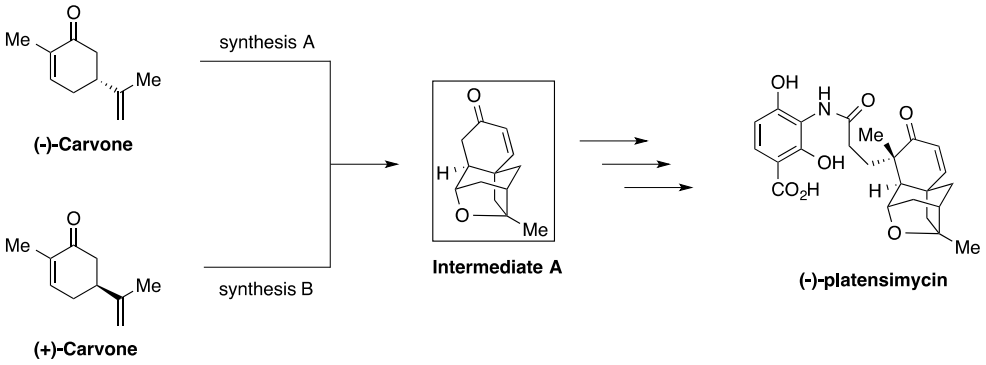
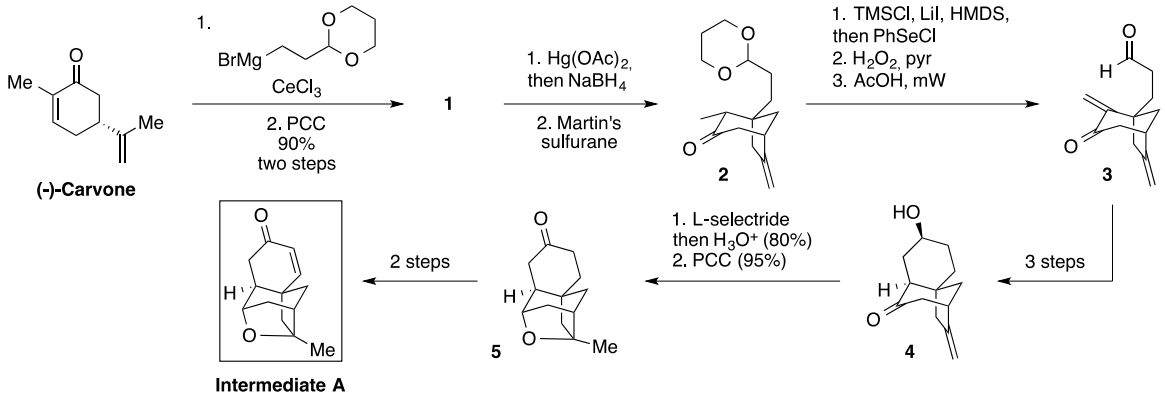
Submitted by Valentin Soulard

Two enantiomers, two pathways, one intermediate



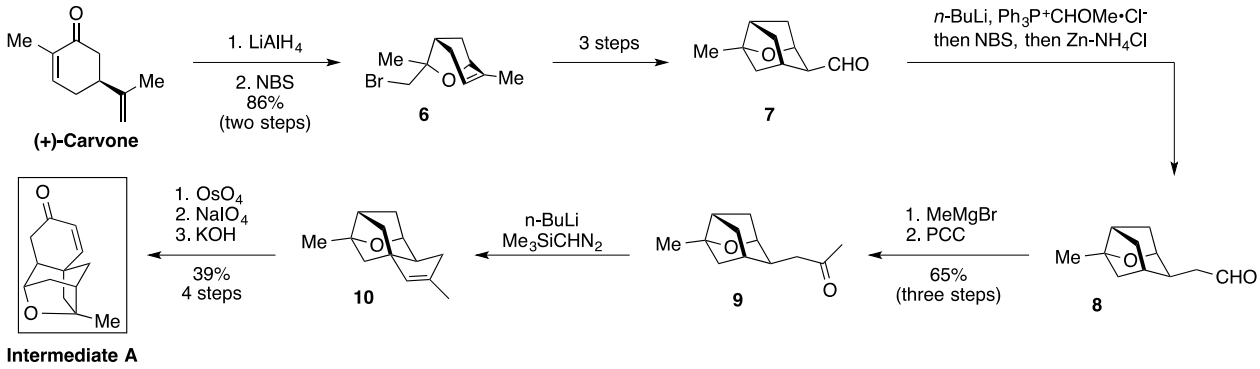
Synthesis A:

