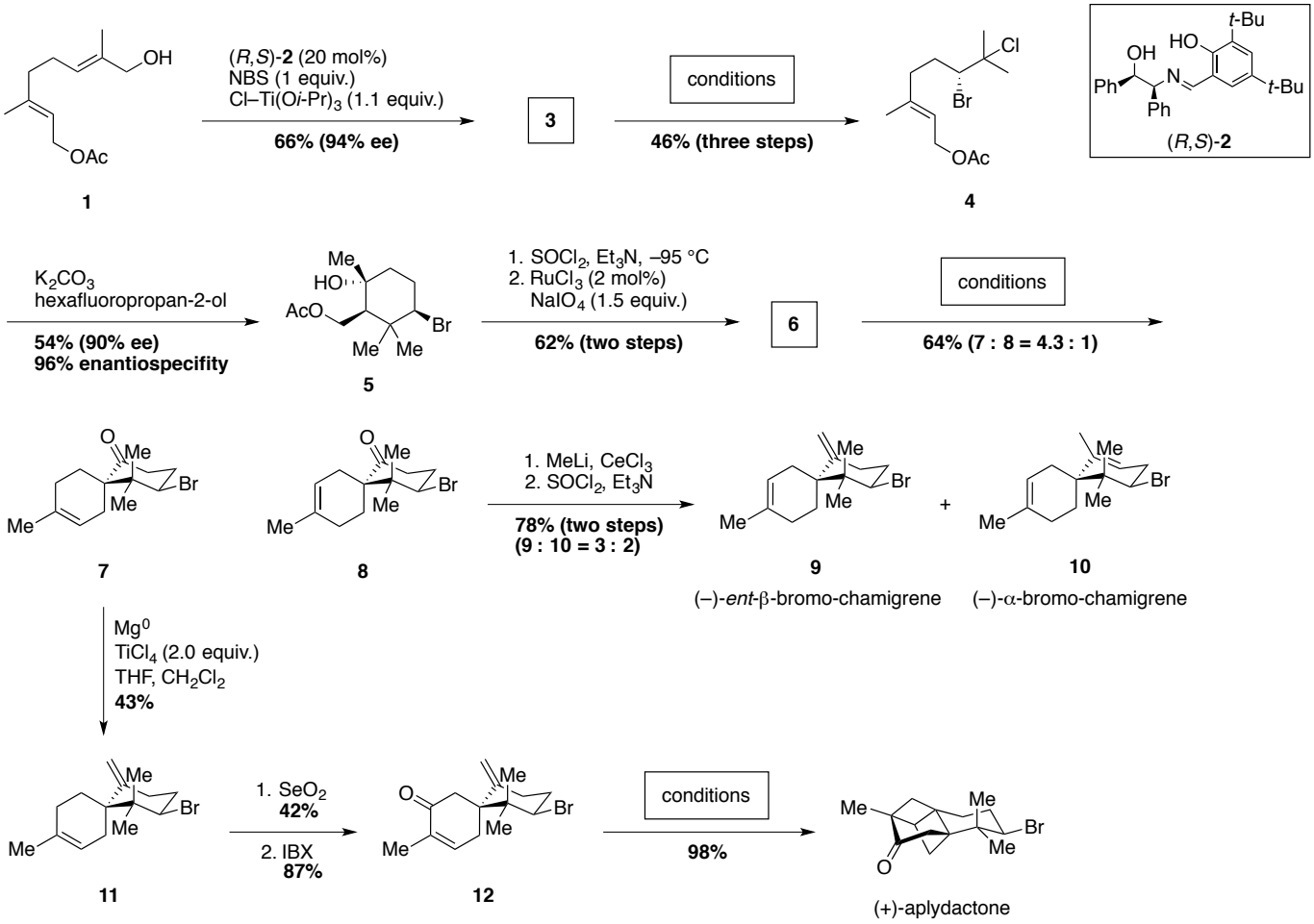
Submitted by Sam

A Unified Approach for the Enantioselective Synthesis of the Brominated Chamigrene Sesquiterpenes

