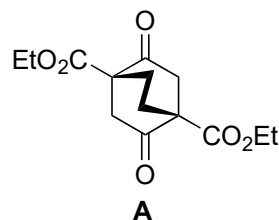


Total Synthesis of (+)-Daphmanidin E

Matthias E. Weiss, Erick M. Carreira, *Angew. Chem. Int. Ed.* **2011**, *50*, 11501–11505.



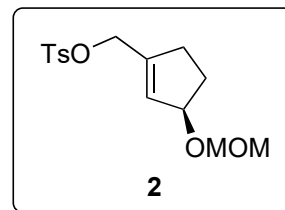
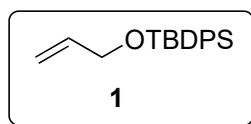
1-8



9-16



- 1) 1,3-propanediol, *p*TsOH (10 mol%), PhH, reflux; then *p*TsOH (10 mol%), acetone, 50°C
- 2) KHMDS, 2-(NTf₂)-pyridine, THF, -40°C
- 3) **1**, 9-BBN, AsPh₃ (16 mol%), [Pd₂(dba)₃]/CHCl₃ (2 mol%), K₃PO₄, DMF/THF/H₂O, 45°C
- 4) BH₃•SMe₂, THF, rt; then NaBO₃•4 H₂O; then DIBAL-H, THF, -25°C
- 5) *p*TsOH (5 mol%), acetone, 50°C
- 6) BzCl, pyridine, DMAP (cat.), CH₂Cl₂, rt
- 7) KHMDS, [18]-crown-6, **2**, THF, -20°C
- 8) nonane, 155°C



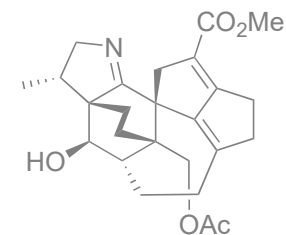
- 9) KHMDS, allyl bromide, [18]-crown-6, THF, -20°C
- 10) *o*-xylene, 165°C
- 11) 9-BBN, THF, rt; then NaBO₃•4 H₂O
- 12) Ac₂O, pyridine, DMAP, CH₂Cl₂, rt; TBAF•3 H₂O, THF, rt
- 13) 2-NO₂-C₆H₄SeCN, PBu₃, THF, rt; H₂O₂, pH 7 buffer, CH₂Cl₂, rt
- 14) CeCl₃•x H₂O, oxalic acid, MeCN, rt
- 15) Me₃Si/imidazole, CH₂Cl₂, rt; MOMCl, *i*Pr₂NEt, CH₂Cl₂, TBAF, THF, rt
- 16) DMP, CH₂Cl₂, rt

Which named reaction takes place in step 3?

Please name the reaction of step 8.

10) Please name the reaction.

Step 13 involves a named reaction. Please provide name and mechanism.

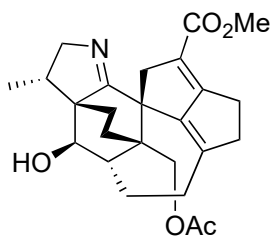


(+)-Daphmanidin E

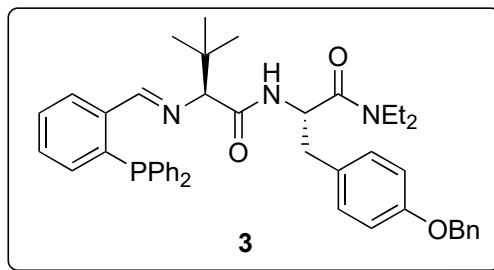
17-23



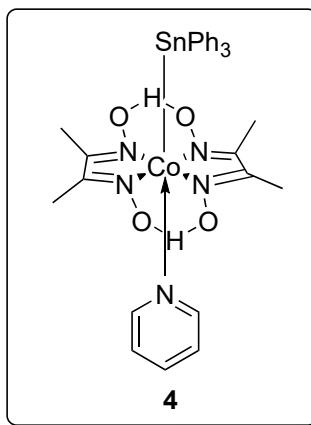
24-29



- 17) MeNO₂, NH₄OAc, 75°C
- 18) ZnMe₂, [Cu(OTf)]₂•toluene, **3**, toluene, 0°C
- 19) Zn, aq. NH₄Cl, EtOH, 40°C; Boc₂O, EtOH, rt
- 20) O₃, PPh₃, CH₂Cl₂, -78°C; NaBH(OAc)₃, AcOH, THF, rt
- 21) MsCl, Et₃N, CH₂Cl₂, 0°C; NaI, acetone
- 22) DBU, toluene, RT
- 23) a) 110 mol% **4**, sunlamp, MeCN, 60°C or
b) 25 mol% **4**, *i*Pr₂NEt, blue LED, MeCN, 23°C



- 24) K₂CO₃, MeOH, 0°C
- 25) PCC, CH₂Cl₂, rt
- 26) Bn₂NH•CF₃CO₂H (1:1), benzene, 50°C
- 27) NaCN, AcOH, MnO₂, MeOH, rt;
K₂CO₃, MeOH, 45°C;
Ac₂O, *i*Pr₂NEt, DMAP, CH₂Cl₂, rt
- 28) CF₃CO₂H, CH₂Cl₂, rt; NH₄Cl, EtOH, 75°C
- 29) Ph₂BBr, CH₂Cl₂, -25°C



Please name the reaction of step 17

Which named reaction takes place in step 23?