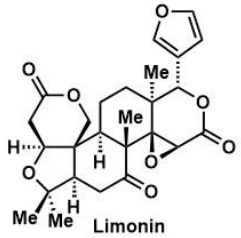
Two concepts:
seco versus abeo

Seco.

seco-steroids are structurally rather close to their parent compound, they exhibit one or more C-C bond scissions

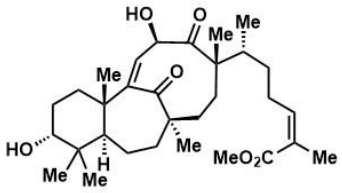


Limonin

Ranging from fungi and plants to bacteria and algae, seco- and abeo-triterperoids are widespread in Nature.

Abeo-

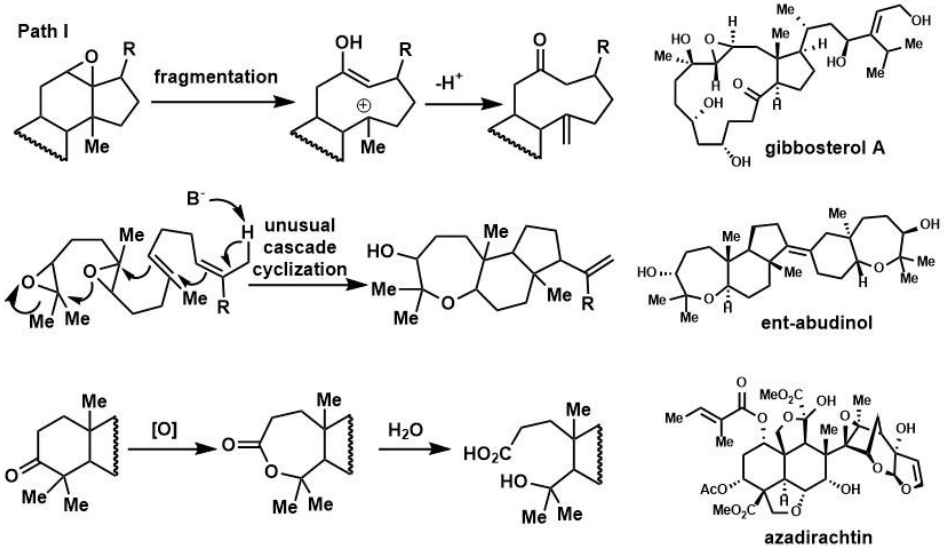
Rearrangements affecting the ring of the original tetracyclic framework and even involving the side chain



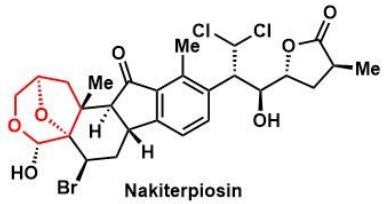
Schiglautone A

Preposed reasons of the C-C bond scissions

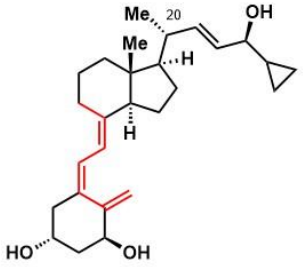
- **cation mediated fragmentation (grobs fragmentation)**
- **unusual cascade cyclization (marine or furgal species)**
- **oxidation or photochemical reaction (like VD_3)**



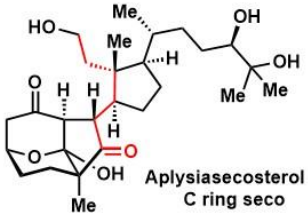
Mentioned synthesis works of the seco-triterpenoids in this Pre.



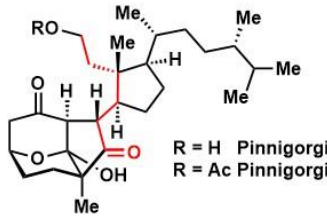
Nakiterpiosin
A ring seco
CD rings abeo



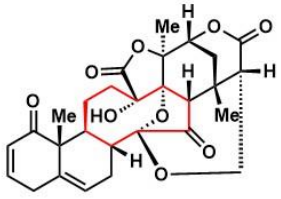
(+)-Calcipotriol
B ring seco



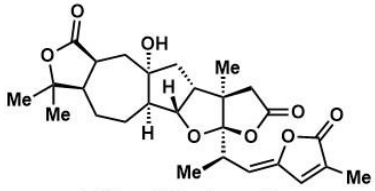
Aplysiasecosterol A
C ring seco



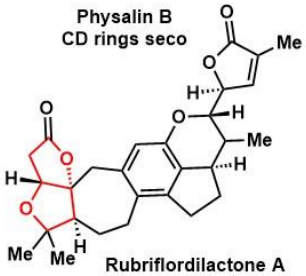
R = H Pinnigorgiol B
R = Ac Pinnigorgiol E



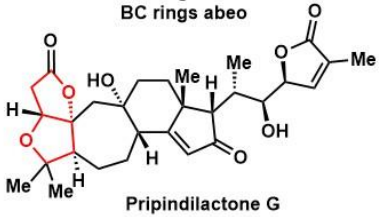
Physalin B
CD rings seco



Schilancitrilactones B
AD rings seco
BC rings abeo

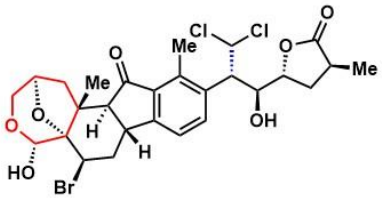


Rubriflordilactone A
A ring seco



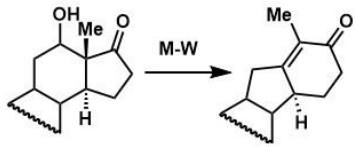
Pripindilactone G
A ring seco
A/B rings abeo

I. Nakiterpiosin



Background

1. proposed structure, this work revised it
2. exhibit cytotoxicity against P388 murine leukemia cell line (GI_{50}=10ng/mL), but molecular target is unknown
3. only 0.4mg was extracted from 30kg sponge

