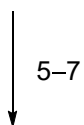
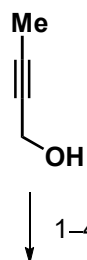
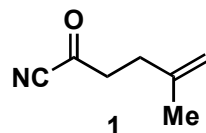


Synthesis of Anhydroryanodol

Kang Du, Matthew J. Kier, Zachary D. Stempel, Valer Jeso, Arnold L. Rheingold, and Glenn C. Micalizio, *J. Am. Chem. Soc.* **2020**, ASAP, <https://doi.org/10.1021/jacs.0c05766>



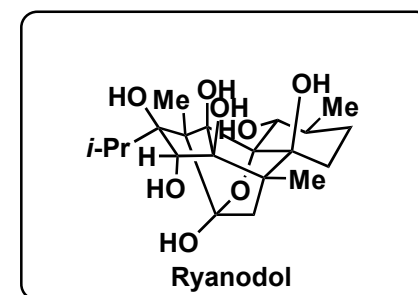
- 1) *i*-PrMgCl, CuI, I₂, then MnO₂
- 2) 2-lithiofuran, THF, then NBS, H₂O
- 3) TBSOTf, lutidine
- 4) H₂, CIRh(PPh₃)₃, PhH

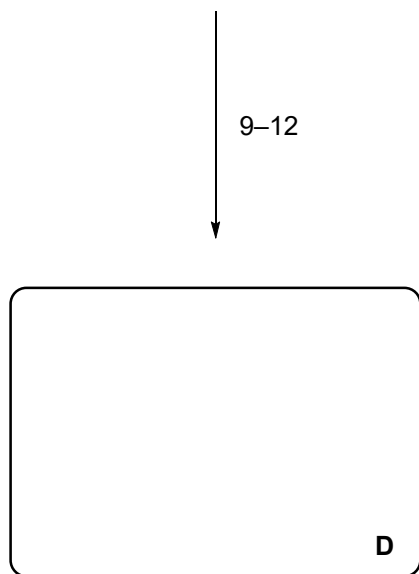
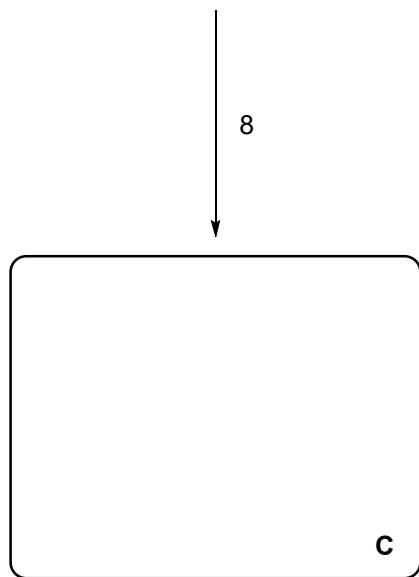


- 5) LiHMDS, **1**, THF
- 6) KHMDS, MeI, THF
- 7) Bu₃SnCC(CH₂)₂OPMB, Pd(PhCN)₂Cl₂, Ph₃As, THF

Step 2: Please provide the name for this transformation.

Step 4: After which Nobel laureate is the catalyst named?





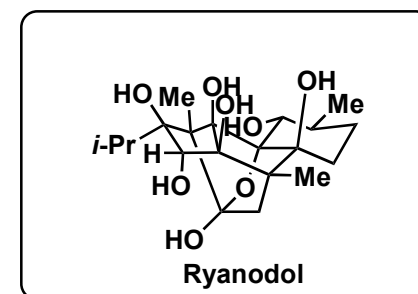
8) $\text{Ti}(\text{O}i\text{-Pr})_4$, $i\text{-PrMgCl}$, THF, -78 to -20 °C

9) TMS-imidazole, DCE
 10) $\text{VO}(\text{O}i\text{-Pr})_3$, $t\text{-BuOOH}$
 11) DDQ, CH_2Cl_2 , pH 7 buffer
 12) $o\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$, PBU_3 , then H_2O_2 , THF

Step 8: Please propose a metallacycle intermediate.

Hint for Step 9: Only one TMS group is attached.

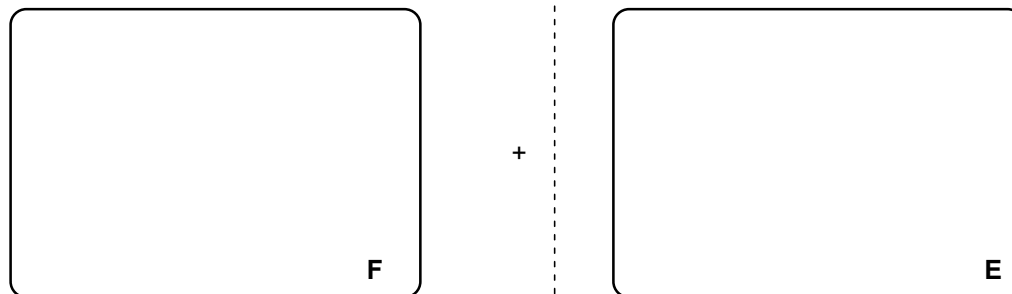
Step 12: What is the name for this transformation?



13–16

- 13) TASF, DMF
- 14) TPAP, NMO
- 15) NaOH, H₂O, DMSO
- 16) Hoveyda-Grubbs II, PhMe, 85 °C

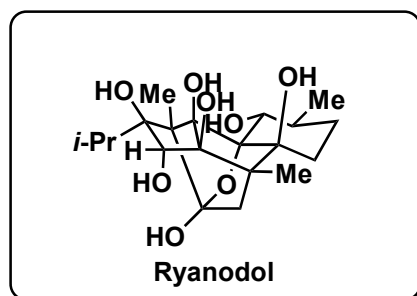
After step 15 and 16: a mixture of 2 compounds is obtained



NaOH, THF,
H₂O

17–22

- 17) TMS-imidazole, 80 °C
- 18) *m*-CPBA, DCE
- 19) Cp₂TiCl₂, Zn, Et₃SiH
- 20) TASF, DMF
- 21) CF₃CO₃H, Na₂HPO₄, DCE
- 22) Li, NH₃, THF, -78 °C



Hint for Step 17: 3 TMS groups are attached.

Hint for Step 20: All TMS groups are removed.