Total Synthesis of the Hexacyclic Sesterterpenoid Niduterpenoid B via Structural Reorganization Strategy

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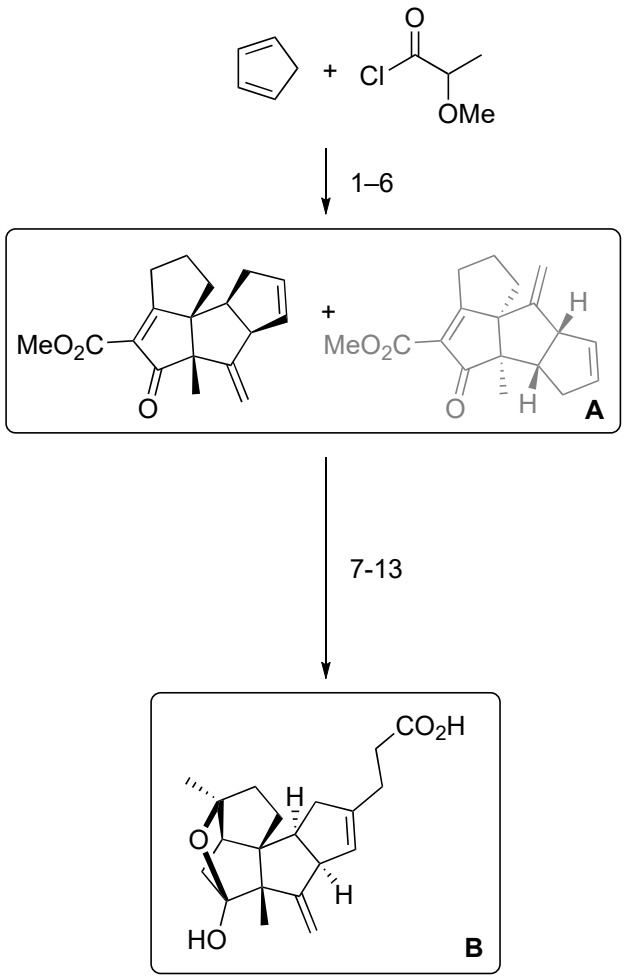
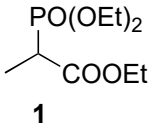


1) Et_3N, cyclohexane
2) NaH, **1**
3) LiOH, EtOH/H_2O
4) CDI, THF; *then* $Mg(MeO_2CCH_2CO_2)_2$
5) Cyclobutanone, $TiCl_4$, pyridine
6) $B(C_6F_5)_3$, CSA, 4Å MS, toluene



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7) LiCl, DMSO
8) NaHMDS, TBSOTf; *then m*-CPBA
9) K_2CO_3, MeOH
10) MeLi, THF
11) TIPSOTf, Et_3N; *then m*-CPBA
12) Me_3SI, *n*-BuLi
13) $MeC(OEt)_3$, EtCOOH; *then* LiOH, EtOH/H_2O

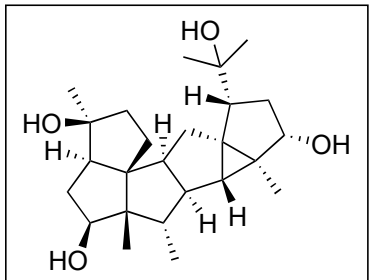
2) Name of the reaction: *Horner-Wadsworth-Emmons (HWE) reaction*

5) Name of the reaction: *Knoevenagel condensation*

6) Name of the reaction: *Nazarov cyclization reaction*
+ Hint: formation of tetraquinane

7) Name of reaction: *Krapcho decarboxylation*

13) Name of the reaction: *Johnson-Claisen rearrangement*



Niduterpenoid B

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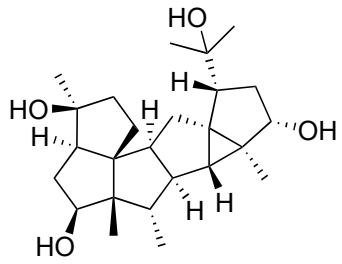

Niduterpenoid B

14) $(COCl)_2$, DMF; *then* $MeCHN_2$
15) $Rh_2(OAc)_4$; *then* TBSOTf, Et_3N
16) $Mn(dpm)_3$, TBHP, Ph(*i*-PrO)SiH_2, *i*-PrOH; *then* HF•pyridine
17) TBSOTf; *then* PhSeCl; *then* H_2O_2
18) *iso*-propenyl MgBr, CuBr
19) $Mn(dpm)_3$, $PhSiH_3$, O_2, EtOH; *then* $NaBH_4$