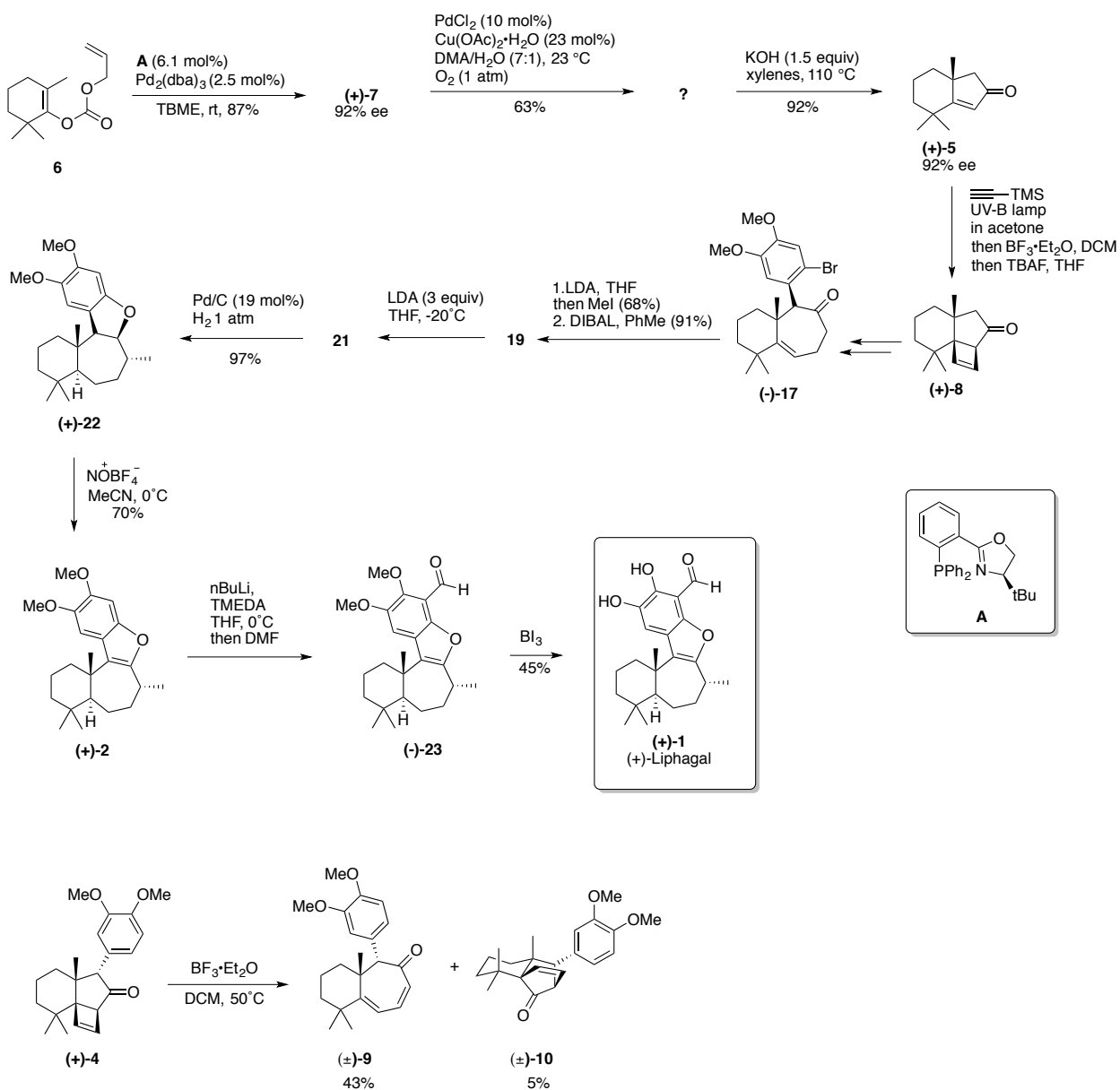


Total synthesis of (+)-Liphagal



1. What is the structure of the compound **7**? How does it form from **6**? What is the name for this reaction?
 2. Through which compound (?) formation of compound **5** is possible? Write the mechanism and which name does this reaction have?
 3. Formation of compound **8** from **5** without $\text{BF}_3 \cdot \text{Et}_2\text{O}$ yields to 45%. Using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ after 3 steps cyclobutene **8** was reached in 68% yield. How can we explain this? Which structure can you propose for other product in case of low yield of target compound?
- Hint: a rearrangement takes place.
4. Give structure of compound **19**.
 5. Propose the structure of compound **21**. Write assumed intermediate on the way from **19** to **21**.