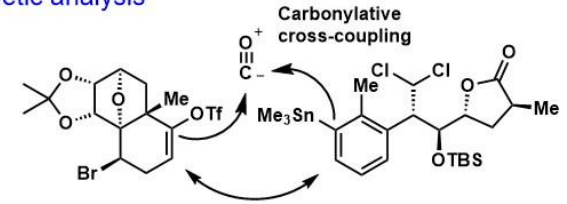


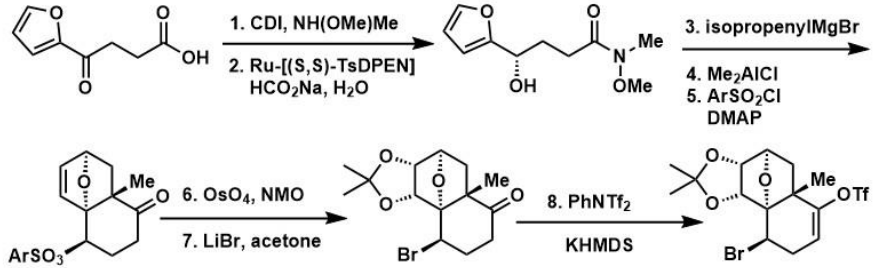
C-nor-D-homosteroids

Structure feature

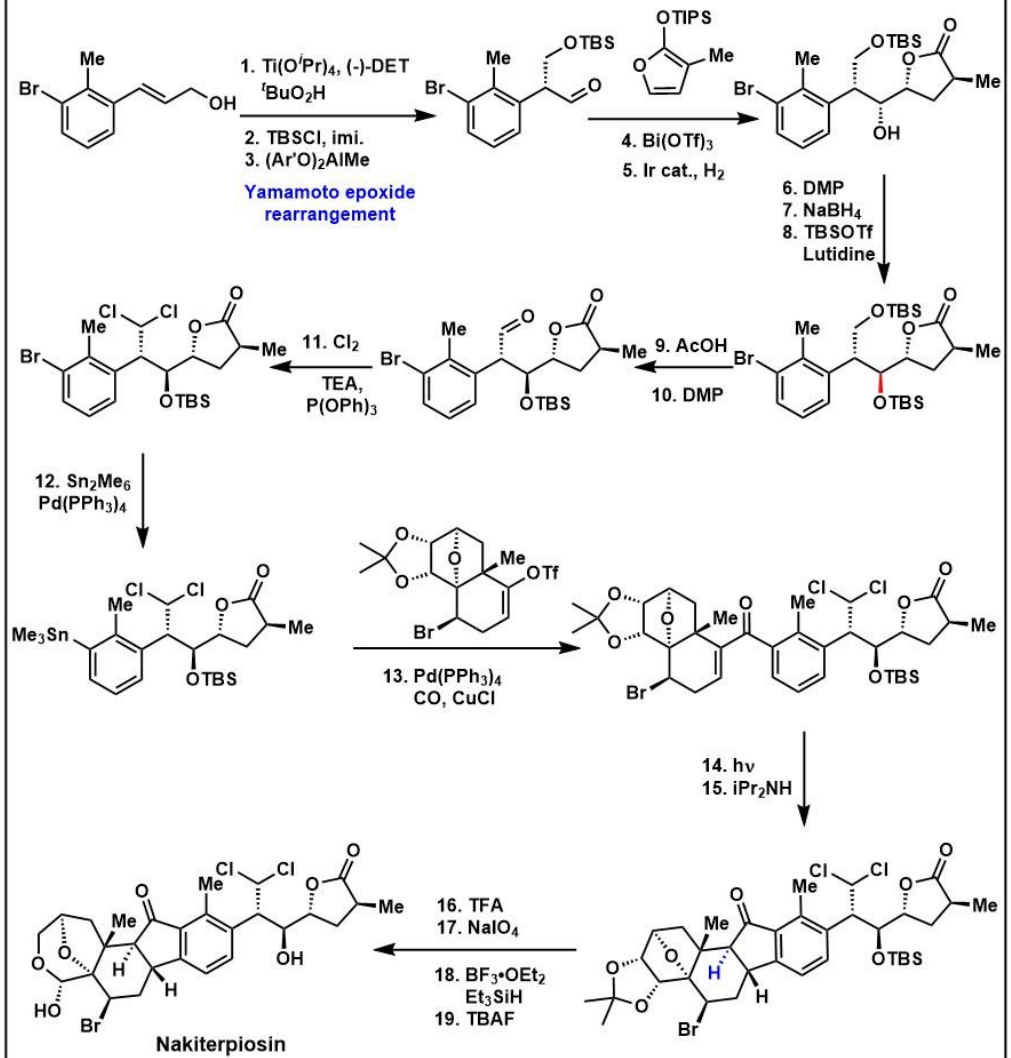
- C-nor-D-homosteroids family (firstly isolated)
- preplex chiral centers
- involve halogen atoms
- unstable hemiacetal

Retrosynthetic analysis



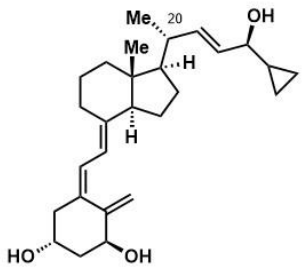


Synthesis of Nakiterpiosin (20 steps)



C. Chen, *JACS*, 2009, *131*, 1410

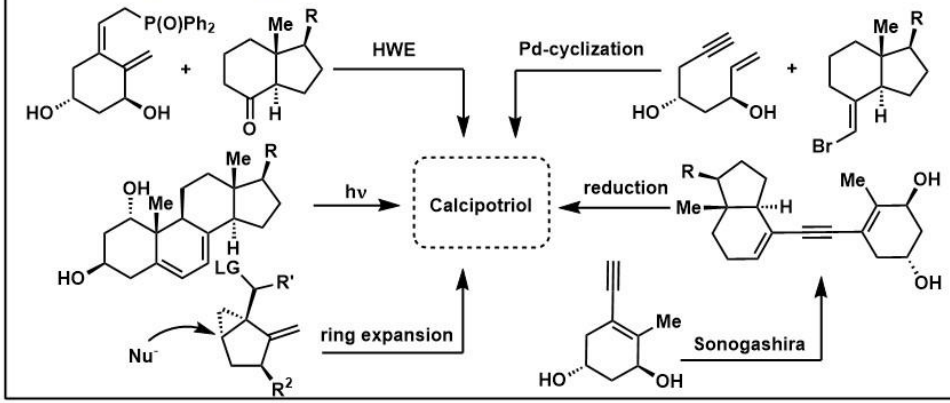
II. Calcipotriol (Dovonex)



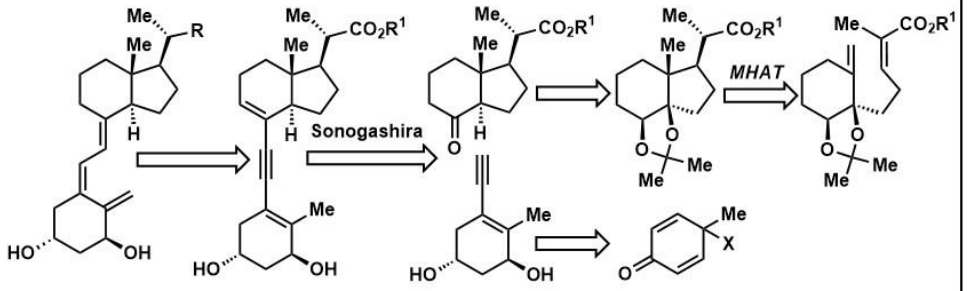
Background

- most successful commercialized VitD analog
- treat psoriasis, an autoimmune skin disease
- traditional approach to synthesis CD rings is degradation of VD_2, causing CD rings are hard to decorate at C20
- scalable synthesis to avoid semisynthesis
- build a platform to gain more VD analogs >3000 analogs

