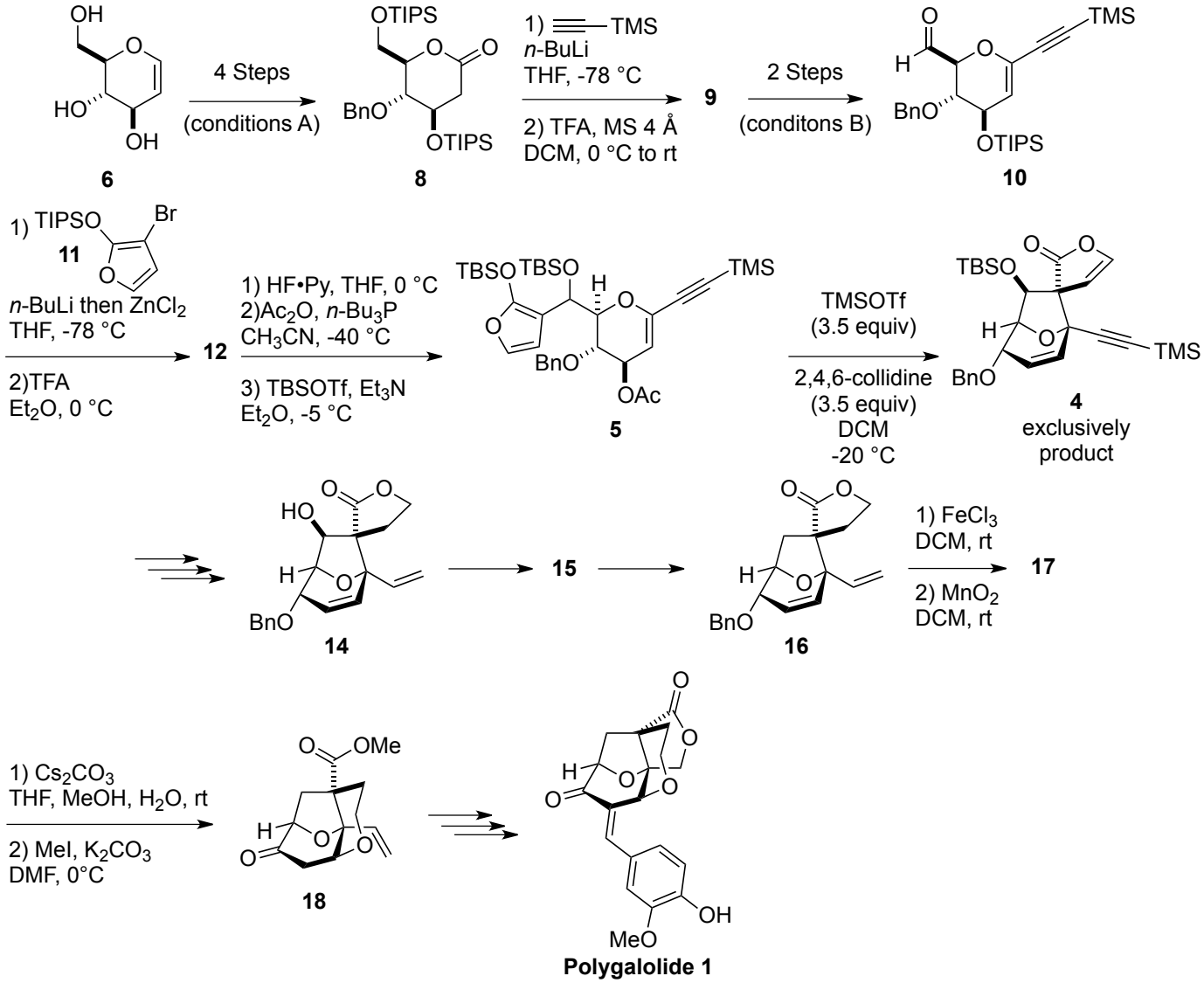
Submitted by Julien

Total Synthesis of Polygalolide A

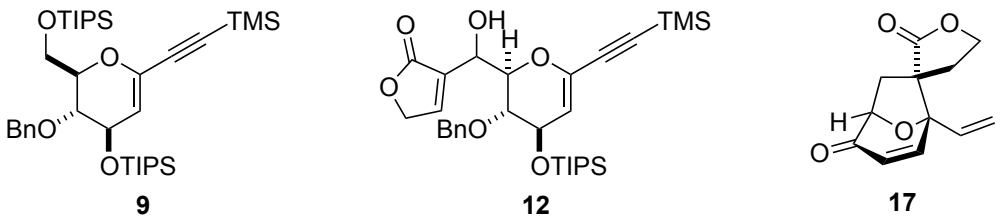
Problem:



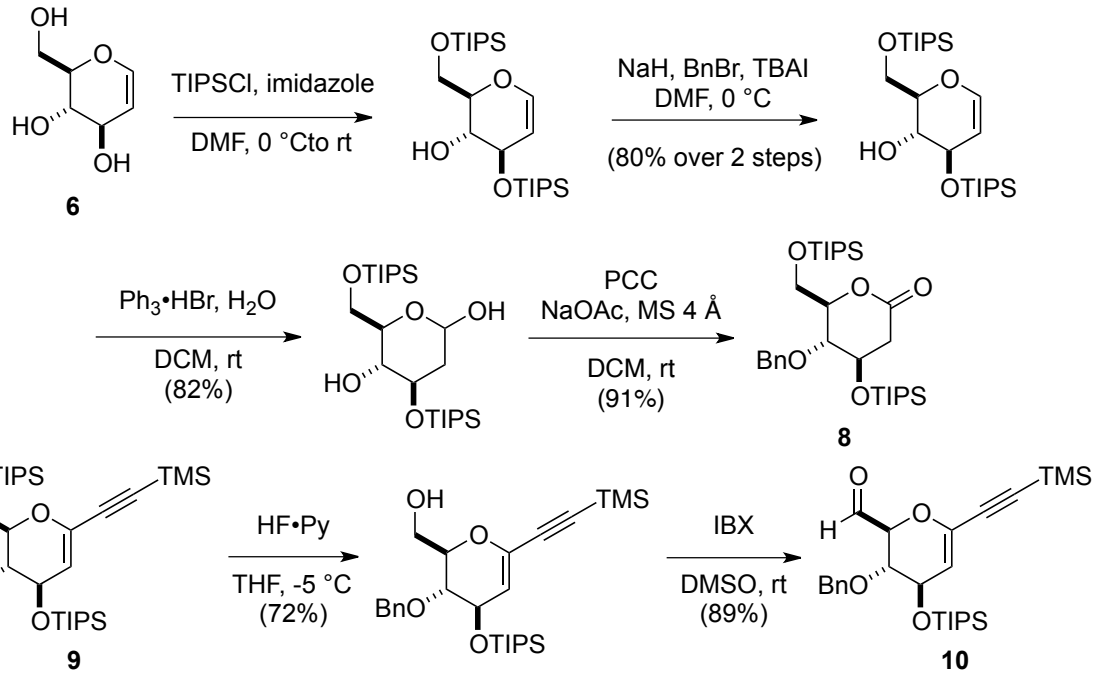
1) Propose a structure for **9**, **12** and **17**.
2) Give the conditions A and B (formation of **8** and **10**).
3) Propose a mechanism for the formation of **4** and explain the stereoselectivity.
4) Propose the condition for the transformation of **14** in **16** and a structure of the intermediate **15** ($C_{21}H_{22}O_5S_2$).
5) Explain the formation of **18**.
6) Propose a preparation of **11** (2 steps from 2-furanone).

Solution:

1)