6. Propose the mechanism of formation compound **2** from **22**.

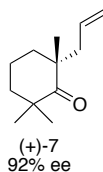
Hint: gas which released has been used in dentistry and surgery, as anaesthetic and analgesic, since 1844.

7. Try to propose possible mechanism for formation compound **9** and **10**.

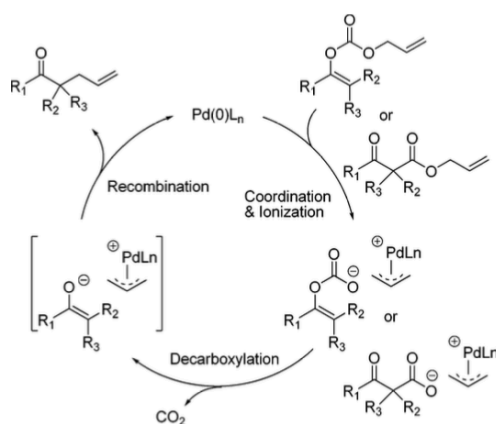
Hint: formation of compound **10** involves two concerted [1,2]-C-C bond migrations.

Total synthesis of (+)-Liphagal

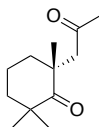
1. What is the structure of the compound **7**? How does it form from **6**? What is the name for this reaction?



Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of Enol Carbonates

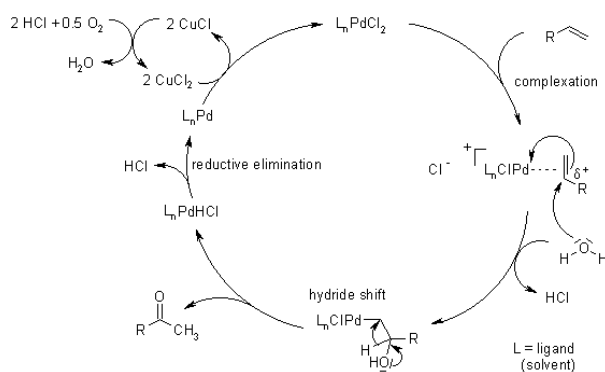


2. Through which compound (?) formation of compound **5** is possible? Write the mechanism and which name does this reaction have?



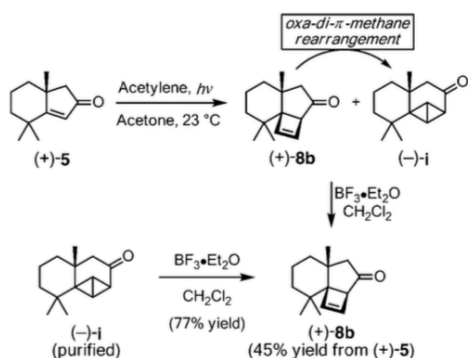
Mechanism of the Wacker-Tsuji Oxidation

The mechanism is typical of palladium olefin chemistry, and water serves as the oxygen source; the reduced palladium is reoxidized by Cu(II) and ultimately by atmospheric oxygen.

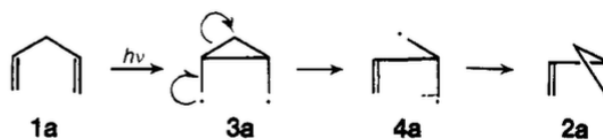
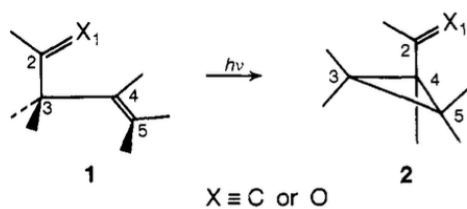


3. Formation of compound **8** from **5** without $\text{BF}_3 \cdot \text{Et}_2\text{O}$ yields to 45%. Using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ after 3 steps cyclobutene **8** was reached in 68% yield. How can we explain this? Which structure can you propose for other product in case of low yield of target compound?