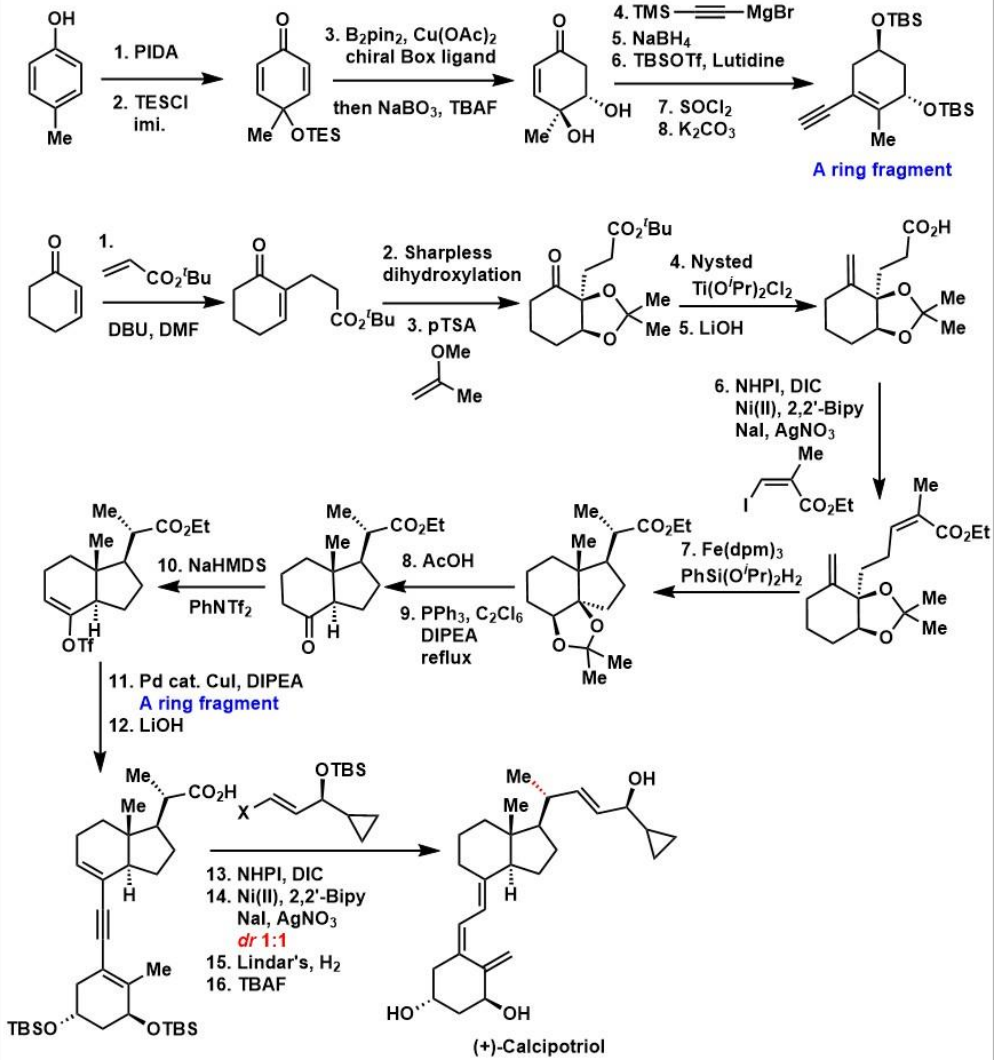
Prominent synthetic approaches



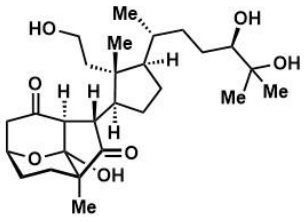
Retrosynthetic analysis



Synthesis of Calcipotriol (16 steps)



