Asymmetric Total Synthesis of Mycoleptodiscin A

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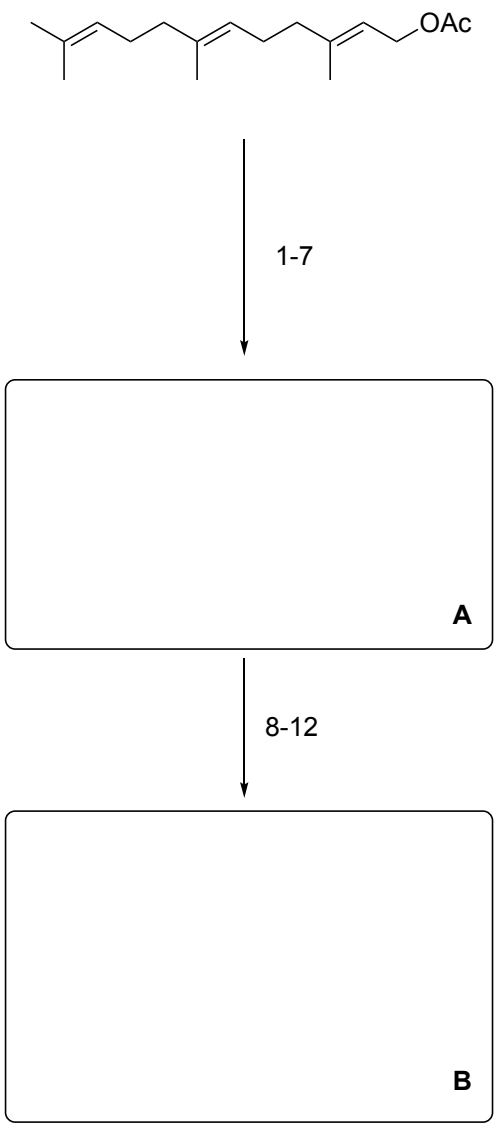


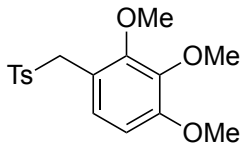
1) OsO_4/NMO, acetone/H_2O
2) $NaIO_4$, 1,4-dioxane/H_2O
3) $MePPh_3Br$, *n*-BuLi, dimethoxyethane
4) 9-BBN, THF, *then* $NaHCO_3/H_2O_2$
5) DMP, CH_2Cl_2
6) Vinylmagnesium bromide, THF
7) TBSCl, imidazole, DMF,
then K_2CO_3, MeOH

8) MsCl, Et_3N, LiBr, THF
9) **E**, KHMDS, THF
10) Na/Hg, Na_2HPO_4, MeOH
11) HF·Py, THF
12) [{Ir(cod)Cl}$_2$], *(R)*-**F**, $Zn(OTf)_2$, DCE,
*exposure of the byproducts to $BF_3{\cdot}OEt_2$ in CH_2Cl_2 gave another portion of **B***

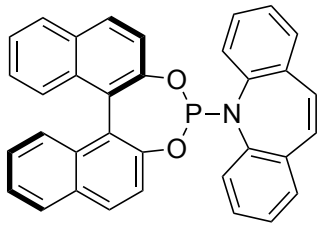
Reference: JACS, 2017, 139, 3603–3606.

What is the name of starting material?

1) + 2) Name reaction?

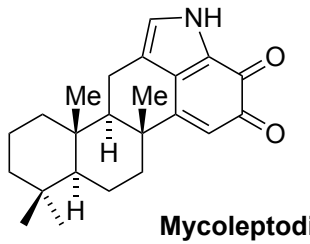


E



(R)-**F**

12) Which by-products might be formed in this step?
Hint: Please think about the possible cascade-interruption.



Mycoleptodiscin A

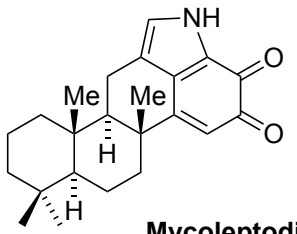
13-16

C

17-21

D

22-25



Mycoleptodiscin A

13) $K_2OsO_2(OH)_4$, $NaIO_4$, 2,6-lutidine, acetone/H_2O
14) *t*-BuOK, MeI, *t*-BuOH
15) $N_2H_4 \cdot H_2O$, KOH, diethylene glycol
16) CrO_3, 3,5-dimethylpyrazole,

17) $AlCl_3$, CH_2Cl_2
18) $NaBH_4$, MeOH/CH_2Cl_2
19) TMSCN (1.2 equiv), $InCl_3$ (10 mol%), TMSBr (20 mol%)
20) $BH_3 \cdot THF$, THF
21) Tf_2O, Et_3N, DMAP, CH_2Cl_2

22) CuI, CsOAc, NMP
23) DDQ, toluene
24) BBr_3, CH_2Cl_2
25) Mg, NH_4Cl, MeOH, *then* work up under an air atmosphere

15) Name reaction? Mechanism?

17) Hint: just a single demethylation