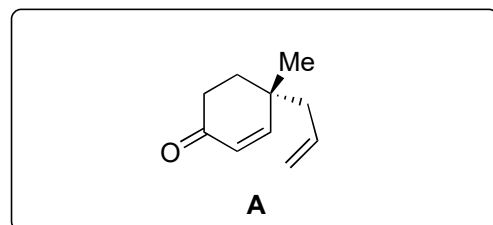
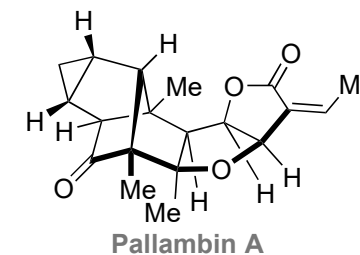


# Enantioselective Total Syntheses of Pallambins A-D

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

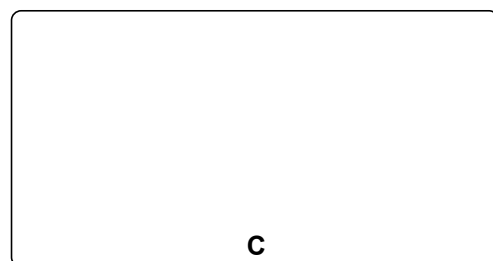
*Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201907523



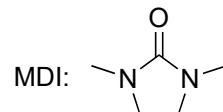
1-5



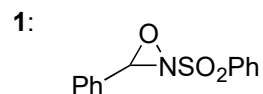
6-9



- 1)  $\text{CH}_2=\text{CHMgBr}$ ,  
 $\text{CuBr}\cdot\text{Me}_2\text{S}$ ,  $-40\text{ }^\circ\text{C}$   
then HMPA, MeI
- 2) TBSCl,  $\text{NEt}_3$ , NaI, MeCN  
then  $\text{Pd}(\text{OAc})_2$ ,  $\text{O}_2$ , DMSO,  $85\text{ }^\circ\text{C}$
- 3) *m*-CPBA,  $\text{CH}_2\text{Cl}_2$
- 4) TsOH, MDI,  $\text{CH}_2\text{Cl}_2$



- 5)   
,  $115\text{ }^\circ\text{C}$
- 6)  $\text{H}_2\text{SO}_4$ , EtOH/ $\text{H}_2\text{O}$ ,  $100\text{ }^\circ\text{C}$
- 7) 3 eq. LiHMDS, **1**,  $-78\text{ }^\circ\text{C}$
- 8) DMP,  $\text{CH}_2\text{Cl}_2$
- 9)  $\text{LiAlH}(\text{O}t\text{-Bu})_3$ ,  $-78\text{ }^\circ\text{C}$



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

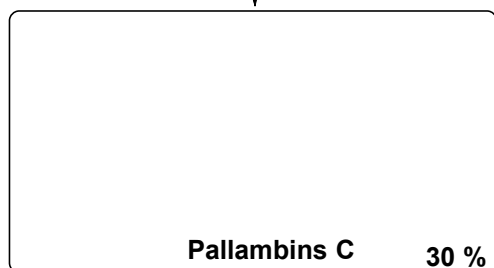
- 3) Name?

- 5) Name?  
Propose a mechanism

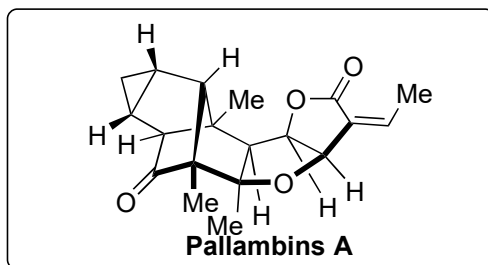
- 7) Name of reagent?



10–14



15



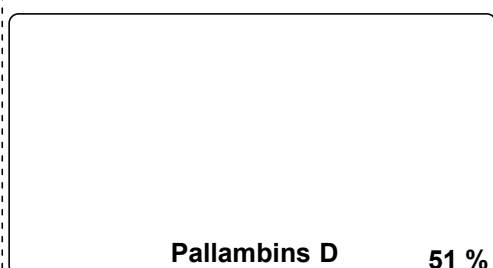
- 10) Ph<sub>3</sub>P=C=C=O, *m*-Xylene, 160 °C
- 11) Red-Al, CuI, THF, -78 °C
- 12) Py·HBr<sub>3</sub>, AcOH
- 13) Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, NEt<sub>3</sub>, DMSO
- 14) LiHMDS, THF, -78 °C, MeCHO
- 15) *hν*, CH<sub>2</sub>Cl<sub>2</sub>

10) Name?

13) What side product would you expect?

15) Mechanism:

+



15

