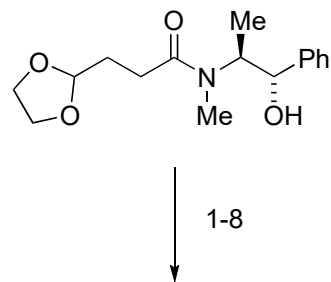
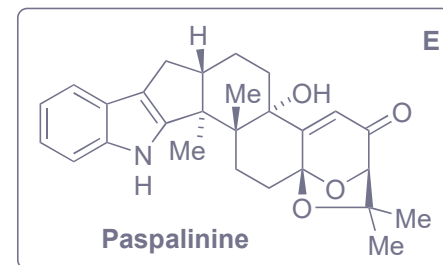
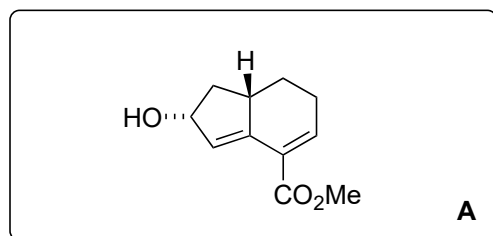


Asymmetric Total Synthesis of Indole Diterpenes Paspalicine, Paspalinine, and Paspalinine-13-ene

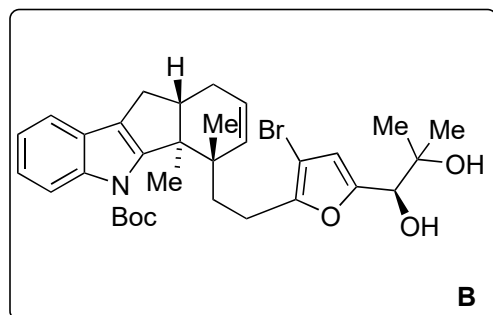
Lian-Dong Guo, Zejun Xu, and Rongbiao Tong
Angew. Chem. Int. Ed. **2022**, *61*, e202115384.



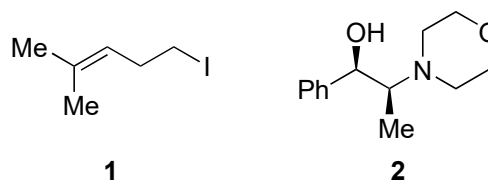
1-8



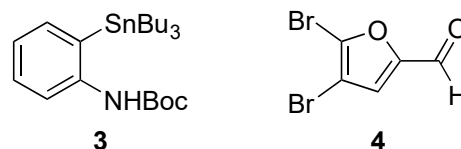
9-20



- 1) LDA, LiCl, then **1**
- 2) MeLi
- 3) KHMDS, Comins reagent
- 4) py
- 5) *n*BuLi, ClCO₂Me
- 6) TMSOTf, 2,6-lutidine, H₂O
- 7) Zn(CHCH₂)₂, **2**, *n*BuLi
- 8) Hoveyda-Grubbs II



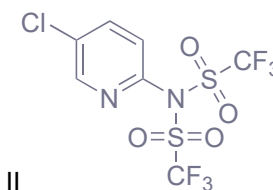
- 9) CH₂I₂, ZnEt₂
- 10) TBSOTf, Et₃N
- 11) LDA, MeI
- 12) DIBAL
- 13) DMP
- 14) Ph₃P=CH₂
- 15) Na-Naph, *t*BuOH, Comins reagent
- 16) Pd(PPh₃)₄, LiCl, CuCl, **3**
- 17) Pd(OCOCF₃)₂
- 18) Cy₂BH, then **4**, PdCl₂(dppf)
- 19) Ph₃P=CMe₂
- 20) AD-mix α



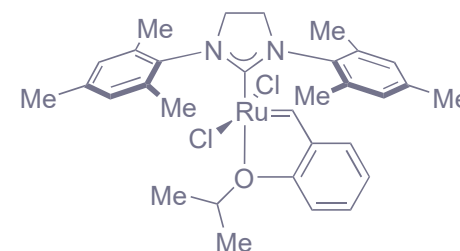
Step 1: Name the reaction

Myer's asymmetric alkylation

Step 3: Structure of Comins reagent



Step 3: Structure of Hoveyda-Grubbs II



Step 9: Name the reaction

Simmons-Smith-cyclopropanation

Step 14: Name the reaction

Wittig olefination

Step 16: Name the reaction

Stille coupling

Step 17: Name the reaction

aza-Wacker reaction

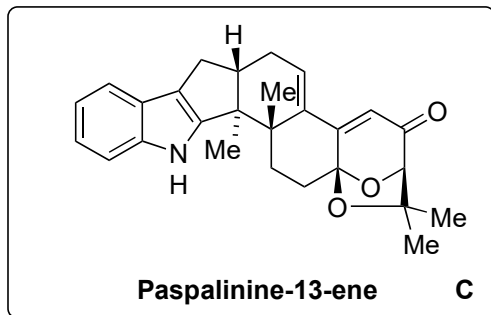
Step 18: Name the reaction

Suzuki-Miyaura coupling

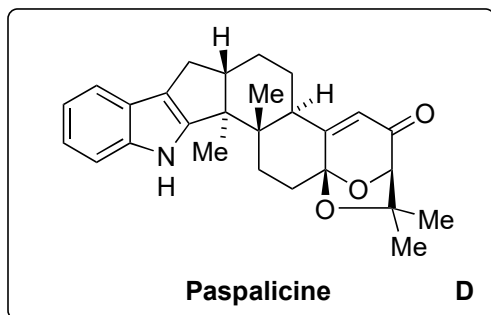
Step 20: Name the reaction and the components of the AD-mix

Sharpless asymmetric dihydroxylation
 (DHQ)₂PHAL, K₂CO₃, K₃[Fe(CN)₆], K₂OsO₄ · 2 H₂O

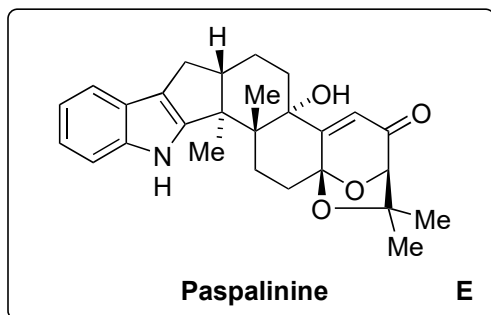
21-26



27



28



- 21) Hermann's cat, TBAC
- 22) CeBr_3 (cat), H_2O_2 , then CuSO_4 , *p*-TSA
- 23) Wilkinson's catalyst, H_2
- 24) TBSOTf, Et_3N
- 25) PhSeCl , H_2O_2
- 26) SiO_2 , 90°C

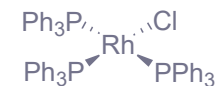
- 27) Lindlar cat, then DDQ

- 28) SeO_2

Step 21: Name the reaction
intramolecular Heck reaction

Step 22: Name the reaction
Achmatowicz rearrangement/ bicycloketalization

Step 23: Structure of Wilkinson's catalyst



Step 27: Name the components of the Lindlar catalyst
 $5\% \text{Pd-CaCO}_3$, Pb(OAc)_2 , quinoline
Step 27: Which by-product is formed?

