Dendritic Copper Catalysts for Homogeneous Click Chemistry in Water

**Significance:** The dendrimer 1 consists of water/organic compatible 27 triethyleneglycol (TEG) termini and a hydrophobic core (for the preparation of 1, see: *Chem. Commun.*, 2013, 49, 8169). [Hexabenzyltren-Cu]Br 3 and 1 promote the click reaction of benzyl azides and phenyl acetylenes in water to give the corresponding triazoles in 89–96% yield. The catalyst 1-CuI (4–200 ppm CuI), prepared from CuSO₄·5H₂O and NaAsc, also catalyzed the click reaction in 81–99% yield.

**Comment:** The TEG termini render the dendrimer 1 water-soluble, and the hydrophobic core allows solubilization of the hydrophobic compound 3 and the substrates in water. The interaction between 1 and 3 was shown by selective ¹H NMR shifts and a NOESY spectrum. The micelle nanoreactor 1 was recycled ten times (10th reuse: 2a, 91% yield). The click reaction was performed with 1 ppm 1-CuI to give 2a in 50% yield, whose turnover number (TON) and turnover frequency (TOF) were 510000 and 21200 h⁻¹, respectively.

**Selected examples:**

- **2a**  
  R¹ = H, R² = Ph  
  conditions A: 91% yield  
  conditions B: 99% yield (4 ppm CuI)

- **2b**  
  R¹ = H, R² = TMS  
  conditions A: 89% yield  
  conditions C: 81% yield (20 ppm CuI)

- **2c**  
  R¹ = Me, R² = Ph  
  conditions A: 90% yield  
  conditions B: 89% yield (20 ppm CuI)

- **2d**  
  R¹ = CN, R² = Ph  
  conditions A: 90% yield  
  conditions B: 90% yield (50 ppm CuI)

- **2e**  
  R¹ = Br, R² = Ph  
  conditions A: 96% yield  
  conditions C: 89% yield (50 ppm CuI)