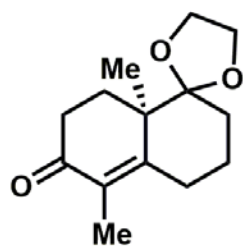


Total Synthesis of (-)-Rhodomollanol A

Till Vogel, 04.03.2020



- 1.) Li, NH₃, -78 °C to -45 °C
- 2.) DIAD, PPh₃, BzOH.
then TsOH•H₂O, acetone
- 3.) IBX, PhMe/DMSO, 85 °C
- 4.) H₂O₂, NaOH, MeOH

A

- 5.) H₂NNHCONH₂•HCl,
NaOAc, EtOH/H₂O
- 6.) Pb(OAc)₄, DCM, -10 °C
- 7.) H₂, Pd/BaSO₄

B

- 8.) n-BuLi, **1**,
then **B**

C

- 9.) DHP, TsOH•H₂O
- 10.) PIFA, Na₂CO₃,
Na₃PO₄, HFIP,
then TFA

D

- 11.) (TMSOCH₂)₂,
TMSOTf

E

- 12.) NaH, CS₂, MeI
- 13.) AIBN, Bu₃SnH
- 14.) DIBAL-H

F

- 15.) VO(acac)₂, TBHP
- 16.) (PhSeO)₂O, py,
PhMe, 90 °C
- 17.) NaBH₄, CeCl₃•7H₂O

G

- 18.) LiHMDS, TMSCl
- 19.) hν, AcOH

H

- 20.) MeSOCH₂Na,
MeI, HMPA

I

- 21.) OsO₄, py,
then aq. NaHSO₃
- 22.) PPTS, 2-methoxypropene

J

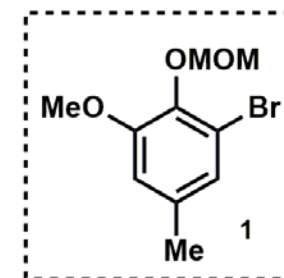
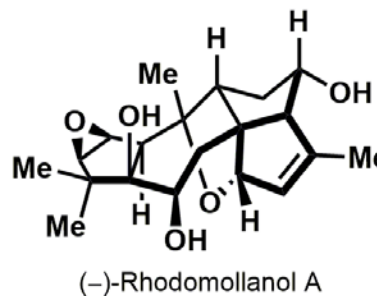
- 23.) LiHMDS, NIS,
then mCPBA
- 24.) TsNHNH₂, PPTS
- 25.) NaBH₃CN, AcCl, MeOH
- 26.) NEt₃, 50 °C

- 27.) Cp₂TiCl₂, Zn, THF, 50 °C
- 28.) NaH, CS₂, MeI
- 29.) dichlorobenzene, 150 °C,
then TsOH•H₂O, MeOH

K

L

- 30.) VO(acac)₂, TBHP
- 31.) NaBH₄, MeOH



Hints: step 5)/(6) traditional conditions; 5) H₂NNHCONH₂•HCl, NaOAc, EtOH/H₂O; 6) base; step 10) cascade of cycloaddition and subsequent rearrangement; step 11) acetal formation + subsequent rearrangement; step 19) two cyclopropane rings are involved in the transformation; carbon skeleton complete after the transformation; step 20) the dmsyl anion is not incorporated in the product