Streamlined Total Synthesis of Uncialamycin and Its Application to the Synthesis of Designed Analogues for Biological Investigations

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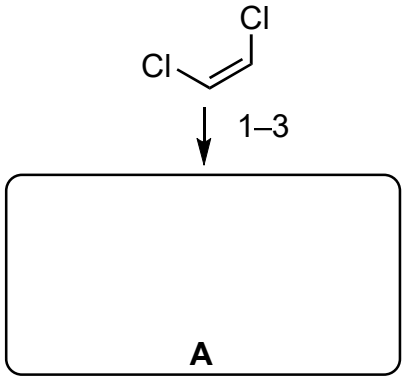
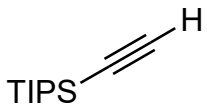
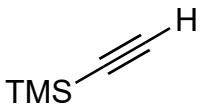


1) $Pd(PPh_3)_4$, CuI, **1**
2) $Pd(PPh_3)_4$, CuI, **2**
3) K_2CO_3

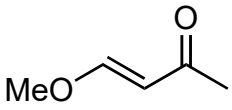


1



2

4) BBr_3
5) NaOH, **4**, H_2O
6) $CsCO_3$, TBAI, DMBBr
7) **5**, HCO_2H, NEt_3
8) DIBALH *then* TESCl, imH



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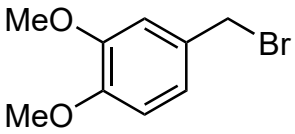
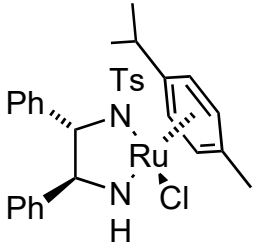
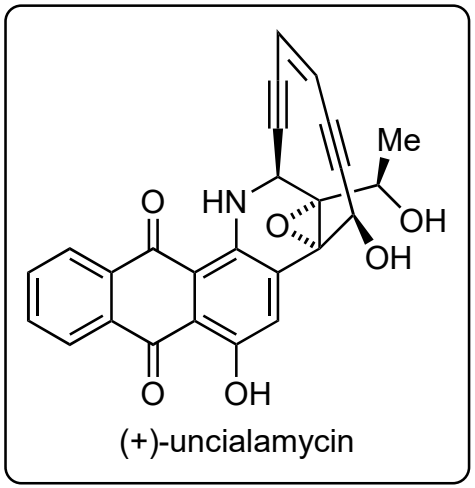


DMBBr



5

1) Name of the reaction
5) Provide a mechanism;
Name of the reaction;
Hint: a new heterocycle is formed
7) Name of the reaction

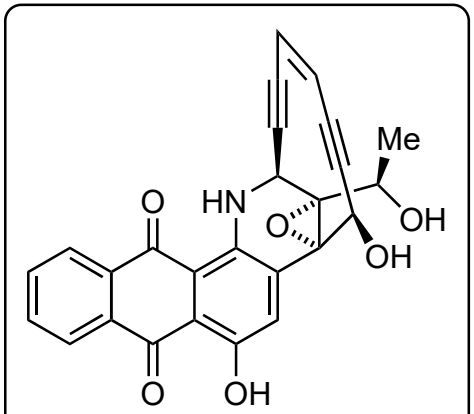


(+)-uncialamycin

9-18

C

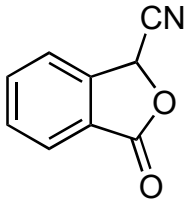
19-22



(+)-uncialamycin

9) **A**, *i*-PrMgCl *then* **B** *then* AllocCl
10) AcOH, H_2O
11) $NaBH_4$ *then* *m*-CPBA, $NaHCO_3$
12) AcCl (1 equiv.), DIPEA
13) DMP, $NaHCO_3$
14) TBAF, AcOH *then* $NaBH_4$
15) TESCl, imH *then* K_2CO_3, MeOH
16) DMP, $NaHCO_3$
17) DDQ, phosphate buffer (pH 6.8)
18) $CeCl_3$, KHMDS

19) PIDA, MeOH
20) **6**, LHMDS
21) $Pd(Ph_3)_4$, morpholine
22) 3 HF · NEt_3



6

9) Structure of AllocCl

9)

20) Provide a mechanism
Name of the reaction