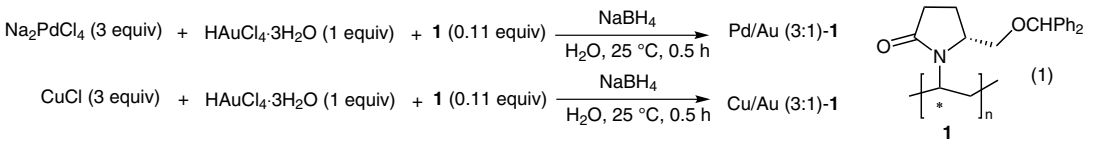
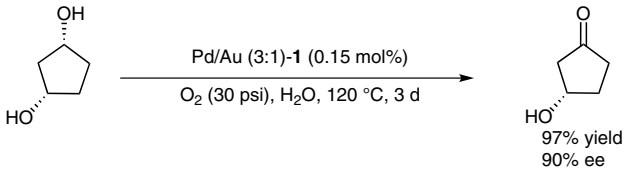
B. HAO, M. J. GUNARATNA, M. ZHANG, S. WEERASEKARA, S. N. SEIWALD, V. T. NGUYEN, A. MEIER, D. H. HUA* (KANSAS STATE UNIVERSITY, MANHATTAN, USA)
Chiral-Substituted Poly-*N*-vinylpyrrolidinones and Bimetallic Nanoclusters in Catalytic Asymmetric Oxidation Reactions
J. Am. Chem. Soc. **2016**, *138*, 16839–16848.

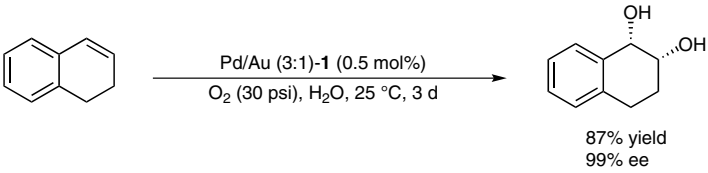
Chiral Polymer Stabilized Bimetallic Nanocatalysts for Asymmetric Oxidations



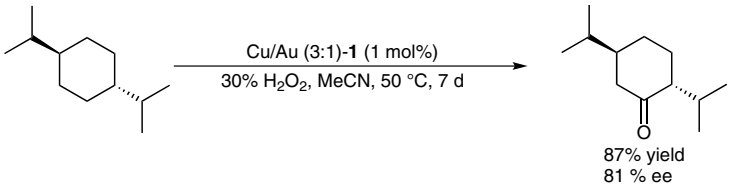
Position-selective oxidation of cyclic diols
Selected example:



Dihydroxylation of alkenes
Selected example:



C–H oxidation of cycloalkanes
Selected example:



Significance: A 3:1 Pd/Au bimetallic nanocatalyst stabilized by the chiral substituted poly(*N*-vinylpyrrolidinone) **1**, prepared according to eq. 1, catalyzed the selective oxidation of 1,2- and 1,3-cyclic diols (eq. 2; 15 examples), and the dihydroxylation of alkenes under oxygen in water (eq. 3; 7 examples, to afford the corresponding chiral products in high yields and high enantiomeric excesses. Cu/Au (3:1)–**1**, prepared by a similar method, catalyzed the C–H oxidation of cycloalkanes with H_2O_2 to give the corresponding ketones with high enantioselectivity (eq. 4).

Comment: In the oxidation of (±)-cyclohexane-1,3-diol, the catalyst was recovered and reused twice with a sharp decrease in its catalytic activity (first run: 49% yield; 99% ee; second run: 39% yield, 99% ee; third run: 18% yield, 98% ee).

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Category
Polymer-Supported Synthesis

Key words
asymmetric catalysis
oxidation
palladium catalysis
gold catalysis
copper catalysis
bimetallic catalyst