

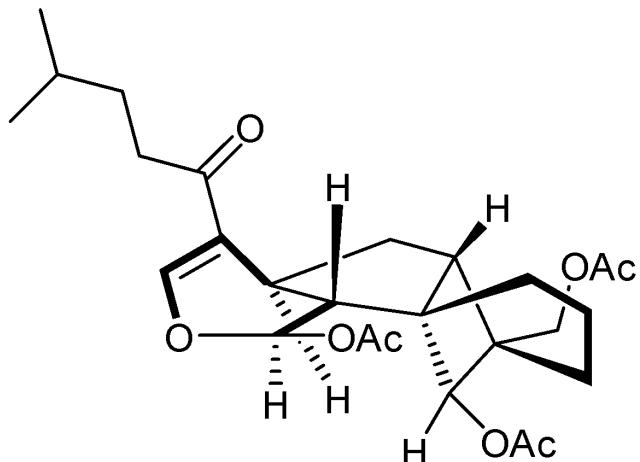


## Total Synthesis

International Edition: DOI: 10.1002/anie.201808517  
German Edition: DOI: 10.1002/ange.201808517

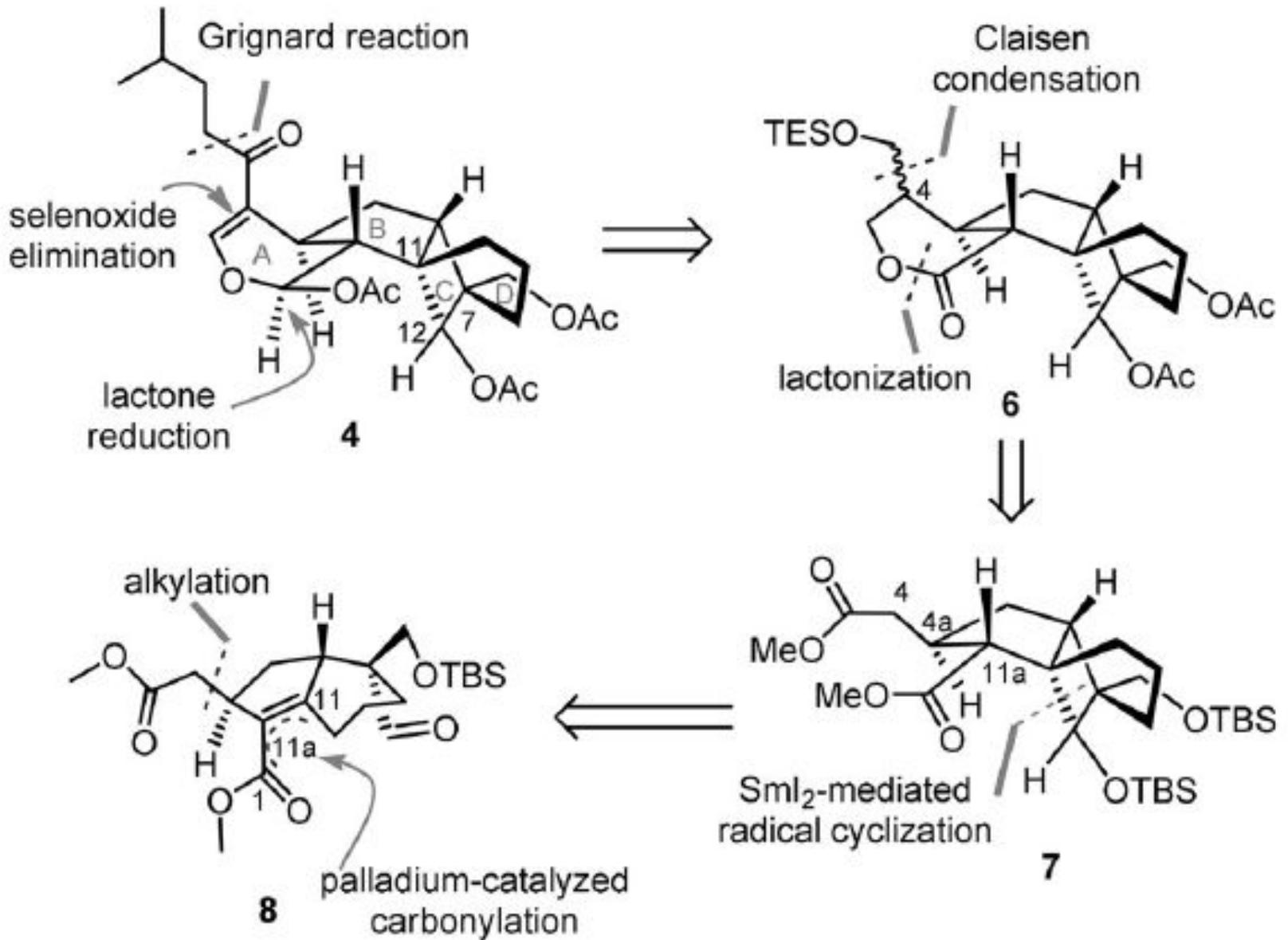
## Enantioselective Total Synthesis of (+)-Plumisclerin A