III. Aplysiasecosterol A

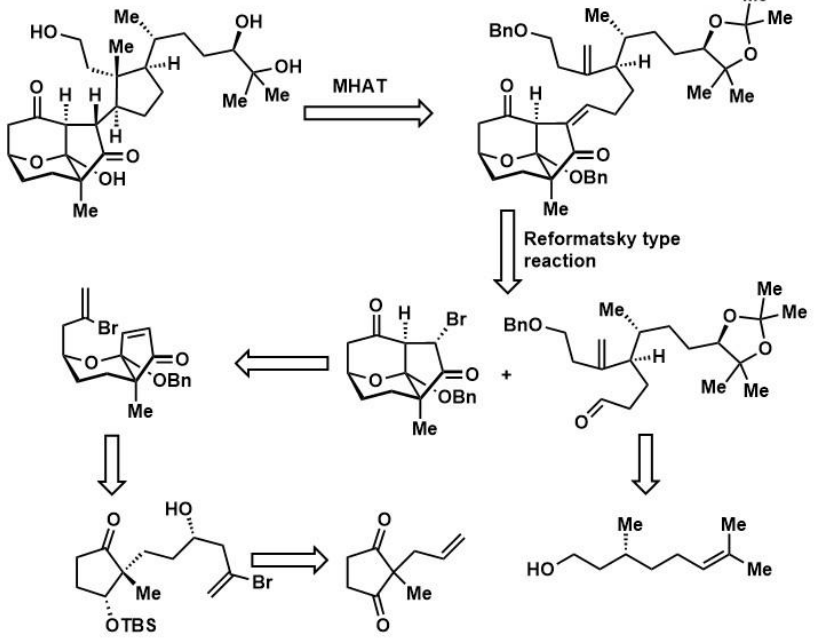


Aplysiasecosterol A

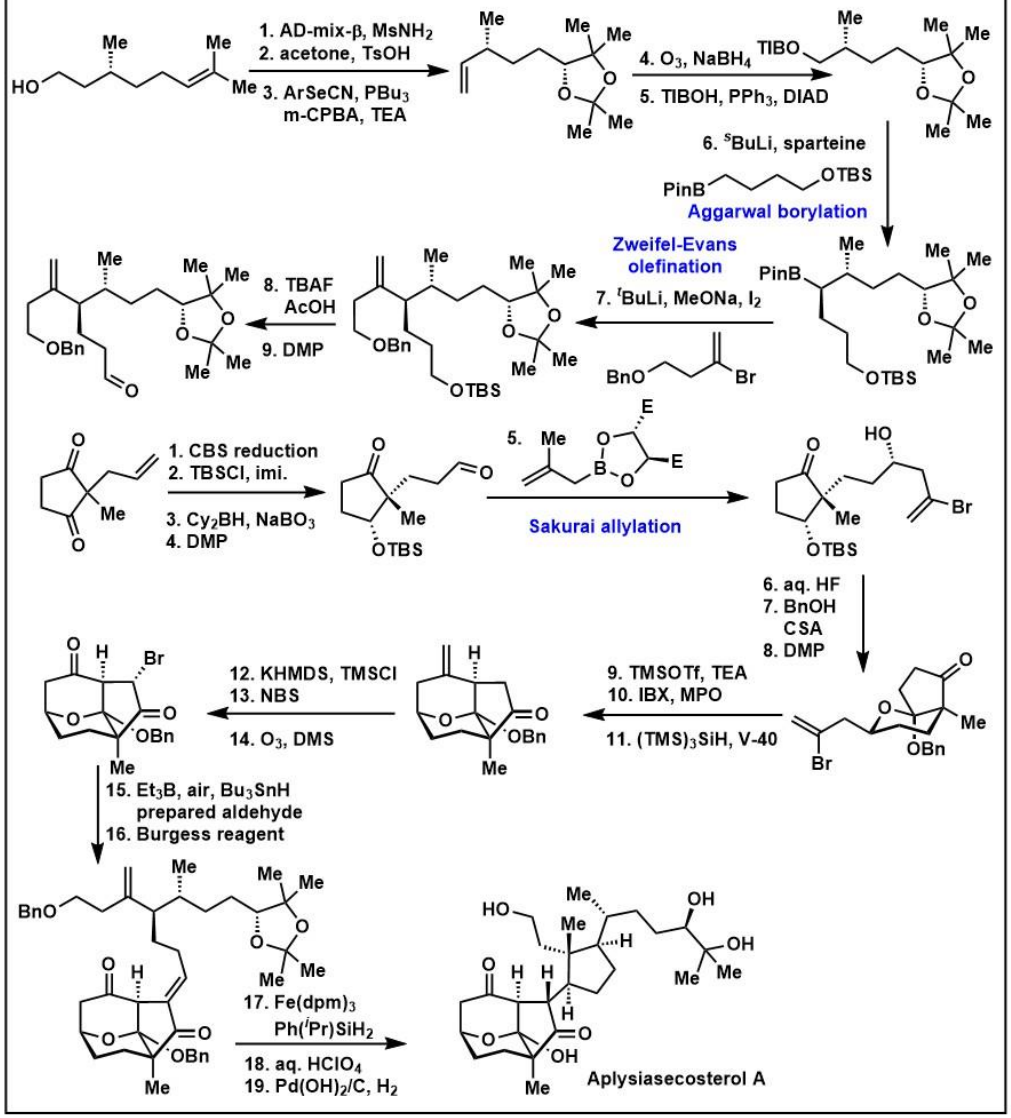
Background

- a 9,11-secosteroid isolated from sea hare
- possess a unique tricyclic γ-diketone core
- 8 consecutive steregenic centers
- high oxidation state
- de novo synthesis
- chiral resources involving CBS cat., AD-mix-β and sparteine

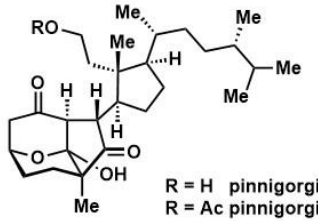
Retrosynthetic analysis



Synthesis of Aplysiasecosterol A (19 steps)



IV. Pinnigorgiols B and E

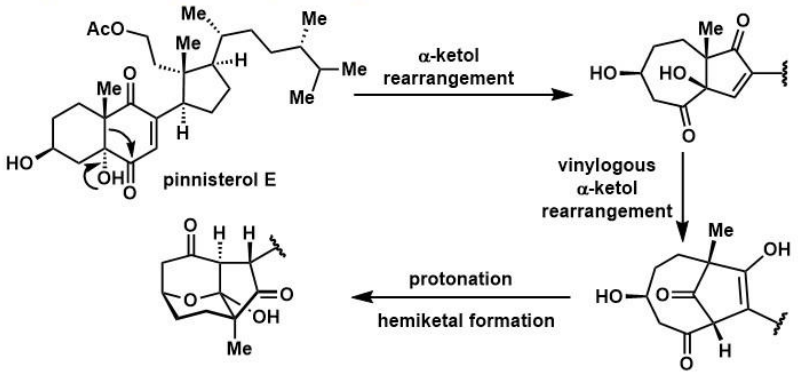


R = H pinnigorgiol B
R = Ac pinnigorgiol E

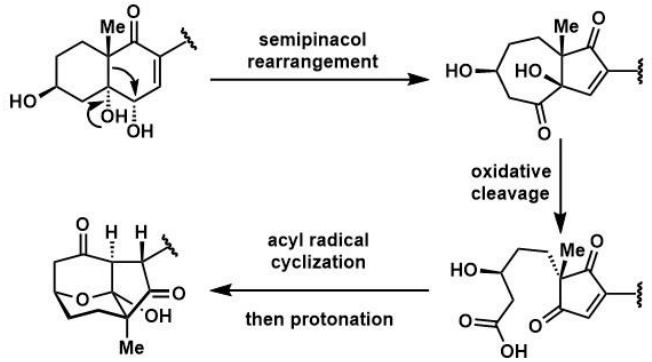
Structure feature

- the same tricyclic γ-diketone core
- 8 consecutive steregenic centers
- the chiral resource is ergosterol
- bioinspired semisynthesis

