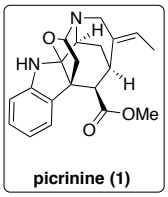
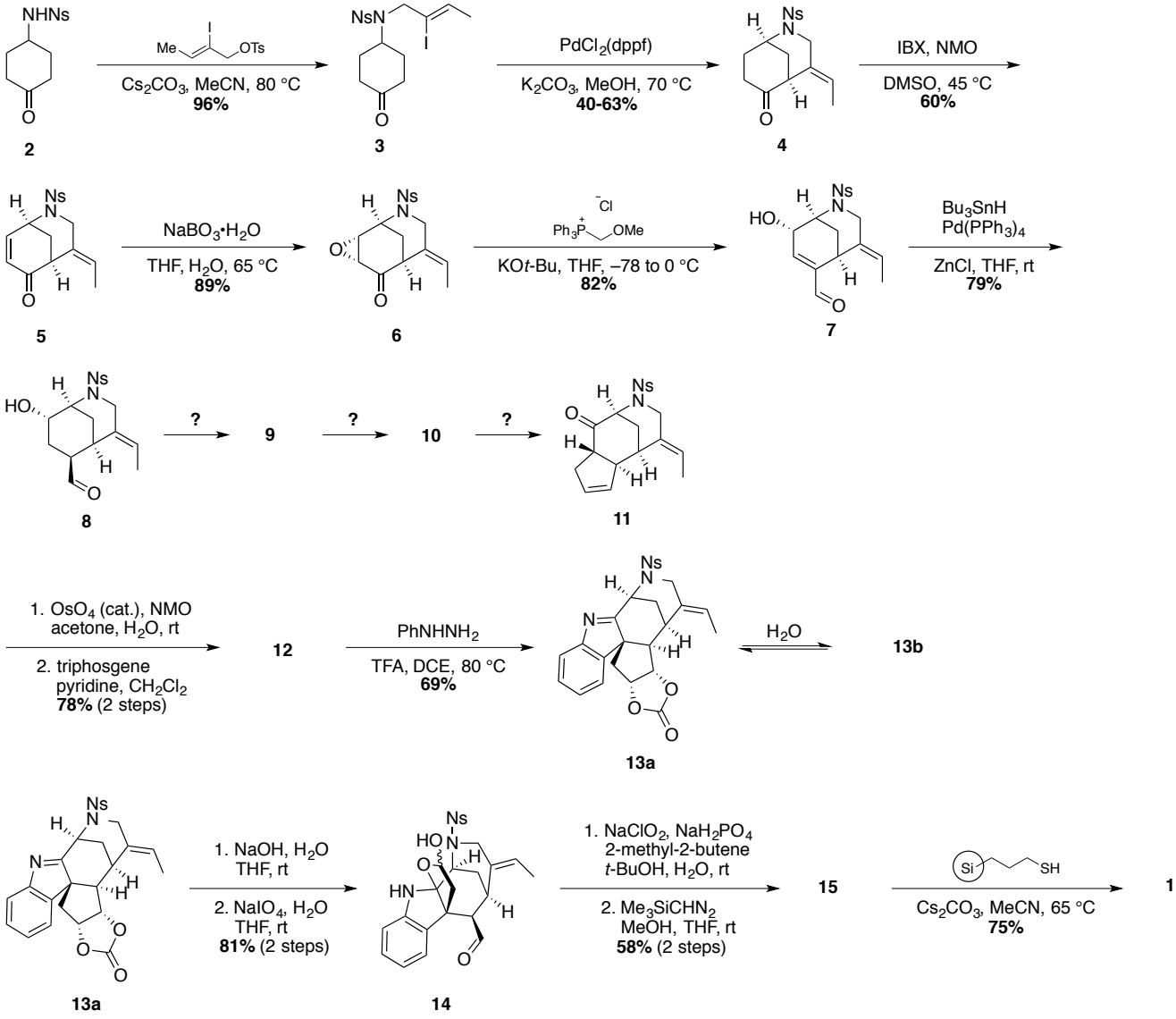
Submitted by Sam

**Total Synthesis oft he Akuammiline Alkaloid Picrinine**




Questions:

1. Propose a mechanism for the oxidation of ketone **4** to enone **5**.
2. Propose a mechanism for the formation of epoxide **6** from enone **5** and aldehyde **8** from enone **7**.
3. Suggest a sequence of reaction for the formation of tricycle **11** starting from aldehyde **8.** Give the intermediates and conditions.
4. In the formation of **12**, triphosgene is used to protect the product. How many equivalents of triphosgene have to be used and what is its reaction with pyridine?
5. What are the names of the reactions in the steps **12→13a** and **14→15**?
6. Propose a mechanism for the formation of **14** from **13a**.
7. *(If time: Suggest a synthesis of the vinyl iodide in the first step, starting from but-2-yn-1-ol using $Bu_3SnH$. How could you synthesize the isomer (with $Bu_3SnH$)?)*

