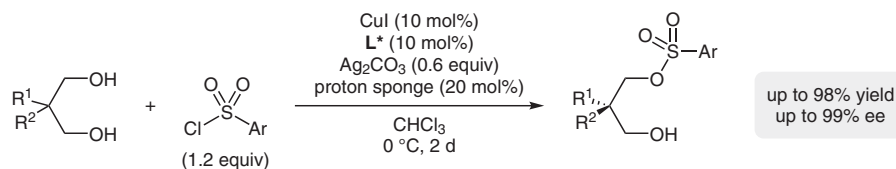


Y.-F. CHENG, Z.-L. YU, Y. TIAN, J.-R. LIU, H.-T. WEN, N.-C. JIANG, J.-Q. BIAN, G.-X. XU, D.-T. XU, Z.-L. LI, Q.-S. GU*, X. HONG*, X.-Y. LIU* (SOUTHERN UNIVERSITY OF SCIENCE AND TECHNOLOGY, SHENZHEN, BEIJING NATIONAL LABORATORY FOR MOLECULAR SCIENCES, ZHEJIANG UNIVERSITY, AND WESTLAKE UNIVERSITY, HANGZHOU, P. R. OF CHINA)

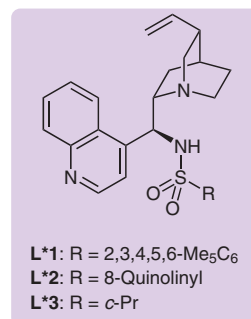
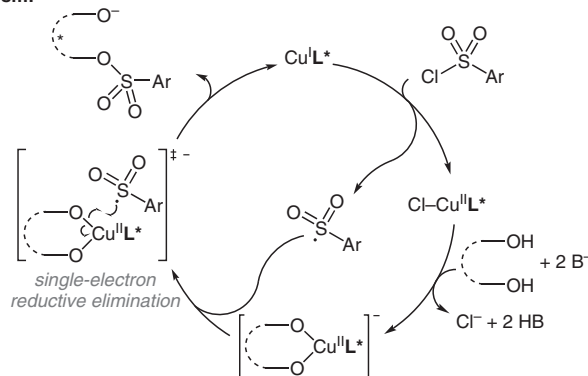
Cu-Catalyzed Enantioselective Radical Heteroatomic S–O Cross-Coupling

Nat. Chem. **2023**, *15*, 395–404, DOI: 10.1038/s41557-022-011102-z.

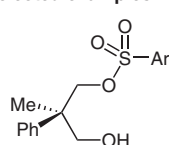
Desymmetrization of 1,3-Diols by Copper(I)-Catalyzed S–O Cross-Coupling with Aryl Sulfonyl Chlorides



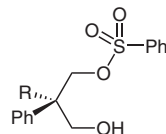
Proposed mechanism:



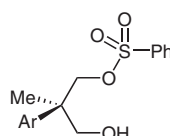
Selected examples:



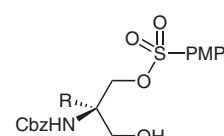
Ar = Ph: 86% yield, 94% ee
Ar = *p*-Tol: 86% yield, 93% ee
Ar = PMP: 57% yield, 92% ee
Ar = Naph: 72% yield, 91% ee



R = Et: 92% yield, 93% ee
R = *i*-Pr: 88% yield, 94% ee
R = *c*-Pr: 89% yield, 96% ee
R = Bn: 97% yield, 98% ee



Ar = 3-CF₃-C₆H₄: 55% yield, 84% ee
Ar = 3-Cl-C₆H₄: 80% yield, 85% ee
Ar = 3-Thionyl: 72% yield, 91% ee
Ar = CO₂Me: 42% yield, 79% ee



R = H: 67% yield, 87% ee
R = Et: 60% yield, 94% ee
R = Vinyl: 52% yield, 95% ee
R = Ph: 86% yield, 95% ee

Significance: Liu, Hong, Gu and co-workers disclosed a copper(I)-catalyzed S–O cross-coupling for the desymmetrization of 1,3-diols. The sulfonyl protected alcohols are obtained in good yields and excellent enantioselectivities.

Comment: The proposed radical mechanism is supported by experimental and theoretical studies. The key step of this challenging heteroatom–heteroatom cross-coupling is a single electron reductive elimination in which only one transition metal–heteroatom bond is cleaved.

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