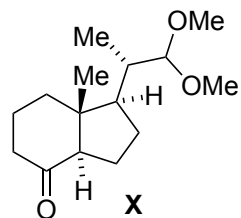


Asymmetric Total Synthesis of Cyclocitrinol

J. Liu, J. Wu, J.-H. Fan, X. Yan, G. Mei, and C.-C. Li
J. Am. Chem. Soc. **2018**, *140*, 5365–5369

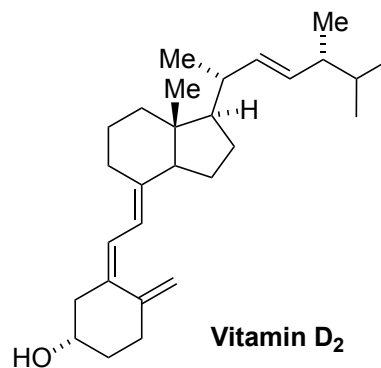


1-6



7-9

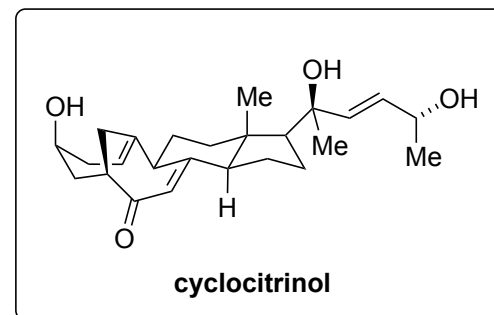
- 1) CuI, vinylMgBr, THF, $-78\text{ }^{\circ}\text{C}$
- 2) TIPSCI (1.1 equiv.), imidazole
- 3) *p*-TsOH, MeOH
- 4) NaIO₄
- 5) NaBH₄
- 6) CBr₄, PPh₃



step 7: X is commercially available. How is it prepared from Vitamin D₂?

step 9: role of TMSN₃

- 7) LDA, TMSCl
- 8) IBX, DMSO
- 9) TMSN₃, pyridine, I₂

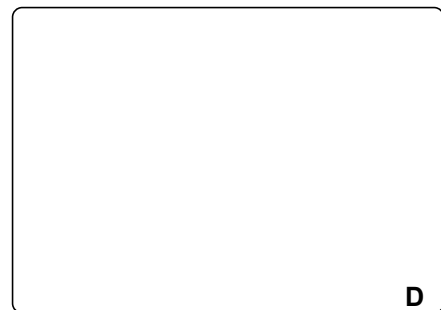




10-13

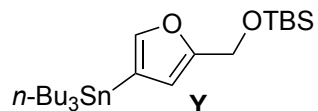


14+15



16-19

- 10) CuTC, LiOAc, NMP, **Y**
- 11) NaBH₄, NiCl₂•H₂O
- 12) **A**, *t*-BuLi, Et₂O, -78 °C
- 13) TBAF, *then* NBS, NaOAc, NaHCO₃, H₂O



- 14) Ac₂O, 2,2,6,6-tetramethylpiperidine (TMP), DMAP
- 15) TMP, MeCN, 155 °C

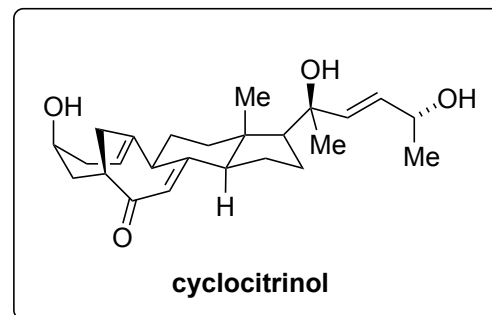
- 16) NaBH₄
- 17) KHMDS, CS₂, MeI
- 18) AIBN, *n*-Bu₃SNH, PhMe, 80 °C
- 19) SOCl₂, pyridine, 2,4,6-trimethylpyridine, 0 °C

step 10: name reaction?

step 13: name reaction?

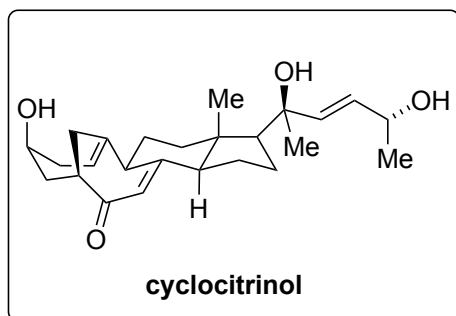
step 14: hint: reaction occurs 2x

step 15: mechanism? which unusual functionality is introduced?

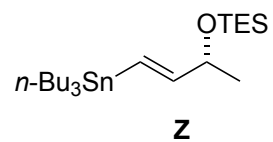




20-24



- 20) Li, EtNH₂
- 21) TEMPO, NCS, TBACl
- 22) TESOTf
- 23) *t*-BuOK, O₂, *t*-BuOH
- 24) **Z**, *n*-BuLi, THF, -78 °C, then TBAF



step 20: hint: two deprotections occur