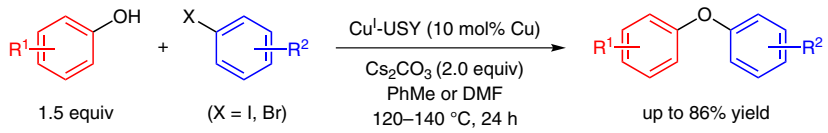
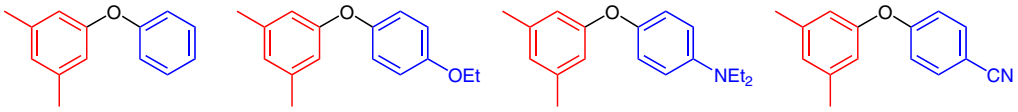
V. MAGNÉ, T. GARNIER, M. DANEL, P. PALE,* S. CHASSAING* (UNIVERSITÉ DE TOULOUSE AND UNIVERSITÉ DE STRASBOURG, FRANCE)
Cu^{I}-USY as a Ligand-Free and Recyclable Catalytic System for the Ullmann-Type Diaryl Ether Synthesis
Org. Lett. **2015**, *17*, 4494–4497.

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

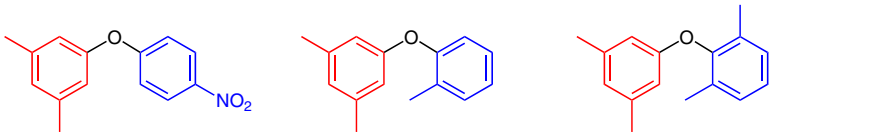


1.5 equiv (X = I, Br) → up to 86% yield

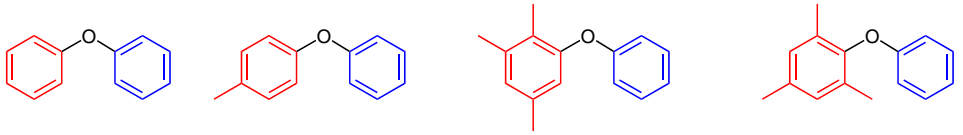
Typical results:



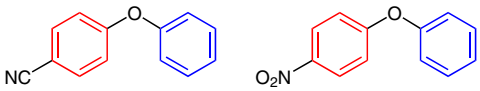
85% yield (X = I) | 84% yield (X = I) | 84% yield (X = Br) | 83% yield (X = Br)



83% yield (X = I) | 85% yield (X = I) | 34% yield (X = Br)



79% yield (X = I) | 86% yield (X = I) | 86% yield (X = I) | 62% yield (X = Br)



0% yield (X = I) | 0% yield (X = I)

Significance: Copper(I)-exchanged zeolite USY (Cu^{I}-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 Cu^{I}-USY (*Org. Lett.* **2007**, *9*, 883; *Eur. J. Org. Chem.* **2009**, 423). The catalytic activity of Cu^{I}-USY for the Ullmann-type coupling was superior to that of the other Cu(I) zeolites, such as Cu^{I}-MOR, Cu^{I}-β, or Cu^{I}-ZSM5. Cu^{I}-USY was ineffective for the reactions of 4-cyano- or 4-nitrophenols with phenyl halides. ICP-AES analysis revealed that no copper leached from the catalyst during the reaction.

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Category
Polymer-Supported Synthesis

Key words
copper
zeolites
Ullmann reaction
phenols
aryl halides