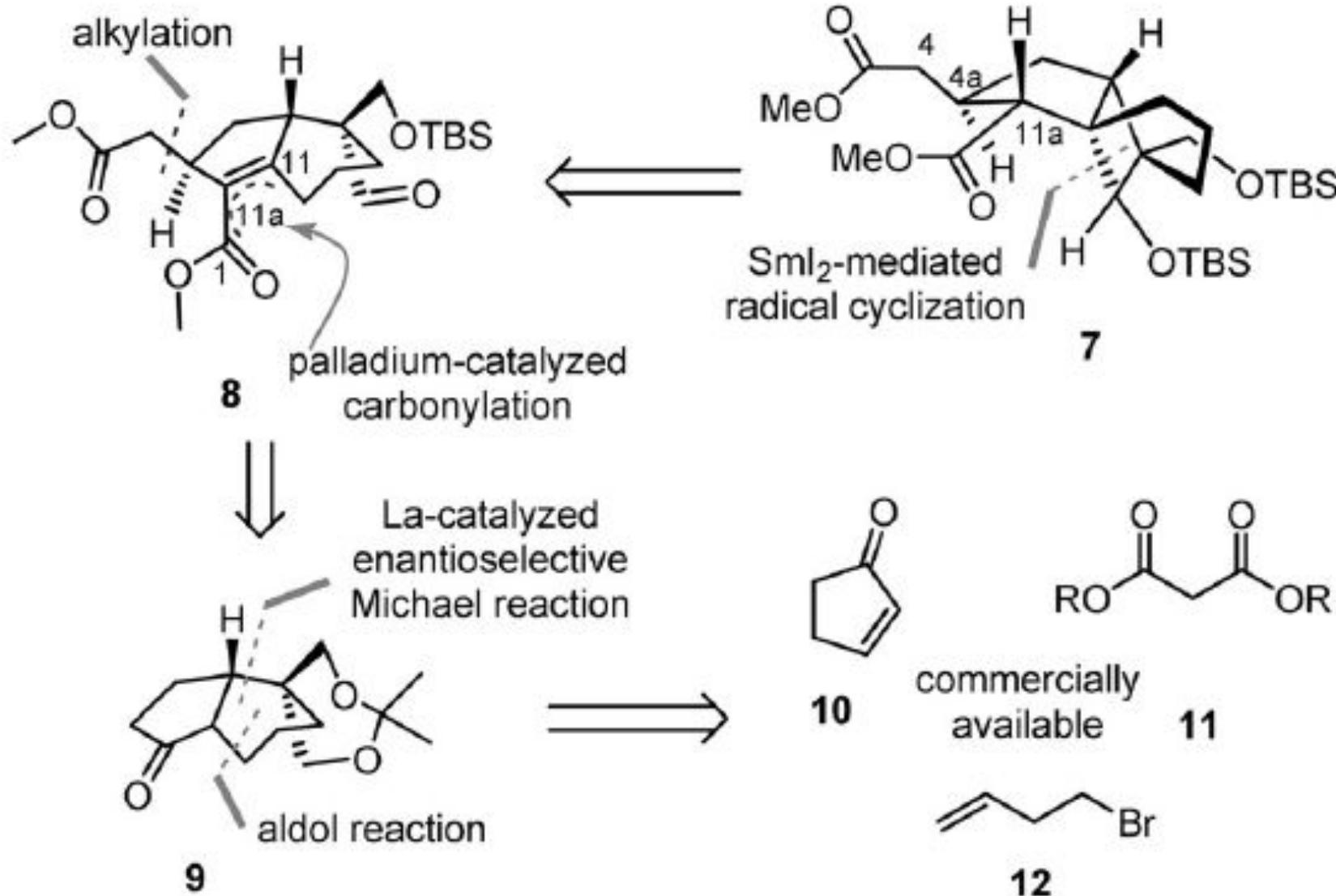
Ming Gao, Ye-Cheng Wang, Kai-Rui Yang, Wei He, Xiao-Liang Yang, and Zhu-Jun Yao\*

