Highly Efficient Heterogeneous Aerobic Cross-Dehydrogenative Coupling via C–H Functionalization of Tertiary Amines Using a Nanoporous Gold Skeleton Catalyst


**Aerobic Cross-Dehydrogenative Coupling with Nanoporous Gold**

![Chemical structure diagram]

**Method:**
- **Method A:** O₂, 80 °C, solvent: nitroalkane or MeOH
- **Method B:** TBHP, r.t. or 80 °C, solvent: nitroalkane, MeOH, or MeCN

**Typical Results:**
- 95% (99%) yield: method A (99% yield): method B, r.t.
- 74% (99%) yield: method A (79% yield): method B, r.t.
- 90% (94%) yield: method A (48% yield): method B, r.t.
- 80% (96%) yield: method A (97% yield): method B, r.t.
- 98% (99%) yield: method A (85% yield): method B, r.t.
- 75% yield, 1:1.7 dr, (99% yield): method A (99% yield): method B, r.t.
- 65% yield: method A
- 85% yield: method A
- 62% yield: method A
- 82% yield: method A
- 85% yield: method A
- 66% yield: method B
- 70% yield: method B
- 52% yield: method B
- NMR yields are shown in parentheses

**Significance:** Zero-valent nanoporous gold (AuNPore) catalyzed the cross-dehydrogenative coupling of tertiary amines with carbon nucleophiles in the presence of oxygen or tert-butyl hydroperoxide to give the corresponding C–C coupling products in ≤98% isolated yield (eq. 1; 24 examples). After the reaction, the catalyst was recovered by filtration and reused nine times without loss of catalytic activity.

**Comment:** The authors previously reported the preparation of AuNPore (J. Am. Chem. Soc. 2012, 134, 17536). The catalytic activity of AuNPore for the cross-dehydrogenative coupling was superior to that of other nanoporous metal catalysts, such as nanoporous silver, copper, palladium, or platinum. An SEM study revealed that the morphology, pore size, and nanoporosity of AuNPore were unchanged after the catalytic reaction. ICP-MS analysis of the reaction solution showed no leaching of gold from the catalyst.