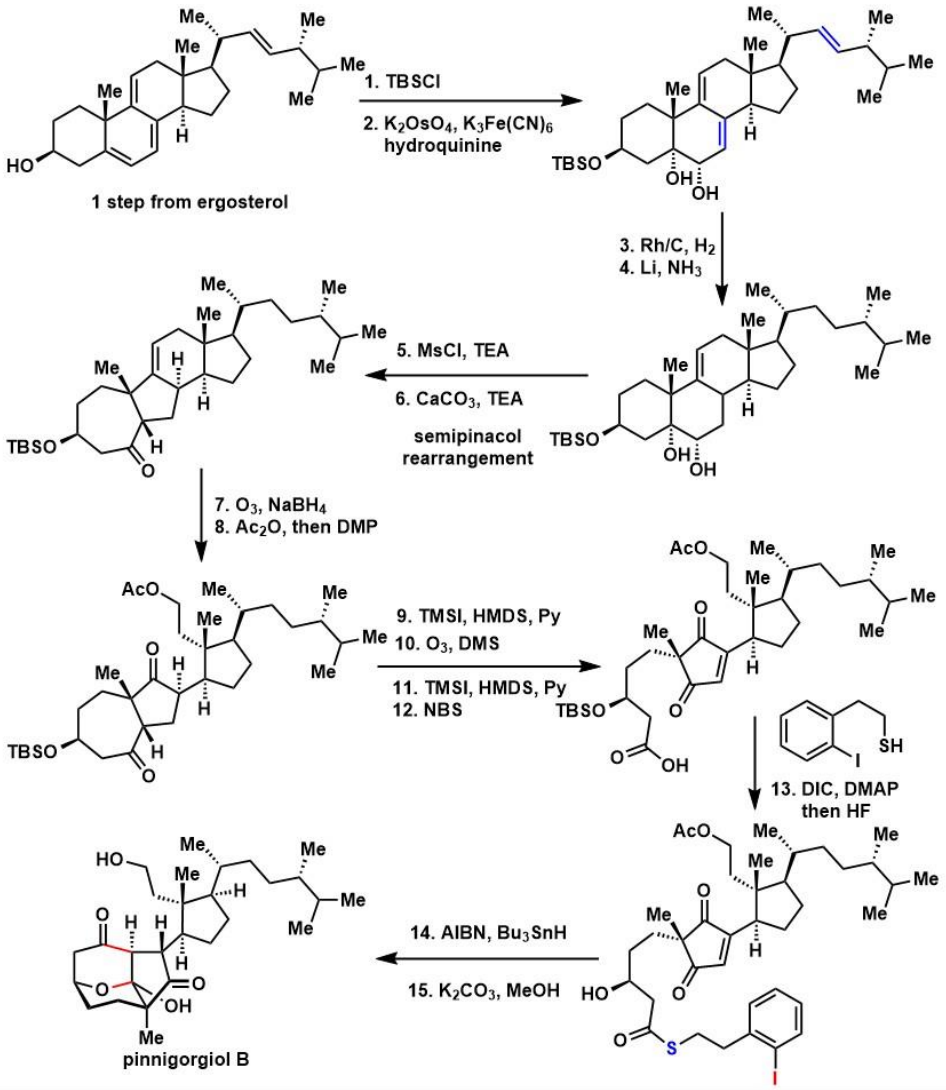
Proposed biosynthetic pathway



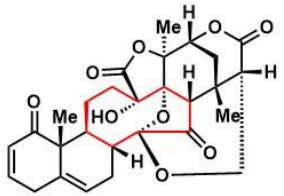
Essential acyl radical cyclization

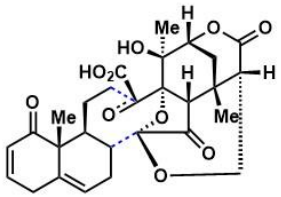


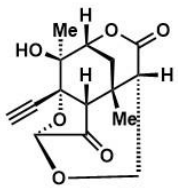
Synthesis of pinnigorgiol B (15 steps)



V. physalin B







synthesis of the DFGH ring system

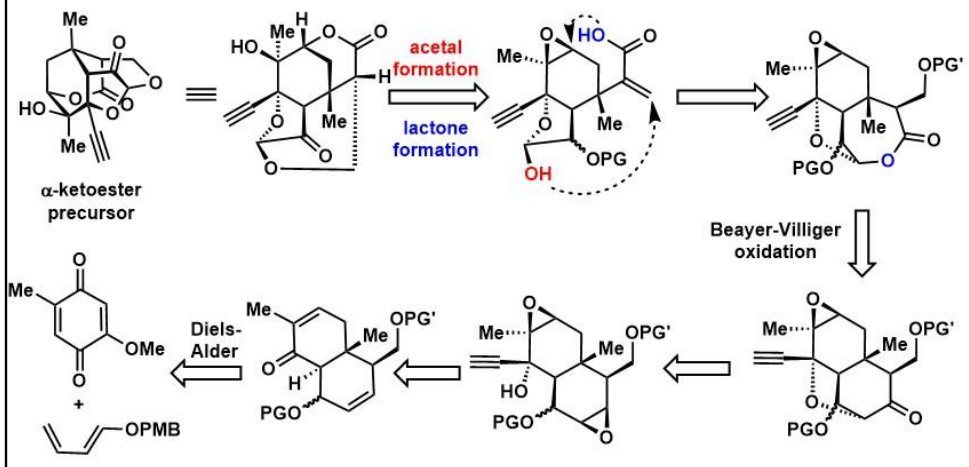
Background

- belonging to the Solanaceae family, mainly in species of the genus *Physalis* spp.
- no report for total synthesis currently
- Due to the fast growth of the plants, an approach for extraction has been established
- the potent anti-inflammatory and immunosuppressive agents

