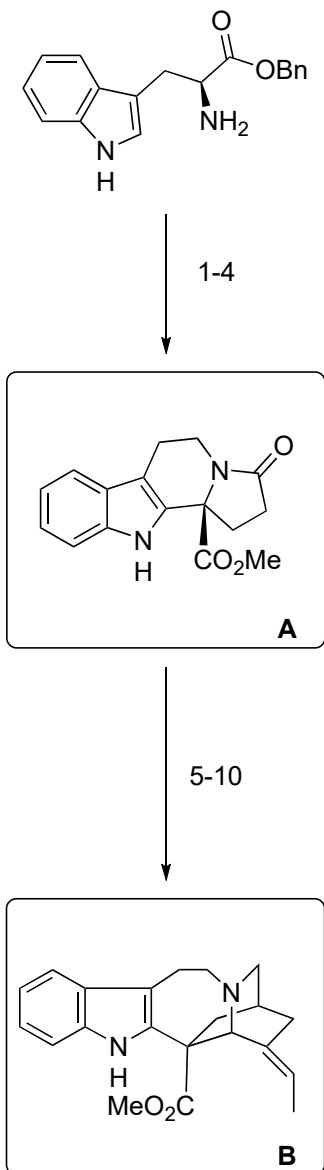
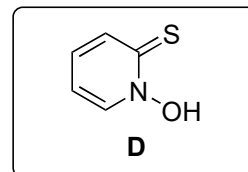
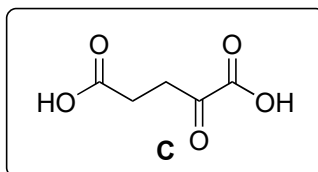


Enantioselective Synthesis of Iboga Alkaloids and Vinblastine Via Rearrangements of Quaternary Ammoniums

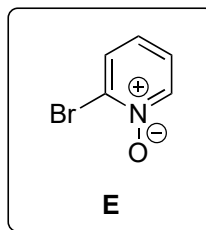
Yun Zhang, Yibin Xue, Gang Li, Haosen Yuan and Tuoping Luo*
Chem. Sci. **2016**, *7*, 5530–5536



- 1) **C**, THF, reflux
- 2) H₂, Pd/C (10% mol)
- 3) isobutyl chloroformate, NMO, then **D**, Et₃N
- 4) *t*-butylthiol, 270W sun lamp



- 5) Boc₂O
- 6) LDA, propargyl bromide
- 7) TFA
- 8) Me₃O⁺BF₄⁻, then NaBH₄
- 9) PPh₃AuNTf₂ (cat.), **E**, MsOH, AgOTf (cat.)
then NaHCO₃ (aq.), Et₃N
- 10) *t*-BuOK, Ph₃PEtBr



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

L-Tryptophan, Pictet-Spengler reaction

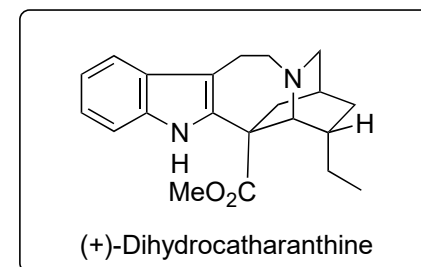
Step 4: Name the reaction

Barton decarboxylation

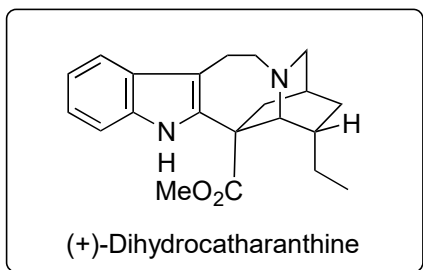
Step 9: During the basic treatment a second reaction happens followed by a rearrangement. Name the rearrangement and provide a mechanism. See attached.

Step 10: Name the reaction

Wittig reaction

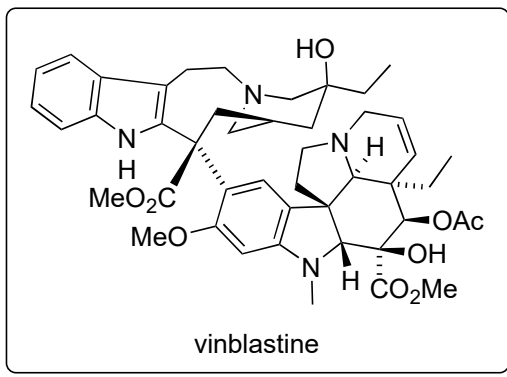


11
↓

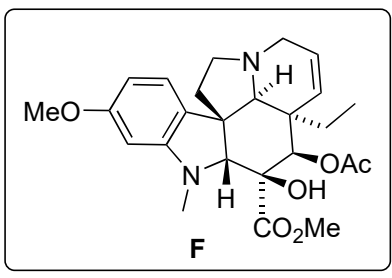


B

12
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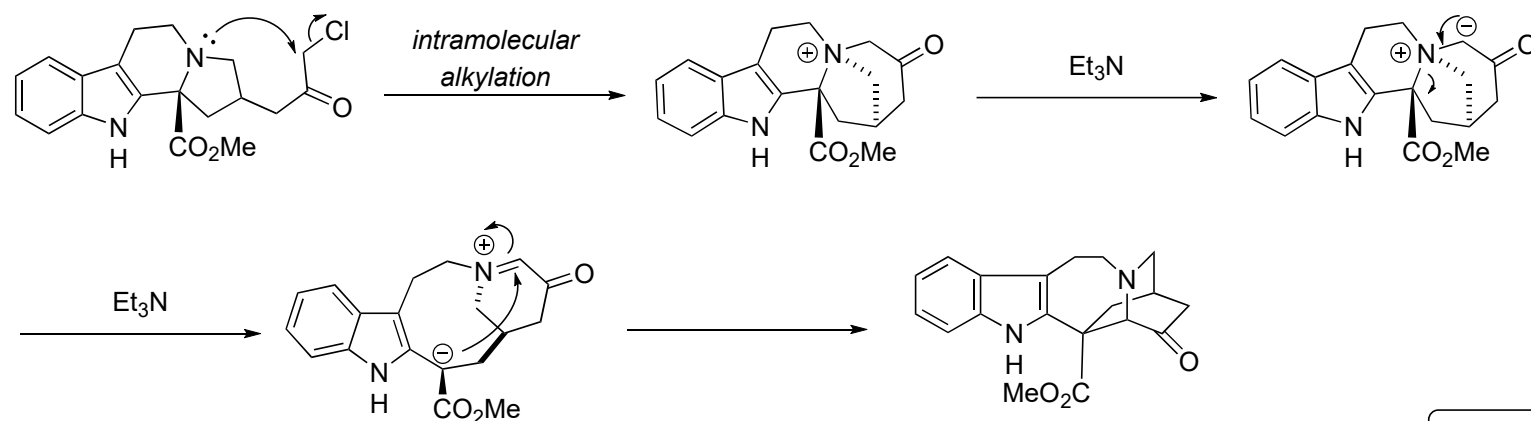
11) H₂, PtO₂



12) **F**, FeCl₃, 0.1N HCl-CF₃CH₂OH
then Fe₂(ox)₃, O₂, NaBH₄

Step 12: Propose a mechanism for this step
See attached.

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



Note: radical mechanism also plausible

Step 12: Oxidative coupling to vinblastine. Proposed mechanism.

