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

Preparation of HKUST-1@Fe₃O₄:

\[ \text{Fe}_3\text{O}_4\text{CO}_2\text{H} \quad \text{Cu(OAc)}_2\text{H}_2\text{O} \quad \text{BTC} \quad \text{Cu(OAc)}_2\text{H}_2\text{O} \]

\[ \text{HKUST-1@Fe}_3\text{O}_4 \]

Oxidation of benzylic hydrocarbons:

\[ \text{HKUST-1@Fe}_3\text{O}_4 (25 \text{ mg}) \quad \text{TBHP (2.5 mol equiv), benzonitrile (0.5 mL)} \]

80 °C, 14 h

\[ \begin{align*}
\text{O} & \quad \text{O} \\
94.7\% \text{ conversion} & \quad 95.2\% \text{ selectivity} \\
\text{O} & \quad \text{O} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*} \]

94.7% 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 Fe₂O₃•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.