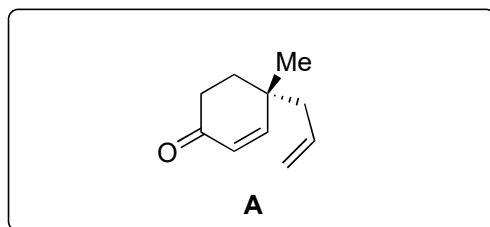
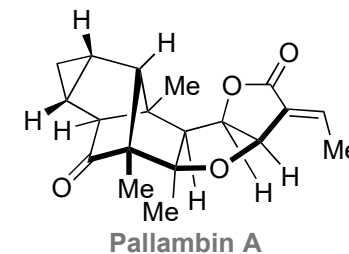


Enantioselective Total Syntheses of Pallambins A-D

Xiwu Zhang, Xinxian Cai, Bin Huang, Lei Guo, Zhongrun Gao, and Yanxing Jia

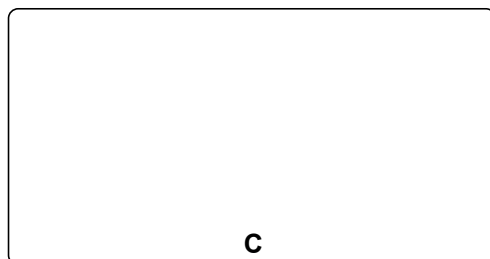
Angew. Chem. Int. Ed. **2019**, DOI: 10.1002/anie.201907523



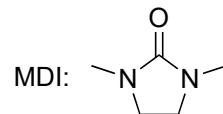
1-5



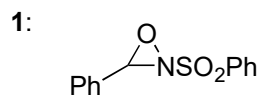
6-9



- 1) $\text{CH}_2=\text{CHMgBr}$,
 $\text{CuBr}\cdot\text{Me}_2\text{S}$, $-40\text{ }^\circ\text{C}$
then HMPA, MeI
- 2) TBSCl, NEt_3 , NaI, MeCN
then $\text{Pd}(\text{OAc})_2$, O_2 , DMSO, $85\text{ }^\circ\text{C}$
- 3) *m*-CPBA, CH_2Cl_2
- 4) TsOH, MDI, CH_2Cl_2



- 5)
, $115\text{ }^\circ\text{C}$
- 6) H_2SO_4 , EtOH/ H_2O , $100\text{ }^\circ\text{C}$
- 7) 3 eq. LiHMDS, **1**, $-78\text{ }^\circ\text{C}$
- 8) DMP, CH_2Cl_2
- 9) $\text{LiAlH}(\text{O}t\text{-Bu})_3$, $-78\text{ }^\circ\text{C}$



- 2) Name? Mechanism:
Hint: A ring is formed

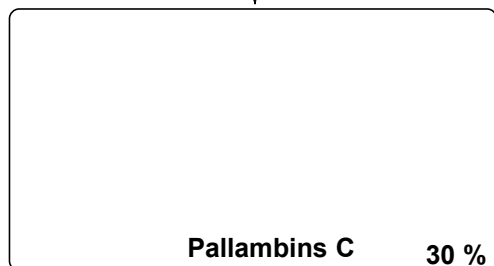
- 3) Name?

- 5) Name?
Propose a mechanism

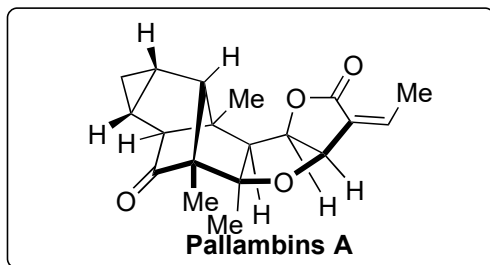
- 7) Name of reagent?



10–14



15



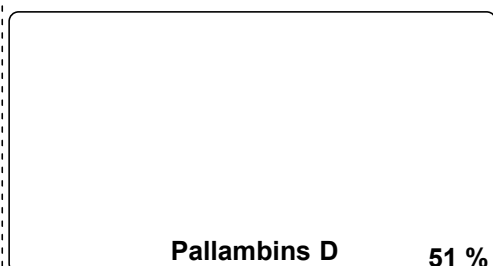
- 10) Ph₃P=C=C=O, *m*-Xylene, 160 °C
- 11) Red-Al, CuI, THF, -78 °C
- 12) Py·HBr₃, AcOH
- 13) Pd(OAc)₂, PPh₃, NEt₃, DMSO
- 14) LiHMDS, THF, -78 °C, MeCHO
- 15) *hν*, CH₂Cl₂

10) Name?

13) What side product would you expect?

15) Mechanism:

+



15

