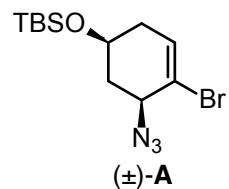
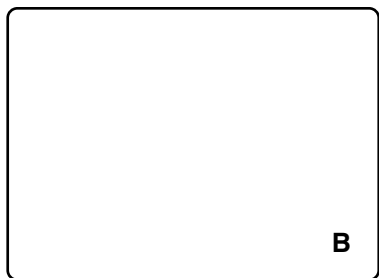


Biomimetic Total Synthesis of the Pentacyclic *Amaryllidaceae* Alkaloid Derivative Gracilamine

Nadia (Yuqian) Gao, Martin G. Banwell and Anthony C. Willis, *Org. Lett.* **2017**, *19*, 162–165.



1-3

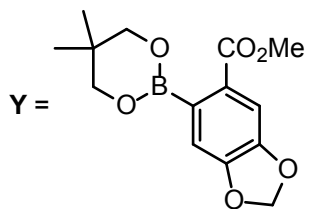


4-5



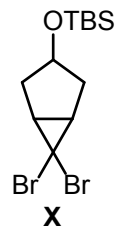
6-9

- 1) PPh_3 , $\text{MeOH}/\text{H}_2\text{O}$
- 2) TsCl , NEt_3
- 3) **Y**, $\text{PdCl}_2\text{dppf}\cdot\text{CH}_2\text{Cl}_2$, KOAc , Cs_2CO_3 ,



- 4) NaH , 1-bromo-2-butyne
- 5) $\text{Pd}(\text{OAc})_2$, *N,N'*-Dibenzylideneethylenediamine, toluene, reflux

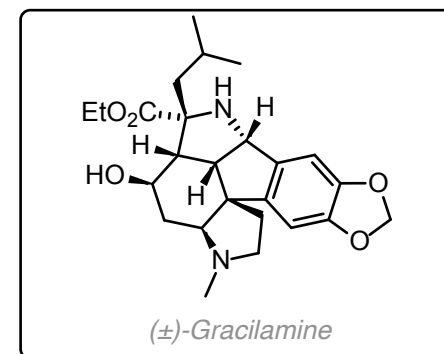
- 6) DIBAL-H
- 7) DMP
- 8) ethyl L-Leucinate $\cdot\text{HCl}$, Et_3N , MgSO_4
- 9) toluene, reflux



The starting material can be prepared within 2 steps from the [3.1.0]-bicyclic **X**. Please think of a possible transformation and the mechanism.

Please sketch the mechanism of the reaction in step 1.

Please provide the name and a detailed mechanism for the reaction in step 5. Could you think of a possible side product (38%)?

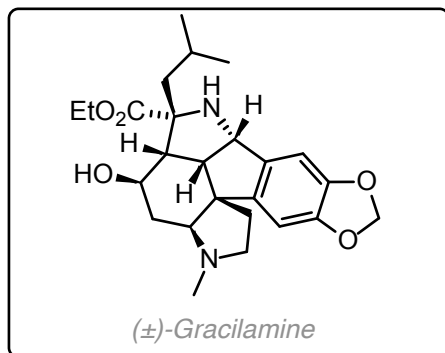




10-12
↓



13-16
↓



10) $\text{K}_2\text{OsO}_4 \cdot 2 \text{H}_2\text{O}$ (10 mol%), NMO (2 eq), citric acid
11) $\text{PhI}(\text{OAc})_2$
12) NaBH_4

What is the role of citric acid in step 10?

13) NaH , CS_2 , MeI
14) $n\text{-Bu}_3\text{SnH}$, AIBN
15) Mg , MeOH, sonication
 then HCl (aq.)
16) H_2CO , NaCNBH_3

Please provide a detailed mechanism for the transformation of step 14.