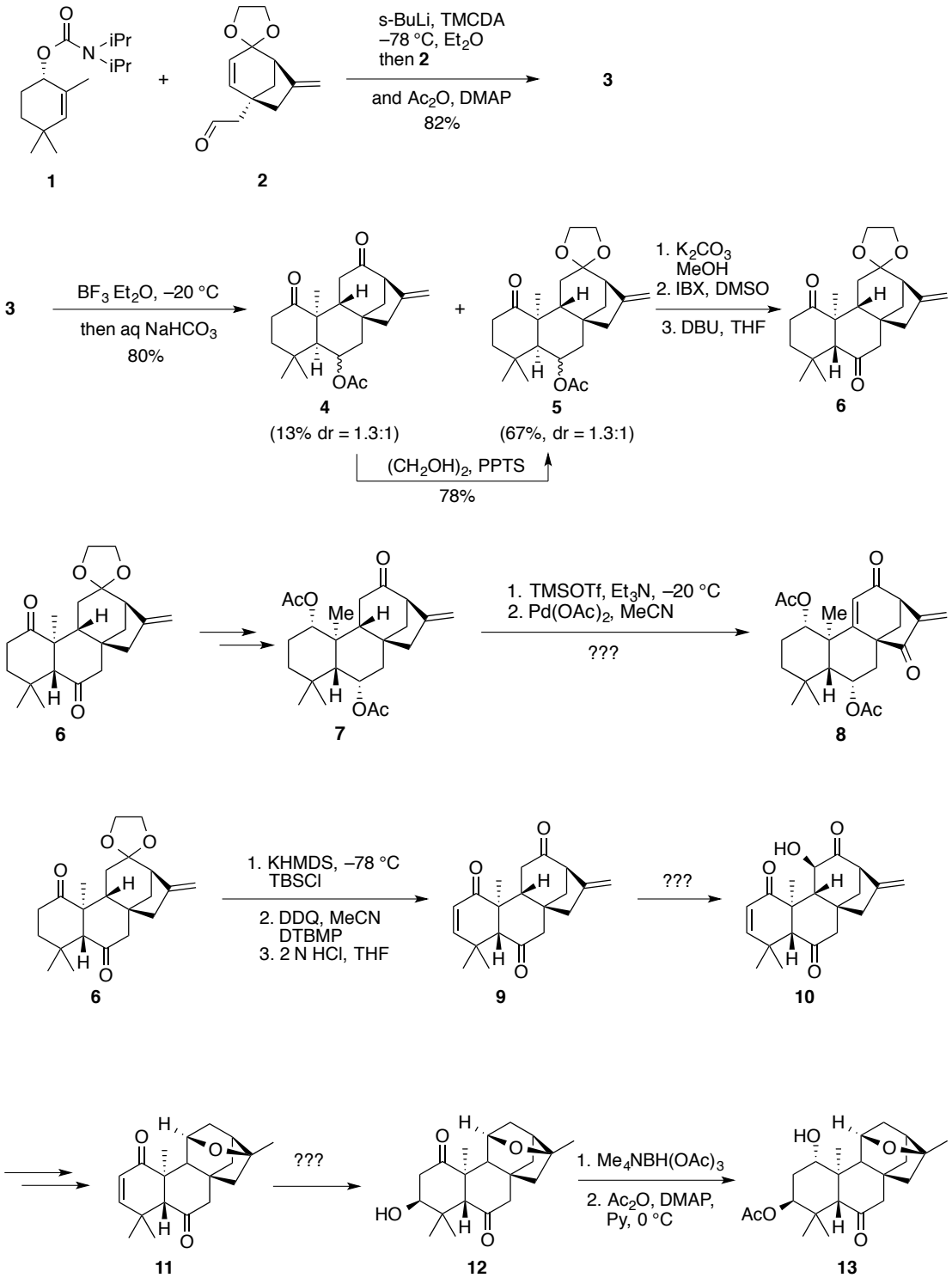
Submitted by Nicolas Volkoff

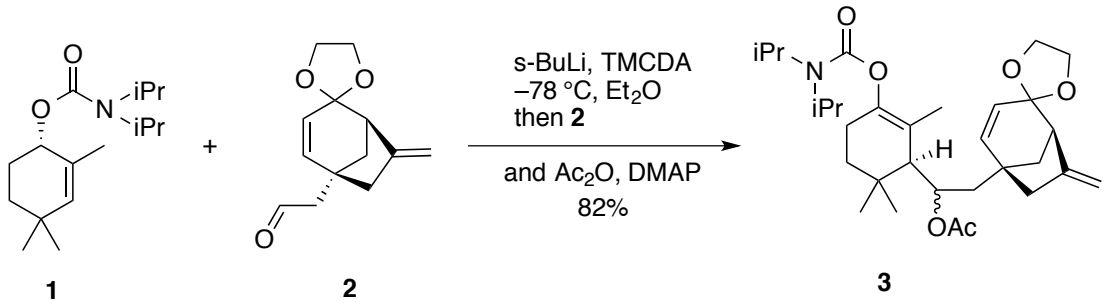
Convergente Route to *ent*-Kaurane Diterpenoids

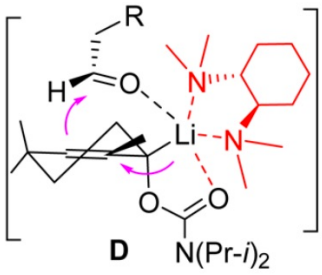


1. **Give the missing structure 3**
2. **Explain the mechanisms to obtain the compound 4/5**