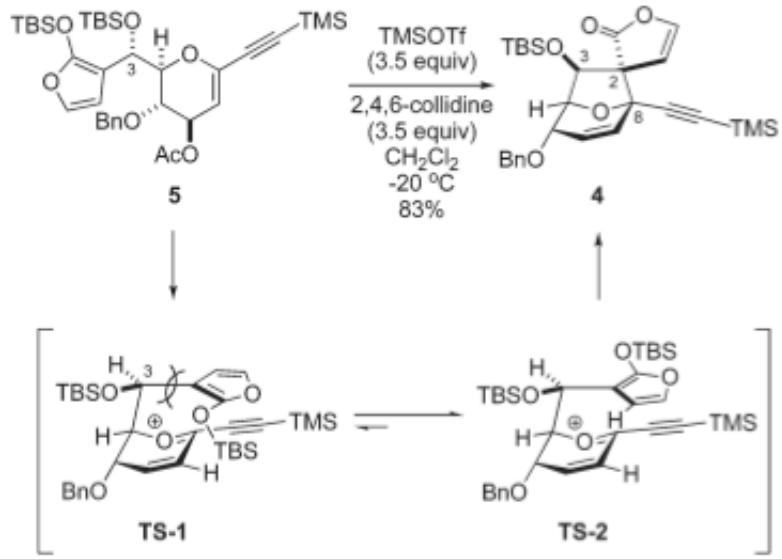


2)

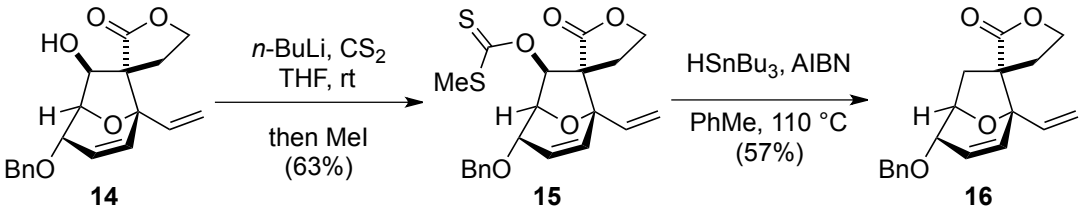


3)

Scheme 3. Synthesis of Oxabicyclo[3.2.1]octene **4** and Proposed Mechanism for the Intramolecular *C*-Glycosylation

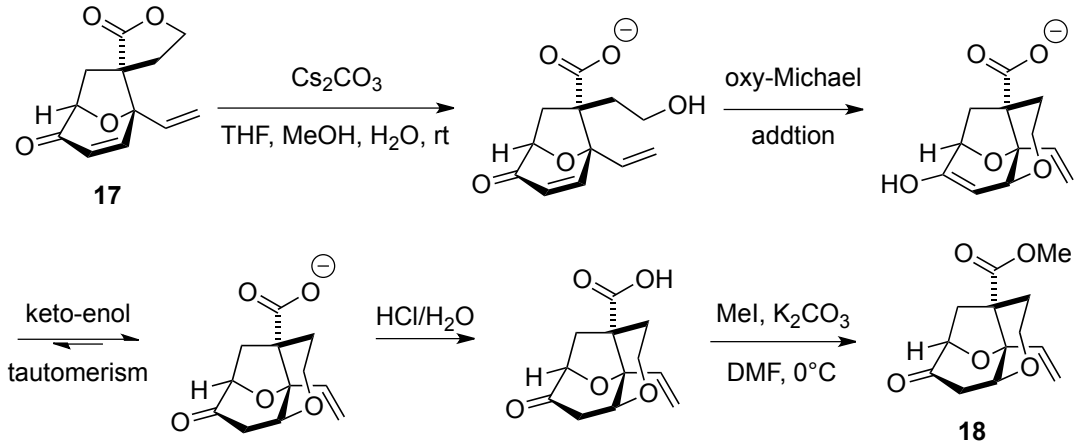


4)



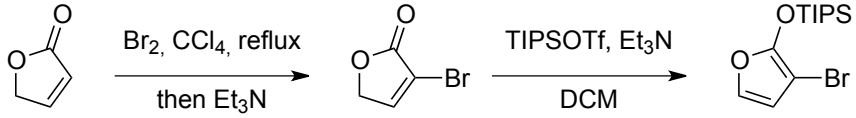
14 **15** **16**

5)



17 **18**

6)



Comments:
The starting material **6** is commercial available. **11** is synthetized from 2-furanone.

References:
Adachi, M.; Yamada, H.; Isobe, M.; Nishikawa, T. *Org. Lett.* **2011**.
Boukouvalas, J.; Marion, O. *Synlett* **2006**, 1511.

Keywords:
Total synthesis, Ferrier type C-Glycosylation, Barton-McCombie deoxygenation, oxidation of allilyc alcohol, oxy-Michael addition.