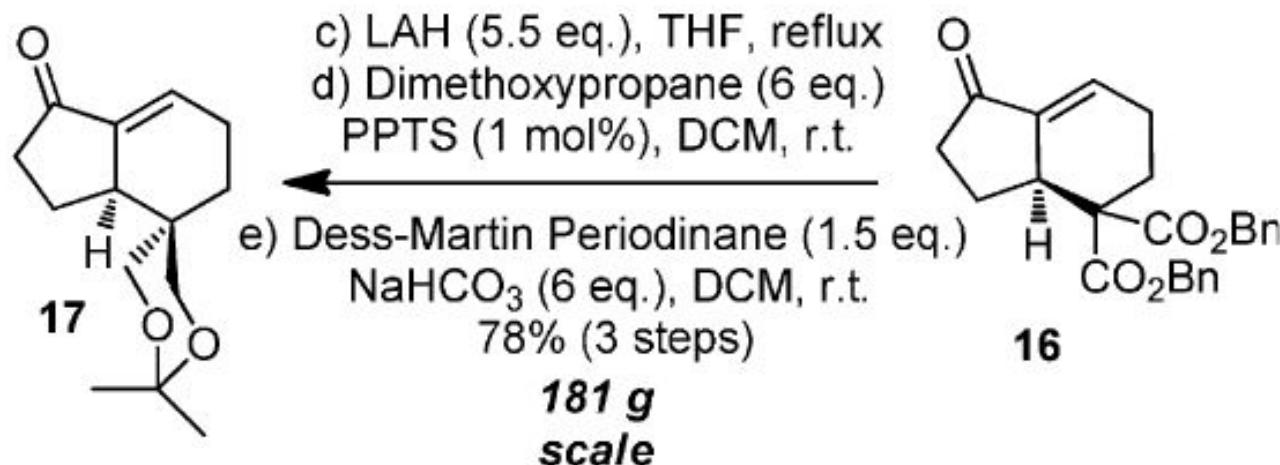
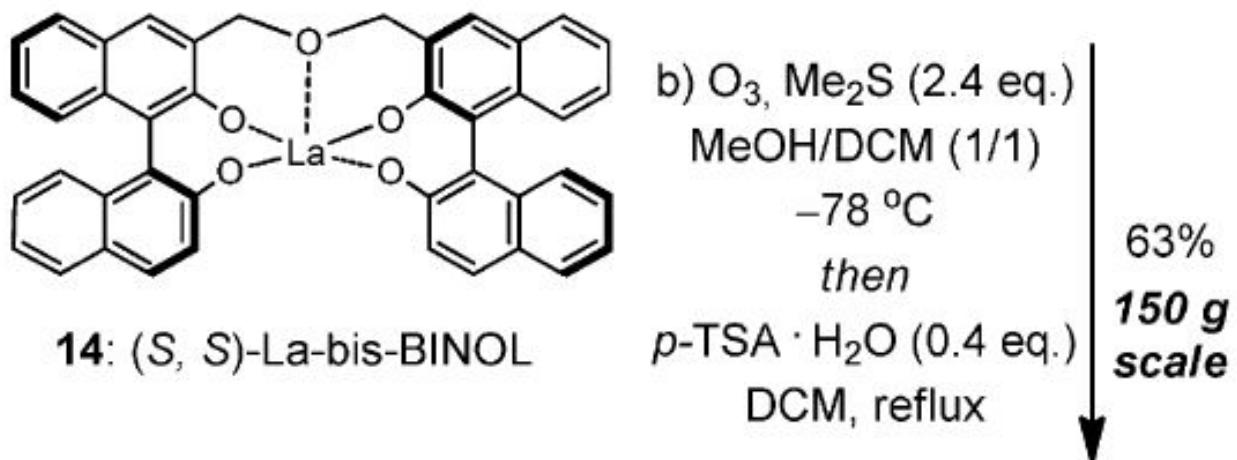
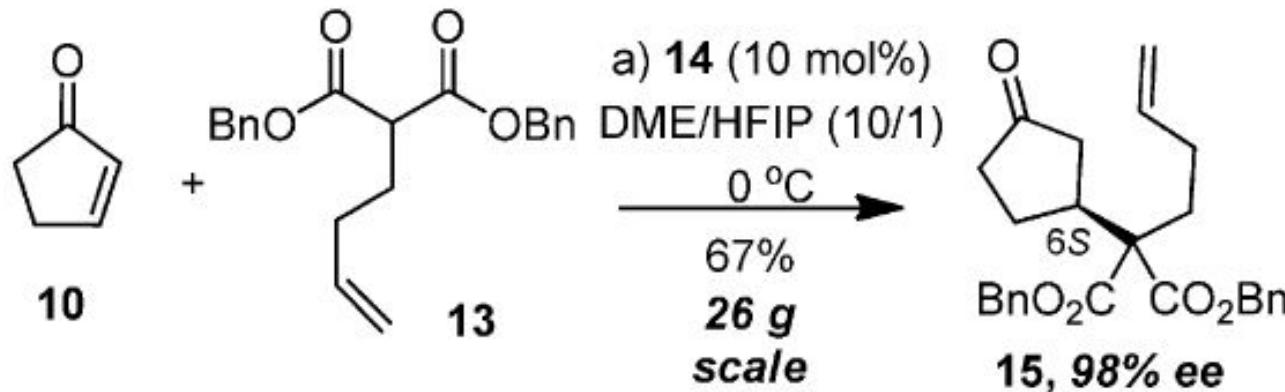


