Total synthesis of solanoeclepin A

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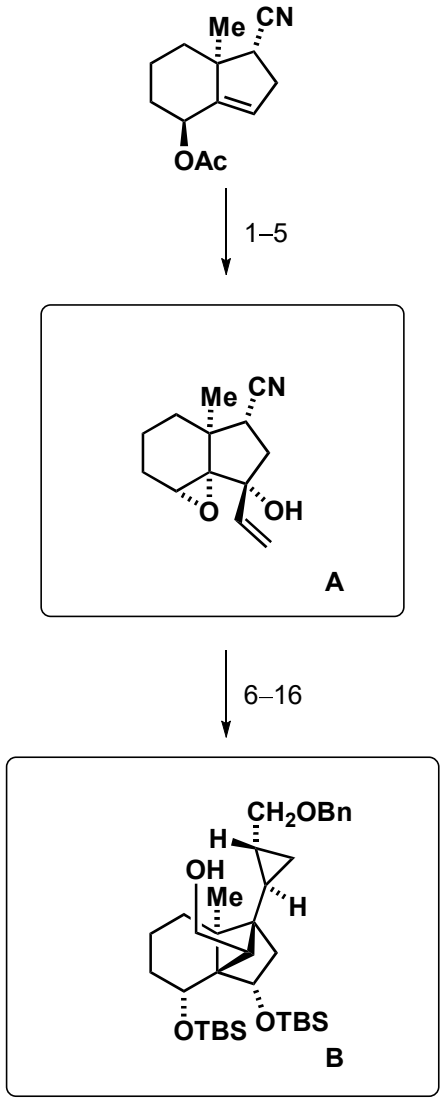
Nat. Chem., **2011**, 3, 484–488.



1) *m*CPBA, CH_2Cl_2
2) Me_3Al, $Al(OTf)_3$, $(CH_2Cl)_2$
3) DBU, CH_2Cl_2
4) CH_2=$CHMgBr$, $CeCl_3$, THF
5) TBHP, $Ti(O\textit{i}\text{-}Pr)_4$, MS4Å, CH_2Cl_2

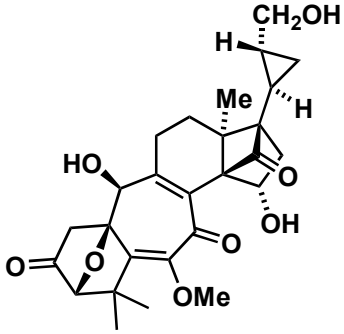
6) TMSOTf, 2,6-lutidine, CH_2Cl_2, then HF•py
7) DIBAL, THF
8) TBSOTf, 2,6-lutidine, CH_2Cl_2
9) *m*CPBA, $(CH_2Cl)_2$
10) LDA, then TBSCl, HMPA, THF
11) DIBAL, CH_2Cl_2
12) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF
13) DIBAL, THF
14) **Z**, Et_2Zn, CH_2I_2, CH_2Cl_2
15) NaH, BnBr, TBAI, DMF
16) TBAF, THF

How would you make the starting material?

