



Key Steps:

- ***SmI*₂-mediated stereoselective cyclizations in two steps, a difference between ^tBu ester and Me ester**
- **Heck reaction**

Significance:

- **First asymmetric total synthesis of Phaeocaulisin A.**
- **Taking advantage of the umpolung carbonyl-olefin coupling reactivity to achieve two sequential *SmI*₂-mediated cyclizations to stereoselectively construct the polycyclic core of the natural product.**