- Why $CeCl_3$ is used for the first step?
- Give the structure of **1**
- Explain the mechanism between **2** and **3**
- Give the 3 missing steps between **3** and **4**
- Give the last 2 steps missing



Synthesis B:

- Give the 3 missing steps between **6** and **7**
- Give the mechanism of the reaction between **7** and **8**
- Explain the formation of **10**



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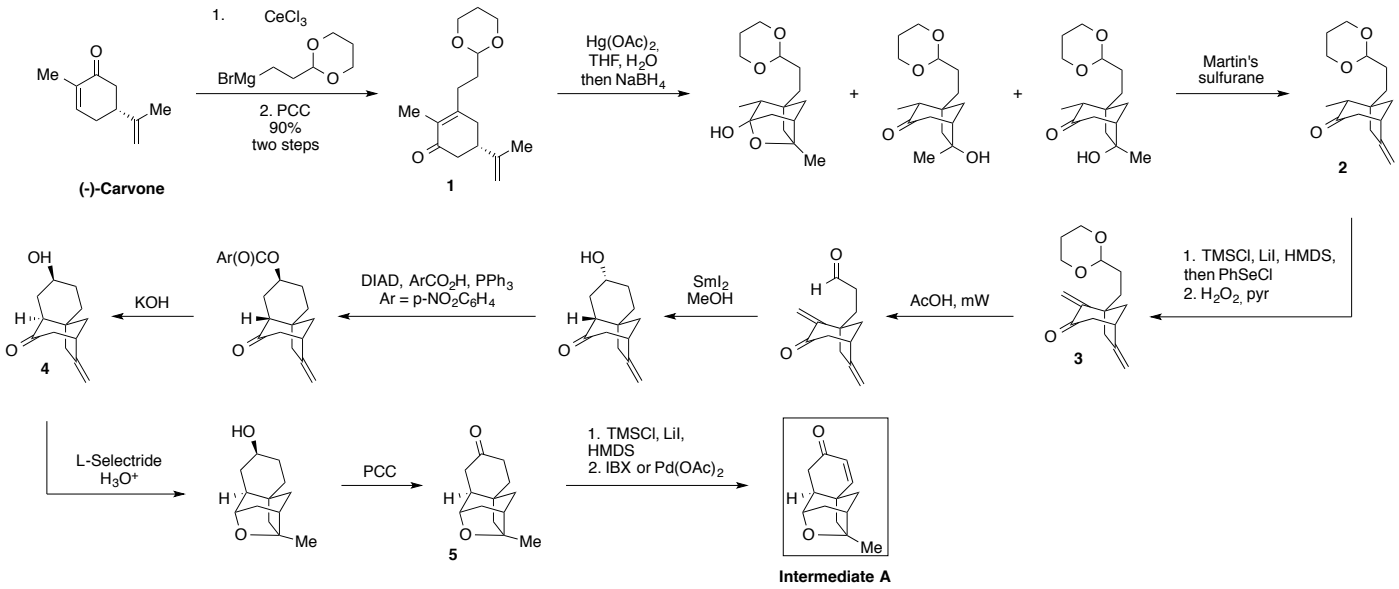
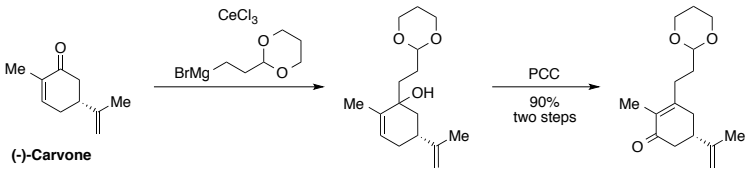
SOLUTIONS

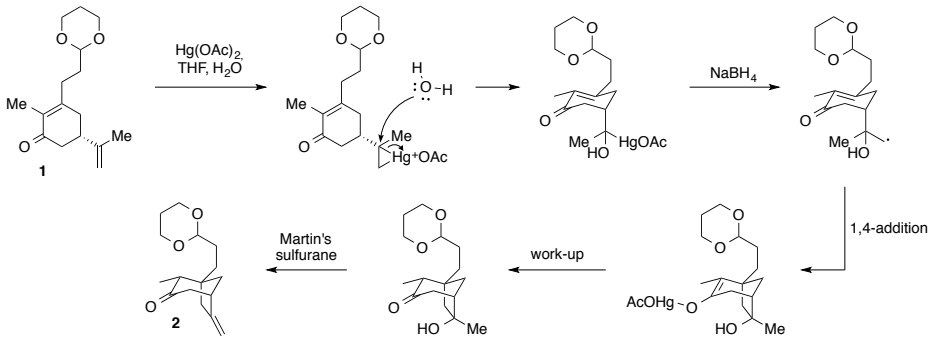
Synthesis A:



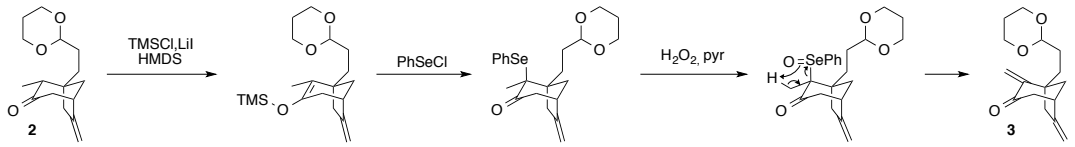
1. 1,2-addition of the Grignard reagents with Luche conditions



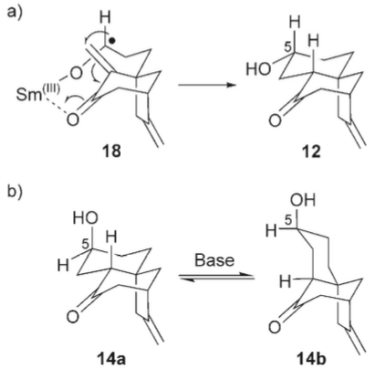
2. Reactions between **1** and **2**



3. Reactions between **2** and **3**



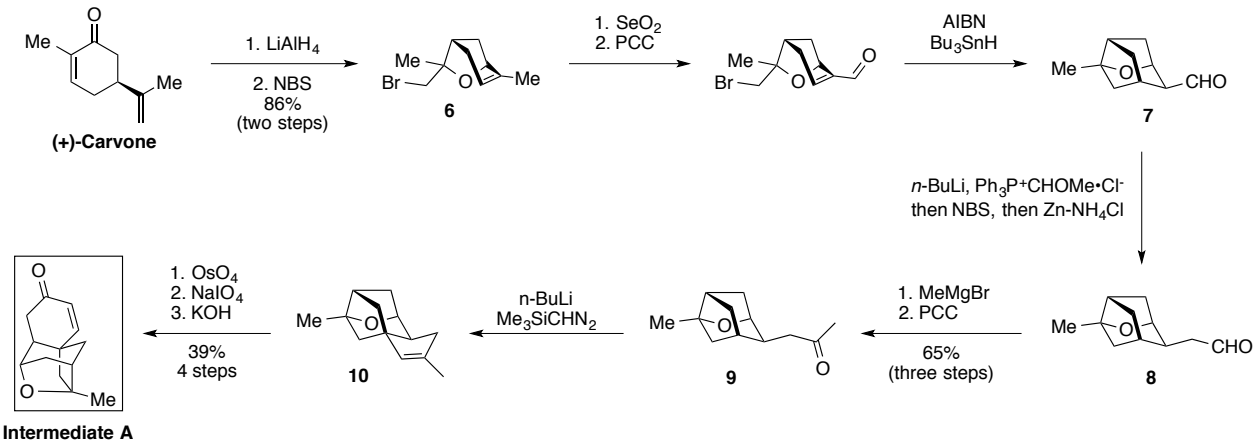
4. Radical Cyclization and epimerization



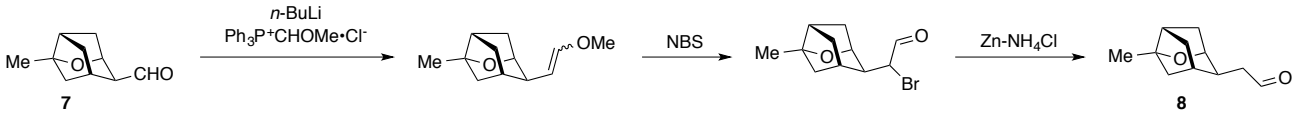
Scheme 4. a) Postulated samarium-templated ring closure of radical **18** to form hydroxy ketone **12**; and b) base-mediated equilibration of of hydroxy ketones **14a** and **14b**.

Synthesis B:

- Give the 3 missing steps between **6** and **7**
- Give the mechanism of the reaction between **7** and **8**
- Explain the formation of **10**



2. Homologation reaction between **7** and **8**



3. Reaction between **9** and **10**

Scheme 1. Selective C–H Insertion of Alkylidene Carbenes