalyst

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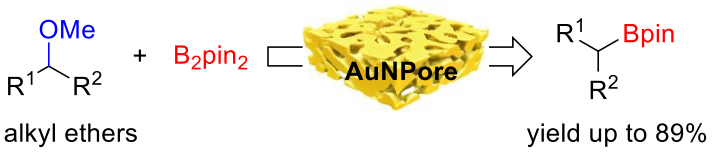
Alkylboron compounds are valuable intermediates with flexible reactivity in organic synthesis, enabling diverse transformations to access useful bioactive molecules and functional organic materials. Among the reported synthetic strategies,[1] substitution borylation via cleavage of the activated C−O bond of the protected alcohols has emerged as a new strategy for the selective synthesis of these alkylboron compounds compared to the classical addition borylation of the C=C bond. However, successful examples of substitution borylation of ethers with inert C-O bonds are rare due to their large bond dissociation energies, despite the abundance of ether feedstocks in nature and petrochemicals. On the other hand, recent studies in our group have shown that nanoporous gold (AuNPore), free of metal oxide supports, is able to cleave the B−B bond of bis(pinacolato)diboron (B_2pin_2), enabling the diboration of alkynes and methylenecyclopropanes.[2] Herein, we demonstrate that AuNPore show remarkable heterogeneous catalytic activity in the selective substitution borylation of unactivated etheric C-O bonds with B_2pin_2.

Borylation of (3-methoxybutyl)benzene with B_2pin_2 in the presence of AuNPore (10 mol%) at 100 °C in toluene for 6 h afforded the corresponding alkylboron product in 80% yield. This selective borylation showed broad substrate scope, accommodating acyclic and cyclic ethers as well as acetals to produce various alkylboronic esters and diesters. The mechanism of this heterogeneous catalytic substitution borylation will be discussed based on experimental results and DFT calculations. Additionally, the heterogeneous nature of AuNPore allows for facile recovery and reuse, maintaining catalytic activity over multiple cycles.



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