Asymmetric Total Synthesis of Pre-schisanartanin C

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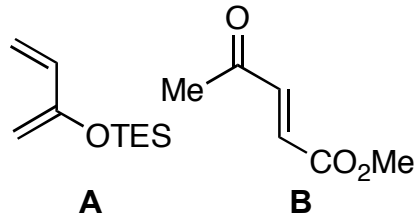
A + **B**

1-4

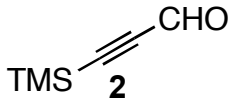
C

6-11



A **B**

1) **1**, TESOTf
2) MeMgCl (1.2 equiv)
3) Et_2Zn, TFA, CH_2I_2
4) $FeCl_3$ then TEA
5) L-selectride, **2**, then PivCl



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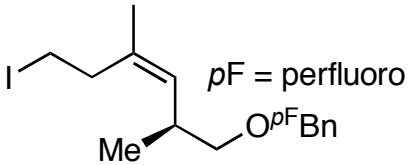
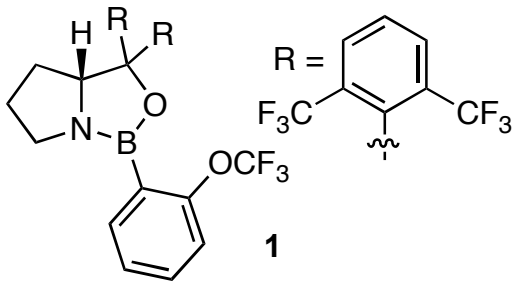


3

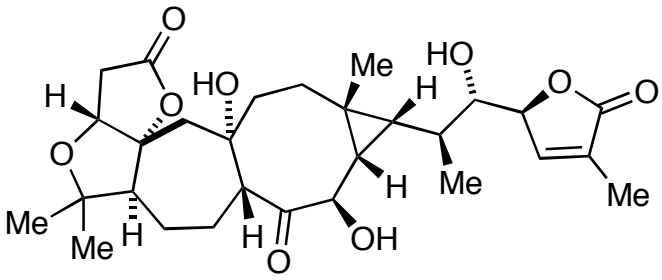
6) **3**, *t*-BuLi, $CeCl_3$ then **C**
7) TBAF
8) DIBAL
9) ^{pF}-BzCl (2 equiv.), DMAP, pyridine
10) mCPBA (1.2 equiv.), $NaHCO_3$ (10 equiv.)
11) NIS, TBAI

step 1: name?
step 2 hint: a ring forms
step 3,4: name, mechanism?



1

hint 8: two moieties are reduced
hint 9: overall 3 reactions
hint 8-10: overall α-oxidation of γ-lactone



Pre-schisanartanin C

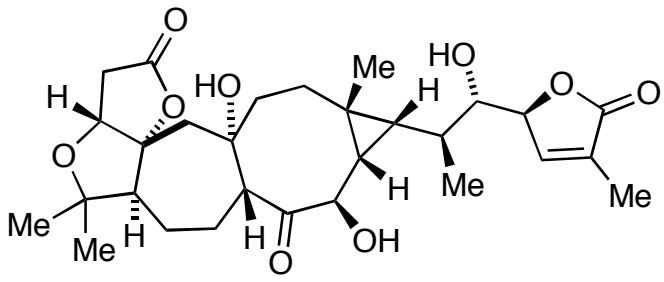
D

12, 13

E

12) *t*-$Bu_2Si(OTf)_2$, lutidine
13) AuCl, DCE, rt, 7 days

step 13 hint: first, propargylic group undergoes a 1,2, shift to form a carbene intermediate

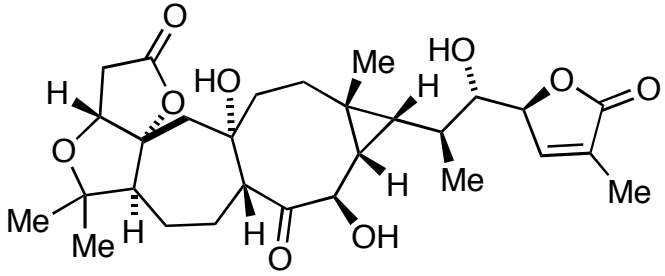


Pre-schisanartanin C

14-18

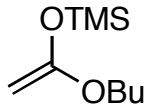
F

19-24



Pre-schisanartanin C

14) MeLi then MeOTf
15) DIBAL then Ac_2O
16) TMSOTf, **4**
17) OsO_4 then $NaHSO_3$
18) $Al(Ot\text{-}Bu)_3$



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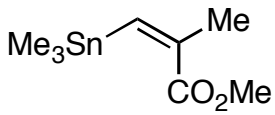

5

19) Raney-Nickel
20) TEMPO, PIDA
21) CHI_3, $CrCl_2$
22) $Pd(PPh_3)_4$, CuTC, **5**
23) HF, py, then DBU
24) AD mix-α

hint 14: MeLi is used for deprotection, MeOTf for reprotection

step 17: name?

hint 19: isomerization to the thermodynamically more stable α-hydroxy ketone