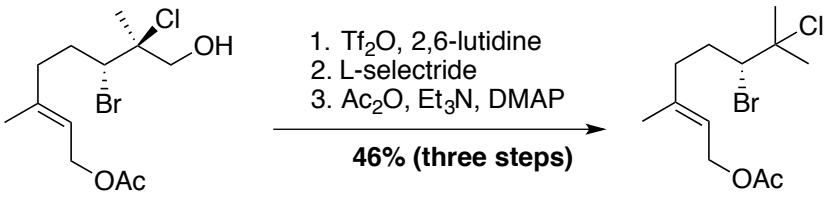


Questions:

1. Give the structure of compound **3** and propose conditions for its transformation to **4**.
2. Cyclohexanol **5** is obtained under ionizing conditions. Propose a mechanism and a rationale for the high enantiospecificity. (Hint: hydroxy-group is obtained after workup)
3. Give the structure of compound **6** and the mechanism for its formation from **5**. With compound **6** in hand, propose LA-catalyzed conditions for the formation of compounds **7** and **8**. (How many products would you expect for this step?)
4. Propose a mechanism for the formation of olefin **11** from ketone **7** and enone **12** from olefin **11**.
5. In the last step, the final product is obtained in very high yield. Propose conditions (1 step) for its formation and give a rationale for your choice.

Solution

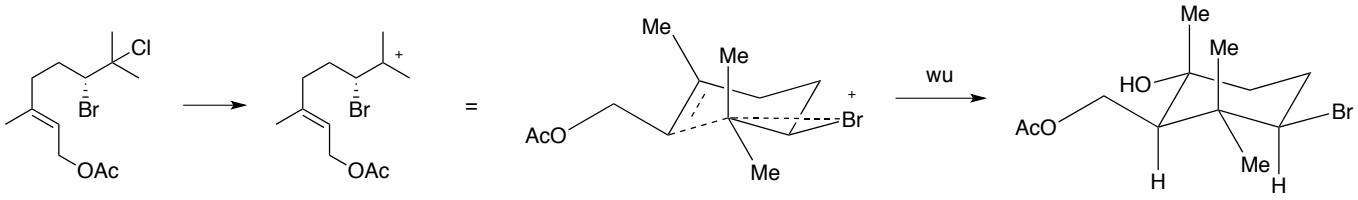
1. Compound **3** and its transformation to **4**



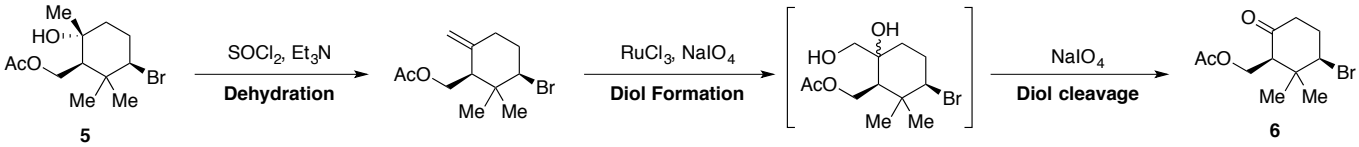
3 **4**

Deoxygenation: *J. Am. Chem. Soc*. **2015**, *137*, 12784–12787

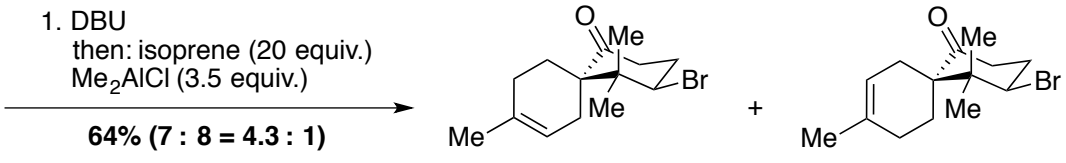
2. Cationic cyclization



3. a.) Formation and structure of ketone **6**



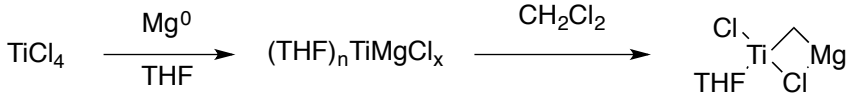
b.) Diels-Alder reaction with isoprene.



