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Cul-Nanoparticles-Catalyzed Selective Synthesis of Phenols, Anilines, and Thiophenols from Aryl Halides in Aqueous Solution


Synthesis of Phenols, Anilines, and Thiophenols with Cul Nanoparticles

**Significance:** Copper iodide nanoparticles catalyzed the hydroxylation and amination of arylhalides with water and ammonia in the presence of tetra-n-butylammonium hydroxide to give the corresponding phenols in up to 99% yield (32 examples) and anilines in up to 97% yield (32 examples), respectively. The catalyst also promoted the reaction of arylhalides with sulfur powder to afford the corresponding thiophenols in up to 94% yield (11 examples).

**Comment:** The catalyst was readily recovered from the reaction mixture by centrifugation and reused twice with slight loss of its catalytic activity for the formation of aniline from iodobenzene (1st reuse: 87% yield, 2nd reuse: 80% yield). TEM and XRPD analyses showed that shape and size of the Cul nanoparticles were not changed after the amination of iodobenzene. ICP analysis revealed that significant copper leaching from the catalyst was not observed during the reaction.

**Synthesis of Phenols from Aryl Halides:**

1. CuI nanoparticles (1.5 mol% Cu) n-Bu₄NOH (3 equiv), H₂O
   - X = I: 60 °C, 24 h
   - X = Br: 80 °C, 48 h
   - X = I: up to 99% yield (16 examples)
   - X = Br: up to 96% yield (16 examples)

2. HCl
   - X = I: up to 87% yield (2 examples)
   - X = Br: up to 91% yield (3 examples)

**Synthesis of Anilines from Aryl Halides:**

1. CuI nanoparticles (1.5 mol% Cu) NH₃ ⋅ H₂O (5 equiv) n-Bu₄NOH (2 equiv) H₂O
   - X = I: r.t., 24 h
   - X = Br: 80 °C, 48 h
   - X = I: up to 97% yield (19 examples)
   - X = Br: up to 91% yield (13 examples)

2. Zn, HCl
   - X = I: up to 94% yield (7 examples)
   - X = Br: up to 87% yield (4 examples)

**Synthesis of Thiophenol from Aryl Halides:**

1. CuI nanoparticles (1.5 mol% Cu) sulfur powder (3 equiv), n-Bu₄NOH (2 equiv) H₂O, 40 °C, 24 h
   - X = I: up to 94% yield (7 examples)
   - X = Br: up to 91% yield (4 examples)

2. Zn, HCl
   - X = I: up to 94% yield (7 examples)
   - X = Br: up to 87% yield (4 examples)