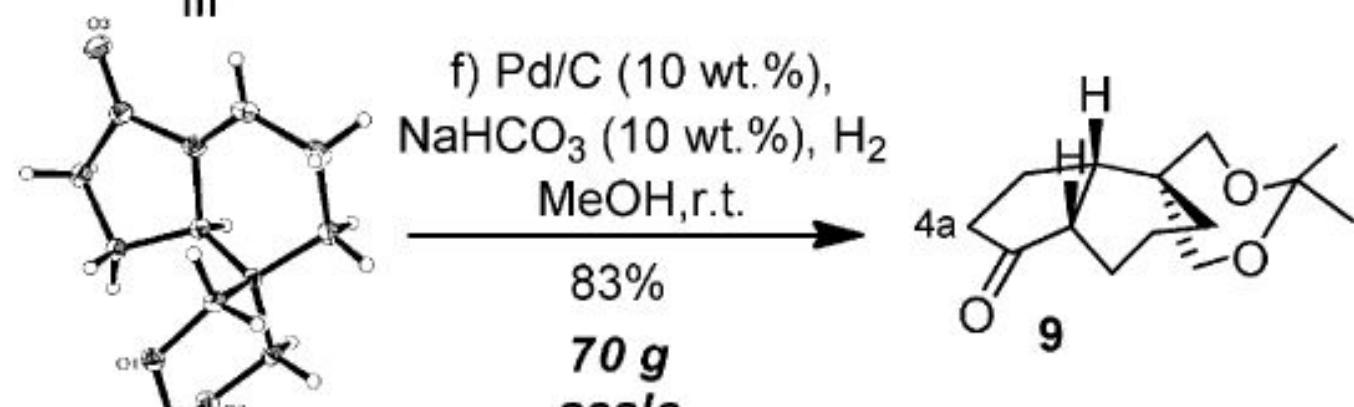
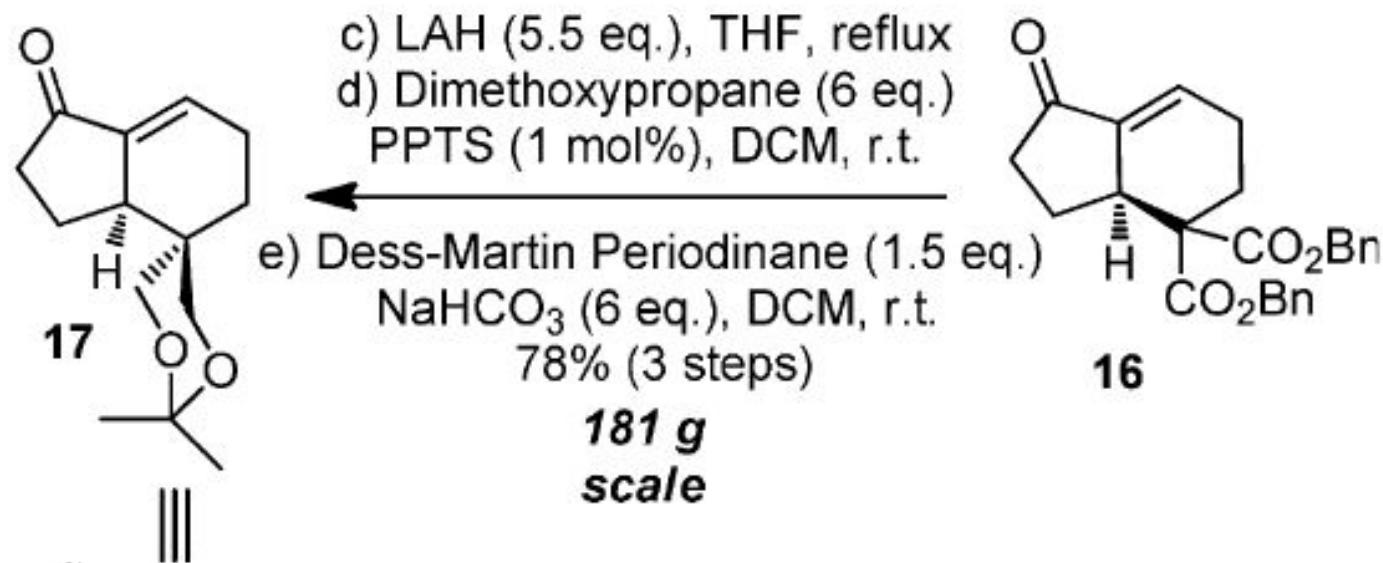
(+)-Plumisclerin A



