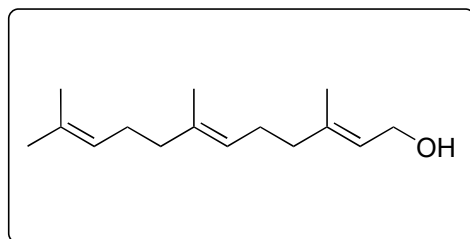
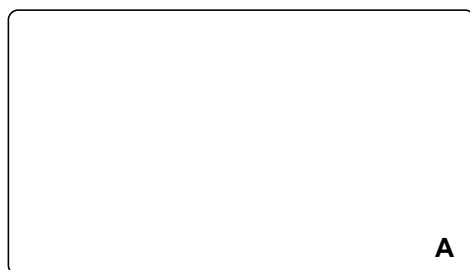


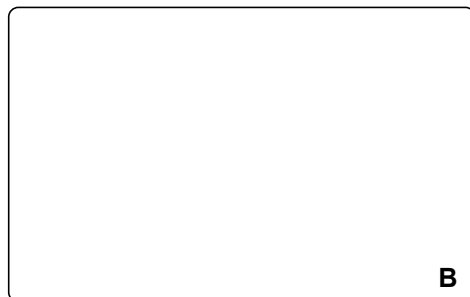
Synthesis of [REDACTED]



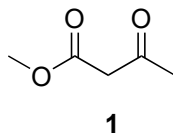
1–5



6–10



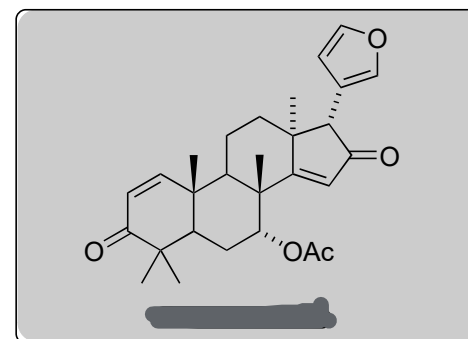
- 1) MsCl, Et₃N then LiBr
- 2) **1** (1.2 eq.), NaH (1.2 eq.)
then *n*-BuLi (1.2 eq.)
then substrate then PO(OEt)₂Cl
- 3) Hg(OAc)₂, CH₃NO₂ then stir in NaCl (aq.)
- 4) NaBH₄ (3 eq.), O₂
- 5) CrO₃, aq. H₂SO₄



- 6) NaH, PO(OEt)₂Cl (1 eq.)
- 7) ethylene glycol, PTSA
- 8) DIBAL
- 9) HO₃SONO
- 10) sunlamp, 50 °C

- 1) Name the starting material.
- 2) Hint: product has a phosphorous NMR shift around 140 ppm.
- 3) Hint: nitromethane is a solvent. A tricyclic system is formed.
- 4) Hint: oxidative demercuration. Can you propose a mechanism?
- 5) Name of reagent?

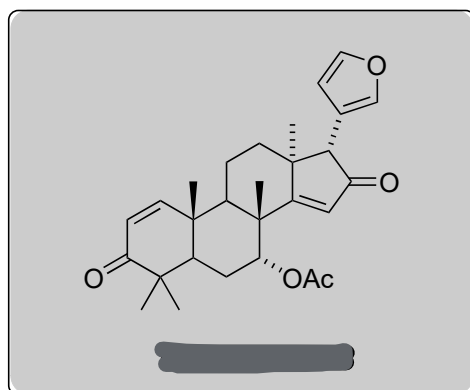
- 9) Hint: an alkyl nitrite is formed.
- 10) Named reaction. Can you come up with a mechanism?



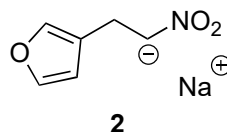
11–15



16–23



- 11) 1M HCl
- 12) $\text{N}(\text{CH}_3)_4\text{BH}(\text{OAc})_3$, $-78\text{ }^\circ\text{C}$
- 13) **2**, EtOH, reflux *then* 12M HCl, $10\text{ }^\circ\text{C}$
- 14) NaOEt, EtOH, $70\text{ }^\circ\text{C}$
- 15) $\text{BrCH}_2\text{OCH}_3$, TBAI, DIPEA, $70\text{ }^\circ\text{C}$



- 16) L-selectride (excess)
- 17) BzOH, DEAD, PPh_3
then NaOH, EtOH
- 18) Zn/Ag, CH_2I_2 *then* substrate, $0\text{ }^\circ\text{C}$
- 19) DMP
- 20) Li, NH_3 , THF *then* DMP
- 21) LDA, PhSeBr
then 30% H_2O_2 in H_2O /pyridine
- 22) TMSBr, DCM
- 23) Ac_2O , DMAP

11) Hint: a hemiacetal is formed. Can you rationalize its diastereoselectivity?

12) Hint: selective hemiacetal reduction.

13) Name the two reactions occurring in this step. How would you prepare **2**?

17) Hint: selective reaction at C16 (according to IUPAC atom numbering for steroids). Name the reaction.

18) Name the reaction.