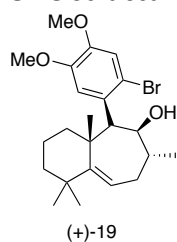
Photocycloaddition of enone **5** with acetylene produced a mixture of cyclobutene photoadduct presumably resulting from *oxa-di- π -methane rearrangement* of **8 b**. Exposure of the mixture to $\text{BF}_3 \cdot \text{OEt}_2$ resulted in conversion of compound **i** into **8 b**.



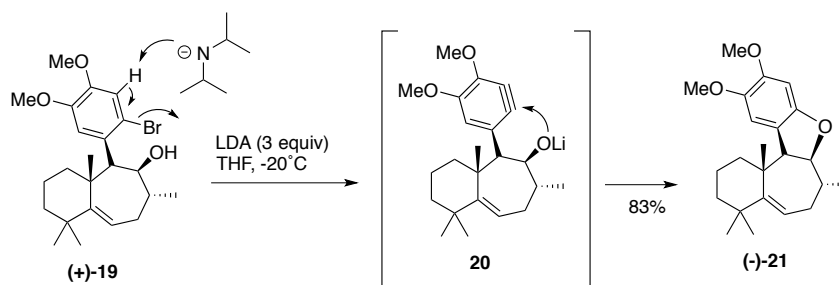
Oxa-di- π -methane rearrangement.



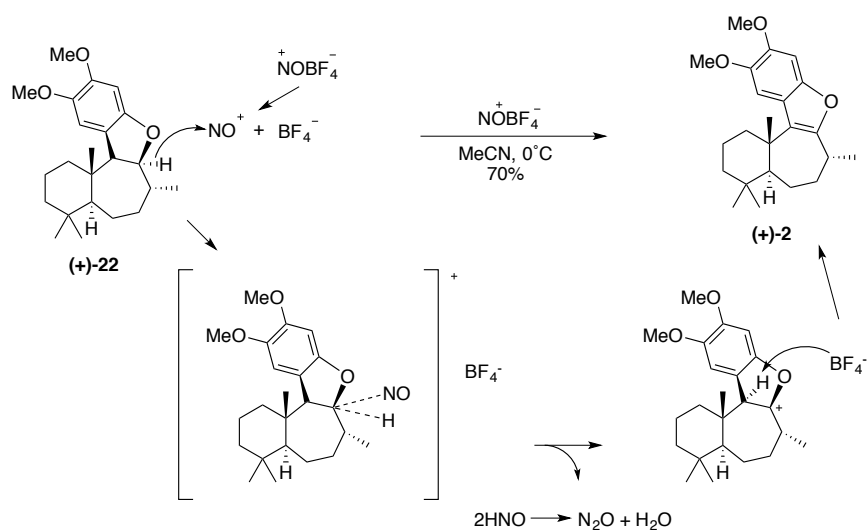
4. Give structure of compound **19**.



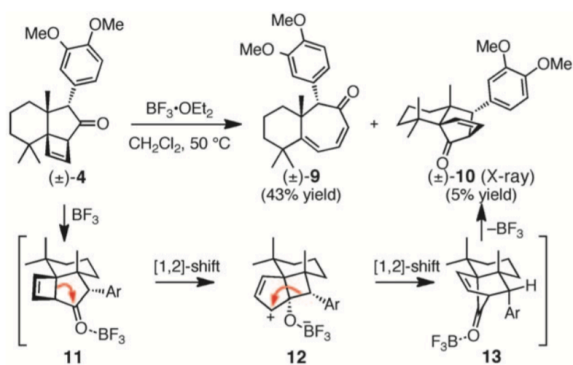
5. Propose the structure of compound **21**. Write assumed intermediate on the way from **19** to **21**.



6. Propose the mechanism of formation compound **2** from **22**.



7. Try to propose possible mechanism for formation compound **9** and **10**.



The synthesis was taken from the paper: *Angew. Chem. Int. Ed.* 2011, 50, 6814–6818