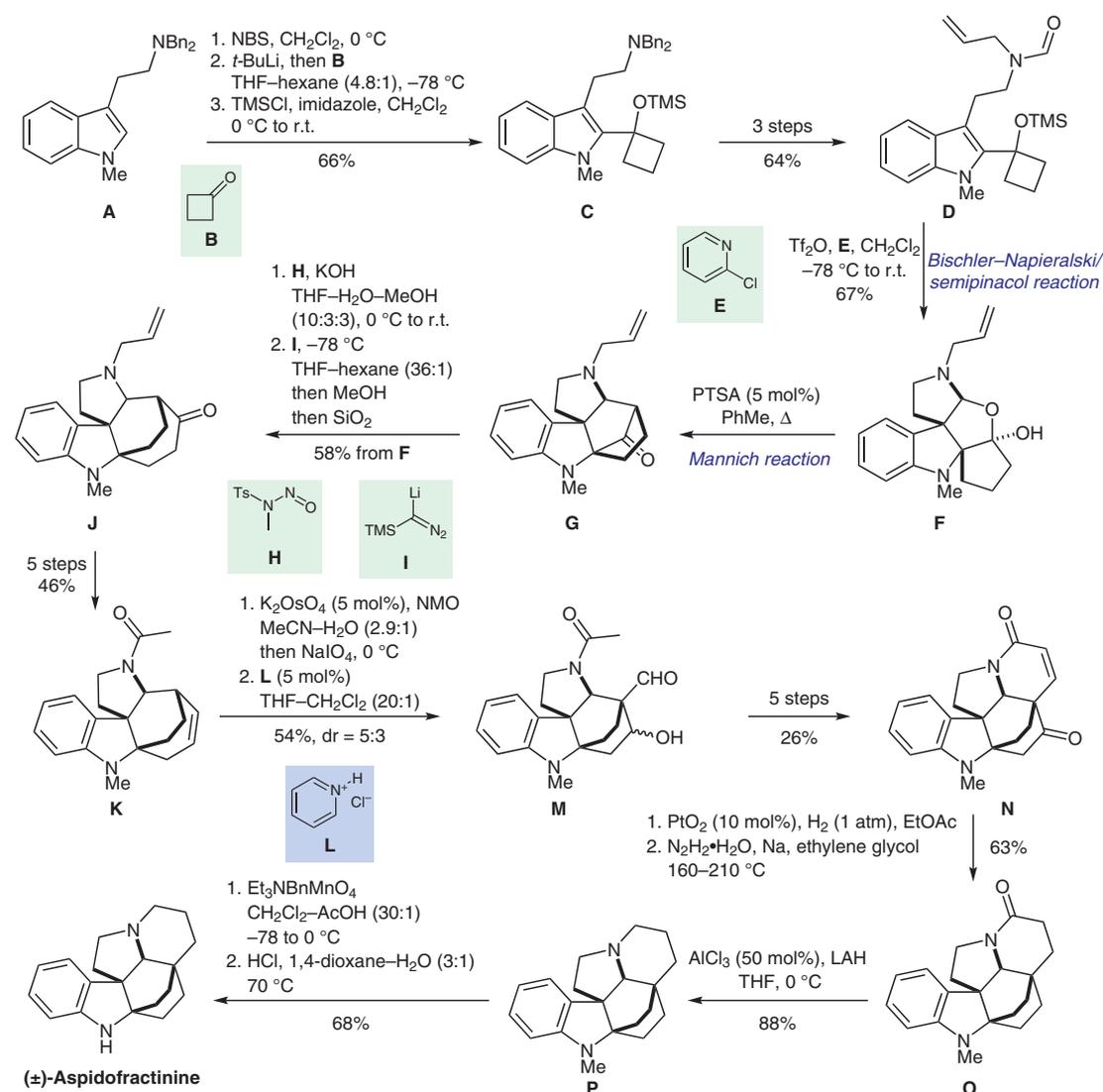


S.-H. WANG, R.-Q. SI, Q.-B. ZHUANG, X. GUO, T. KE, X.-M. ZHANG*, F.-M. ZHANG*, Y.-Q. TU* (LANZHOU UNIVERSITY AND SHANGHAI JIAO TONG UNIVERSITY, P. R. OF CHINA)

Collective Total Synthesis of Aspidofractinine Alkaloids through the Development of a Bischler–Napieralski/Semipinacol Rearrangement Reaction

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Total Synthesis of (±)-Aspidofractinine



Significance: The authors report the total synthesis of (±)-aspidofractinine employing a Bischler–Napieralski/semipinacol sequence as key step. In combination with a Mannich reaction, four aspidofractinine alkaloids were synthesized, all containing a bicyclo[2.2.2]octane framework.

Comment: Treatment of formamide **D** with Tf₂O triggered the Bischler–Napieralski/semipinacol cascade furnishing hemiacetal **F**, which underwent a Mannich reaction to give ketone **G**. Ring expansion followed by glycol-cleavage and aldol condensation led to enone **N**, which was transformed to the natural product after functional group interconversions.

SYNFACTS Contributors: Erick M. Carreira, Fabian Glatz
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