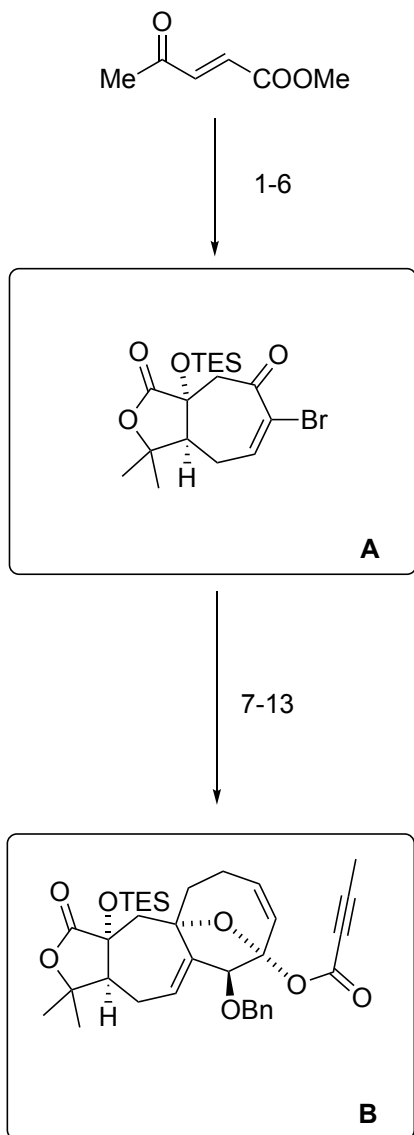
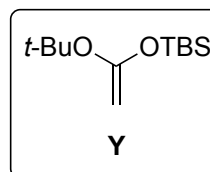
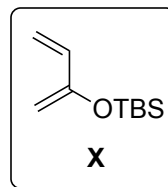


## Diastereoselective Total Synthesis of ( $\pm$ )-Schindilactone A

Qing Xiao, Wei-Wu Ren, Zhi-Xing Chen, Tian-Wen Sun, Yong Li, Qin-Da Ye, Jian-Xian Gong, Fan-Ke Meng, Lin You, Yi-Fan Liu, Ming-Zhe Zhao, Ling-Min Xu, Zhen-Hua Shan, Ying Shi, Ye-Feng Tang, Jia-Hua Chen, Zhen Yang  
*Angew. Chem. Int. Ed.* **2011**, *50*, 7373–7377.

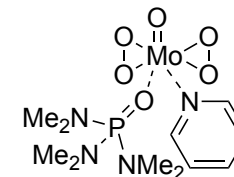


- 1) Et<sub>2</sub>AlCl, **X**
- 2) CH<sub>3</sub>MgBr
- 3) KHMDS, then O<sub>2</sub>, P(OMe)<sub>3</sub>
- 4) TESOTf, 2,6-lutidine
- 5) KO<sup>t</sup>-Bu, CHBr<sub>3</sub>
- 6) AgClO<sub>4</sub>•H<sub>2</sub>O, 30°C

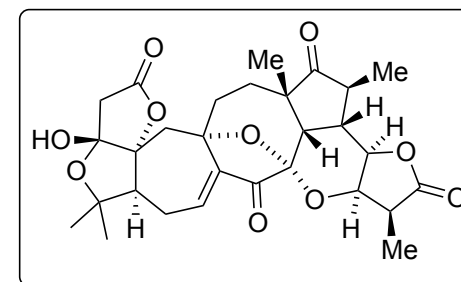


- 7) Pd(o-tol<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub> (cat.), CuF<sub>2</sub>, **Y**
- 8) but-3-enylmagnesium bromide
- 9) KHMDS, then MoOPH
- 10) benzyl 2,2,2-trichloroacetimidate, TfOH
- 11) vinylmagnesium bromide
- 12) Grubbs<sup>2nd</sup> generation catalyst, MgBr<sub>2</sub>
- 13) KHMDS, but-2-ynoic pivalic anhydride

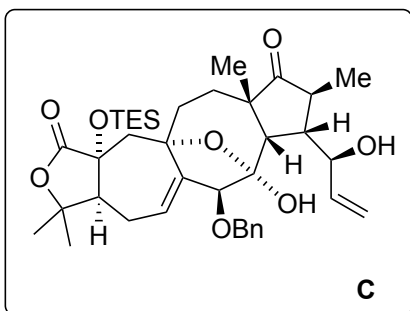
Structure of MoOPH?



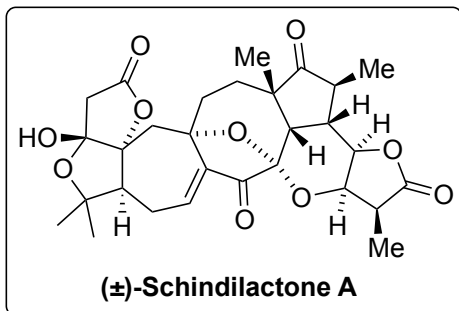
Structure of Grubbs<sup>2nd</sup> generation catalyst?



