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Facile Fabrication of Magnetically Recyclable Metal-Organic Framework Nanocomposites for Highly Efficient and Selective Catalytic Oxidation of Benzylic C–H Bonds

Oxidation of Benzylic C–H Bonds with HKUST-1@Fe₃O₄

**Preparation of HKUST-1@Fe₃O₄:**

\[
\text{Fe₃O₄-CO₂H} \rightarrow \text{HKUST-1@Fe₃O₄}
\]

\[\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \rightarrow \text{BTC}
\]

Oxidation of benzylic hydrocarbons:

\[
\begin{align*}
\text{O} & \quad \text{HKUST-1@Fe₃O₄ (25 mg)} \\
\text{O} & \quad \text{TBHP (2.5 mol equiv), benzonitrile (0.5 mL)} \\
\text{O} & \quad 80 °C, 14 h
\end{align*}
\]

94.7% conversion 95.2% selectivity
>99% conversion >99% selectivity
>99% conversion >99% selectivity
>99% conversion 98.3% selectivity
>99% conversion 97.1% selectivity

**Significance:** The magnetic core–shell nanocomposites HKUST-1@Fe₃O₄ were prepared from Fe₃O₄-CO₂H (Φ 20 nm), polyvinylpyrrolidone (PVP), Cu(OAc)₂, and trimesic acid (BTC), in which the iron-based nanoparticles were encapsulated by the resulting HKUST-1 shell [for the copper-organic framework of Cu(OAc)₂ and trimesic acid, see: Chui et al. Science 1999, 283, 1148]. The oxidation of benzylic C–H bonds was carried out with HKUST-1@Fe₃O₄ and TBHP to give the corresponding desired carbonyl products in up to >99% conversion and >99% selectivity.

**Comment:** The catalyst was characterized by SEM, HR-TEM, PXRD, BET, and FT-IR analyses. Elemental analysis revealed a ratio of copper and iron of 19.34% and 28.63%. The catalyst was recovered by an external magnet and reused twice without significant loss of the catalytic activity.