7 **8**

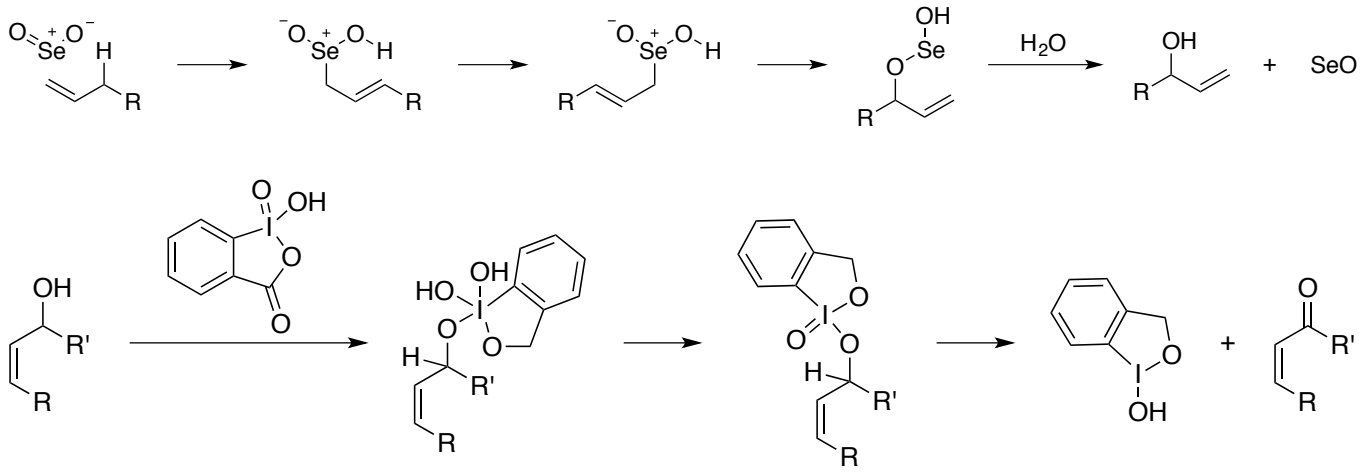
Four products. 2 endo, 2 exo products. Only two are obtained probably due to steric interactions between the methyl-group of isoprene and the ketone of the enone.

4. a.) Olefination of **7** using $TiCl_4$/Mg and CH_2Cl_2.



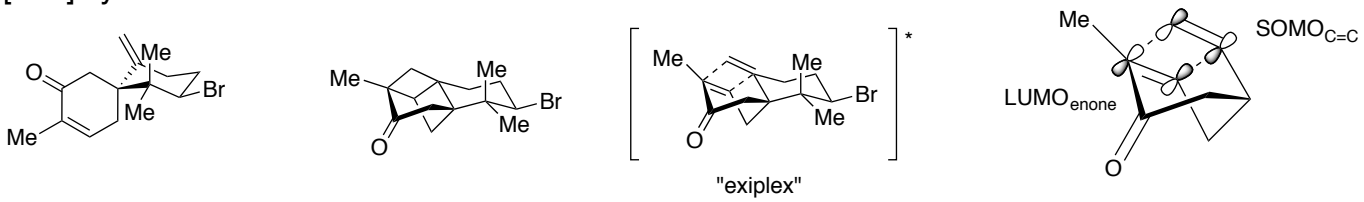
Org. Lett. **2004**, *6* (26), 4961–4963

b.) Riley Oxidation and IBX oxidation



5. Last step

[2+2] cycloaddition



thermal [2+2] cycloaddition forbidden → orbital missmatch