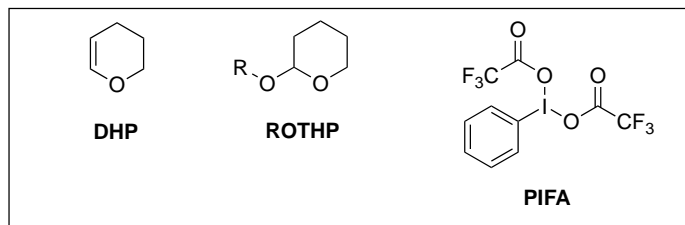
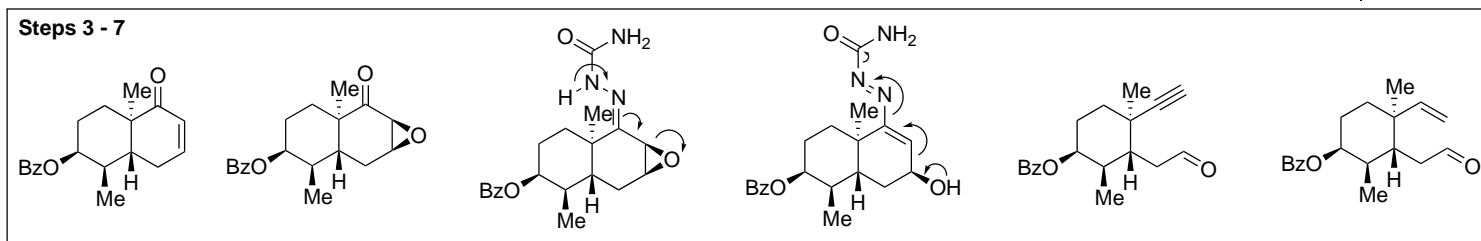
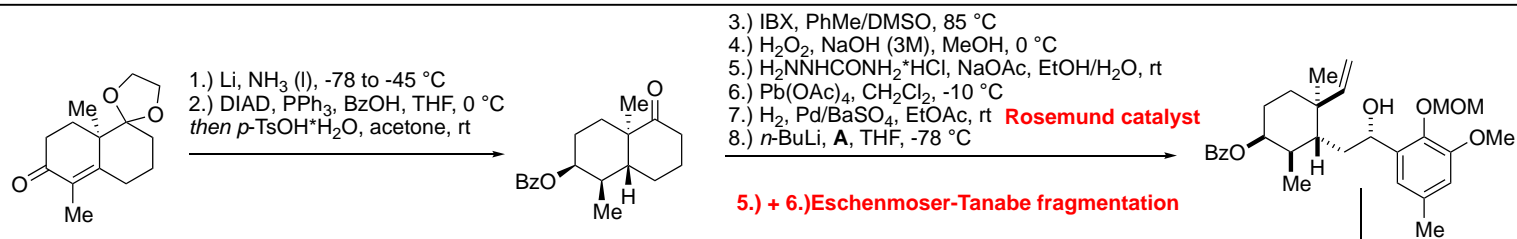
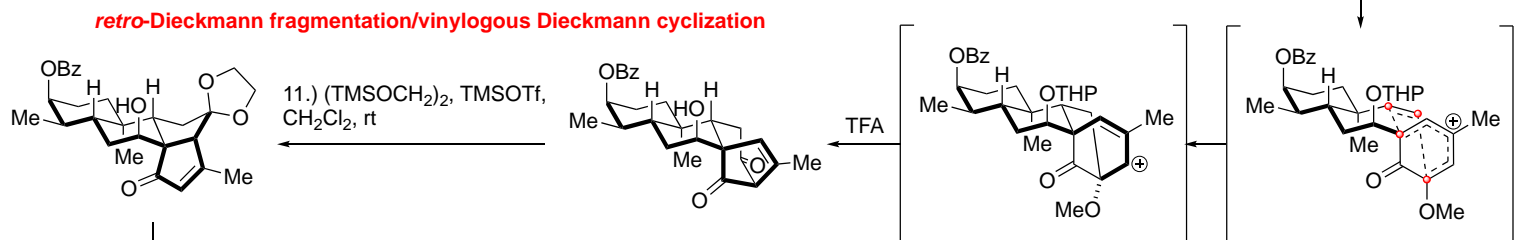


