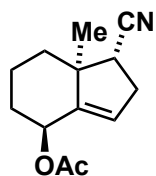


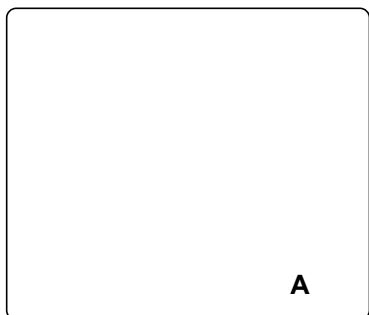
Total synthesis of solanoeclepin A

K. Tanino, M. Takahashi, Y. Tomata, H. Tokura, T. Uehara, T. Narabu and M. Miyashita

Nat. Chem., **2011**, 3, 484–488.

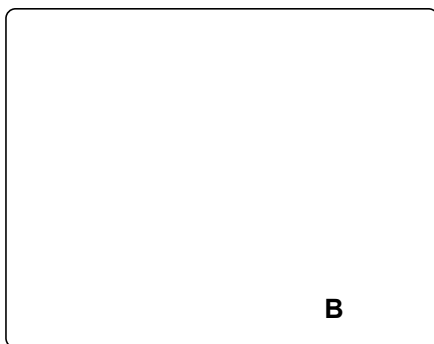


1-5



A

6-16



B

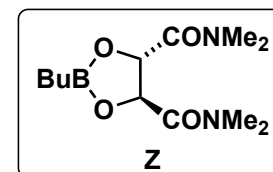
- 1) *m*-CPBA, CH₂Cl₂
- 2) Me₃Al, Al(OTf)₃, (CH₂Cl)₂
- 3) DBU, CH₂Cl₂
- 4) CH₂=CHMgBr, CeCl₃, THF
- 5) TBHP, Ti(O*i*-Pr)₄, MS4Å, CH₂Cl₂

- 6) TMSOTf, 2,6-lutidine, (CH₂Cl)₂, then HF·py
- 7) DIBAL, THF
- 8) TBSOTf, 2,6-lutidine, CH₂Cl₂
- 9) *m*-CPBA, (CH₂Cl)₂
- 10) LDA, then TBSCl, HMPA, THF
- 11) DIBAL, CH₂Cl₂
- 12) (EtO)₂P(O)CH₂CO₂Et, NaH, THF
- 13) DIBAL, THF
- 14) **Z**, Et₂Zn, CH₂I₂, CH₂Cl₂
- 15) NaH, BnBr, TBAI, DMF
- 16) TBAF, THF

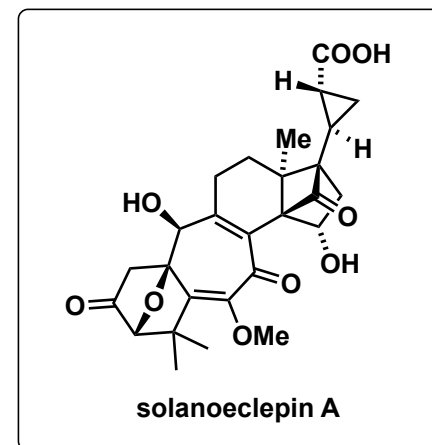
How would you make the starting material?

Step 2: Name the reaction!

