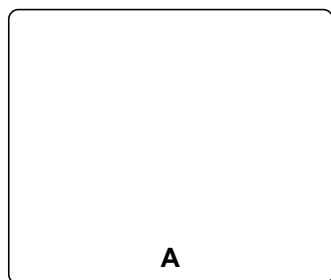


Enantioselective Total Synthesis of (-)-Pavidolide B

Zhang, P.-P., Yang, Z.-M., L, Y.-H., Gong, J.-X., Yang, Z. *J. Am. Chem. Soc.* **2017**, *139*, 13989-13992.

(S)-Carvone

1-2

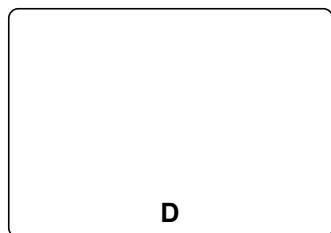


1) Cu-Al Ox, air, *t*-BuOK (0.5 eq)
2) RhCl(PPh₃) (5 mol %), H₂ (1 atm), RT

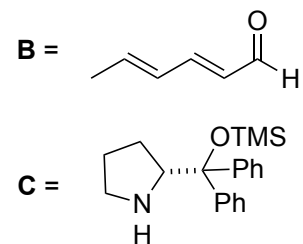
step 2: name the catalyst

dimethyl bromomalonate

3-5



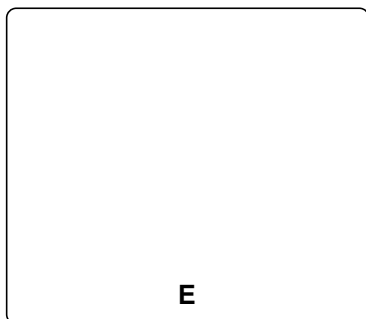
3) **B** (1.2 eq), **C** (20 mol %), Et₃N (1 eq)
4) CH(OEt)₃ (1.5 eq), PTSA (0.1 eq)
5) NH₄OH (1.1 eq), *i*PrOH, H₂O



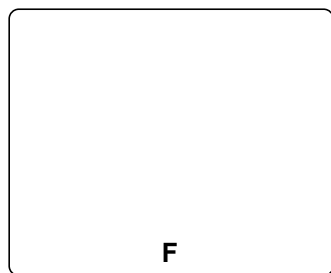
How would you prepare **C**?

D

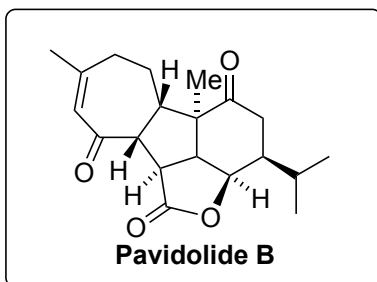
6



7-9



10-13



6) PPh_3 , DEAD, **A**

7) PhSH , $\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})\text{PF}_6$,
p-toluidine, blue LEDs, MECN
8) Me_4NOH , *i*PrOH, H_2O , *then* toluene, $120\text{ }^\circ\text{C}$
9) HCl (2M)

step 7: please come up with a mechanism

10) $\text{Ni}(\text{acac})_2$, Et_2Zn , isoprene
11) Martin's reagent
12) Grubbs II, DCM , reflux
13) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (20 mol %), EtOH , $100\text{ }^\circ\text{C}$

step 10: please come up with a mechanism