Chiral Polymer Stabilized Bimetallic Nanocatalysts for Asymmetric Oxidations

**Position-selective oxidation of cyclic diols**

Selected example:

\[
\text{Na}_2\text{PdCl}_4 \text{ (3 equiv)} + \text{HAuCl}_4 \text{ (1 equiv)} + \text{Pd/Au (3:1)-1} (0.15 \text{ mol%}) \quad \text{NaBH}_4 \quad \text{H}_2\text{O}, 25 \degree \text{C}, 0.5 \text{ h} \\
\text{CuCl} \text{ (3 equiv)} + \text{HAuCl}_4 \text{ (1 equiv)} + \text{Cu/Au (3:1)-1} (0.11 \text{ equiv}) \quad \text{NaBH}_4 \quad \text{H}_2\text{O}, 25 \degree \text{C}, 0.5 \text{ h} \\
\]

\[
\text{O}_2 (30 \text{ psi}), \text{H}_2\text{O}, 120 \degree \text{C}, 3 \text{ d} \\
\text{O}_2 (30 \text{ psi}), \text{H}_2\text{O}, 25 \degree \text{C}, 3 \text{ d} \\
\]

**Dihydroxylation of alkenes**

Selected example:

\[
\begin{align*}
\text{Pd/Au (3:1)-1 (0.5 mol%)} & \quad \text{O}_2 (30 \text{ psi}), \text{H}_2\text{O}, 25 \degree \text{C}, 3 \text{ d} \\
\text{87% yield} & \quad 99\% \text{ ee} \\
\end{align*}
\]

**C–H oxidation of cycloalkanes**

Selected example:

\[
\begin{align*}
\text{Cu/Au (3:1)-1 (1 mol%)} & \quad 30\% \text{ H}_2\text{O}_2, \text{MeCN}, 50 \degree \text{C}, 7 \text{ d} \\
\text{87% yield} & \quad 81\% \text{ ee} \\
\end{align*}
\]

**Significance:** A 3:1 Pd/Au bimetallic nanocatalyst stabilized by the chiral substituted poly(\text{N-vinylpyrrolidinone}) \text{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; 90% ee; second run: 39% yield, 99% ee; third run: 18% yield, 98% ee).