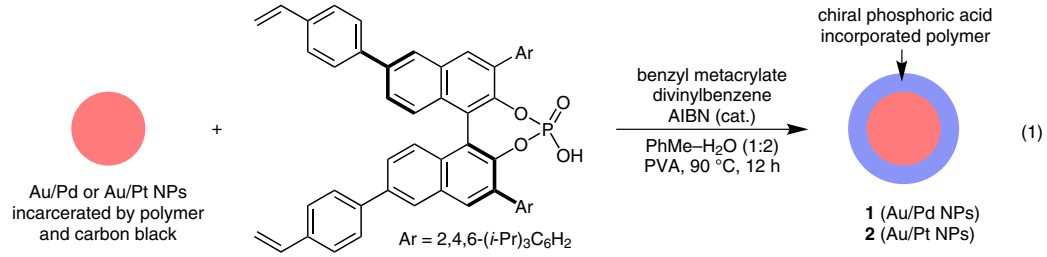
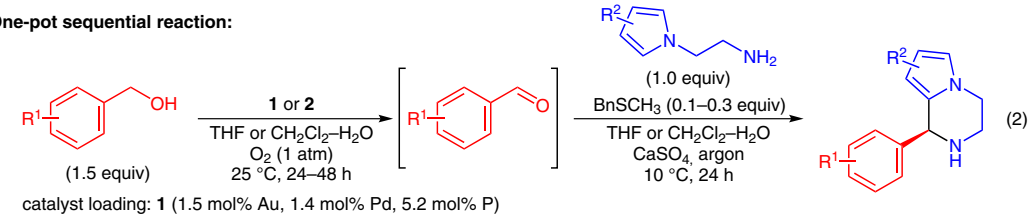
H.-G. CHENG, J. MIGUÉLEZ, H. MIYAMURA, W.-J. YOO, S. KOBAYASHI* (THE UNIVERSITY OF TOKYO, JAPAN)

Integration of Aerobic Oxidation and Intermolecular Asymmetric Aza-Friedel–Crafts Reactions with a Chiral Bifunctional Heterogeneous Catalyst
Chem. Sci. **2017**, *8*, 1356–1359.

Chiral Piperazines by Phosphoric Acid/Metal Nanoparticle Catalysis

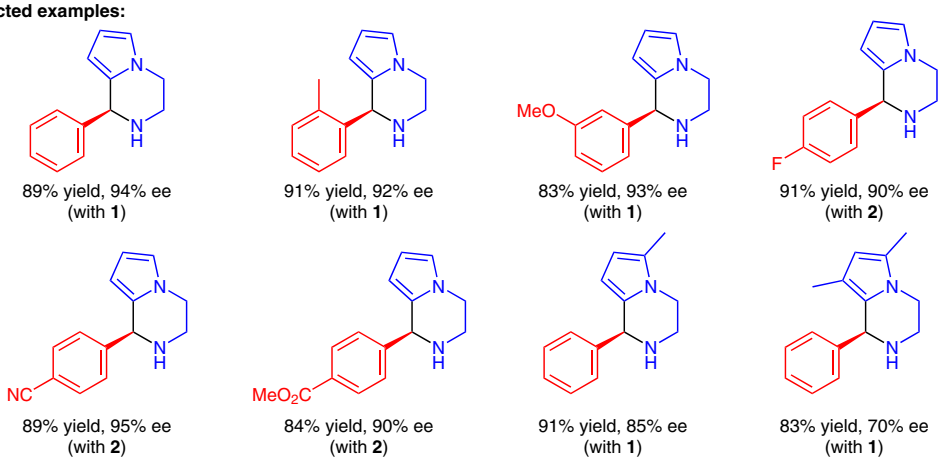


One-pot sequential reaction:



catalyst loading: **1** (1.5 mol% Au, 1.4 mol% Pd, 5.2 mol% P)
2 (3.0 mol% Au, 4.8 mol% Pt, 8.8 mol% P)

Selected examples:



Significance: Chiral phosphoric acids immobilized on polymer/carbon black-entrapped Au/Pd or Au/Pt nanoparticles (**1** and **2**, respectively) were prepared according to eq. 1. Catalysts **1** and **2** promoted an aerobic oxidation of benzyl alcohols and subsequent asymmetric aza-Friedel–Crafts reaction with *N*-(2-aminoethyl)pyrroles in one pot to give the corresponding chiral piperazines in ≤91% yield and ≤95% ee (eq. 2).

Comment: Benzyl methyl sulfide prevents oxidation of the resulting piperazine products to their imine forms. In the sequential reactions of benzyl alcohol and [2-(1*H*-pyrrol-1-yl)ethyl]amine, catalyst **1** was recovered by filtration and reused five times without significant loss of its catalytic performance (first run: 92% yield, 89% ee, sixth run: 85% yield, 84% ee).

SYNFACTS Contributors: Yasuhiro Uozumi, Shun Ichii
Synfacts 2017, 13(05), 0545 Published online: 18.04.2017
DOI: 10.1055/s-0036-1590234; **Reg-No.:** Y04317SF