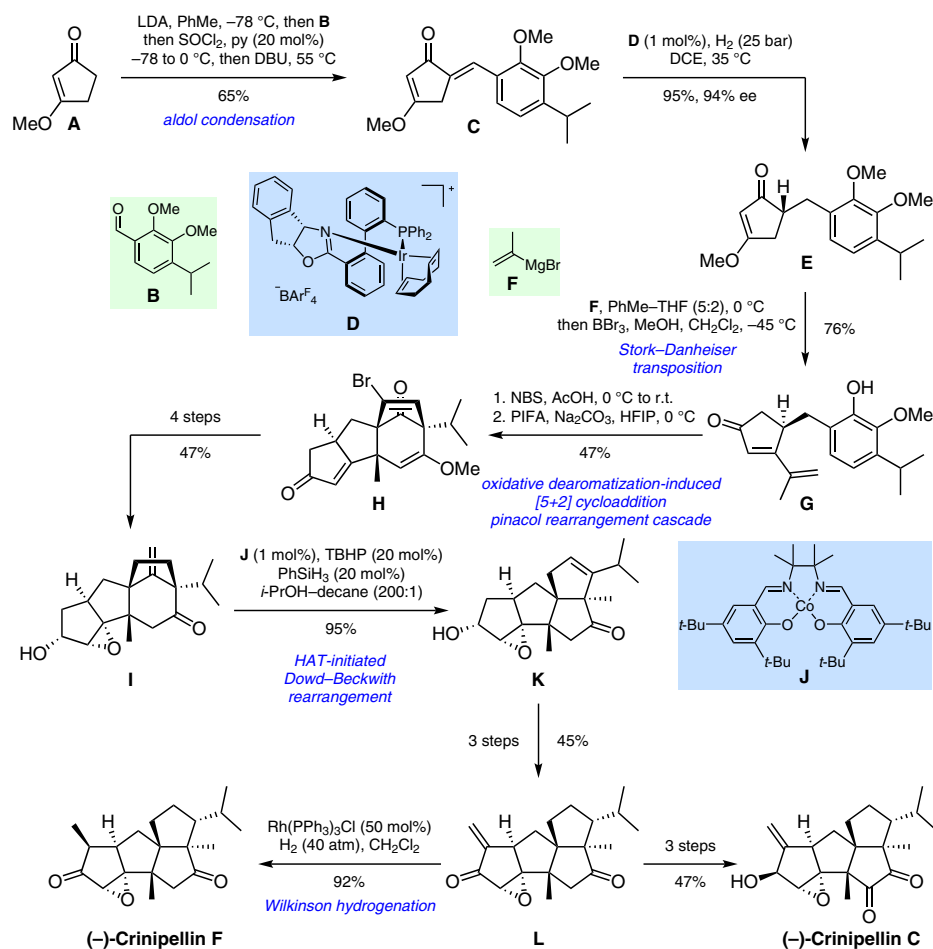


Y. ZHAO, J. HU, R. CHEN, F. XIONG, H. XIE*, H. DING* (ZHEJIANG UNIVERSITY AND ZHEJIANG GONGSHANG UNIVERSITY, HANGZHOU, P. R. OF CHINA)

Divergent Total Syntheses of (–)-Crinipellins Facilitated by a HAT-Initiated Dowd–Beckwith Rearrangement

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Syntheses of (–)-Crinipellins C and F



Significance: The crinipellins are highly oxygenated tetraquinane natural products. Ding, Xie, and co-workers present their total syntheses featuring a HAT-initiated Dowd–Beckwith rearrangement. With enone **L** as a common intermediate, the authors were able to access eight natural products of the crinipellin family.

Comment: Cycloaddition precursor **G** was synthesized by Stork–Danheiser transposition of vinylogous ester **E**. An oxidative dearomatization-induced [5+2] cycloaddition pinacol rearrangement cascade yielded tetracycle **H**. Alkene **I** underwent a hydrogen atom transfer initiated Dowd–Beckwith rearrangement furnishing the tetraquinane framework.

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(–)-crinipellins

Stork–Danheiser transposition

[5+2] cycloaddition

Dowd–Beckwith rearrangement

Wilkinson hydrogenation

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