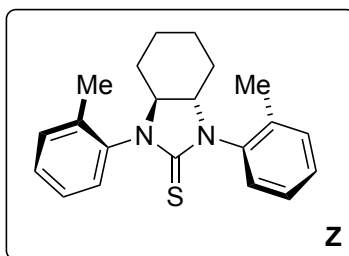
14-22



23-29



- 14)  $\text{Co}_2(\text{CO})_8$  (cat.), TMTU, CO
- 15) NaOMe, MeOH
- 16) TMS-imidazole
- 17) KHMDS, *then* MeI
- 18) DIBALH
- 19) DMP,  $\text{NaHCO}_3$
- 20) vinylmagnesium bromide
- 21) TBAF, AcOH
- 22)  $\text{LiAlH}_2(\text{OMe})_2$



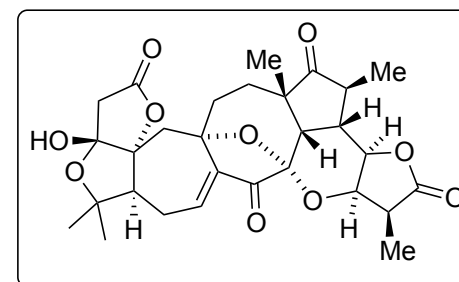
- 23)  $\text{Pd}(\text{OAc})_2$  (cat.), Z,  $\text{CuCl}_2$ , CO
- 24) LHMDS, *then* MeI
- 25) LiTMP
- 26)  $\text{Ac}_2\text{O}$ ,  $\text{Sc}(\text{OTf})_3$
- 27)  $\text{Pd}(\text{OH})_2$  (cat.),  $\text{H}_2$
- 28) LHMDS
- 29) DMP,  $\text{NaHCO}_3$

Name of step 14?

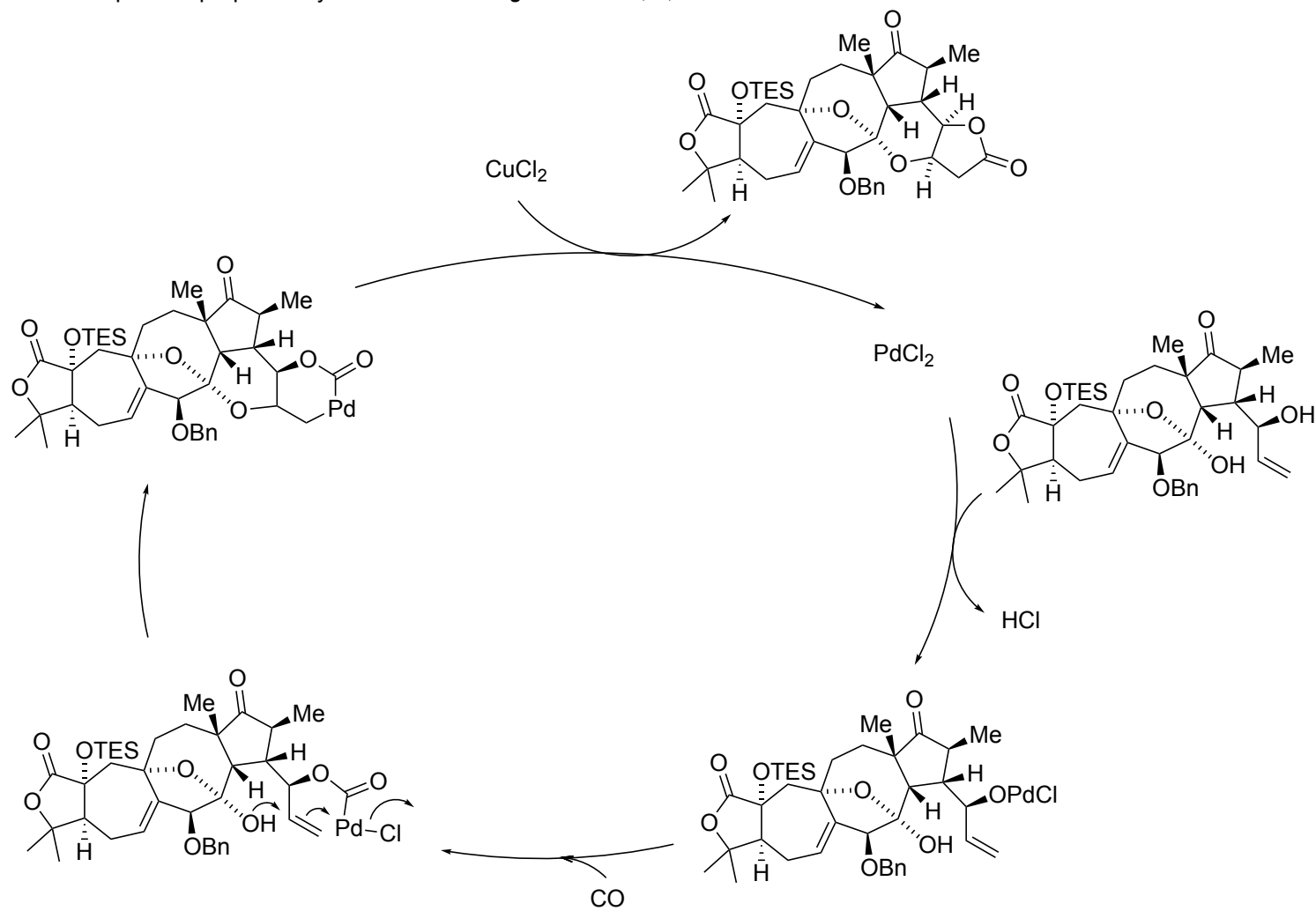
Pauson-Khand reaction

Come up with a mechanism for step 23!

see below



Mechanism of step 23 as proposed by the authors in *Org. Lett.* **2005**, 7, 885 – 888.:



first formation of a butenolide, which then gets attacked by the alcohol might also be possible