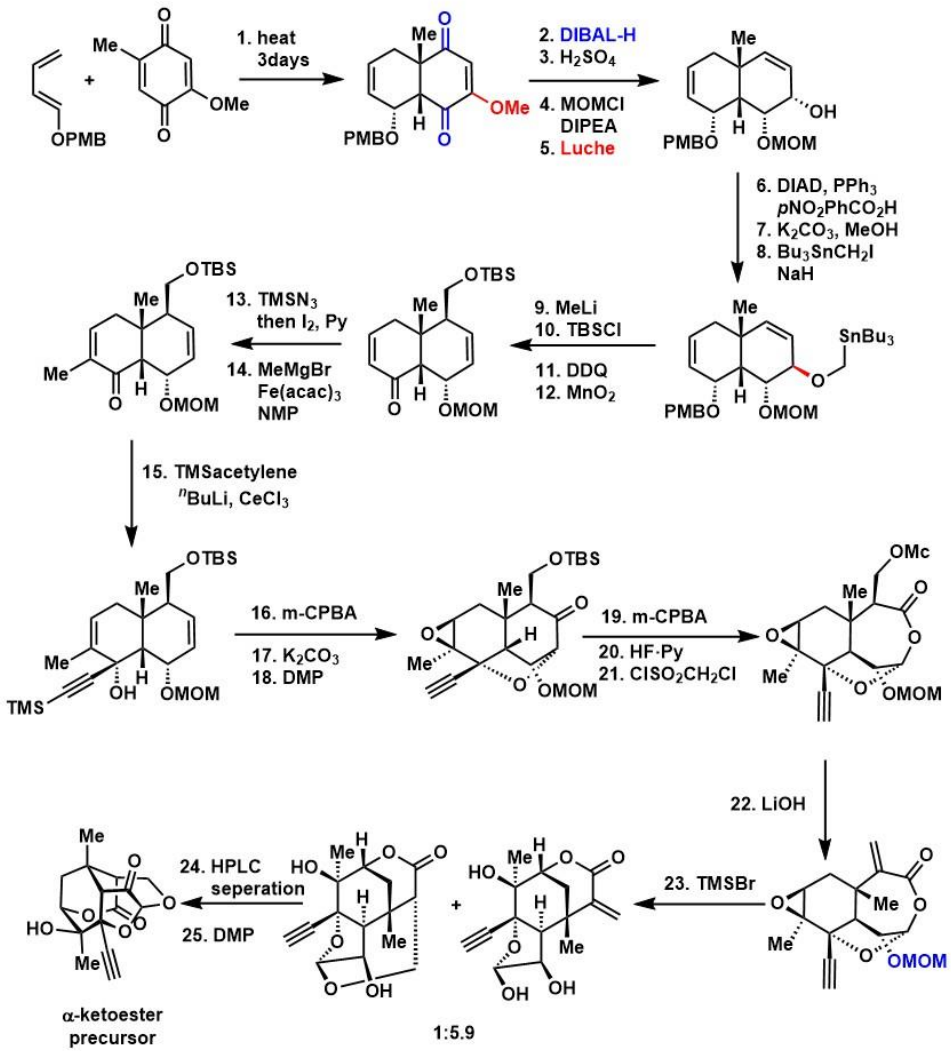
Structure feature

- a 13,14-*seco*-16,24-cycloergostane skeleton
- terrified chiral centers
- complex fuse rings system (8 rings)
- extremely high oxidation state
- various oxygen functional groups

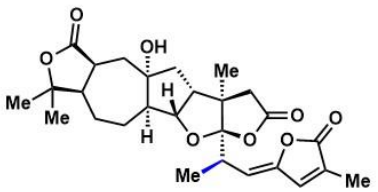
Retrosynthetic analysis of the DFGH ring systhem



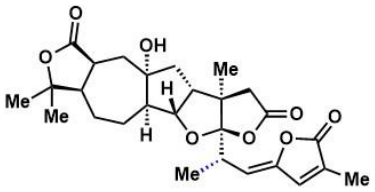
Synthesis of the DFGH ring systhem (25 steps)



VI. Schilancitrilactones B and C



Schilancitrilactones B



Schilancitrilactones C

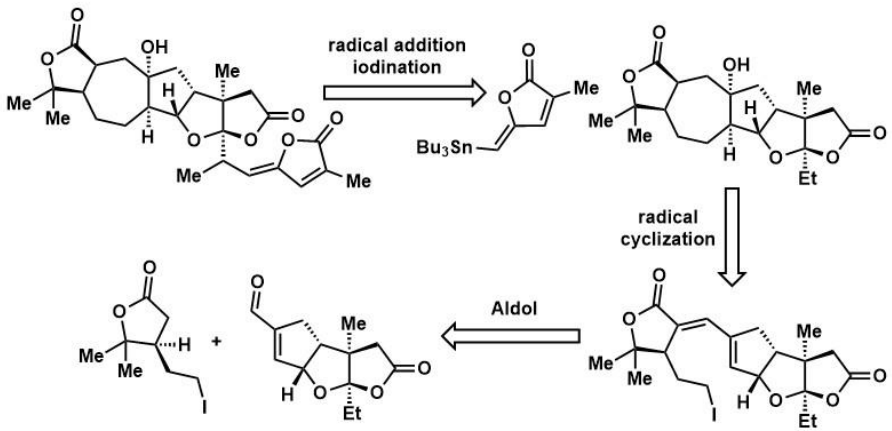
Structure feature

- nortriterpenoid family
- 7 consecutive chiral centers
- 3 lactone rings
- 3 cis-fused five membered rings
- relatively high oxidation state

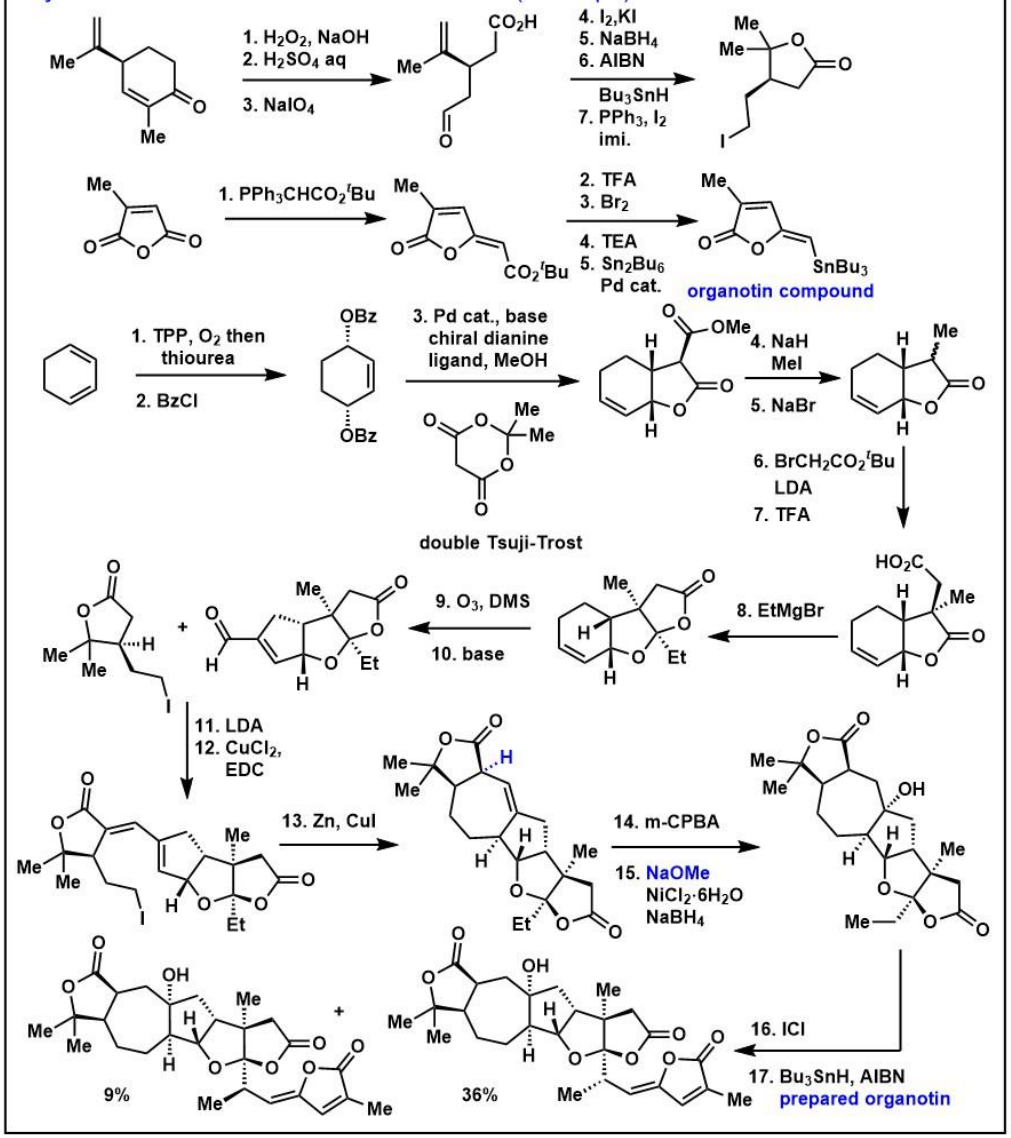
Background

- isolated in 2012 by Sun and coworkers from the stems of Schisandra Lancifolia
- Schilancitrilactones C showed anti-HIV biological activities but B is not bioactive
- chiral resource: carvone, chiral ligand