Hint: electronics



Z

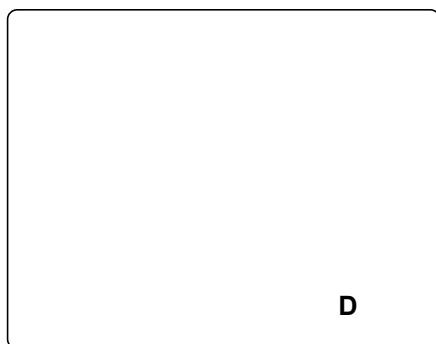


solanoeclepin A

17-25

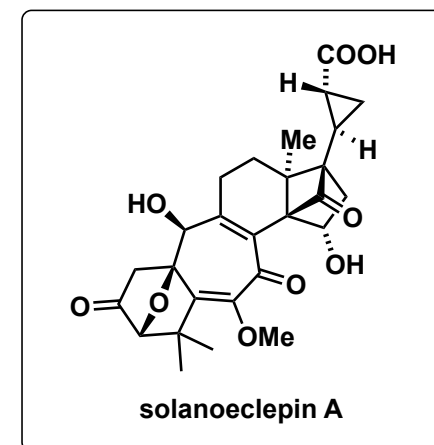
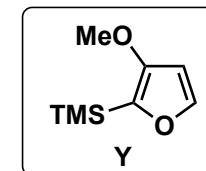
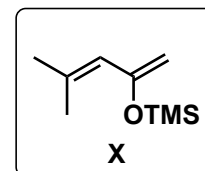


26-30

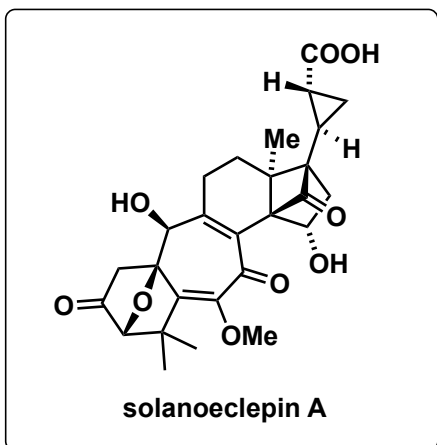
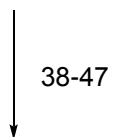
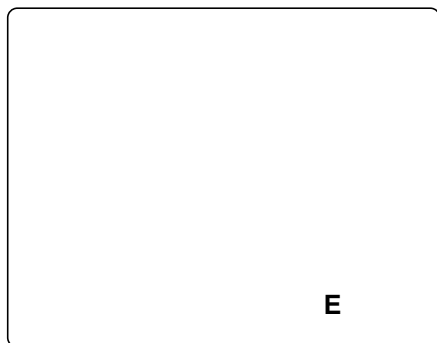
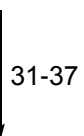


- 17) o -NO₂C₆H₄SeCN, Bu₃P, THF
- 18) H₂O₂, THF
- 19) HF•py, THF
- 20) TBSCl, imidazole, DMF
- 21) DMP, CH₂Cl₂
- 22) HF•py, THF
- 23) BOMCl, DIPEA, TBAI, CH₂Cl₂
- 24) *t*-BuOCH(NMe₂)₂, DMF
- 25) Tf₂O, 2,6-(*t*-Bu)₂Py, CH₂Cl₂

- 26) **Y**, *t*-BuLi, THF
- 27) PPTS, DMF, H₂O
- 28) TMSCl, imidazole, DMF
- 29) **X**, Bu₃SnF, PdCl₂[P(*o*-tol)₃]₂, DMF
- 30) Me₂AlCl, Et₂O



D



- 31) $\text{CH}_3\text{CO}_2\text{H}$, H_2O
- 32) DMP, CH_2Cl_2
- 33) SeO_2 , 1,4-dioxane, H_2O
- 34) $\text{Cu}(\text{OAc})_2$, MeOH
- 35) MeI, Ag_2O , DMF
- 36) DIBAL, PhMe
- 37) IBX, CH_2Cl_2 , DMSO

- 38) TMSCl, imidazole, DMF
- 39) OsO_4 , pyridine, *t*-BuOH
- 40) NaIO_4 , MeCN
- 41) TMSCl, imidazole, DMF
- 42) H_2 , $\text{Pd}(\text{OH})_2$, THF
- 43) $\text{CH}_3\text{CO}_2\text{H}$, H_2O
- 44) TMSCl, imidazole, DMF, then aq. THF
- 45) DMP, CH_2Cl_2
- 46) NaClO_2 , NaH_2PO_4 , 2-methyl-2-butene, *t*-BuOH, H_2O
- 47) 3 M HCl, $\text{CH}_3\text{CO}_2\text{H}$, H_2O