



Significance:

Ding and coworkers reported the first asymmetric total syntheses of (+)-vulgarisin A–E, which contain an unprecedented and highly oxygenated [5-6-4-5] tetracyclic carbon framework.

Comment:

- A CAIMCP approach to forge A ring bearing desired stereochemistry at C14.
- A **borylation/conjugate addition** process connect two segments in one pot.
- A **2,3-Wittig rearrangement** to forge the quaternary center at C10.
- Samarium(II) mediate **stereocontrolled Pinacol cyclization** for construction of the B ring.