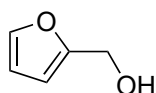
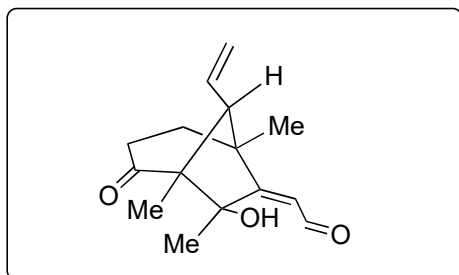


11-Step Total Synthesis of Pallambins C and D

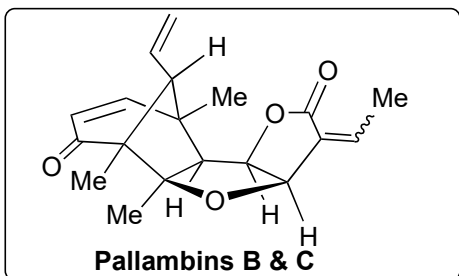
Luisruben P. Martinez, Shigenobu Umemiyu, Sarah E. Wengryniuk, and Phil S. Baran
Journal of the American Chemical Society 2016 138 (24), 7536-7539



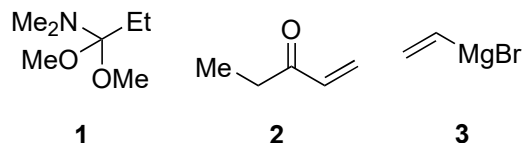
1-5



6-11



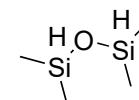
- 1) **1**, Δ , then TMDS, $\text{Ti}(\text{OiPr})_4$
- 2) **2**, Bu_4NBr , KOH
- 3) **3**, $\text{CuBr} \cdot \text{DMS}$, TMSCl , HMPA
- 4) O_2 , $h\nu$, methylene blue, then thiourea
- 5) TiCl_4



- 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 ?

Eschenmoser - Claisen rearrangement



2) Name of the reaction ?

Robinson annulation

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

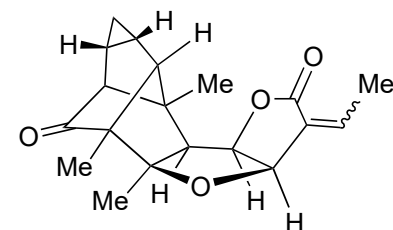
Photosensitizer necessary for singlet oxygen generation

5) Name of the reaction ?

Mukaiyama aldol reaction

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

Jiao-Zhen Zhang, Rong-Xiu Zhu, Gang Li, Li-Ning Wang, Bin Sun, Wen-Fang Chen, Lei Liu, and Hong-Xiang Lou
Organic Letters 2012 14 (22), 5624-5627



Pallambins A & D

$h\nu$

