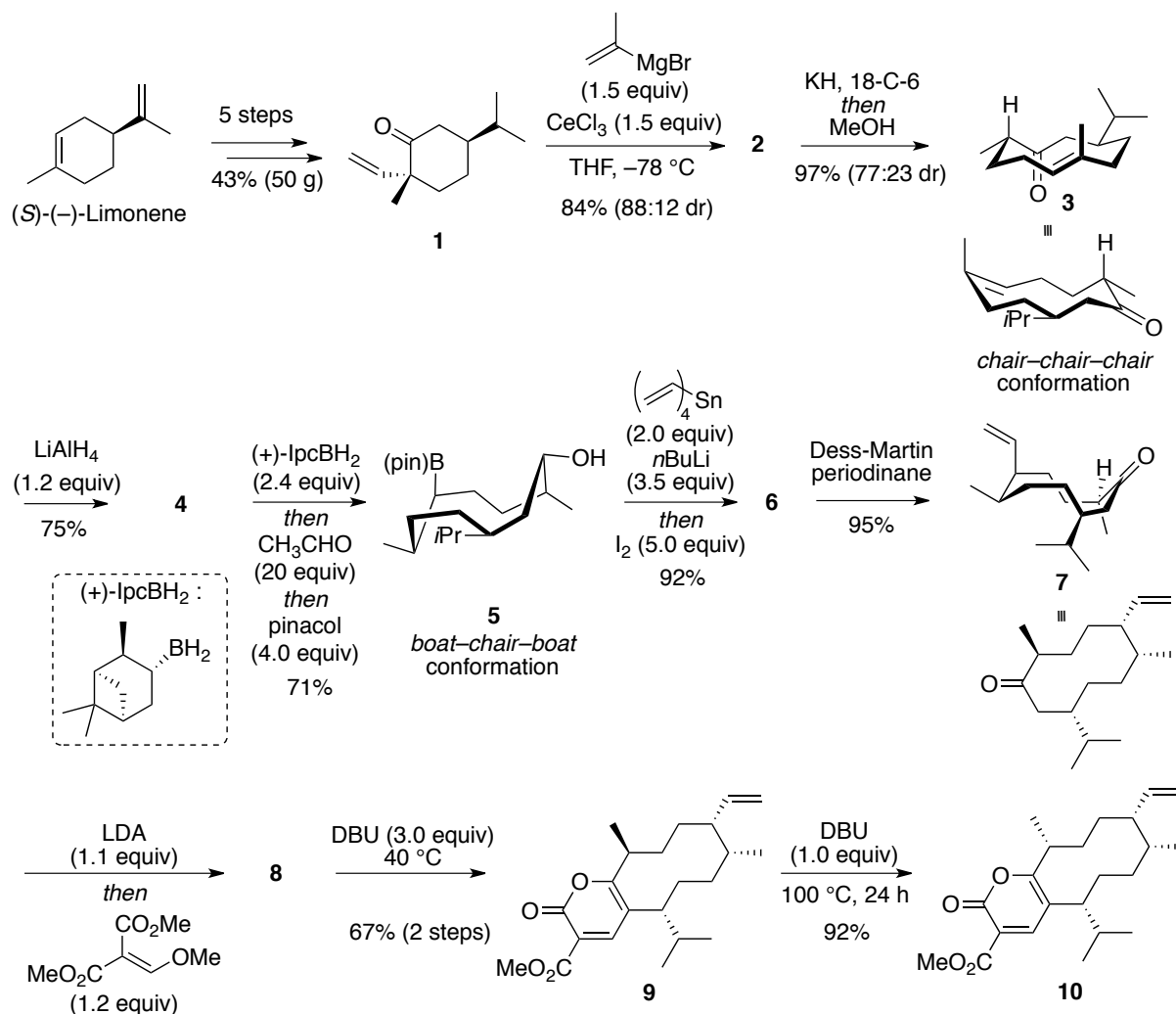


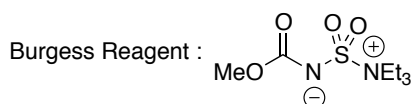
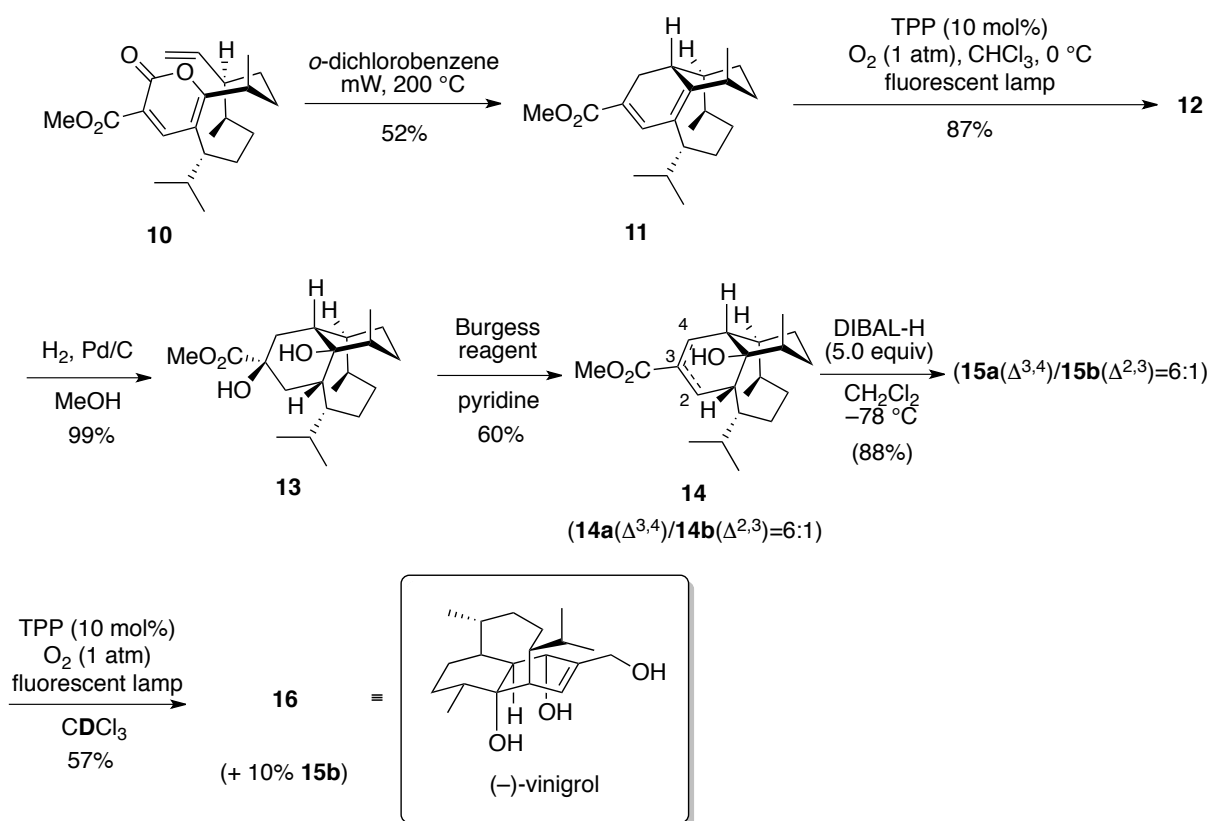
## ROCS Synthesis Seminars – 10/05/2019

### Total Synthesis of (-)-Vinigrol (Luo, 2019)

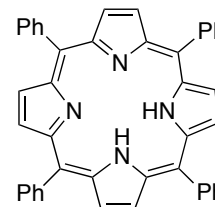
Vinigrol is a structurally and stereochemically complex natural product that displays various potent pharmacological activities. Vinigrol is the only terpenoid that is characterized by the 6–6–8 tricyclic ring system with the axial four-carbon tether bridging the densely decorated cis-decalin. Vinigrol was first isolated from a fungal strain in Japan in 1987 by Hashimoto and co-workers. To date there are only three total synthesis reported. A new synthetic route toward this natural product has been developed to complete the asymmetric synthesis of (-)-vinigrol and provide over 600 mg of material.



- 1) Give the structure of **2** and suggest a stereoselectivity model.
- 2) Give the mechanism **2** → **3**.
- 3) Give the structure of **4**.
- 4) Give the mechanism **4** → **5**. What is the role of acetaldehyde ?
- 5) Give the structure of **6** and the mechanism **5** → **6**.
- 6) Give the mechanism **7** → **8** → **9**.



TPP (Photosensitizer):



7) Give the mechanism  $\text{10} \rightarrow \text{11}$ .

8) Give the structure of  $\text{12}$  and the mechanism  $\text{11} \rightarrow \text{12}$ .

9) Give the mechanism  $\text{13} \rightarrow \text{14}$ .

10) Give the structure of  $\text{16}$  and check that it corresponds to (-)-vinigrol !