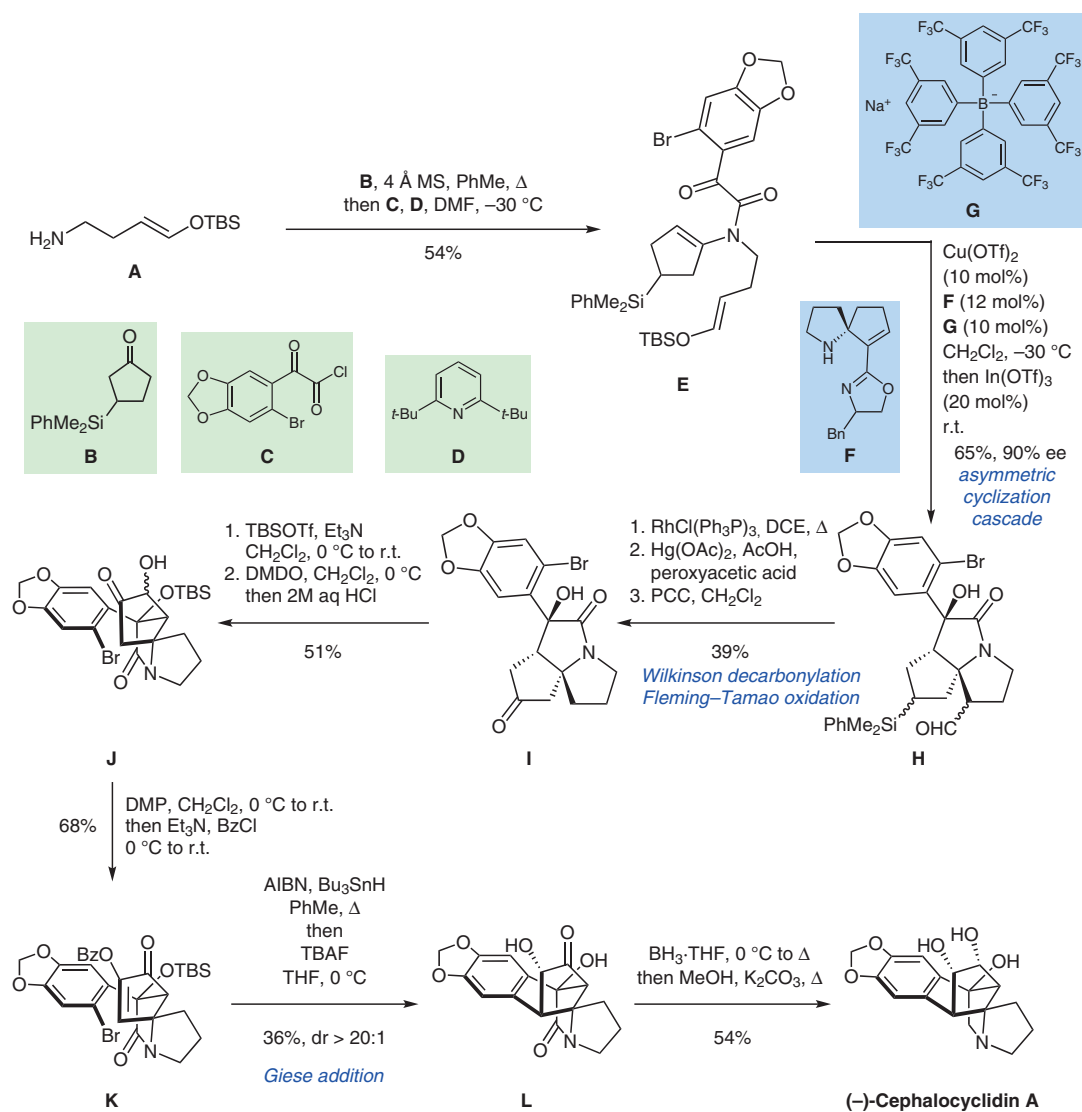


Q.-B. ZHUANG, J.-R. TIAN, K. LU, X.-M. ZHANG*, F.-M. ZHANG, Y.-Q. TU*, R. FAN, Z.-H. LI, Y.-D. ZHANG (LANZHOU UNIVERSITY AND SHANGHAI JIAO TONG UNIVERSITY, P. R. OF CHINA)

Catalytic Asymmetric Polycyclization of Tertiary Enamides with Silyl Enol Ethers: Total Synthesis of (–)-Cephalocyclidin A
J. Am. Chem. Soc. **2023**, *145*, 26550–26556, DOI: 10.1021/jacs.3c11178.

Total Synthesis of (–)-Cephalocyclidin A



Significance: Zhang, Tu and co-workers report a concise total synthesis of (–)-cephalocyclidin A. Key to their approach is a Cu(II)-catalyzed enantioselective polycyclization cascade of tertiary enamides with terminal silyl enol ethers. The development and scope of this methodology is also reported in the highlighted paper.

Comment: Enamide **E** undergoes an intramolecular cyclization cascade to give **H** via nucleophilic attack of the enamine onto the carbonyl and subsequent trapping of the generated iminium with the enol ether. A second salient feature is the Giese addition, from **K** to **L**, furnishing the last carbocycle in the caged natural product.

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Category

Synthesis of Natural Products

Key words

(–)-cephalocyclidin A

asymmetric cyclization cascade

Wilkinson decarbonylation

Fleming–Tamao oxidation

Giese addition

Synfact of the Month

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