Synthesis of (–)-Asperchalasine A

**Significance:** The unique cytochalasan dimer asperchalasine A, which possesses a decacyclic ring system and twenty chiral centers, was among cytochalasan alkaloids recently isolated from the culture broth of *Aspergillus flavipes*. Deng and co-workers took on the synthetic challenges associated with the preparation of the structurally intriguing asperchalasines A in the laboratory and report its first total synthesis. Furthermore, asperchalasines D, E, and H were accessed from shared intermediates.

**Comment:** The enantioselective synthesis began with the preparation of triene segment C and dienophile D from L-arabinose and Boc-L-leucine, respectively. Diels–Alder cycloaddition crafted intermediate E, which was elaborated further to give 17-epi-asporchalasin B (H). Diels–Alder reaction of this tricycle with epicoccine-derived I provided hexacycle J, which was subsequently converted into the target structure by formal [5+2] cycloaddition with an additional equivalent of H.