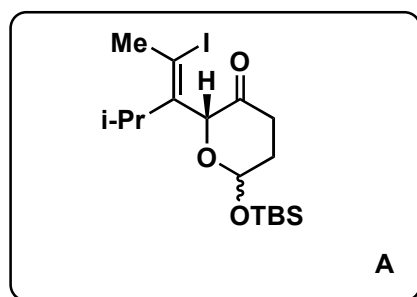


## Synthesis of Anhydroryanodol

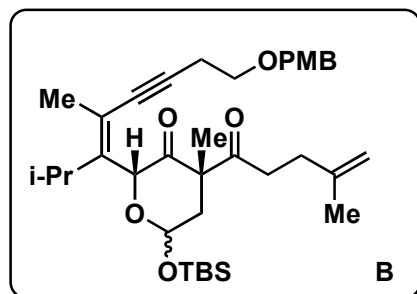
Kang Du, Matthew J. Kier, Zachary D. Stempel, Valer Jeso, Arnold L. Rheingold, and Glenn C. Micalizio, *J. Am. Chem. Soc.* **2020**, ASAP, <https://doi.org/10.1021/jacs.0c05766>



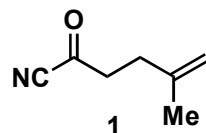
1-4



5-7



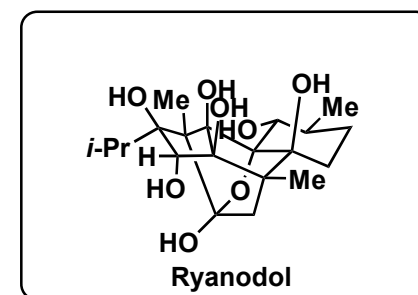
- 1) *i*-PrMgCl, CuI, I<sub>2</sub>, then MnO<sub>2</sub>
- 2) 2-lithiofuran, THF, then NBS, H<sub>2</sub>O
- 3) TBSOTf, lutidine
- 4) H<sub>2</sub>, CIRh(PPh<sub>3</sub>)<sub>3</sub>, PhH

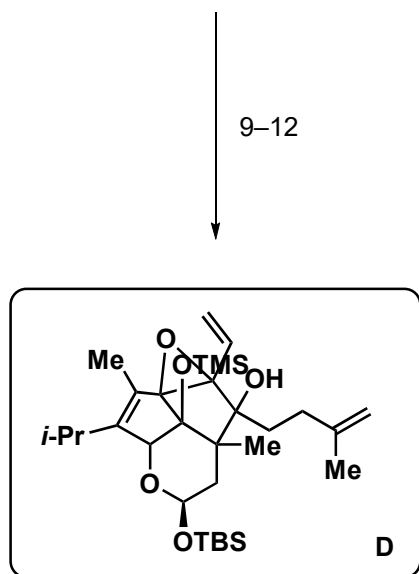
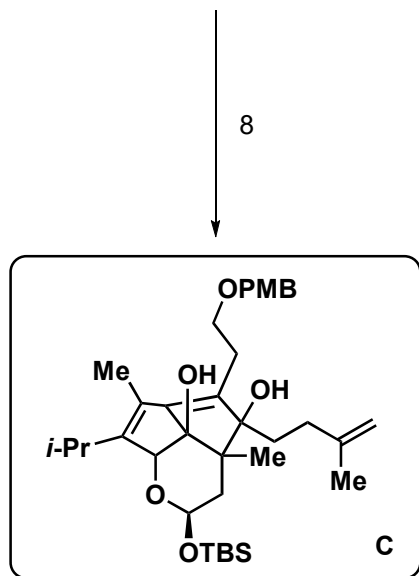


- 5) LiHMDS, **1**, THF
- 6) KHMDS, MeI, THF
- 7) Bu<sub>3</sub>SnCC(CH<sub>2</sub>)<sub>2</sub>OPMB, Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, Ph<sub>3</sub>As, THF

