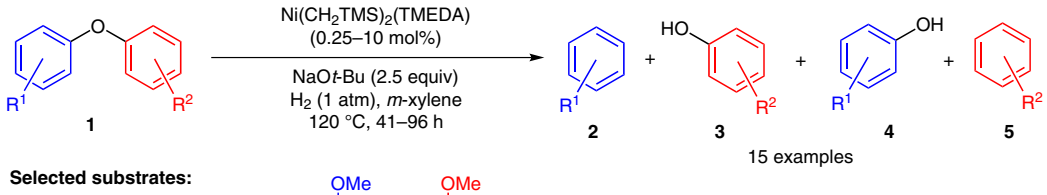
A. G. SERGEEV, J. D. WEBB, J. F. HARTWIG* (UNIVERSITY OF CALIFORNIA, BERKELEY, USA)

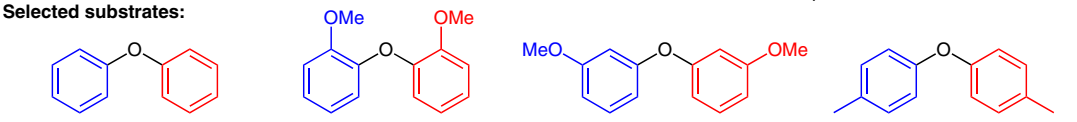
A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation
J. Am. Chem. Soc. **2012**, *134*, 20226–20229.

Hydrogenolysis of Aryl or Benzyl Ethers Using Nickel Nanoparticles

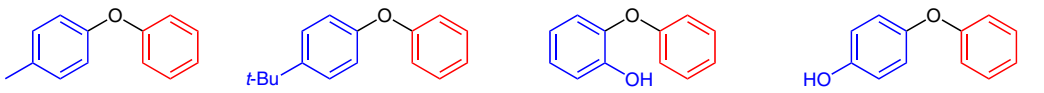
Hydrogenolysis of aryl ethers:



Selected substrates:

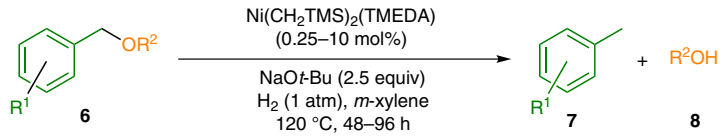


2a 99% yield, **3a** 99% yield | **2b** 99% yield, **3b** 99% yield | **2c** 68% yield, **3c** 66% yield | **2d** 94% yield, **3d** 91% yield

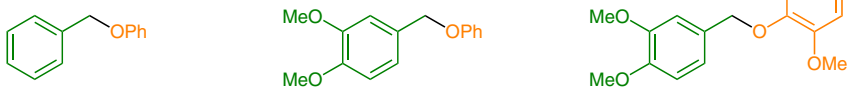


2e 13% yield, **3e** 11% yield, **4e** 81% yield, **5e** 85% yield | **2f** 3% yield, **3f** 3% yield, **4f** 90% yield, **5f** 90% yield | **2g**+**3g** 160% yield (based on **1**), **5g** 9% yield | **2h**+**3h** 194% yield (based on **1**)

Hydrogenolysis of benzyl ethers:



Selected results:



7a 98% yield, **8a** 95% yield | **7b** 81% yield, **8b** 87% yield | **7c** 93% yield, **8c** 98% yield

Significance: Nickel nanoparticles, generated in situ from $Ni(CH_2TMS)_2(TMEDA)$ and *t*-BuONa, catalyzed the hydrogenolysis of aryl ethers **1** under H_2 in *m*-xylene to give the corresponding products **2**–**5** (15 examples). The hydrogenolysis of benzyl ethers **6** also proceeded in the presence of the nickel nanoparticles under H_2 atmosphere to afford the corresponding toluenes **7** and phenols **8** (4 examples).

Comment: The nickel nanoparticles were characterized by TEM, STEM, and EDS analyses. EDS analysis showed that the catalyst contained both nickel and sodium. From this result, the authors propose that *t*-BuONa stabilizes the nickel nanoparticles.

SYNFACTS Contributors: Yasuhiro Uozumi, Hiroaki Tsuji
Synfacts 2013, 9(3), 0337 Published online: 15.02.2013
DOI: 10.1055/s-0032-1318224; **Reg-No.:** Y00213SF

Category
Polymer-Supported Synthesis

Key words
nickel nanoparticles
hydrogenolysis
aryl ethers
benzyl ethers