Source:

J. M. Smith, J. Moreno, B. W. Boal, N. K. Garg, *J. Am. Chem. Soc.* **2014**, *136*, 4504–4507.

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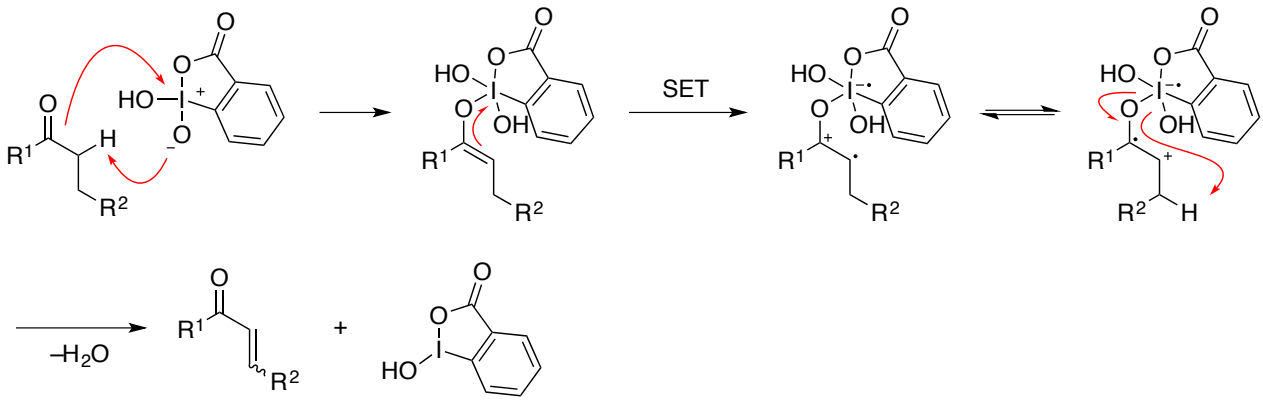
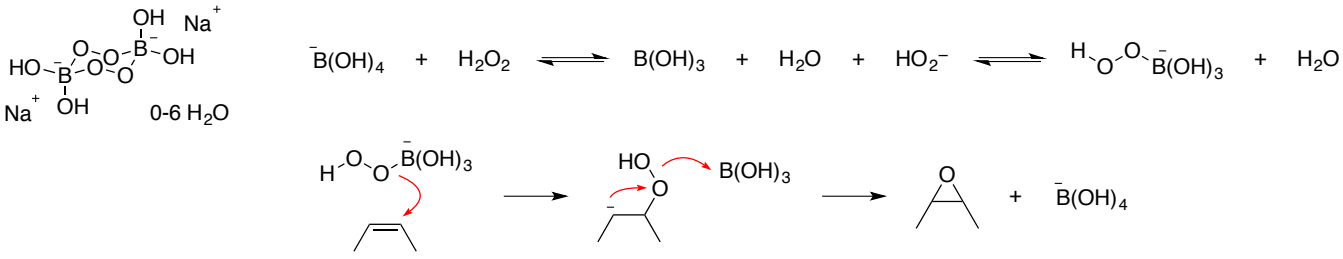
Solutions:

## 1. Oxidation of ketone with IBX

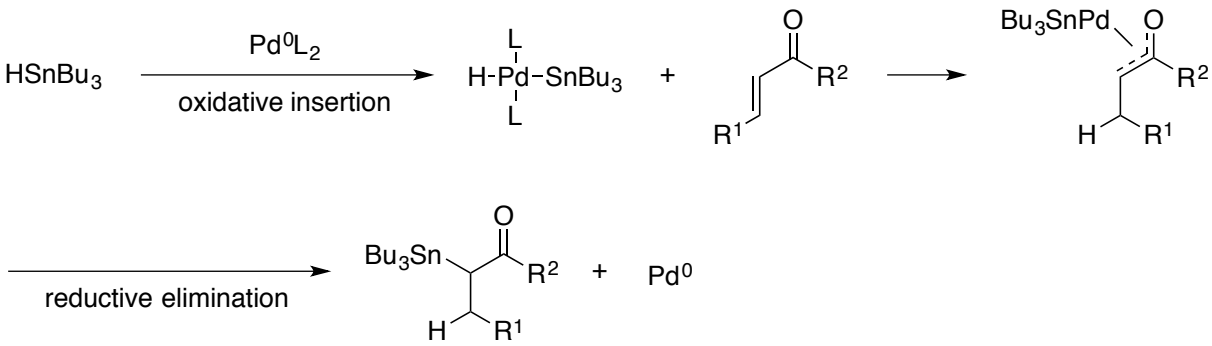



Ref.: K. C. Nicolaou, T. Montagnon, P. S. Baran, *Angew. Chem. Int. Ed.* **2002**, *41*, 993–996.