3. **Propose conditions to obtain 8 from 7 (2 steps missing)**
4. **Find some conditions to obtain 10 from 9 and 12 from 11**

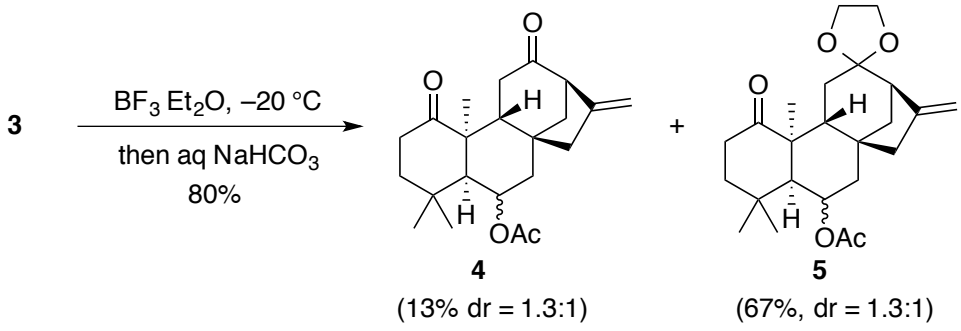
Solution

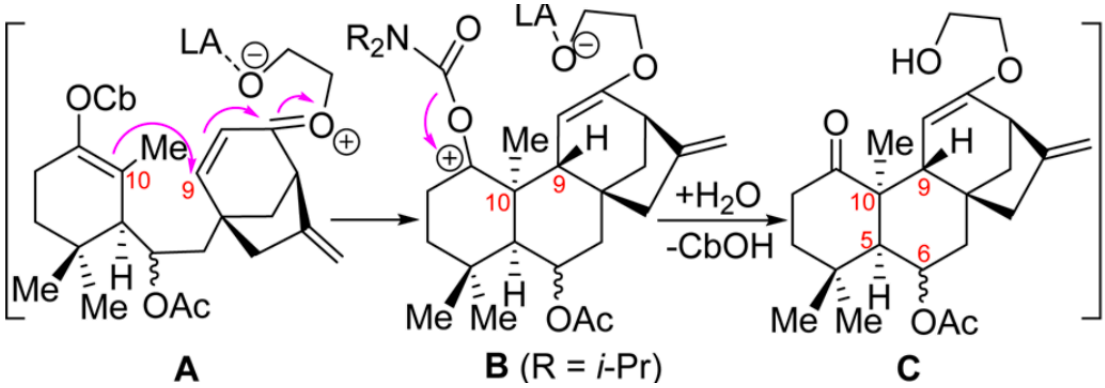
homoaldol reaction (Hoppe's Homoaldol) deprotonation in alpha of the carbamate



