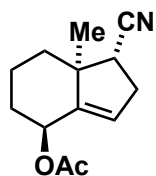


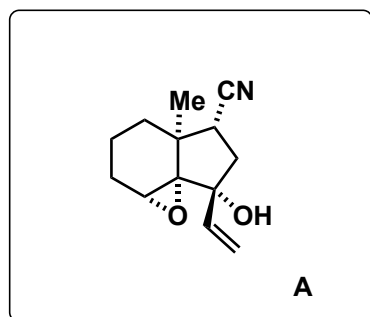
## Total synthesis of solanoeclepin A

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

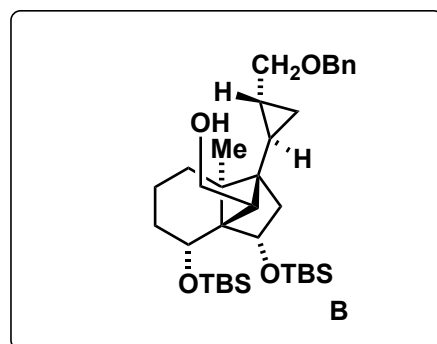
*Nat. Chem.*, **2011**, 3, 484–488.



1-5



6-16



- 1) *m*CPBA, CH<sub>2</sub>Cl<sub>2</sub>
- 2) Me<sub>3</sub>Al, Al(OTf)<sub>3</sub>, (CH<sub>2</sub>Cl)<sub>2</sub>
- 3) DBU, CH<sub>2</sub>Cl<sub>2</sub>
- 4) CH<sub>2</sub>=CHMgBr, CeCl<sub>3</sub>, THF
- 5) TBHP, Ti(O*i*-Pr)<sub>4</sub>, MS4Å, CH<sub>2</sub>Cl<sub>2</sub>

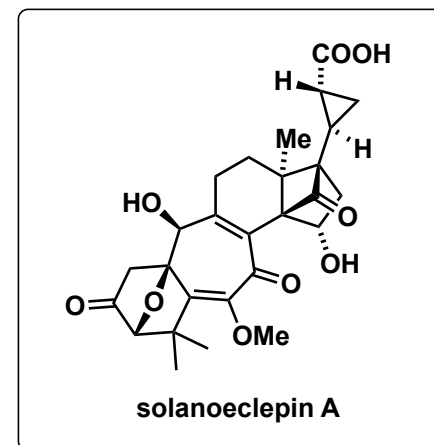
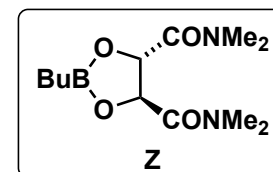
- 6) TMSOTf, 2,6-lutidine, (CH<sub>2</sub>Cl)<sub>2</sub>, then HF·py
- 7) DIBAL, THF
- 8) TBSOTf, 2,6-lutidine, CH<sub>2</sub>Cl<sub>2</sub>
- 9) *m*-CPBA, (CH<sub>2</sub>Cl)<sub>2</sub>
- 10) LDA, then TBSCl, HMPA, THF
- 11) DIBAL, CH<sub>2</sub>Cl<sub>2</sub>
- 12) (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CO<sub>2</sub>Et, NaH, THF
- 13) DIBAL, THF
- 14) **Z**, Et<sub>2</sub>Zn, CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>
- 15) NaH, BnBr, TBAI, DMF
- 16) TBAF, THF

How would you make the starting material?

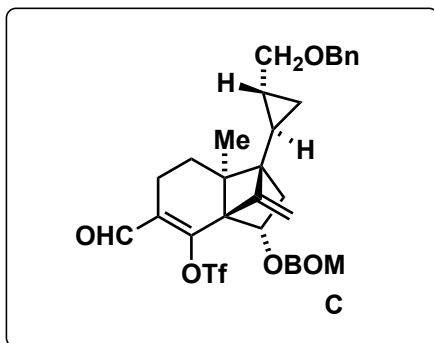
*Eur. J. Org. Chem.* **2006**, 328-334.

