GROUP MEETING - EXERCISE 29
02.11.2017 – Beltran Raphaël.

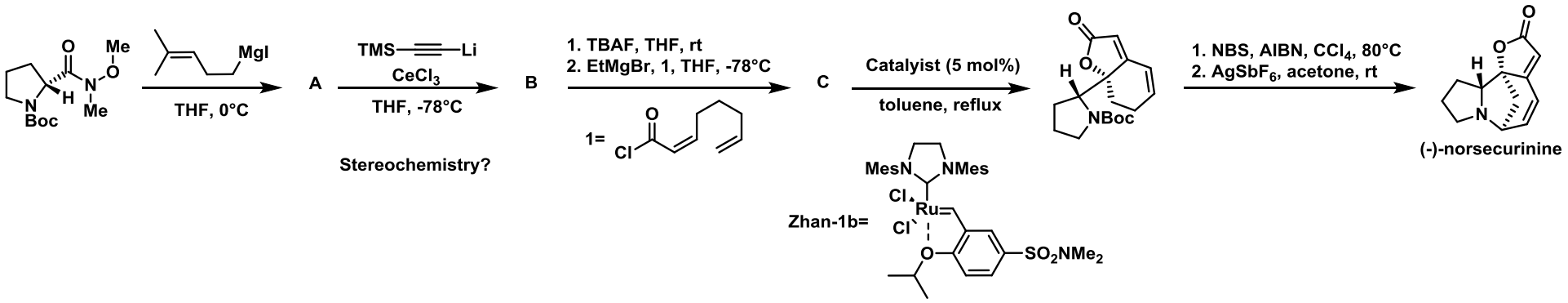
Access to (-)-flueggine A, (+)-virosaine B and (-)-virosaine A, from *Securinega* alkaloids

Securinega alkaloids are a family of bridged tetracyclic compounds mainly found on the plants of the Euphorbiaceae family. Most of these alkaloids contain an interesting α,β,γ,δ-unsaturated lactone moiety. These compounds have drawn increasing interest from synthetic chemists, resulting in a number of innovative total syntheses. *Nat. Prod. Rep*., **2009**, *26*, 758–775

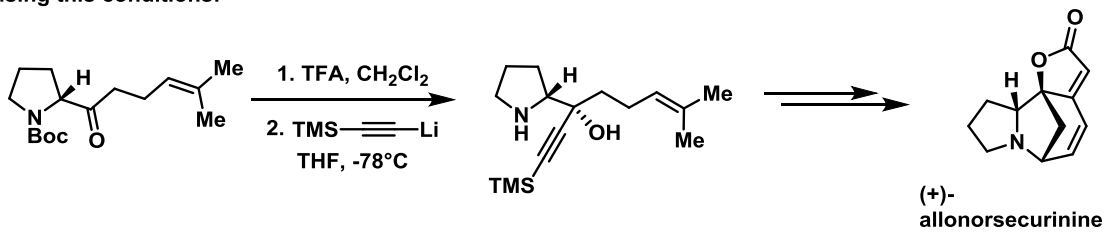
Part I: Total synthesis of (-)-flueggine A and (+)-virosaine B.

In 2013, Zhen Yang, Chuang-chuang Li and coworkers reported the first total synthesis of (-)-flueggine A and (+)-virosaine B *via* (-)-norsecurinine and (+)-allonorsecurinine respectively. *Angew. Chem. Int. Ed.* **2013**, *52*, 620-624.

I: Synthesis of (-)-norsecurinine & (+)-allonorsecurinine. *Give a mechanism of each reaction.*

