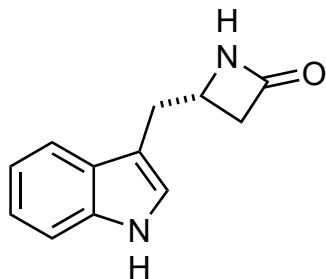
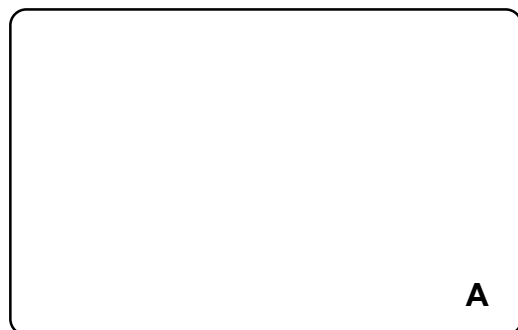


# Total Synthesis of Indole Alkaloid (+)-Alstonlarsine A

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1-8

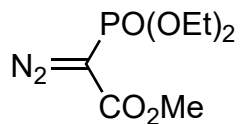


9



- 1) DMAP (cat.), TBSCl, Et<sub>3</sub>N
- 2) NaH, TBSCl, 0 °C to r.t.
3. LDA, THF, –78 °C then MeI
- 4) Et<sub>2</sub>NLi, THF, –78 °C  
*then* MeCHO, –100 °C
- 5) DMAP (cat.), Ac<sub>2</sub>O, Et<sub>3</sub>N
- 6) KF, MeOH, 0 °C
- 7) DMAP (cat.), (Boc)<sub>2</sub>O, Et<sub>3</sub>N
- 8) 50% aq HF

- 9) Cu(acac)<sub>2</sub> (2 mol%), **1**, 120 °C

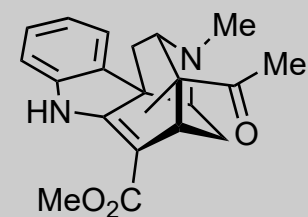


**1**

- 1) The starting material is a non-natural structural derivative of which amino acid? Name the 3- and 1-letter codes.
- 4) Name the reaction.

- 6) *Hint*: monodeprotection of the β-lactam.

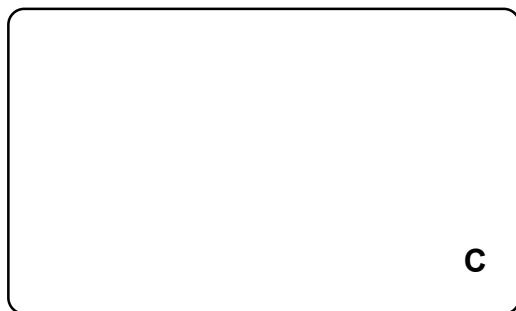
- 9) *Hint*: a formal C-H insertion occurs.



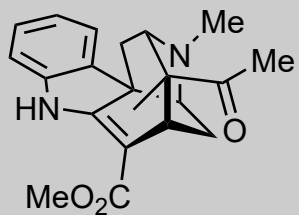
**(+)-alstonlarsine**

**B**

10-15



16-18



**(+)-alstonlarsine**

- 10)  $\text{NaBH}_4$ ,  $\text{MeOH}/\text{H}_2\text{O}$ ,  $0\text{ }^\circ\text{C}$
- 11) IBX,  $75\text{ }^\circ\text{C}$
- 12)  $\text{LiBr}$ ,  $\text{Et}_3\text{N}$
- 13)  $(\text{Boc})_2\text{O}$ ,  $\text{Et}_3\text{N}$ , DMAP (10 mol%)
- 14)  $\text{NaH}$ ,  $0\text{ }^\circ\text{C}$   
then  $\text{MeI}$ ,  $0\text{ }^\circ\text{C}$  to r.t.
- 15) TFA

- 16)  $\text{MeCHO}$ ,  $\text{PhMe}$ ,  $100\text{ }^\circ\text{C}$
- 17)  $\text{NaH}$ ,  $\text{LiAlH}_4$ ,  $\text{THF}$ ,  $0\text{ }^\circ\text{C}$
- 18)  $\text{Me}_2\text{S}$ ,  $\text{NCS}$ ,  $0\text{ }^\circ\text{C}$   
then **substrate**,  $-78$  to  $-50\text{ }^\circ\text{C}$ ,  
then  $\text{Et}_3\text{N}$ ,  $-50\text{ }^\circ\text{C}$

10) *Hint*: acetate is unreacted.

11) Draw the structure of IBX.

12) Name the reaction.

16) Name the reaction.

17) The acetate, resistant to acidic or basic hydrolysis, was selectively removed under reductive conditions with  $\text{LiAlH}_4$ . Reason the inclusion of  $\text{NaH}$ .

18) Name the reaction.