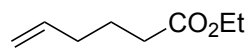


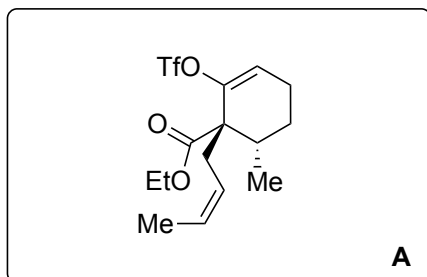
# Total Syntheses of Various Amphilectane and Serrulatane Diterpenoids

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

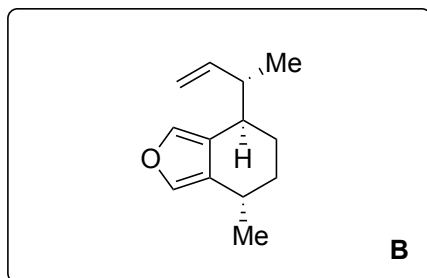
*J. Am. Chem. Soc.* **2016**, *138*, 6261



1-6



7-10



11-14

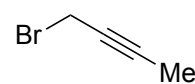
**Caribanol A**

- 1) O<sub>3</sub>, DMS
- 2) Ph<sub>3</sub>P=CHCO<sub>2</sub>Et
- 3) MeMgCl, CuCl
- 4) NaH, **i**
- 5) H<sub>2</sub>, Pd-CaCO<sub>3</sub>, Pb(OAc)<sub>2</sub>, quinoline
- 6) LiHMDS, PhNTf<sub>2</sub>

- 7) DIBAL-H
- 8) Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, Et<sub>3</sub>N, CO
- 9) PhCl, mW, 200°C
- 10) DIBAL-H then HCl

- 11) 9-BBN, **ii**, Pd(dppf)Cl<sub>2</sub>, AsPh<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>
- 12) AuCl<sub>3</sub>
- 13) TMSCHN<sub>2</sub>, *n*-BuLi
- 14) NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O

**i**:

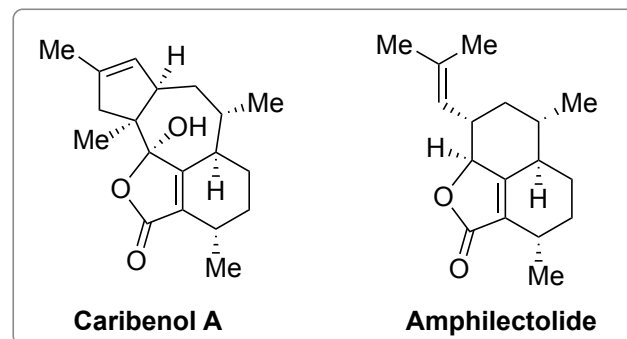


Provide the name of the catalytic system used in step 5

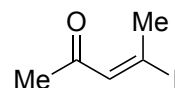
**answer: Lindlar catalyst**

Which reaction takes place in step 9

**answer: Cope rearrangement**

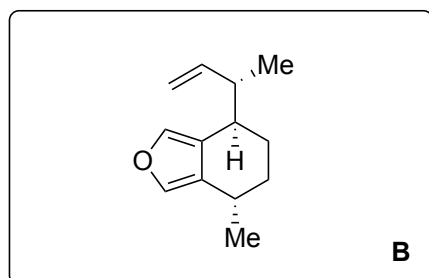


**ii**:



Provide a mechanism for step 13

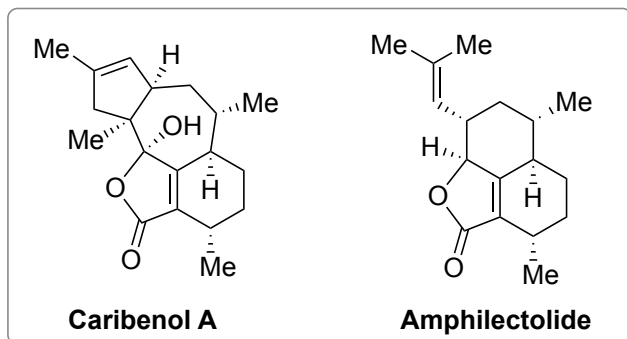
**answer of mechanism 13:** By exposing **I** to lithio-TMS-diazomethane, an alkylidene carbene-mediated 1,5-CH insertion was achieved, presumably via intermediate **II**, and tetracycle **III** was isolated in 37% yield as a pair of diastereomer ( $\alpha$ -H: $\beta$ -H = 3:1).



15-18

**Amphilectolide**

- 15) 9-BBN, H<sub>2</sub>O<sub>2</sub>
- 16) Tf<sub>2</sub>O, 2,6-lutidine
- 17) NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O then TfOH
- 18) 1-bromo-2-methylpropene, *t*-BuLi, CuI



**mechanism of step 13:**