E133: (-)-rhodomollanol



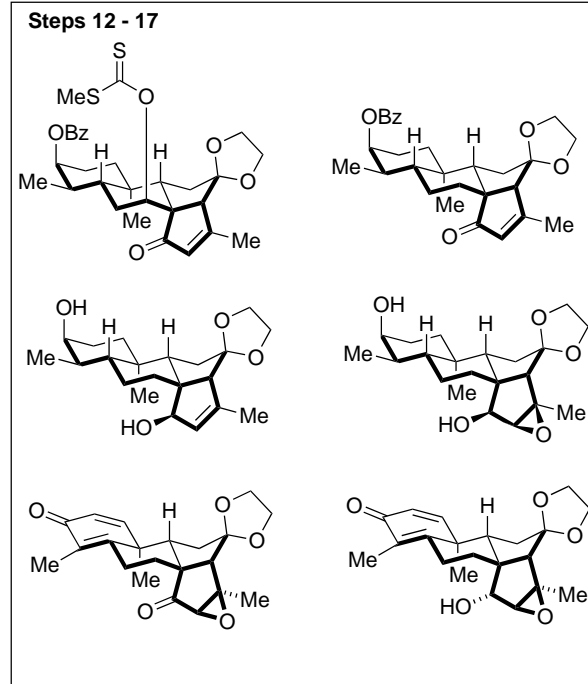
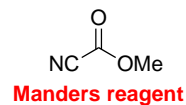
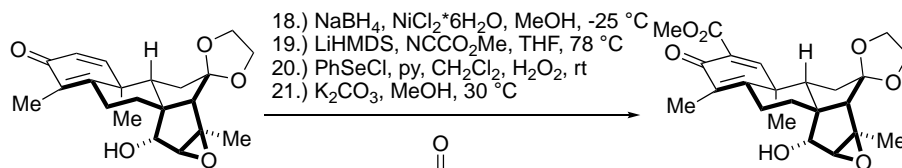
9.) DHP, *p*-TsOH·H₂O
 10.) PIFA, Na₂CO₃, Na₃PO₄, HFIP, 0 °C

Oxidative dearomatization-induced (ODI)-(5+2) cycloaddition/pinacol-type 1,2-acyl migration



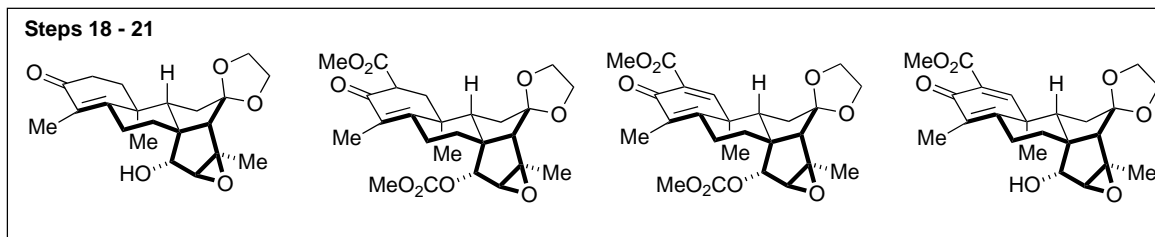
E133: (-)-rhodomollanol

- 12.) NaH, CS₂, MeI, THF, 65 °C **Barton-McCombie Deoxygenation**
- 13.) AIBN, *n*-Bu₃SnH, toluene, 60 °C
- 14.) DIBAL-H, CH₂Cl₂, -78 °C
- 15.) VO(acac)₂, TBHP, CH₂Cl₂, 0 °C
- 16.) (PhSeO)₂O, py, toluene, 90 °C
- 17.) NaBH₄, CeCl₃·7 H₂O, MeOH/CH₂Cl₂, -20 °C **Luche reduction**