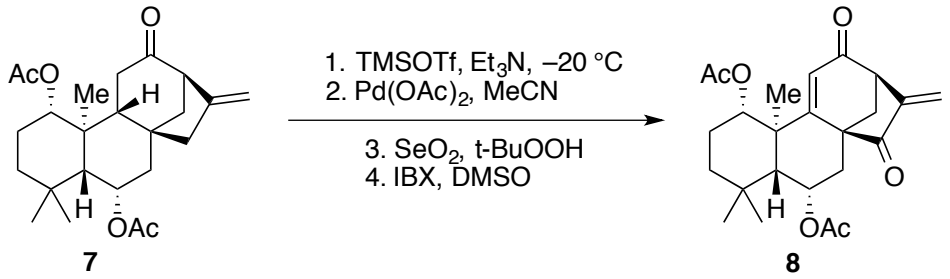


Mukaiyama–Michael-type reaction

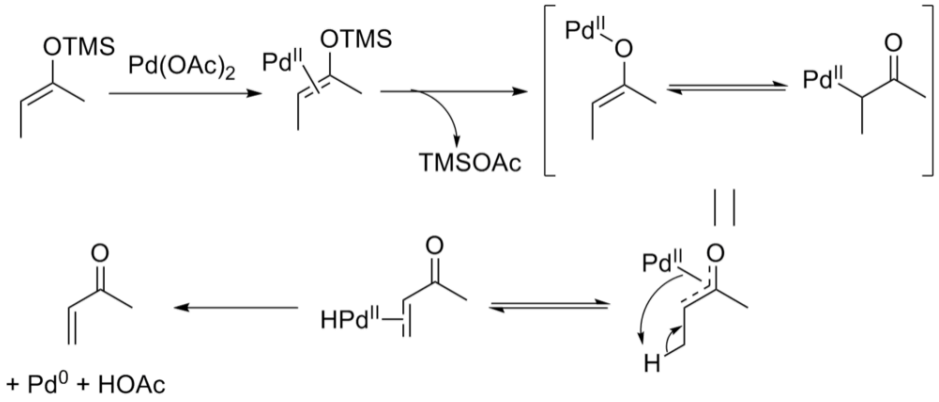


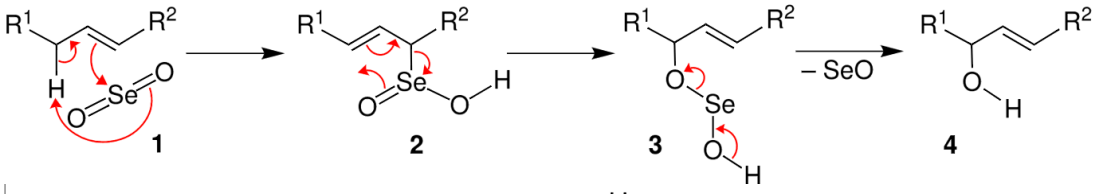


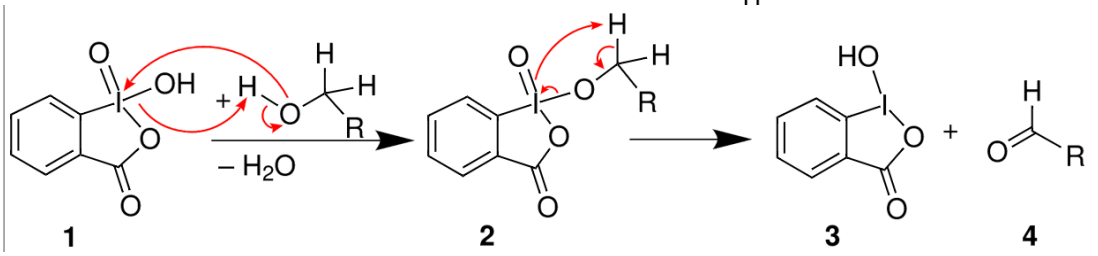
Saegusa's condition for the formation of the enone
Riley oxidation to obtain the allylic alcohol followed by IBX oxidation to obtain the corresponding enone