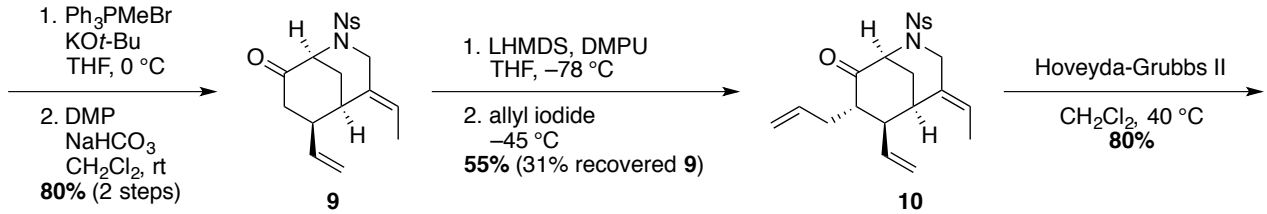
## 2. Epoxidation with $NaBO_3$



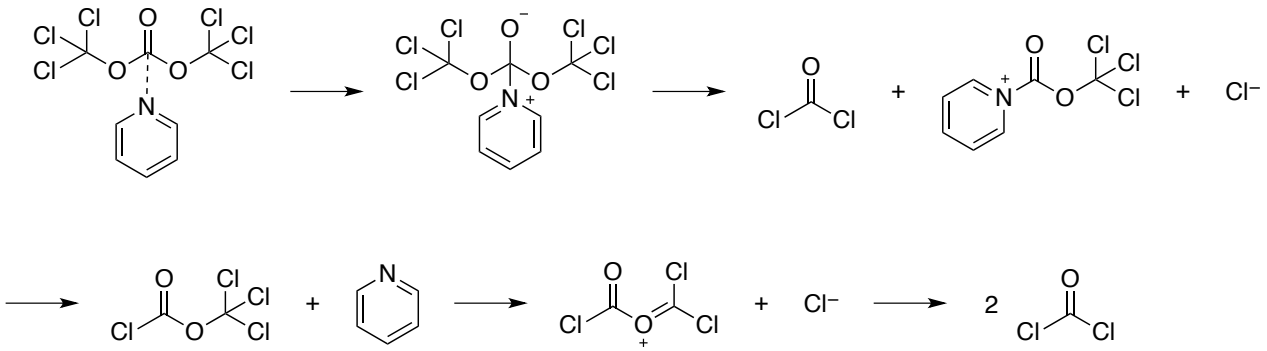

### Hydrostannylation




## 3. Reaction sequence

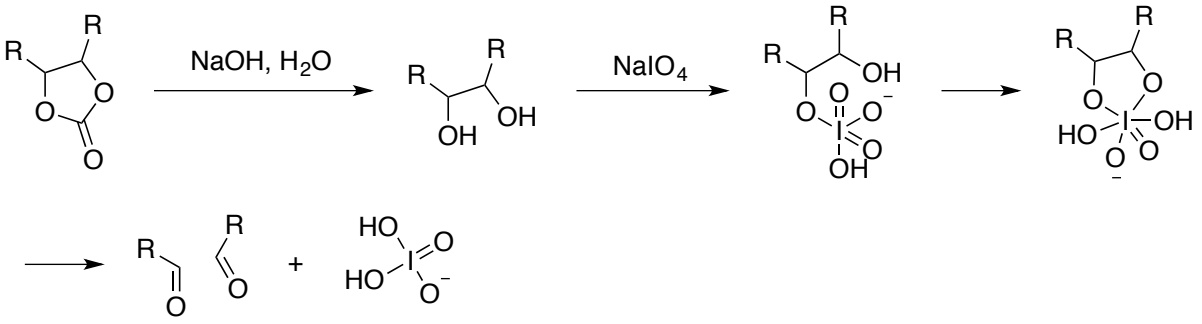


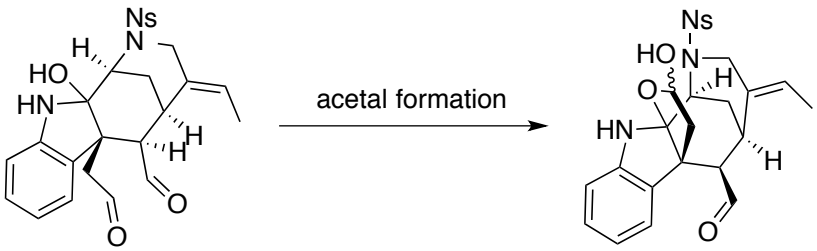
**4. 0.33 equiv. of triphosgene are used in an ideal case.**



**5. Fischer Indole Synthesis, Pinnick Oxidation**

**6. Diol cleavage**




**13b** **14**

**7. Precursor Synthesis**