Step 2: Please provide the name for this transformation.  
Achmatowicz

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

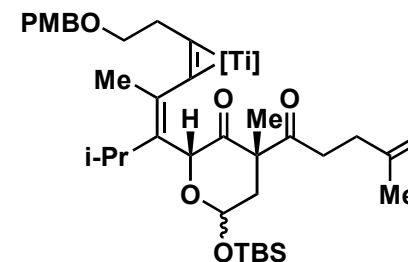




8)  $\text{Ti}(\text{O}i\text{-Pr})_4$ ,  $i\text{-PrMgCl}$ , THF,  $-78$  to  $-20$  °C

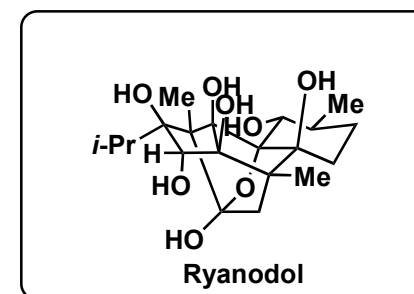
9) TMS-imidazole, DCE  
 10)  $\text{VO}(\text{O}i\text{-Pr})_3$ ,  $t\text{-BuOOH}$   
 11) DDQ,  $\text{CH}_2\text{Cl}_2$ , pH 7 buffer  
 12)  $o\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$ ,  $\text{PBU}_3$ , then  $\text{H}_2\text{O}_2$ , THF

Step 8: Please propose a metallacycle intermediate.



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

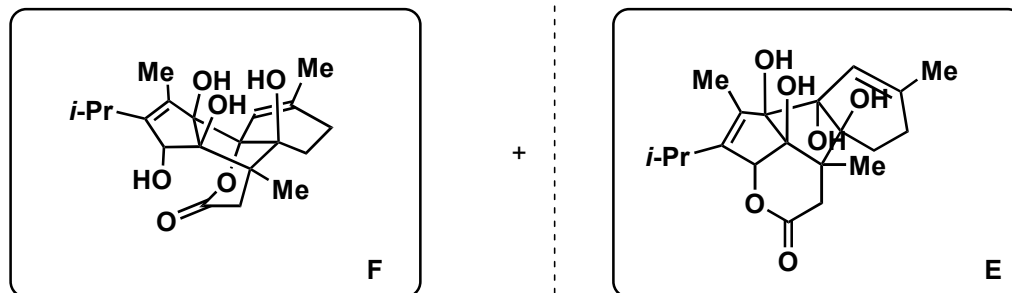
Step 12: What is the name for this transformation?  
 Grieco elimination



13–16

- 13) TASF, DMF
- 14) TPAP, NMO
- 15) NaOH, H<sub>2</sub>O, DMSO
- 16) Hoveyda-Grubbs II, PhMe, 85 °C

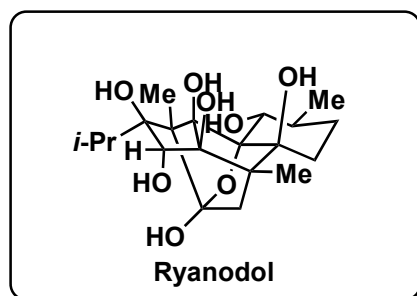
After step 15 and 16: a mixture of 2 compounds is obtained



NaOH, THF,  
H<sub>2</sub>O

17–22

- 17) TMS-imidazole, 80 °C
- 18) *m*-CPBA, DCE
- 19) Cp<sub>2</sub>TiCl<sub>2</sub>, Zn, Et<sub>3</sub>SiH
- 20) TASF, DMF
- 21) CF<sub>3</sub>CO<sub>3</sub>H, Na<sub>2</sub>HPO<sub>4</sub>, DCE
- 22) Li, NH<sub>3</sub>, THF, -78 °C



Hint for Step 17: 3 TMS groups are attached.

Hint for Step 20: All TMS groups are removed.