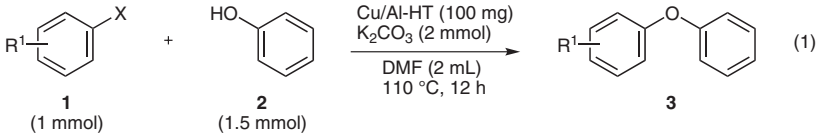
B. SREEDHAR,* R. ARUNDHATHI, M. A. REDDY, M. L. KANTAM (INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY, HYDERABAD, INDIA)

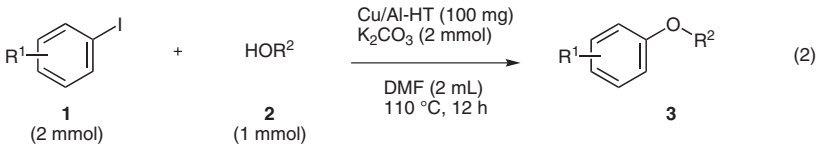
Efficient Catalytic Activity of Copper/Aluminum Hydrotalcite in Diaryl Ether Synthesis
Synthesis **2009**, 483-487.

Copper/Aluminum Hydrotalcite Catalyzed O-Arylation of Phenols/Alcohols with Aryl Halides



1 (1 mmol) + **2** (1.5 mmol) → **3**

R^1 = H, X = I (97% yield)
R^1 = H, X = Br (65% yield)
R^1 = H, X = Cl (47% yield)
R^1 = 4-NO_2, X = I (96% yield)
R^1 = 2-NO_2, X = I (69% yield)
R^1 = 4-NO_2, X = Cl (82% yield)
R^1 = 4-Cl, X = I (89% yield)
R^1 = 4-Br, X = I (85% yield)
R^1 = 4-F, X = I (78% yield)
R^1 = 4-Cl, X = Br (97% yield)
R^1 = 4-CO_2Et, X = I (92% yield)
R^1 = 4-OMe, X = I (97% yield)



1 (2 mmol) + **2** (1 mmol) → **3**

R^1 = H, R^2 = Ph (97% yield)
R^1 = H, R^2 = 4-ClC_6H_4 (57% yield)
R^1 = H, R^2 = 4-FC_6H_4 (83% yield)
R^1 = H, R^2 = 4-MeC_6H_4 (97% yield)
R^1 = H, R^2 = 4-$MeOC_6H_4$ (85% yield)
R^1 = H, R^2 = 4-$EtO_2CC_6H_4$ (78% yield)
R^1 = H, R^2 = 4-PhC_6H_4 (92% yield)
R^1 = H, R^2 = 4-*t*-BuC_6H_4 (97% yield)
R^1 = H, R^2 = 3,4-$Me_2C_6H_3$ (85% yield)
R^1 = H, R^2 = 2-Naph (94% yield)
R^1 = 4-NO_2, R^2 = Bn (93% yield)
R^1 = 4-NO_2, R^2 = Cy (86% yield)
R^1 = 4-MeO, R^2 = Cy (91% yield)
R^1 = 4-Br, R^2 = 4-BrC_6H_4 (85% yield)
R^1 = 4-NO_2, R^2 = 4-$MeOC_6H_4$ (91% yield)
R^1 = 4-MeO, R^2 = 4-BrC_6H_4 (89% yield)

Significance: Copper/aluminum hydrotalcite (Cu/Al-HF, Cu:Al = 2.5:1, 34.94 atm% Cu) was found to catalyze O-arylation of various phenols and alcohols **2** with aryl halides **1**. Thus, the reaction of **1** with **2** was carried out in the presence of Cu/Al-HF and K_2CO_3 in DMF to give the corresponding aryl ethers **3** in 47–97% yield. The Cu/Al-HF catalyst was recovered by filtration and reused four times with slight loss of catalytic activity.

Comment: The Cu/Al-HF catalyst has been developed by Velu and Swamy (S. Velu, C. S. Swamy *Appl. Catal., A: Gen.* **1996**, *145*, 141; see also: M. L. Kantam et al. *Org. Lett.* **2008**, *10*, 2979). The authors reported the Cu/Al-HT catalyzed N-arylation of amines with aryl chlorides (P. R. Likhar, R. Arundhathi, M. L. Kantam *Tetrahedron Lett.* **2007**, *48*, 3911) and the copper fluoroapatite catalyzed N-arylation of N-heterocycles with chloro- and fluoroarenes (B. M. Choudary, C. Sridhar, M. L. Kantam, G. T. Venkanna, B. Sreedhar *J. Am. Chem. Soc.* **2005**, *127*, 9948).

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Hidetoshi Ohta
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Category
Polymer-Supported Synthesis

Key words
hydrotalcite
phenols
copper