Syntheses of Daphniphyllum Alkaloids

**Significance:** The first total synthesis of (–)-hybridaphniphylline B in addition to three other daphniphyllum alkaloids was accomplished. The synthetic strategy relied on a biomimetic Diels–Alder cycloaddition to forge the stereochemically dense decacyclic skeleton.

**Comment:** Utilizing previously synthesized A (J. Am. Chem. Soc. 2017, 139, 14893), hexacycle D was accessed in eleven steps through an optimized Claisen rearrangement. D served as a common intermediate for the synthesis of four natural products.