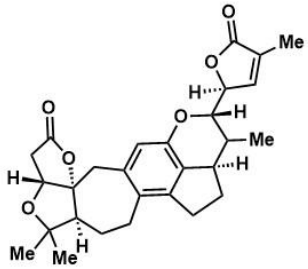
Retrosynthetic analysis



Synthesis of Schilancitrilactones B and C (17 steps)



VII. Rubriflordilactone A



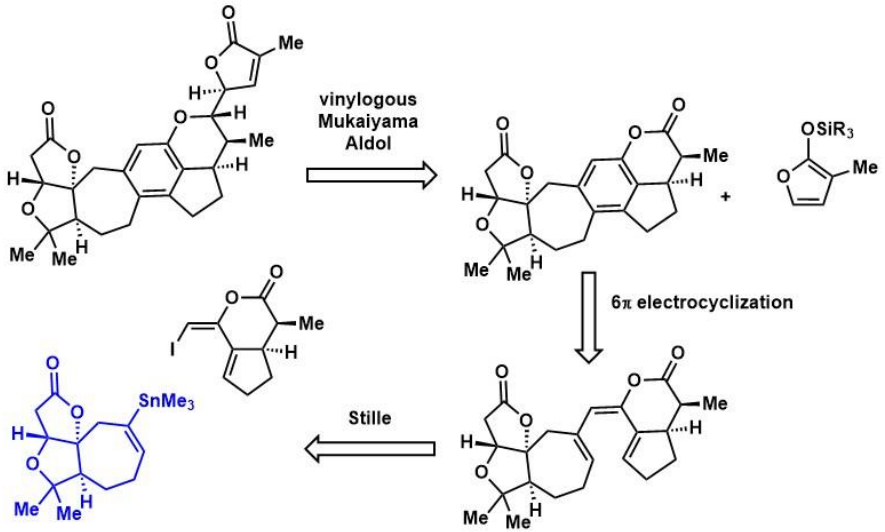
Structure feature

- nortriterpenoid family
- contain a benzene ring
- 2 lactones
- relatively high oxidation state

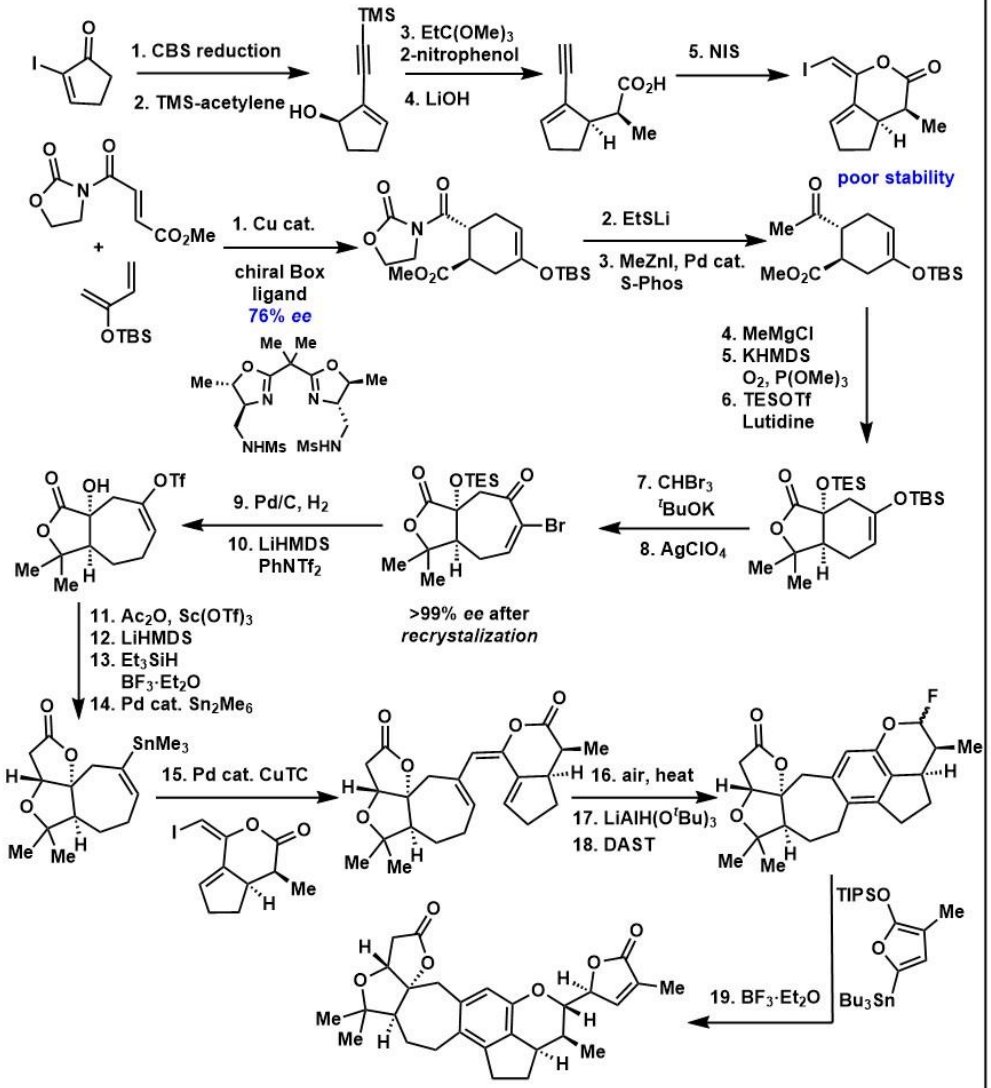
Background

- a bisnortriterpenoid isolated from Schisandra rubriflora by Sun and co-workers
- the strategy of 6p electrocyclization and oxidative aromatization is applied
- chiral resource CBS cat., Chiral Box ligand

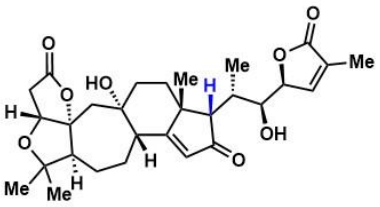
Retrosynthetic analysis



Synthesis of Rubriflordilactone A (19 steps)



VIII. Pripindilactone G



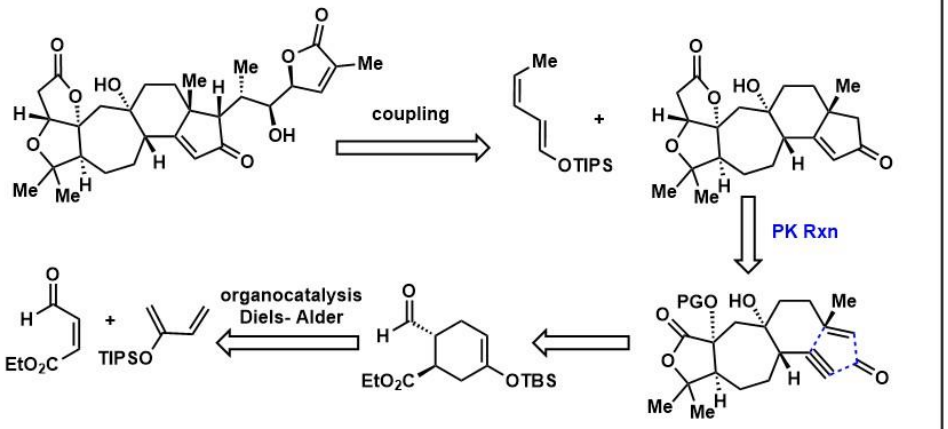
Structure feature

- nortriterpenoid family
- a unique 5/5/7/6/5 pentacyclic**core**
- relatively **high** oxidation state
- 2 lactones

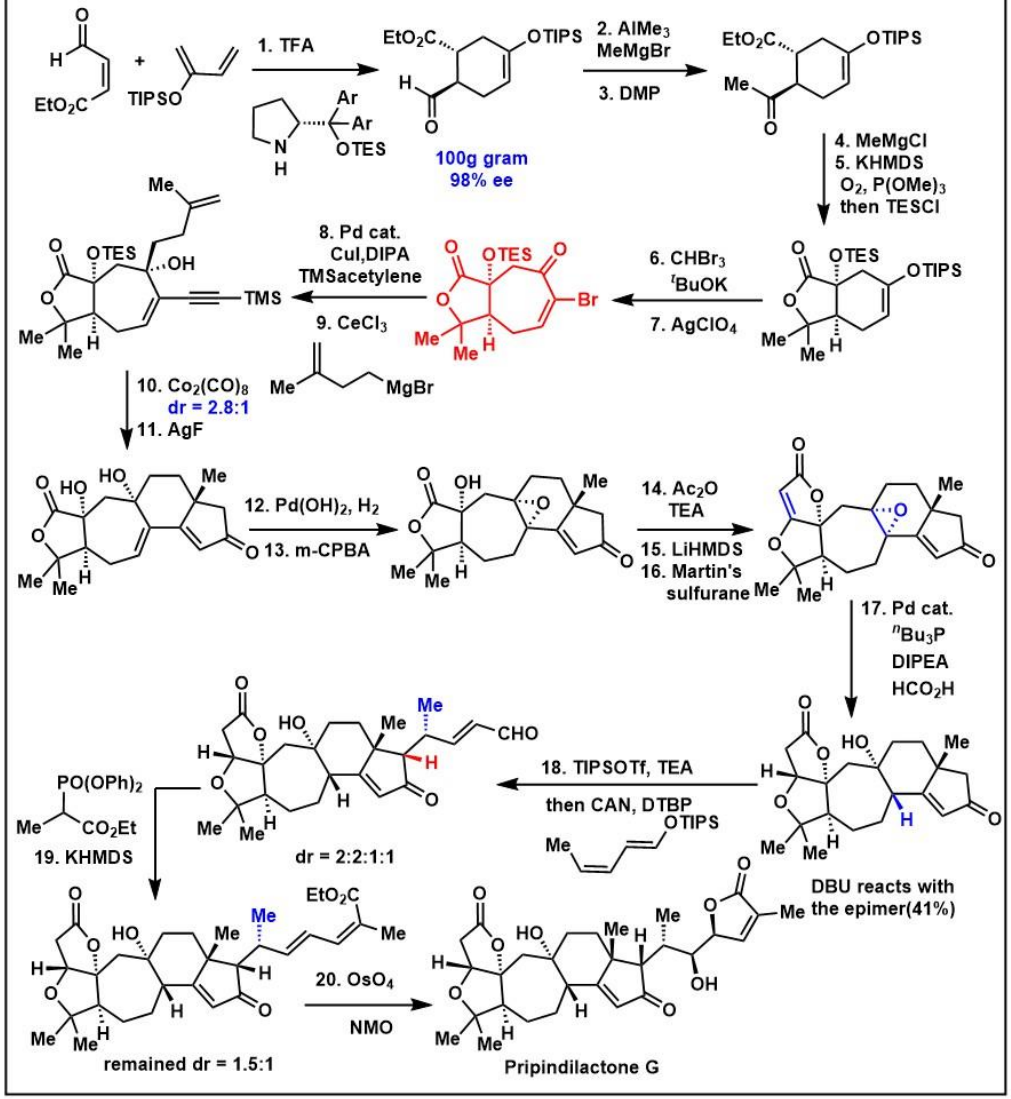
Background

- isolated from**various species of**Schisandraceafamily by Sun et al
- the structure of (+)-propindilactone G has been revised by this study
- chiral resource only is **Hayashi ligand**
- munipulating the stereocenters C_{13}, C_{17} and C_{20} is a big issue
- de novo synthesis

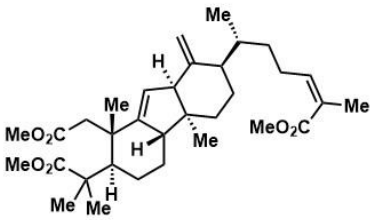
Retrosynthetic analysis



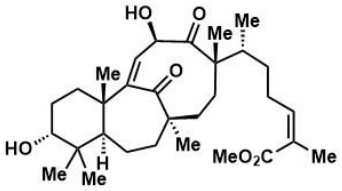
Synthesis of Pripindilactone G (20 steps)



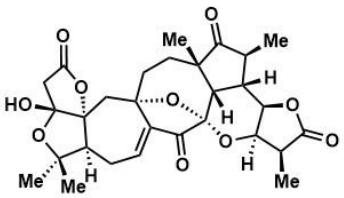
Suggested further reading ...



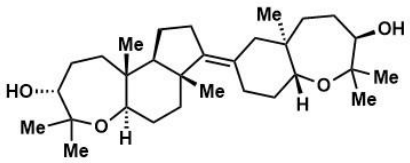
Kadcoccinic Acid A Trimethyl Ester
Trost, *J. Am. Chem. Soc.* 2021, *143*, 12286



SchiglautoneA
DING, *ACIE* 2018, *57*, 15567



Schindilactone A
Yang, *ACIE* 2011, *50*, 7373



ent-abudinol
Hardcastle *J. Am. Chem. Soc.* 2010, *132*, 5300