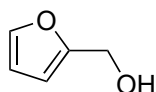


11-Step Total Synthesis of Pallambins C and D

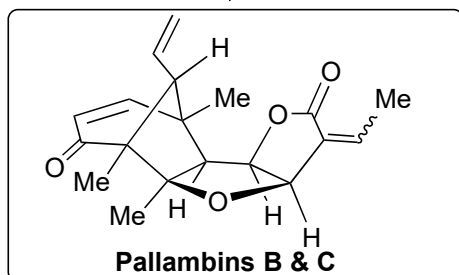
Luisruben P. Martinez, Shigenobu Umemiyu, Sarah E. Wengryniuk, and Phil S. Baran
Journal of the American Chemical Society 2016 138 (24), 7536-7539



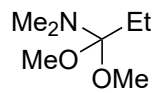
1-5



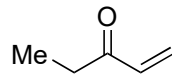
6-11



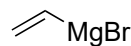
- 1) **1**, Δ , then TMDS, $\text{Ti}(\text{OiPr})_4$
- 2) **2**, Bu_4NBr , KOH
- 3) **3**, $\text{CuBr} \cdot \text{DMS}$, TMSCl , HMPA
- 4) O_2 , $h\nu$, methylene blue, then thiourea
- 5) TiCl_4



1



2



3

- 6) $\text{CH}(\text{OMe})_3$, $\text{BF}_3 \cdot \text{OEt}_2$ then AcBr
- 7) Bu_3SnH , AIBN
- 8) LiHMDS , PhSeCl , H_2O_2
- 9) PPTS , pyridine
- 10) dimethyl malonate, SnCl_4 , DBU , I_2
- 11) NaOH , MeOH , then Et_3N , MeCN , 60°C , then LiHMDS , MeCHO , then Et_3N , MsCl , DMAP

1) Name of the reaction ? TMDS structure ?

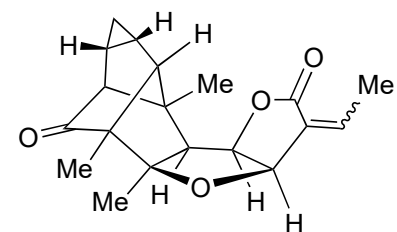
2) Name of the reaction ?

4) Role of methylene blue ? Why is it mandatory ?

5) Name of the reaction ?

Propose a mechanism for the literature known photochemical rearrangement between pallambins B&C and pallambins A&D

$h\nu$



Pallambins A & D