Step 2: Meinwald rearrangement

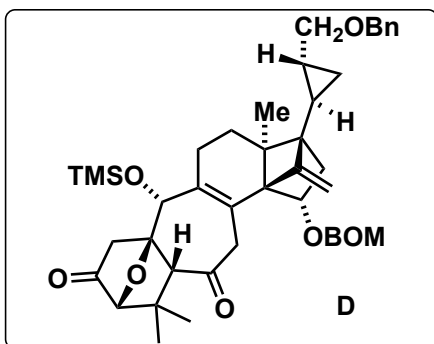
*Hint*: electronics



17-25

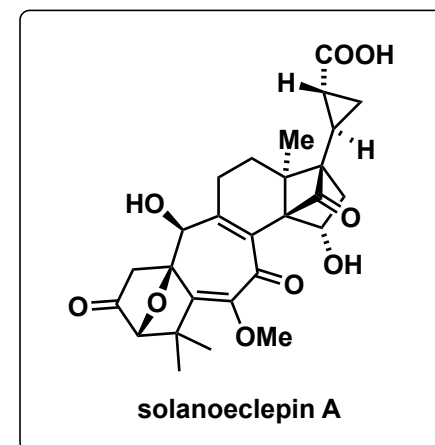
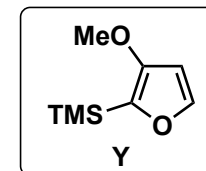
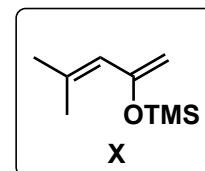


26-30

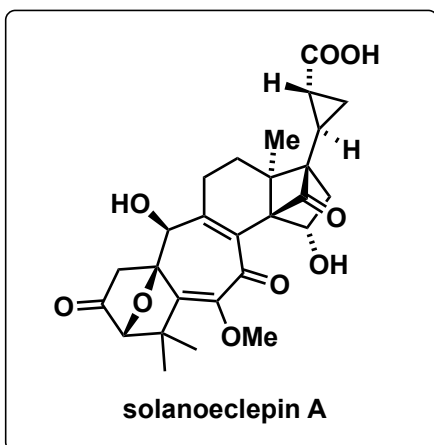
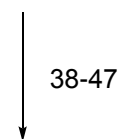
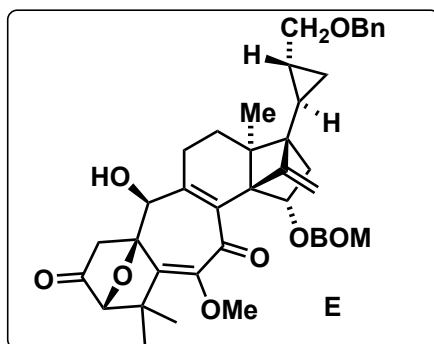
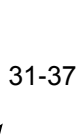


- 17)  $o\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$ ,  $\text{Bu}_3\text{P}$ , THF
- 18)  $\text{H}_2\text{O}_2$ , THF
- 19)  $\text{HF}\cdot\text{py}$ , THF
- 20) TBSCl, imidazole, DMF
- 21) DMP,  $\text{CH}_2\text{Cl}_2$
- 22)  $\text{HF}\cdot\text{py}$ , THF
- 23) BOMCl, DIPEA, TBAI,  $\text{CH}_2\text{Cl}_2$
- 24)  $t\text{-BuOCH}(\text{NMe}_2)_2$ , DMF
- 25)  $\text{Tf}_2\text{O}$ , 2,6- $(t\text{-Bu})_2\text{Py}$ ,  $\text{CH}_2\text{Cl}_2$

- 26) Y,  $t\text{-BuLi}$ , THF
- 27) PPTS, DMF,  $\text{H}_2\text{O}$
- 28) TMSCl, imidazole, DMF
- 29) X,  $\text{Bu}_3\text{SnF}$ ,  $\text{PdCl}_2[\text{P}(o\text{-tol})_3]_2$ , DMF
- 30)  $\text{Me}_2\text{AlCl}$ ,  $\text{Et}_2\text{O}$



D



- 31) CH<sub>3</sub>CO<sub>2</sub>H, H<sub>2</sub>O
- 32) DMP, CH<sub>2</sub>Cl<sub>2</sub>
- 33) SeO<sub>2</sub>, 1,4-dioxane, H<sub>2</sub>O
- 34) Cu(OAc)<sub>2</sub>, MeOH
- 35) MeI, Ag<sub>2</sub>O, DMF
- 36) DIBAL, PhMe
- 37) IBX, CH<sub>2</sub>Cl<sub>2</sub>, DMSO

- 38) TMSCl, imidazole, DMF
- 39) OsO<sub>4</sub>, pyridine, *t*-BuOH
- 40) NaIO<sub>4</sub>, MeCN
- 41) TMSCl, imidazole, DMF
- 42) H<sub>2</sub>, Pd(OH)<sub>2</sub>, THF
- 43) CH<sub>3</sub>CO<sub>2</sub>H, H<sub>2</sub>O
- 44) TMSCl, imidazole, DMF, then aq. THF
- 45) DMP, CH<sub>2</sub>Cl<sub>2</sub>
- 46) NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, 2-methyl-2-butene, *t*-BuOH, H<sub>2</sub>O
- 47) 3 M HCl, CH<sub>3</sub>CO<sub>2</sub>H, H<sub>2</sub>O