Chiral Polymer Stabilized Bimetallic Nanocatalysts for Asymmetric Oxidations

**Position-selective oxidation of cyclic diols**

Selected example:

\[
\text{Na}_2\text{PdCl}_4 (3 \text{ equiv}) + \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} (1 \text{ equiv}) + 1 (0.11 \text{ equiv}) \xrightarrow{\text{H}_2\text{O}, 25^\circ \text{C}, 0.5 \text{ h}} \text{NaBH}_4 \xrightarrow{\text{Pd/Au (3:1)-1}} \text{Cu/Au (3:1)-1} \]

**Dihydroxylation of alkenes**

Selected example:

\[
\text{CuCl (3 equiv)} + \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} (1 \text{ equiv}) + 1 (0.11 \text{ equiv}) \xrightarrow{\text{H}_2\text{O}, 25^\circ \text{C}, 0.5 \text{ h}} \text{NaBH}_4 \xrightarrow{\text{Pd/Au (3:1)-1}} \text{Cu/Au (3:1)-1} \]

**C–H oxidation of cycloalkanes**

Selected example:

\[
\text{Na}_2\text{PdCl}_4 (3 \text{ equiv}) + \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} (1 \text{ equiv}) + 1 (0.11 \text{ equiv}) \xrightarrow{\text{H}_2\text{O}, 25^\circ \text{C}, 0.5 \text{ h}} \text{NaBH}_4 \xrightarrow{\text{Pd/Au (3:1)-1}} \text{Cu/Au (3:1)-1} \]

**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 \( \text{H}_2\text{O}_2 \) 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).