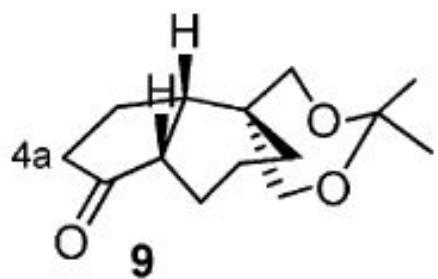




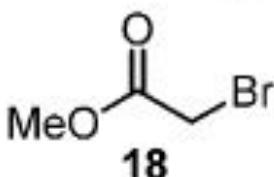
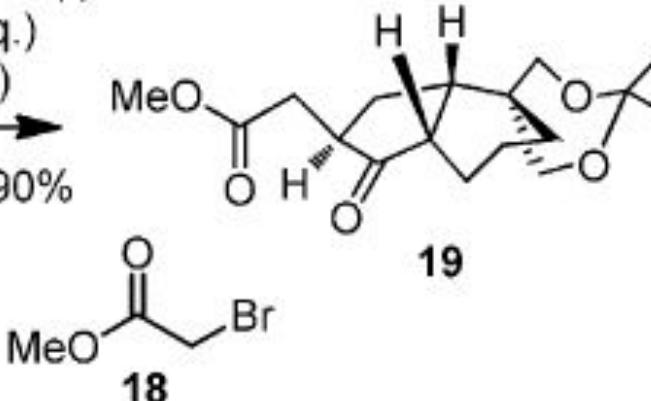




X-ray of 17

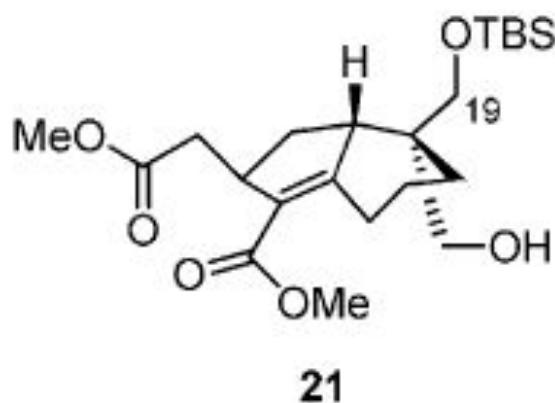


a) LiHMDS (1.2 eq.)  
HMPA (3 eq.)  
**18** (1.5 eq.)  
**9**  $\xrightarrow[\text{THF, -78 } ^\circ\text{C, 90\%}]{}$   
**30 g scale**



b) NaHMDS (1.2 eq.)  
 $\text{Tf}_2\text{NPh}$  (1.3 eq.)  
 $\text{THF/HMPA (10/1), -78 } ^\circ\text{C}$   
c)  $\text{Pd}(\text{PPh}_3)_4$  (8 mol%)  
DIPEA (5 eq.), CO  
MeOH/DMF (10/1),  $60$   $^\circ\text{C}$   
51% (2 steps)

