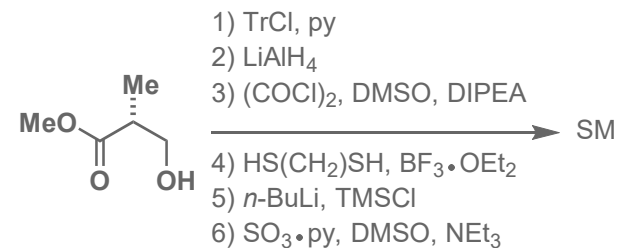
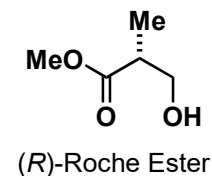


Total Synthesis of (-)-Nahuoic Acid C_i (B_{ii})

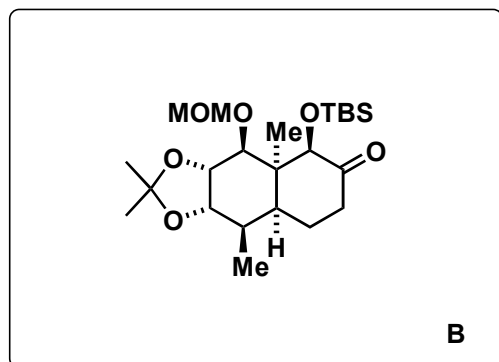
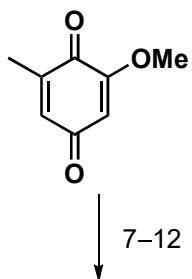
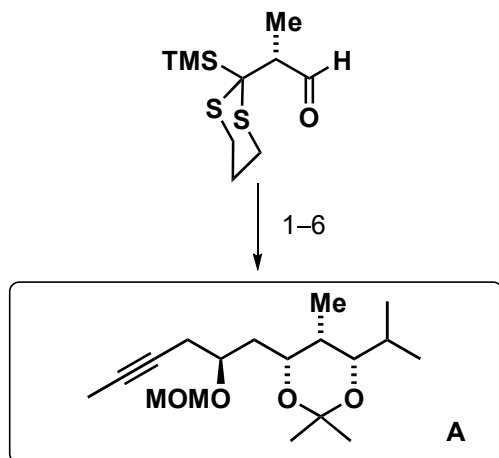
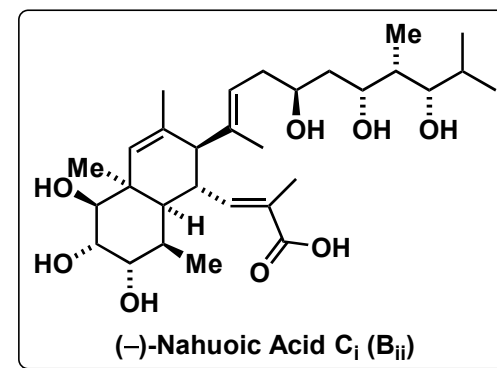
Q. Liu, Y. Deng, A. B. Smith III,
J. Am. Chem. Soc. **2017**, *139*, 13668–13671.



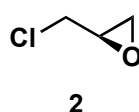
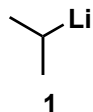
How would you synthesize the SM starting from (*R*)-Roche Ester in six steps?



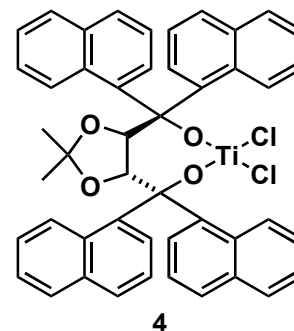
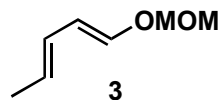
Step 1: Please classify this reaction.
 Anion Relay Chemistry (ARC)



