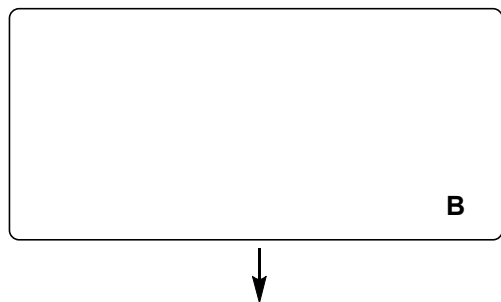
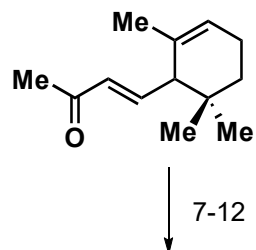
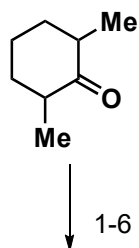
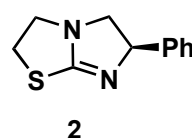
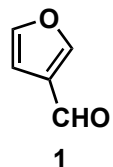


Total Synthesis of (+)-Granatumine A and Related Bislactone Limonoid Alkaloids via a Pyran to Pyridine Interconversion

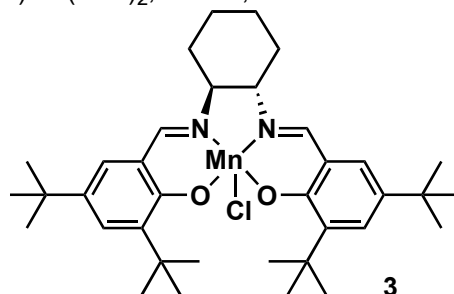
A. Schuppe, Y. Zhao, Y. Liu and T. Newhouse
J. Am. Chem. Soc. **2019**



- 1) LDA(1.5 eq), ZnCl₂, THF, -40°C, then allyl acetate, [Pd(Allyl)Cl]₂, 60°C
- 2) LDA, **1**, THF, -78 °C
- 3) Ac₂O, **2** (cat.), PhMe
- 4) LiHMDS, then Burgess reagent
- 5) SeO₂, Na₂HPO₄, 1,4-dioxane, 100°C
- 6) DMP



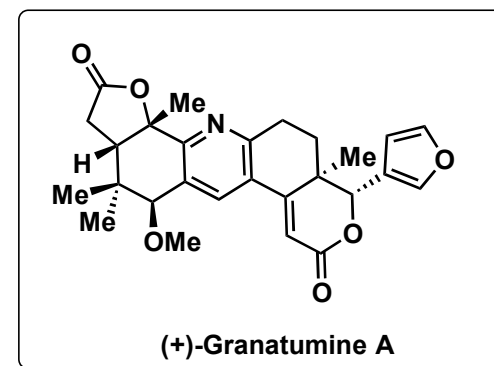
- 7) **3** (cat.), 4-PPNO, NaOCl
- 8) [Rh(cod)(OH)]₂, PhMe₂SiH
- 9) O₃, then Jones reagent
- 10) Pd(TFA)₂, DMSO, O₂, 80°C
- 11) urea•H₂O₂, DBN, H₂O
- 12) Pd(OAc)₂, XPhos, toluene

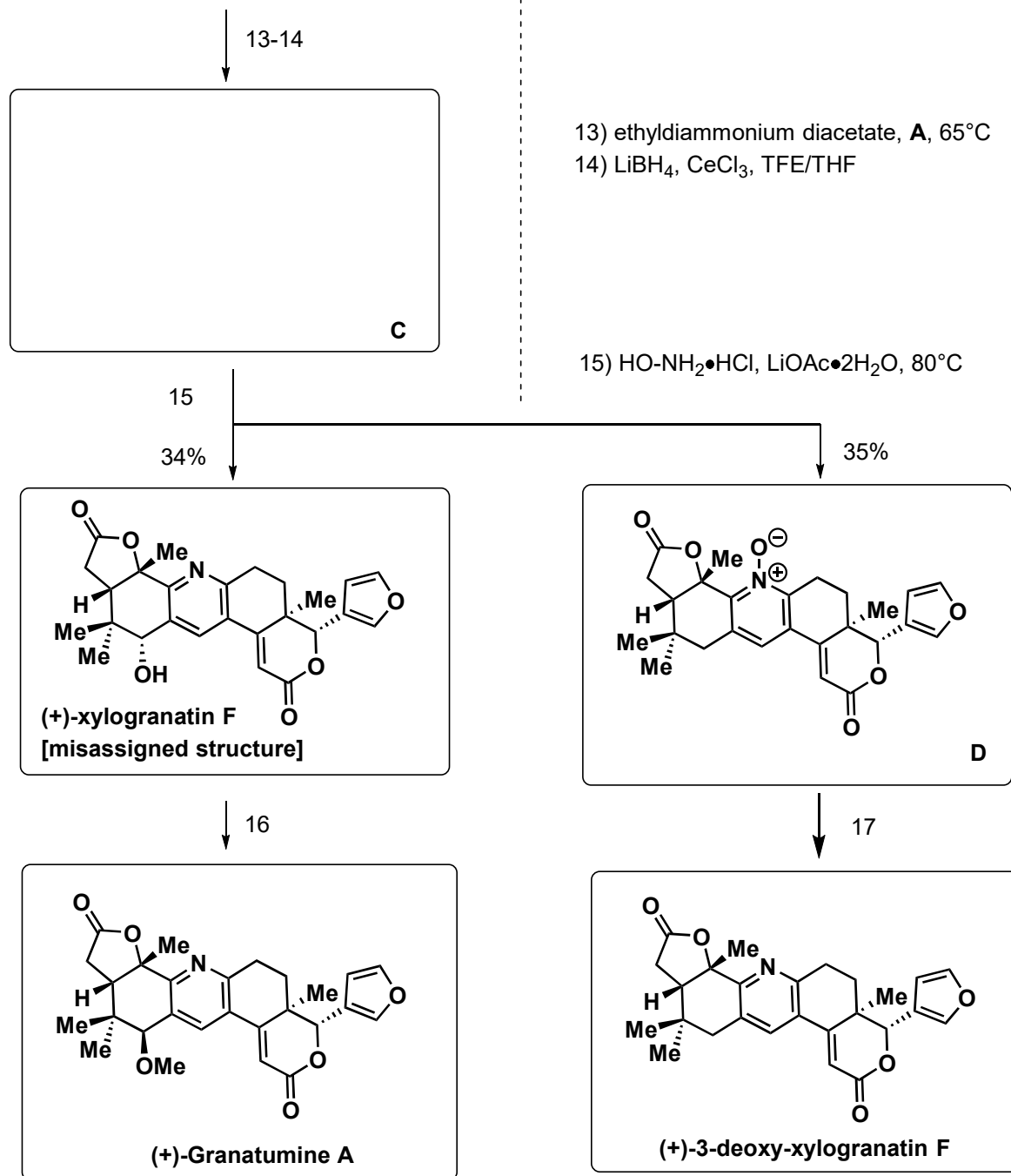


Step 1: Please provide a mechanism and at least one alternative approach (more than one step might be necessary).

Step 9: A heterocycle is formed, please provide a mechanism.

Step 12: It is believed that this reaction is Pd⁰ mediated. Please provide a plausible mechanism





Step 13: A cyclization occurs. Provide a mechanism for it and classify it.

Step 15: Yields two products. Propose mechanisms for the formation of each.

Step 16 and 17: Propose conditions for the conversions.