Enantioselective Total Synthesis of (−)-Ambiguine P

**Significance:** Isolated from the cultured cyanobacterium *Fischerella ambigua* in 2010, ambiguine P belongs to the hapalindole alkaloid family. The pentacyclic natural product contains a seven-membered ring and an embedded indole, which pose significant synthetic challenges. The authors report an enantioselective total synthesis of the target employing a stepwise [4+3]-cycloaddition strategy.

**Comment:** Ketone B, accessible from limonene (A), was transformed into enol ether D in four steps. A net [4+3] cycloaddition of this diene with indole E and subsequent intramolecular Friedel–Crafts reaction installed the target’s pentacyclic core. Functional group manipulations furnished diene I, which was transformed into the natural product by NBS-mediated regioselective oxidation.