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

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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 vinyllogous ester E. An oxidative dearomatization-initiated [5+2] cycloaddition pinacol rearrangement cascade yielded tetracycle H. Alkene I underwent a hydrogen atom transfer initiated Dowd–Beckwith rearrangement furnishing the tetraquinane framework.

Key words
(−)-crinipellins
Stork–Danheiser transposition
[5+2] cycloaddition
Dowd–Beckwith rearrangement
Wilkinson hydrogenation