**30 g scale**



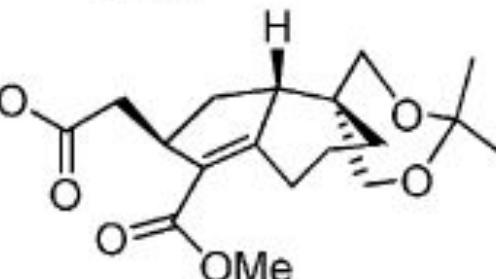
d)  $\text{TsOH}\cdot\text{H}_2\text{O}$  (15 mol%)  
MeOH/ $\text{H}_2\text{O}$  (10/1)  
 $40$   $^\circ\text{C}$   
e) Imidazole (1.4 eq.)  
 $\text{TBSCl}$  (1 eq.), DMF, r.t.  
80% (2 steps)

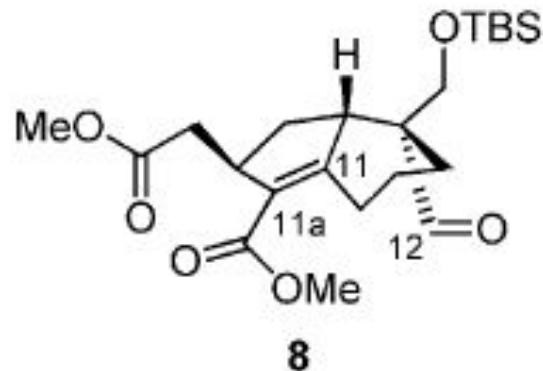
**20, 98% ee**

**20 g scale**

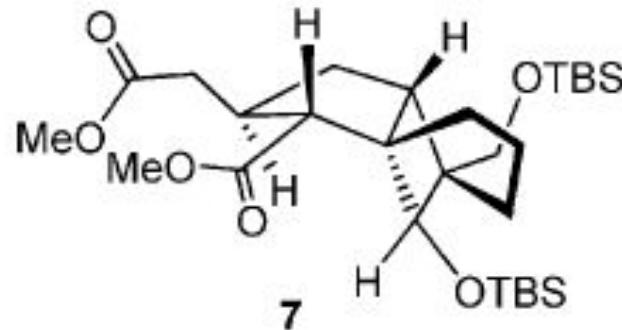
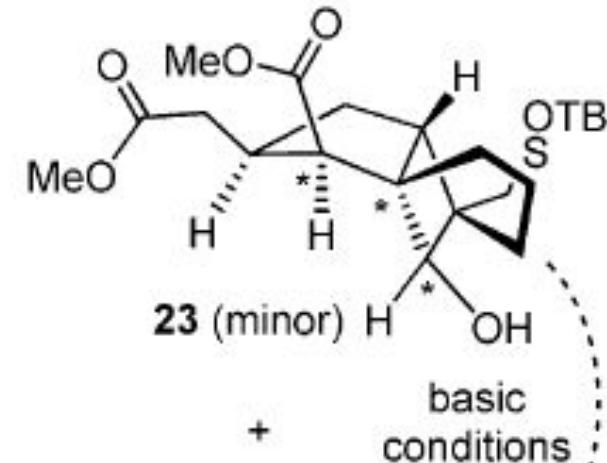
f) PCC (2 eq.)  
DCM, r.t.  
99%

**5 g scale**





j) HMPA (15 eq.)  
 $\text{SmI}_2$  (5 eq.)  
 THF/*t*-BuOH (10/1)  
 $-78^\circ\text{C}$ , 86%  
**23/22 = 1/3.3**  
**5 g scale**



h)  $\text{Et}_3\text{N}$  (4 eq.)  
 $\text{TBSOTf}$  (2 eq.)  
 DCM, r.t., 91%  
**3.2 g scale**