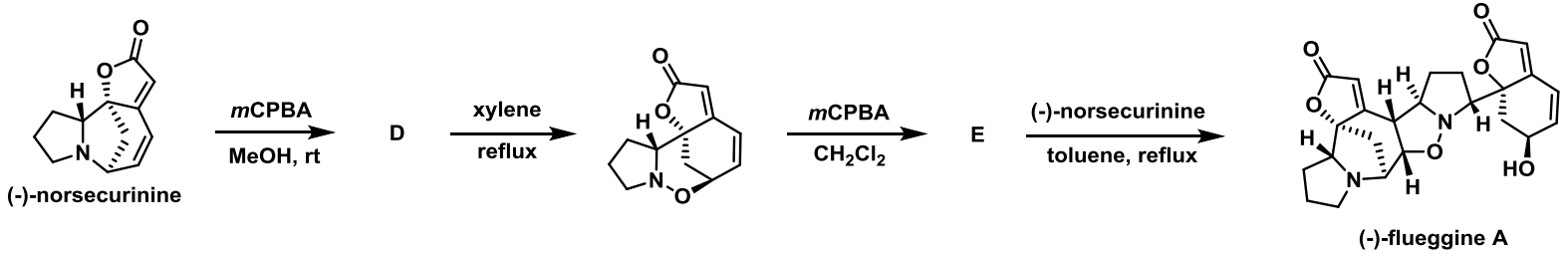


Using a similar sequence, (+)-allonorsecurinine, a diastereoisomer of (-)-norsecurinine, was obtained. The inversion of the stereochemistry at the quaternary center was performed using this conditions:

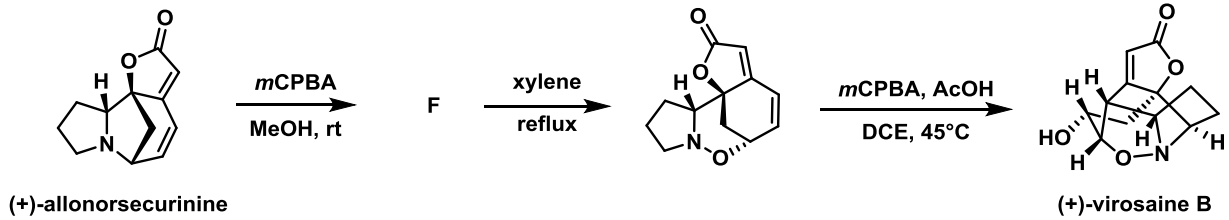


Provide an explanation for the stereochemistry.

II: Synthesis of (-)-flueggine A from (-)-norsecurinine. *Give a mechanism of each reaction.*



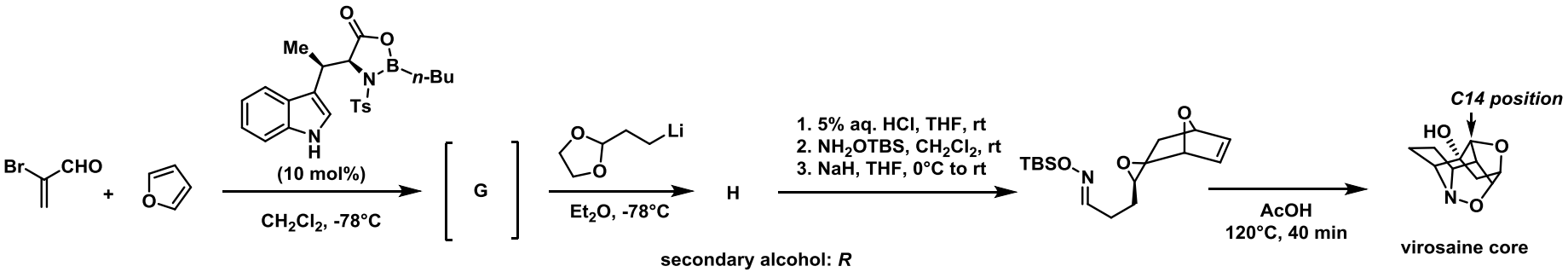
III: Synthesis of (+)-virosaine B from (+)-allonorsecurinine. *Give a mechanism of each reaction.*



Part II: Total synthesis of (-)-virosaine A.

In 2017, Hughes and Gleason reported the first total synthesis of (-)-virosaine A. This work was distinguished by the rapid construction of the carbocyclic framework. *Angew. Chem. Int. Ed.* **2017**, *56*, 10830-10834.

I: Efficient route to the virosaine core. *Give a mechanism of each reaction.*



II: Toward the C14 functionalization. *Give a mechanism of each reaction.*