Ullmann-Type Coupling of Phenols with Aryl Halides on Cuprian Zeolite USY

**Significance:** Copper(I)-exchanged zeolite USY (CuI-USY) catalyzed the Ullmann-type coupling of phenols with aryl iodides or bromides in the presence of cesium carbonate to give the corresponding diaryl ethers in up to 86% yield. In the reaction of 3,5-dimethylphenol with iodobenzene, the catalyst was recovered by simple filtration and reused four times without loss of catalytic activity.

**Comment:** The authors have previously reported a Huisgen cycloaddition and a Glaser coupling with CuI-USY (Org. Lett. 2007, 9, 883; Eur. J. Org. Chem. 2009, 423). The catalytic activity of CuI-USY for the Ullmann-type coupling was superior to that of the other Cu(I) zeolites, such as CuI-MOR, CuI-β, or CuI-ZSM5. CuI-USY was ineffective for the reactions of 4-cyano- or 4-nitrophnols with phenyl halides. ICP-AES analysis revealed that no copper leaked from the catalyst during the reaction.

**Equation:**

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\begin{align*}
R_1\text{-}OH + X\text{-}R_2 & \xrightarrow{\text{CuI-USY (10 mol% Cu)}} R_1\text{-}O\text{-}R_2 \\
\text{(X = I, Br)} & \xrightarrow{\text{Cs}_2\text{CO}_3 (2.0 equiv)} \text{PhMe or DMF} \\
& \xrightarrow{120\text{–}140 ^\circ \text{C}, 24 \text{ h}} \text{up to 86% yield}
\end{align*}
\]