Total Synthesis of (–)-Pavidolide B

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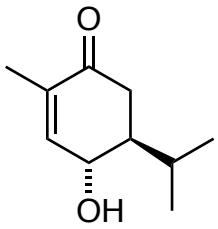
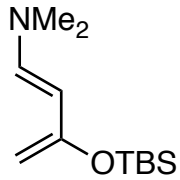


1-4

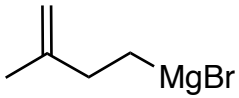
A

5-9

1) Bz_2O, NEt_3, DMAP
2) **1** (2 eq., neat), 70 °C *then* HF –78 °C - r.t.
3) $TMSN_3$, I_2, pyridine
4) n-Bu_3Sn(allyl), $Pd(PPh_3)_4$



1



2

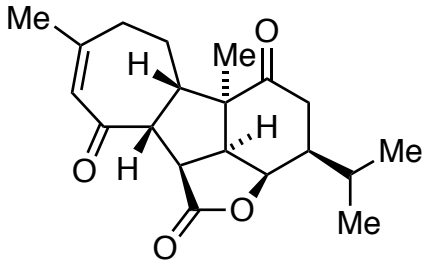
5) **2**, CuBr · SMe_2, HMPA, TMSCl
then AcOH
6) Grubbs II
7) trisylN_3, KOH, TBAB, 18-crown-6
then KOH/MeOH
8) MsCl, NEt_3, DMAP
9) hv (500 W med. p. Hg lamp), THF, r.t.

How can the strating material be accessed?

2) please name the transformation.
Who introduced dienes of type **1**?
note: the silyl group translocates during the first step.

trisylN_3 =
2,4,6-triisopropylbenzenesulfonyl azide

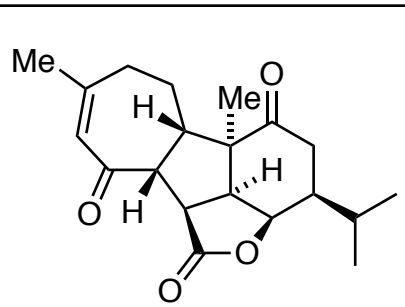
9) Please name the reaction



(–)-pavidolide B

B

10-13



(–)-pavidolide B

10) K_2CO_3, 18-crown-6, heat
11) TPPO *then* PPh_3
12) $TEMPO^+BF_4^-$
then DMP, $NaHCO_3$
13) DBU

TPPO = triphenyl phosphite ozonide

11) Name and Mechanism?
selectivity 4.2:1 for desired
12) How does this transformation work?