

C.-Y. CAI, X.-L. LAI, Y. WANG, H.-H. HU, J. SONG, Y. YANG, C. WANG, H.-C. XU\*  
(XIAMEN UNIVERSITY, P. R. OF CHINA)

Photoelectrochemical Asymmetric Catalysis Enables Site- and Enantioselective Cyanation of Benzylic C–H Bonds  
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# Selective Cyanation of Benzylic C(sp<sup>3</sup>)–H Bonds Using Photoelectrochemical Asymmetric Catalysis

Category

Metals in Synthesis

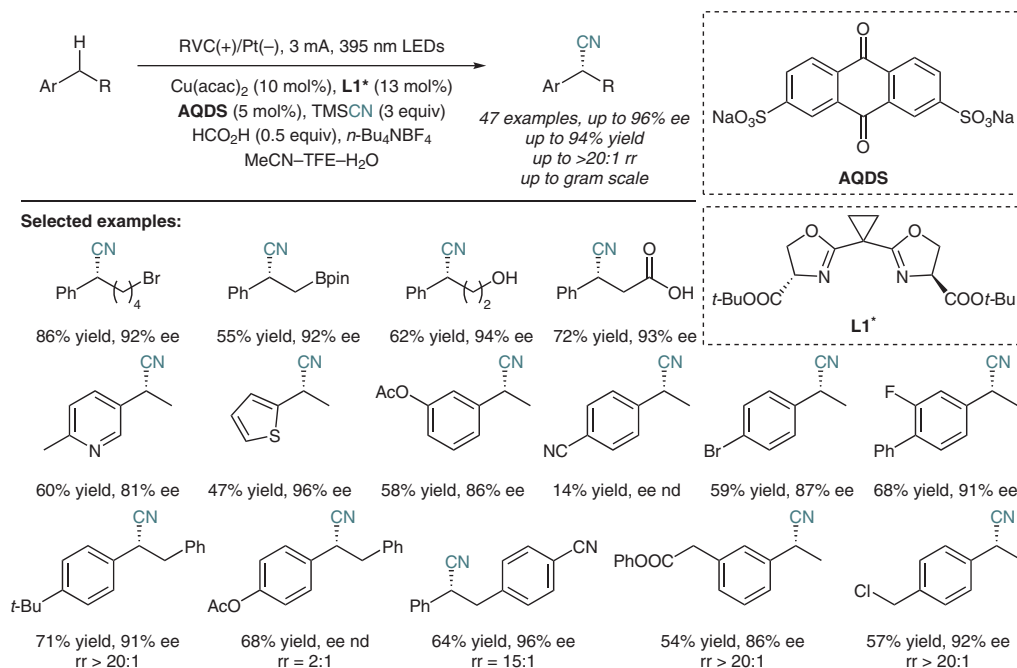
Key words

copper catalysis

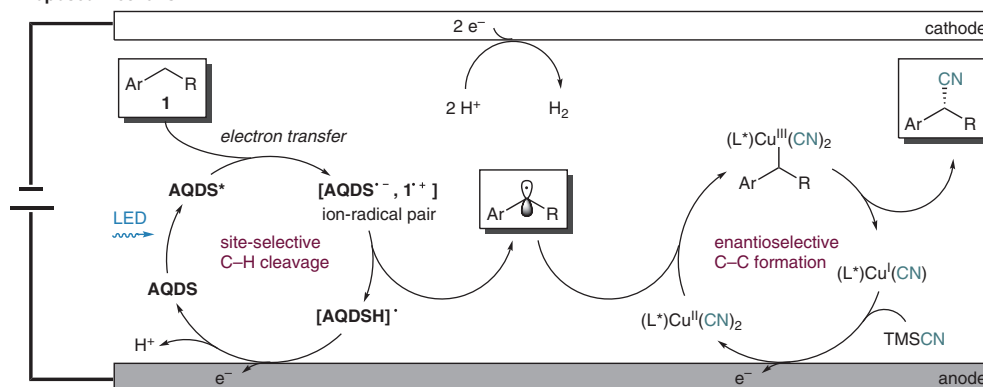
enantioselectivity

photoelectrochemistry

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Proposed mechanism:



**Significance:** In this report, photoelectrochemistry is paired with asymmetric catalysis for the site- and enantioselective cyanation of benzylic C(sp<sup>3</sup>)–H bonds. Mechanistic experiments were used to elucidate the reaction pathway, in which the authors propose the benzylic C(sp<sup>3</sup>)–H cleavage to proceed through two tandem catalytic cycles: a photocatalyzed electron transfer and a subsequent copper-catalyzed asymmetric C–C bond formation.

**Comment:** The reaction was compatible with various functionalized alkylbenzenes, including electron-rich and electron-deficient substrates. Notably, for systems bearing multiple potential sites for cyanation, functionalization occurs in a predictable and selective fashion at the most electron-rich site or sterically accessible benzylic C–H bond.

**SYNFACTS Contributors:** Mark Lautens, Alexa Torelli  
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