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

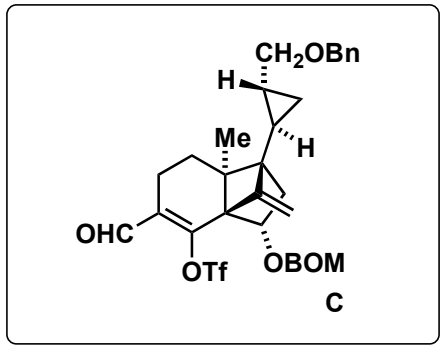
Step 2: Meinwald rearrangement

Hint: electronics

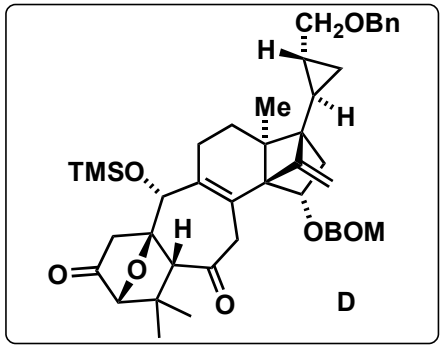


solanoeclipin A

17–25

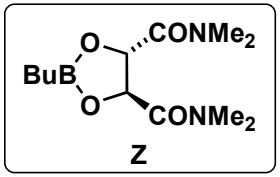


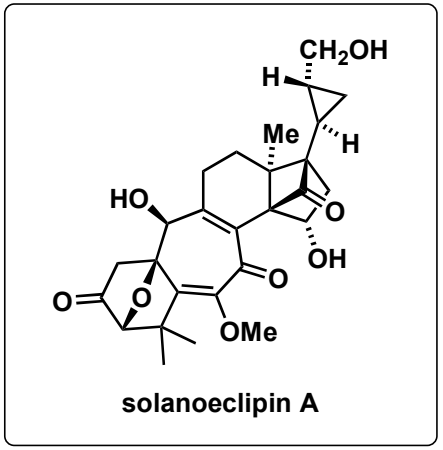
26–30



17) *o*-$NO_2C_6H_4SeCN$, Bu_3P, THF
18) H_2O_2, THF
19) HF•py, THF
20) TBSCl, imidazole, DMF
21) DMP, CH_2Cl_2
22) HF•py, THF
23) BOMCl, DIPEA, TBAI, CH_2Cl_2
24) *t*-$BuOCH(NMe_2)_2$, DMF
25) Tf_2O, 2,6-(*t*-Bu)$_2$Py, CH_2Cl_2

26) **Y**, *t*-BuLi, THF
27) PPTS, DMF,H_2O
28) TMSCl, imidazole, DMF
29) **X**, Bu_3SnF, $PdCl_2[P(o\text{-tol})_3]_2$,DMF
30) Me_2AlCl, Et_2O





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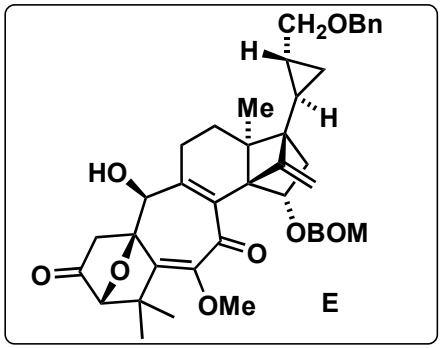
31–37



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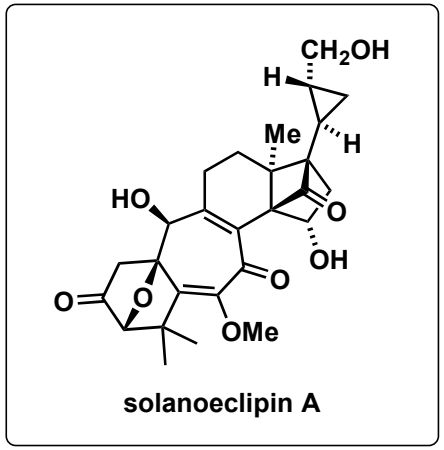
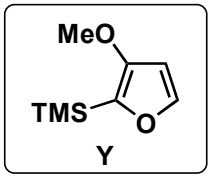
38–47



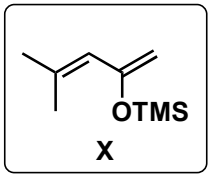
solanoeclipin A

31) CH_3CO_2H, H_2O
32) DMP, CH_2Cl_2
33) SeO_2,1,4-dioxane, H_2O
34) $Cu(OAc)_2$,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, $Pd(OH)_2$, THF
43) CH_3CO_2H, 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, CH_3CO_2, H_2O



Y



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