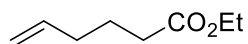


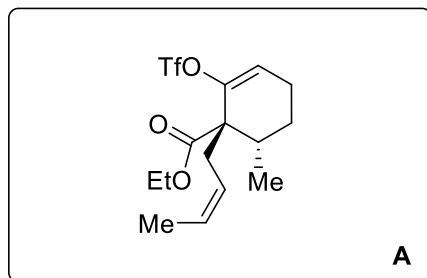
Total Syntheses of Various Amphilectane and Serrulatane Diterpenoids

X. Yu, F. Su, C. Liu, H. Yuan, S. Zhao, Z. Zhou, T. Quan, and T. Luo*

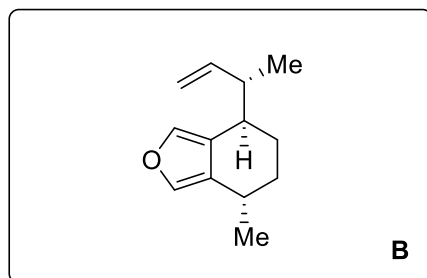
J. Am. Chem. Soc. **2016**, *138*, 6261



1–6



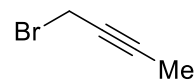
7–10



- 1) O₃, DMS
- 2) Ph₃P=CHCO₂Et
- 3) MeMgCl, CuCl
- 4) NaH, **i**
- 5) H₂, Pd-CaCO₃, Pb(OAc)₂, quinoline
- 6) LiHMDS, PhNTf₂

- 7) DIBAL-H
- 8) Pd(OAc)₂, PPh₃, Et₃N, CO
- 9) PhCl, mW, 200°C
- 10) DIBAL-H then HCl

i:

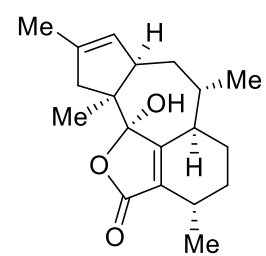


Provide the name of the catalytic system used in step 5

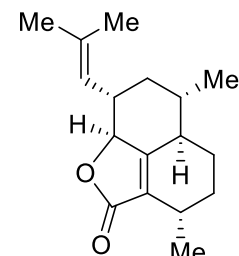
answer: Lindlar catalyst

Which reaction takes place in step 9

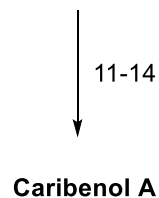
answer: Cope rearrangement



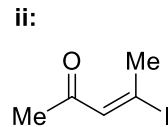
Caribenol A



Amphilectolide

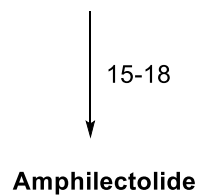
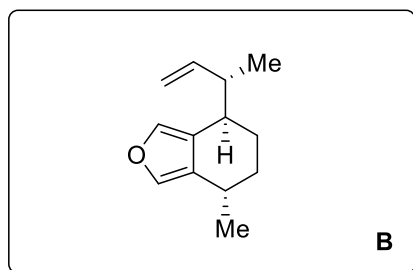


- 11) 9-BBN, **ii**, Pd(dppf)Cl₂, AsPh₃, Cs₂CO₃
- 12) AuCl₃
- 13) TMSCHN₂, *n*-BuLi
- 14) NaClO₂, NaH₂PO₄•2H₂O

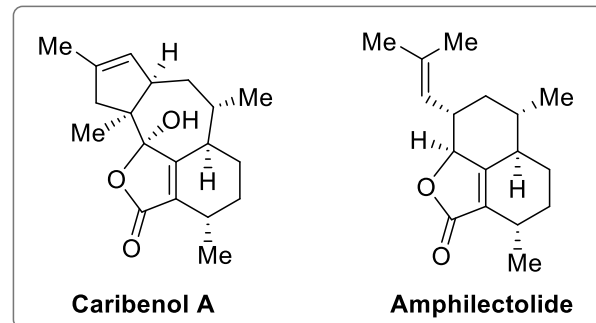


Provide a mechanism for step 13

answer of mechanism 13: By exposing **I** to lithio-TMS-diazomethane, an alkyldiene carbene-mediated 1,5-CH insertion was achieved, presumably via intermediate **II**, and tetracycle **III** was isolated in 37% yield as a pair of diastereomer (α -H: β -H = 3:1).



- 15) 9-BBN, H₂O₂
- 16) Tf₂O, 2,6-lutidine
- 17) NaClO₂, NaH₂PO₄•2H₂O then TfOH
- 18) 1-bromo-2-methylpropene, *t*-BuLi, CuI



mechanism of step 13:

