Synthesis of Eupalinilide E, a Promoter of Human Hematopoietic Stem and Progenitor Cell Expansion

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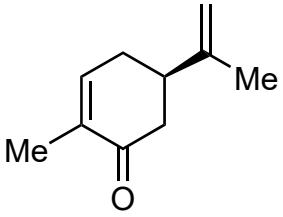
J. Am. Chem. Soc. **2016**, *138*, 6068-6073



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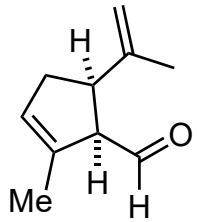
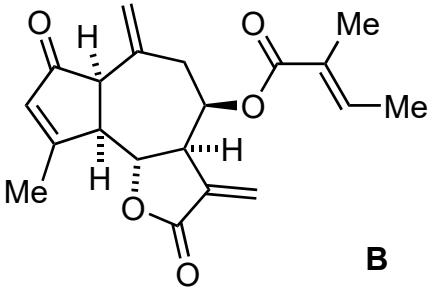


A

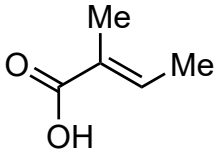
9-16



B

1) HBr, AcOH
2) Br_2, AcOH
3) *i*$PrNH_2$, Et_2O
4) AcOH (10% aq.), THF, 50 °C
5) $LiAlH_4$, Et_2O
6) Ac_2O, 150 °C
7) $LiAlH_4$, Et_2O
8) DMP, $NaHCO_3$, CH_2Cl_2

9) *n*-BuLi, tetravinyltin, -78 to 23 °C,
then **A**, -78 °C
then HMPA, propargyl bromide
10) *n*-BuLi, -78 °C *then* TMSCl
11) $Pd(OAc)_2$ (5 mol %), B_2pin_2, PhMe, MeOH
then H_2O_2, NaOH, THF
12) $(COCl)_2$, DMSO, Et_3N
13) Et_2AlCl, CH_2Cl_2
14) tiglic acid, 2,4,6-TCBC, Et_3N, DMAP
15) TFA, CH_2Cl_2
16) CrO_3, 3,5-DMP, CH_2Cl_2



tiglic acid

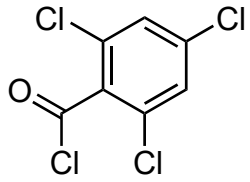
1) Starting material name - *R-carvone*

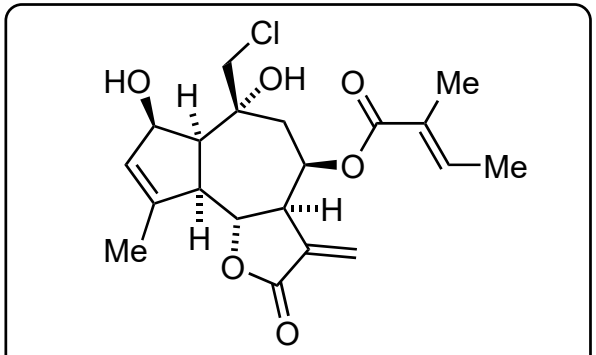
2) *Hint:* after *step 2* you have a tri-Br compound

11) *Hint:* borylative enyne cyclization

12) Name reaction - *Swern oxidation*

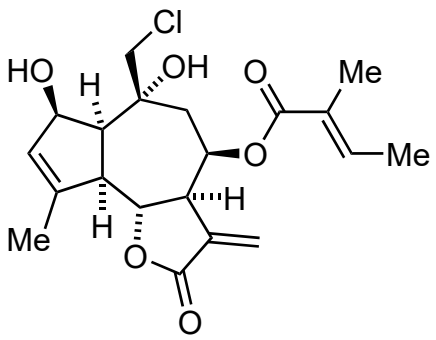
14) Name reaction and structure of 2,4,6-TCBC - *Yamaguchi esterification*





Eupalinilide E

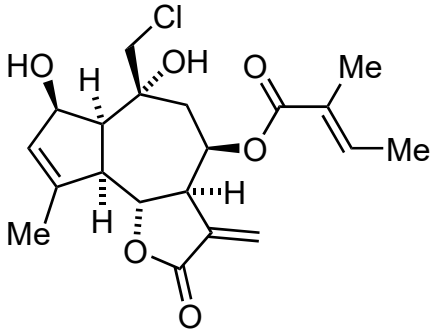
17-20



Eupalinilide E

17) $Yb(OTf)_3$, $NaBH_4$,MeOH/THF
18) $Al(Osec\text{-}Bu)_3$, TBHP, CH_2Cl_2
19) LiCl, HCl, THF

17) Name reaction - *Luche reduction*



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