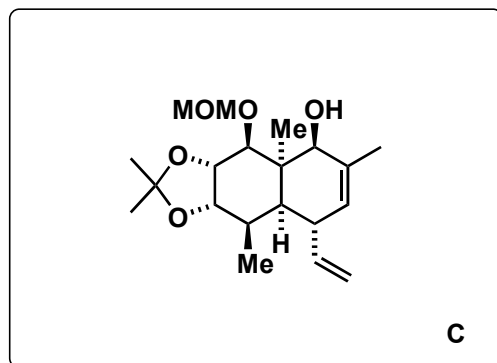
- 1) **1**, Et₂O, -78 °C, then **2**, HMPA, -50 °C to rt
- 2) Hg(ClO₄)₂, CaCO₃
- 3) Et₂BOMe, NaBH₄
- 4) 2-methoxypropene, PPTS
- 5) CH₃CCLi, BF₃·THF
- 6) MOMCl, DIPEA, TBAI



- 7) **3**, **4**, 4 Å MS, -78 °C to -40 °C
- 8) LiAlH₄, then 1 M HCl
- 9) TBSOTf, 2,6-lutidine
- 10) Lindlar catalyst, H₂
- 11) OsO₄, MeSO₂NH₂, NMO
- 12) 2,2-dimethoxy propane, PPTS

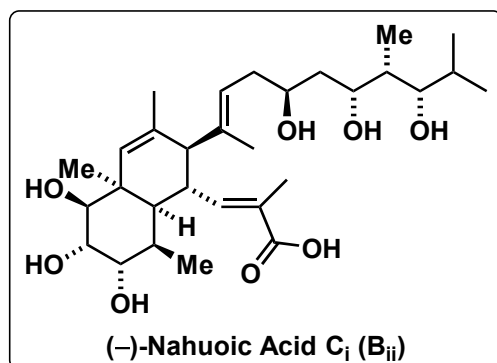


13–18



C

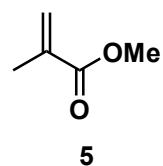
19–22



(-)-Nahuoic Acid **C_i** (**B_{ij}**)

- 13) LiHMDS, TMSCl
- 14) Pd(OAc)₂, O₂
- 15) vinylMgBr, CuBr•DMS, HMPA
- 16) LiHMDS, Tf₂O
- 17) MeMgBr, Fe(acac)₃, Pd(dppf)Cl₂•DCM
- 18) TBAF

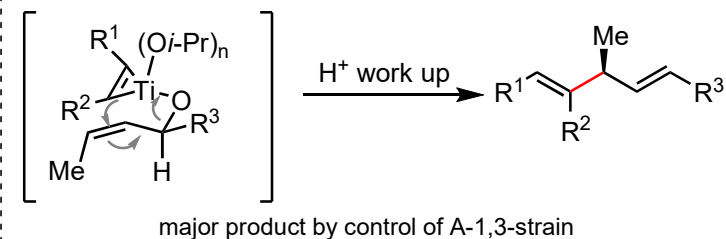
- 19) *n*-BuLi, then added to a mixture of **A** and TiCl(O*i*-Pr)₃ (2.2 equiv), *c*-C₅H₉MgCl (4.4 equiv)
- 20) **5**, HG-II
- 21) LiBF₄, MeCN/H₂O
- 22) LiOH, MeOH/H₂O, then TFA



5

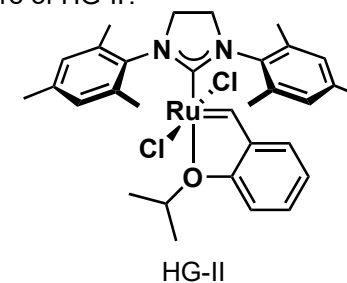
Step 14: Please name the reaction.
Saegusa–Ito reaction

Step 19: Please name the reaction and come up with a mechanism.
Micalizio reaction



reductive coupling of alkynes and lithiated allyl alcohols with transfer of the oxygen to the titanium catalyst

Step 20: What is the structure of HG-II?



HG-II