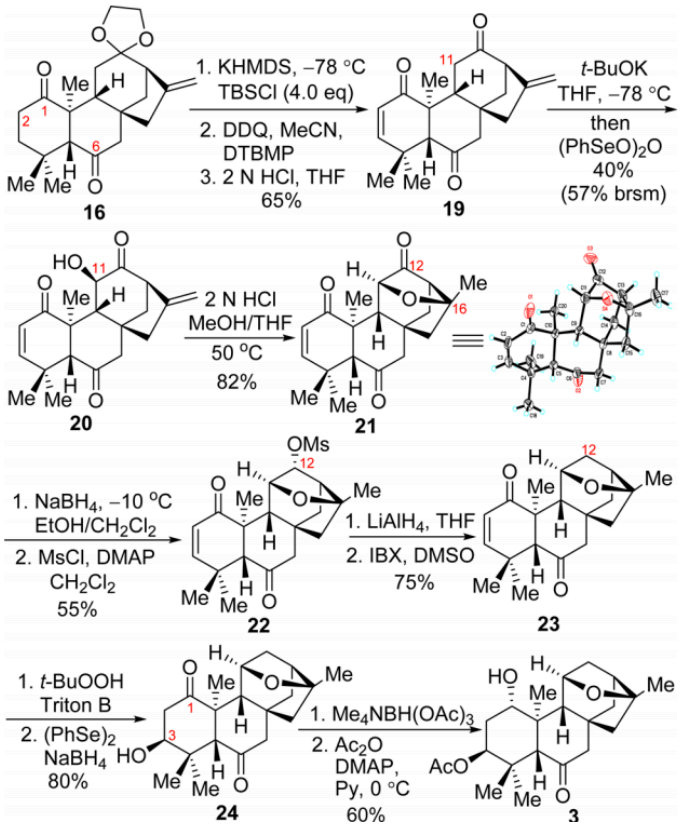
7 8



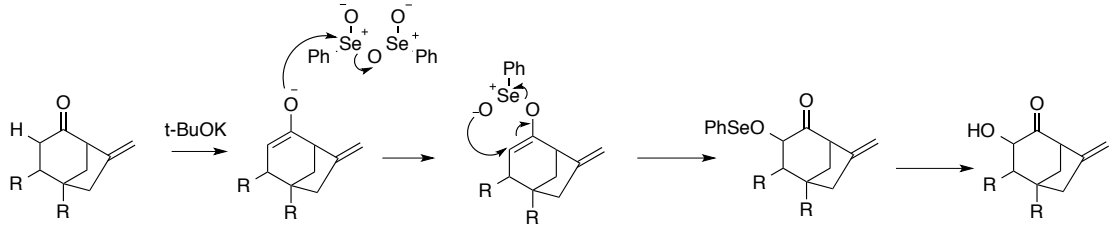


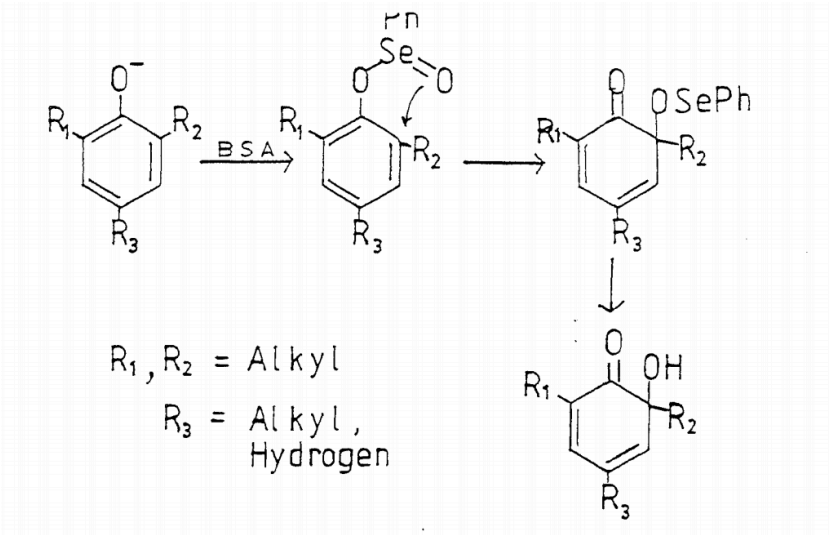


Scheme 5. Total Synthesis of Lungshengenin D



9 to 10 alpha hydroxylation
proposed mechanism from analogy with the oxidation of phenol
ref J.Chem.Soc. Perkin Trans. 1 1977 567





11 to 12
epoxydation with t-BuOOH followed by reduction with PhSeNa
ref tetrahedron Lett. 1987 4293 ; tetrahedron Lett. 1988 347