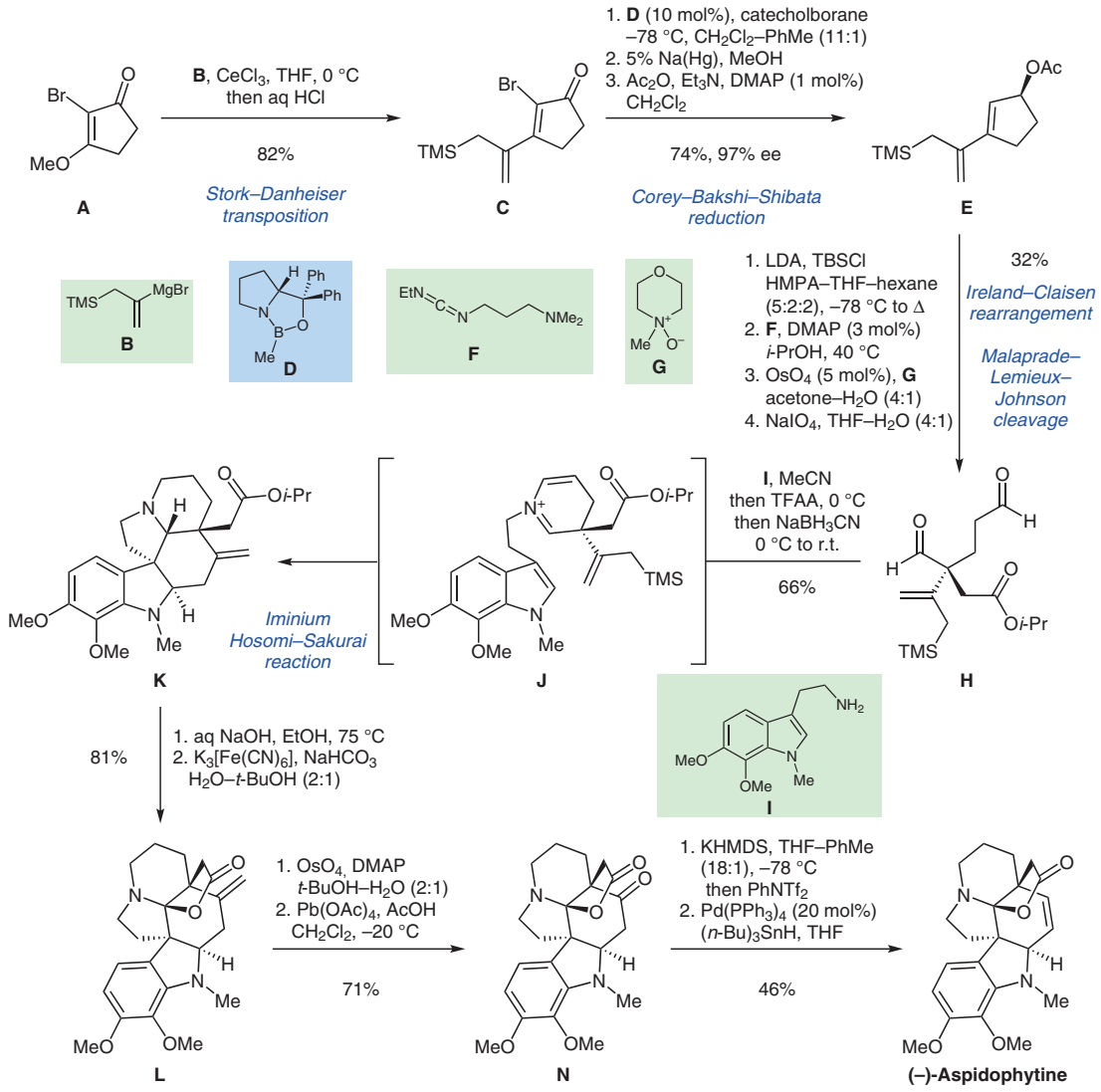
F. HE, Y. BO, J. D. ALTOM, E. J. COREY* (HARVARD UNIVERSITY, CAMBRIDGE, USA)
Enantioselective Total Synthesis of Aspidophytine
J. Am. Chem. Soc. **1999**, *121*, 6771–6772, DOI: 10.1021/ja9915201.

Synthesis of (–)-Aspidophytine



Significance: The authors present the enantioselective synthesis of (–)-Aspidophytine, isolated from *Haplophyton cimicidum* leaves and used in Central America as an anticockroach and insecticide. Despite of remarkable achievements towards the synthesis of apsidospermine alkaloids, the complex structure of (–)-aspidophytine remained a challenge for more than 20 years.

Comment: The synthesis commences with the preparation of key intermediate **H** using a Corey–Bakshi–Shibata reduction followed by Ireland–Claisen rearrangement. Intermediates **H** and **I** are combined to form the pentacyclic core structure **K** in an iminium Hosomi–Sakurai reaction. The synthesis of (–)-aspidophytine is finished via lactonization and installation of the last remaining olefin.

SYNFACTS Contributors: Erick M. Carreira, Sander Folkerts
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Haplophyton cimicidum
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Corey–Bakshi–Shibata reduction
Ireland–Claisen rearrangement
Malaprade–Lemieux–Johnson cleavage
iminium Hosomi–Sakurai reaction

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