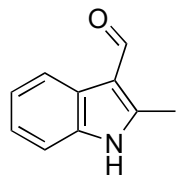


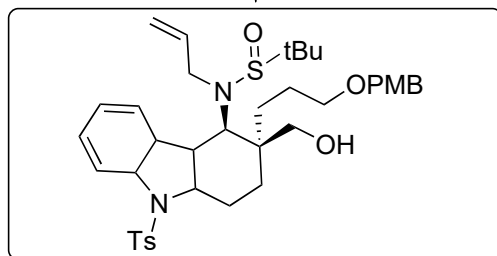
Asymmetric Total Syntheses of Kopsane Alkaloids

Xuelel Jia, Dr. Honghui Lei, Feipeng Han, Tao Zhang, Ying Chen, Dr. Zhengshuang Xu, Dr. Pratanphorn Nakliang, Prof. Dr. Sun Choi, Dr. Yian Guo, Prof. Dr. Tao Ye

Angew. Chem., Int. Ed., **2020**, 59, 12832-12836.

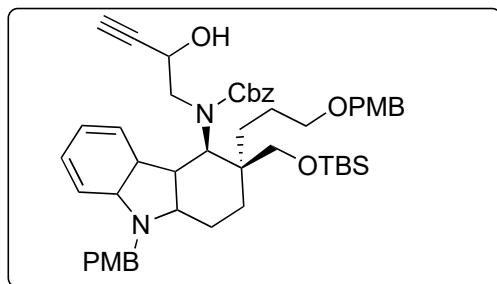


1 - 4

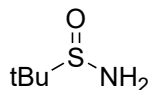


A

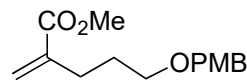
5 - 12



- 1) pTsCl, iPr₂NEt, MeCN
- 2) Ti(OEt)₄, **1**, CH₂Cl₂
- 3) **2**, LiHMDS, THF, -78°C then allyl-Br, DMF, 0°C to 23°C
- 4) DIBAL-H, CH₂Cl₂, 0°C

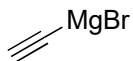


1



2

- 5) HCl, MeOH, CH₂Cl₂, 0°C
- 6) TBSCl, ImH, DMAP, CH₂Cl₂, 0°C to 23°C
- 7) CbzCl, K₂CO₃, CH₂Cl₂
- 8) Mg, MeOH, ultrasonic
- 9) PMBBBr, NaH, DMF, 0°C to 23°C
- 10) OsO₄, NMO, acetone, H₂O
- 11) NaIO₄, CH₂Cl₂
- 12) **3**, LiHMDS, THF, -20°C

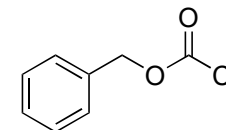


3

- 3) *Hint*: 1 ring is formed, names of the reactions ? Provide a mechanism

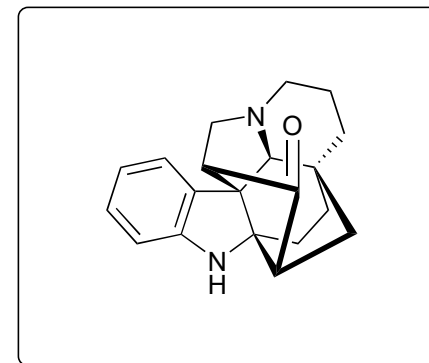
Michael/Mannich domino

- 7) Structure of Cbz ?



- 10) and 11) Name of both reactions ?

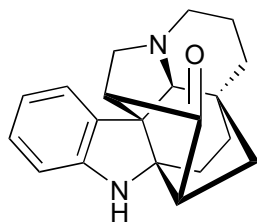
Lemieux-Johnson



B

B

13-21



(-)-Kopsanone

- 13) **4**, PPTS
- 14) PtCl_2 , DCE, 85°C
- 15) PTSA, MeOH, 0°C
- 16) MsCl, Et_3N , DMAP, CH_2Cl_2 , 0°C
- 17) HCl, THF, 0°C
- 18) NaH, THF, 0°C to 23°C
- 19) DDQ, CH_2Cl_2 , 0°C to 23°C
- 20) DMP, NaHCO_3 , CH_2Cl_2 , 0°C
- 21) H_2 , Pd/C, MeOH

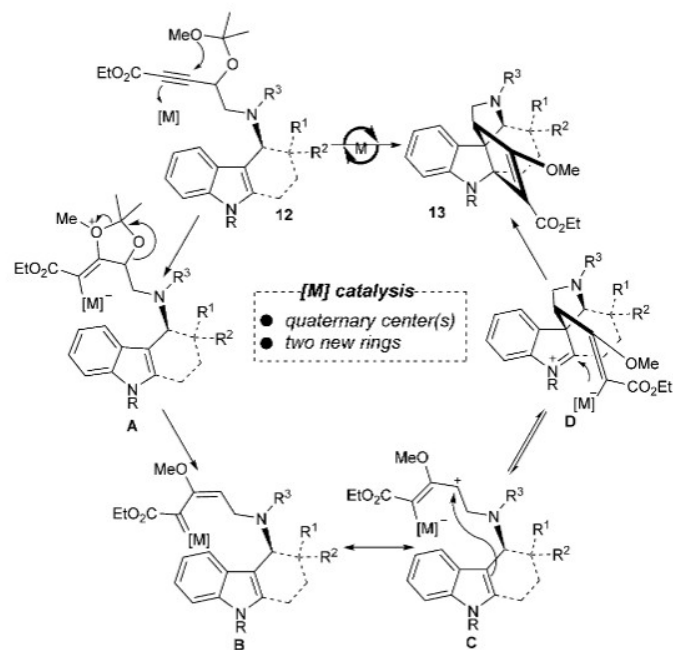


4

(-)-Kopsanone

- 14) *Hint*: 2 rings are formed, propose a mechanism.

Mechanism for 14



Mechanism for 3

