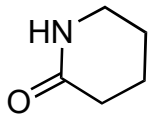
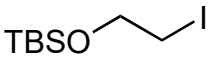
Total Synthesis of Aspidophytine

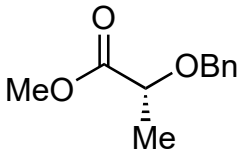
K. C. Nicolaou, S. M. Dalby, U. Majumder, *J. Am. Chem. Soc.* **2008**, *130*, 14942–14943.





1

1) NaH, **1**
2) LDA, **2**
3) KHMDS, **3**
4) $Pd(OH)_2$, H_2
5) $NaBH_4$, $NaIO_4$
6) NaHMDS, **4**



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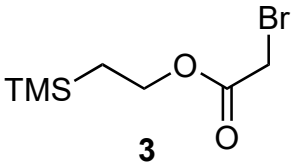

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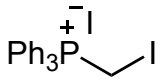
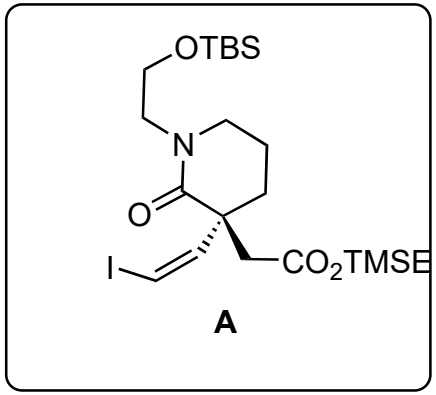
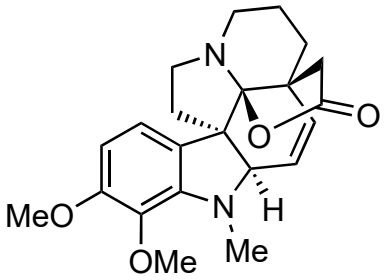


4

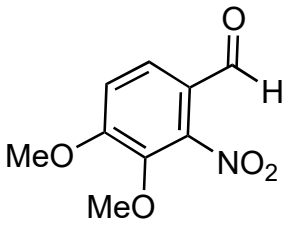


A

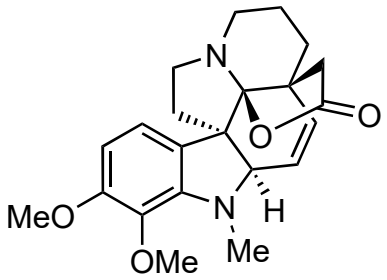
1) Name of the starting material?
   Valerolactone
2) From what chiral pool molecule can **2** be made from?
   (*R*)-Lactic acid
4) Name of the Pd catalyst?
   Pearlmans Catalyst
5) *Hint:* This is diol chemistry; also look at step 6
6) Name of the Reaction? What geometry is formed? Which conditions would give the inverse geometry?
   Stork-Zhao olefination, Z-geometry, Takai-Utimoto Olefination



Aspidophytine



7) $MeNO_2$, KOH
8) Ac_2O NaOAc reflux
9) Fe, AcOH, EtOH reflux
10) MeI, KOH, TBAI
11) *t*-BuLi, $B(OMe)_3$, NH_4Cl
12) **A**, $PdCl_2$(dppf), Cs_2CO_3, H_2O
13) Tf_2O, 2,6-di-tert-butyl-methylpyridine *then* $NaBH_4$
14) HF•py
15) NaH, CS_2, MeI
16) *n*-Bu_3SnH, AIBN
17) TBAF
18) $K_3Fe(CN)_6$, $NaHCO_3$, *t*-BuOH, H_2O



Aspidophytine

7) Name of the reaction?
Henry reaction
9) *Hint:* 2 types of transformations take place
11) *Hint*: C2
12) Name of the reaction?
Suzuki coupling
13) Classify the cyclization according to the Baldwin rules
6-exo-trig
14) *Hint*: Single cleavage, mind 15)