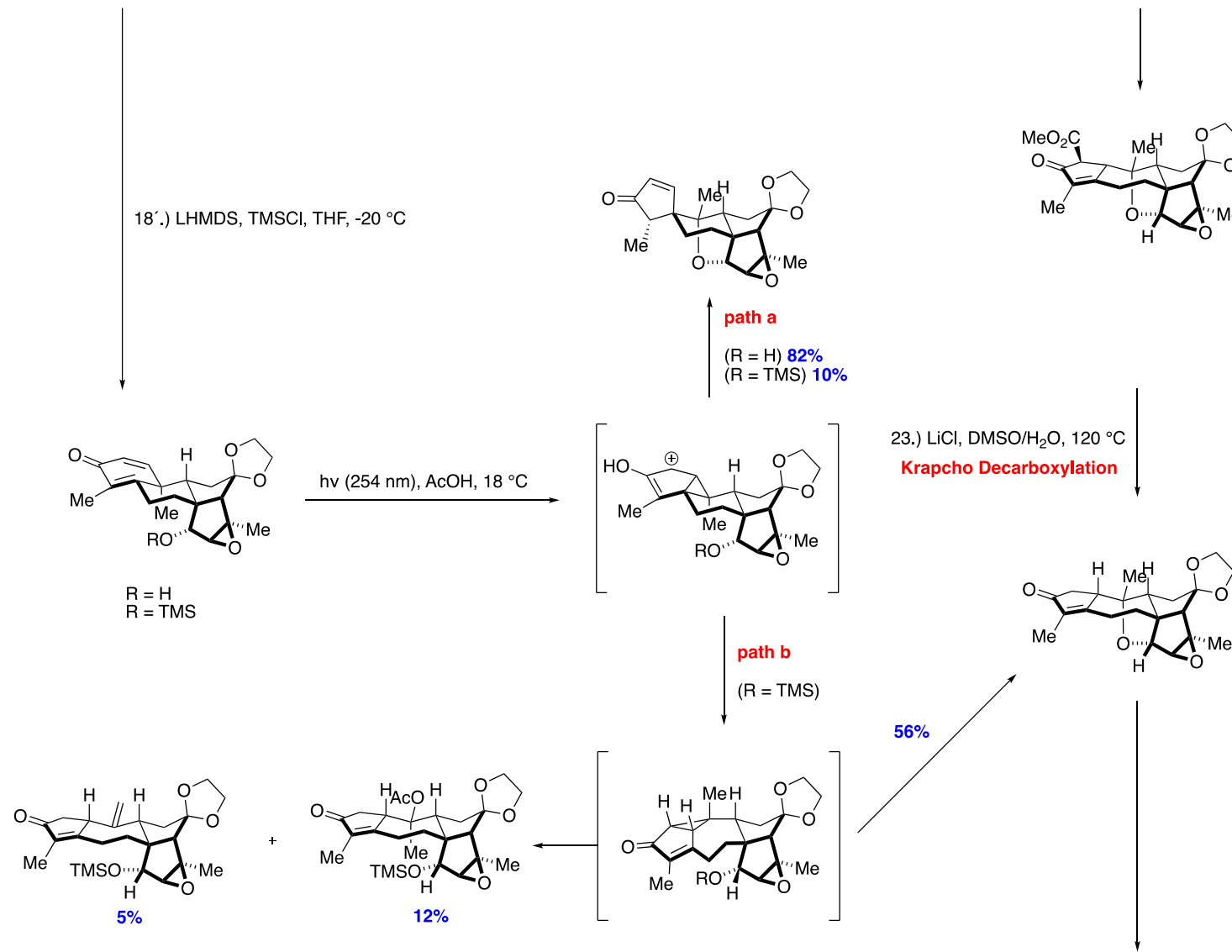


22.) hv (254 nm),
 AcOH, 18 °C

Photo-Nazarov cyclization/intramolecular cycloetherification cascade

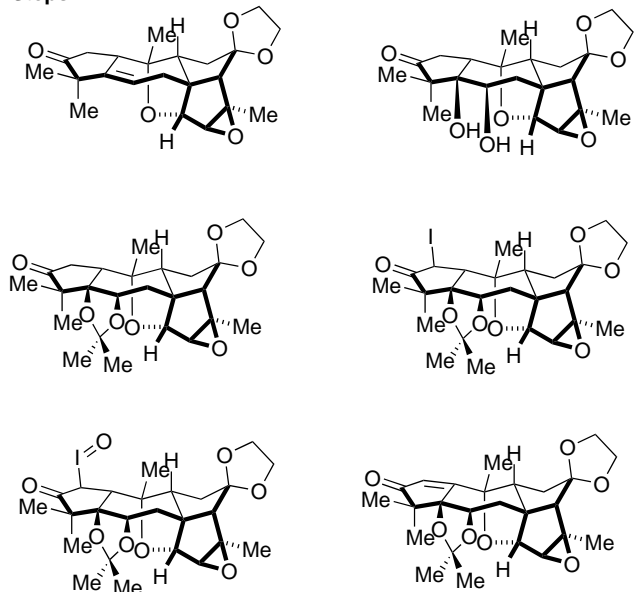


E133: (-)-rhodomollanol



E133: (-)-rhodomollanol

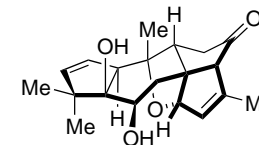
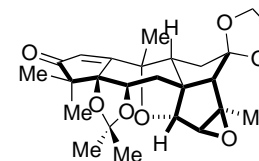
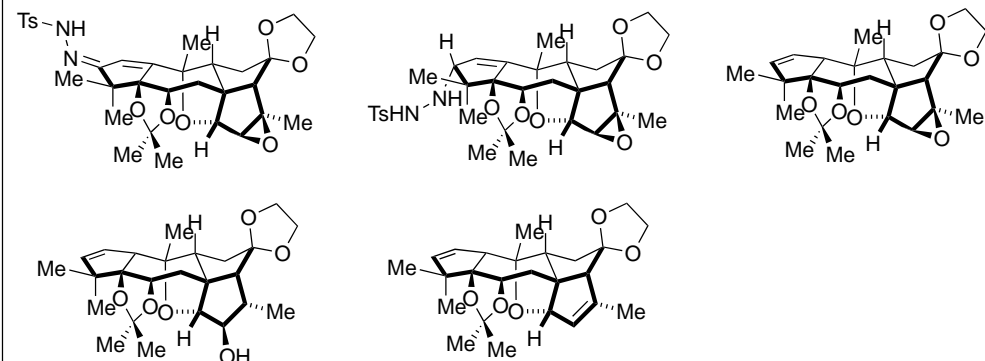
Steps 24 - 27



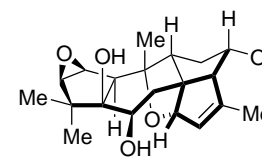
28.) TsNHNH₂, PPTS, THF, 60 °C
 29.) NaBH₃CN, AcCl, MeOH, rt
 then Et₃N
 30.) Cp₂TiCl₂, Zn, THF, 50 °C
 31.) NaH, CS₂, MeI, THF, rt
 32.) *o*-DCB, 150 °C
 then *p*-TsOH·H₂O, MeOH, 30 °C

31.) + 32.) Chugaev Elimination

Steps 28 - 32



33.) VO(acac)₂, TBHP,
 CH₂Cl₂, 0 °C
 34.) NaBH₄, MeOH, 0 °C



(-)-rhodomollanol

