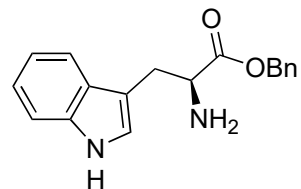
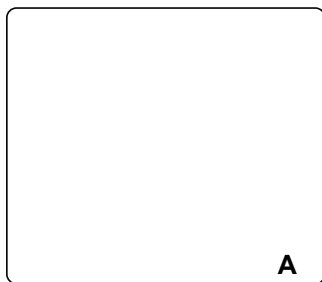


## Enantioselective Synthesis of Iboga Alkaloids and Vinblastine Via Rearrangements of Quaternary Ammoniums

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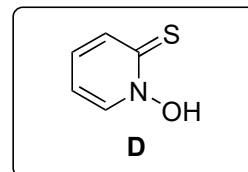
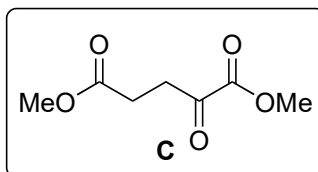
1-4



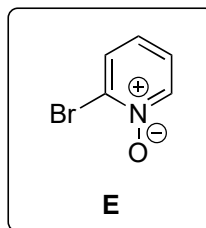
5-10



- 1) **C**, THF, reflux
- 2) H<sub>2</sub>, Pd/C (10% mol)
- 3) isobutyl chloroformate, NMO, *then* **D**, Et<sub>3</sub>N
- 4) *t*-butylthiol, 270W sun lamp



- 5) Boc<sub>2</sub>O
- 6) LDA, propargyl bromide
- 7) TFA
- 8) Me<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup>, *then* NaBH<sub>4</sub>
- 9) PPh<sub>3</sub>AuNTf<sub>2</sub> (cat.), **E**, MsOH, AgOTf (cat.)  
*then* NaHCO<sub>3</sub> (aq.), Et<sub>3</sub>N
- 10) *t*-BuOK, Ph<sub>3</sub>PEtBr

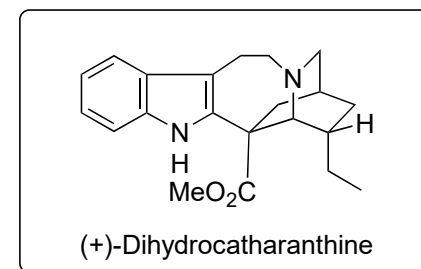


Step 1: What is the name of the amino acid that the starting material comes from? Name the reaction.

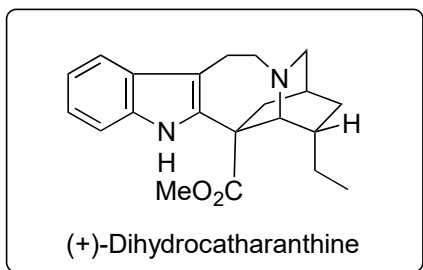
Step 4: Name the reaction

Step 9: During the basic treatment a second reaction happens followed by a rearrangement. Name the rearrangement and provide a mechanism.

Step 10: Name the reaction

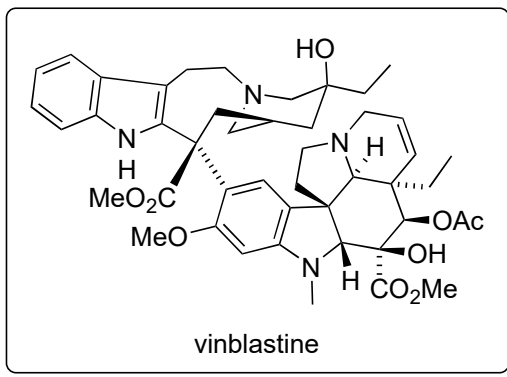


11

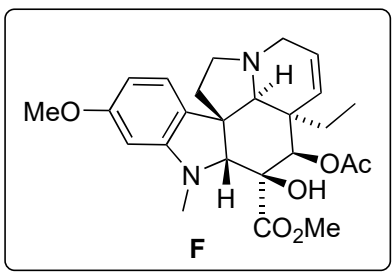


**B**

12



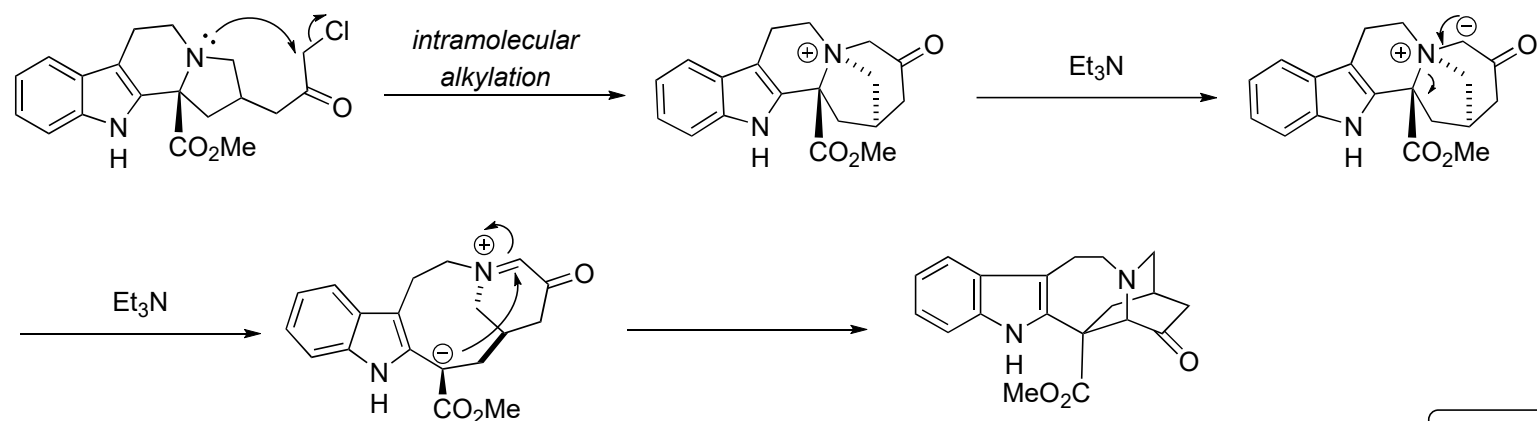
11) H<sub>2</sub>, PtO<sub>2</sub>



12) **F**, FeCl<sub>3</sub>, 0.1N HCl-CF<sub>3</sub>CH<sub>2</sub>OH  
then Fe<sub>2</sub>(ox)<sub>3</sub>, O<sub>2</sub>, NaBH<sub>4</sub>

Step 12: Propose a mechanism for this step

Step 9: [1,2]-Stevens rearrangement. Proposed mechanism:



Note: radical mechanism also plausible

Step 12: Oxidative coupling to vinblastine. Proposed mechanism.

