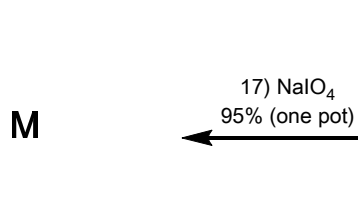
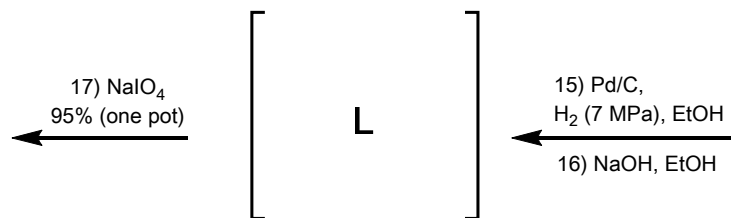
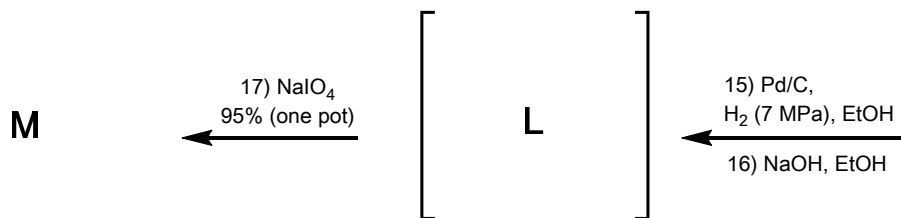
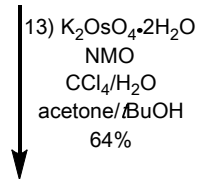
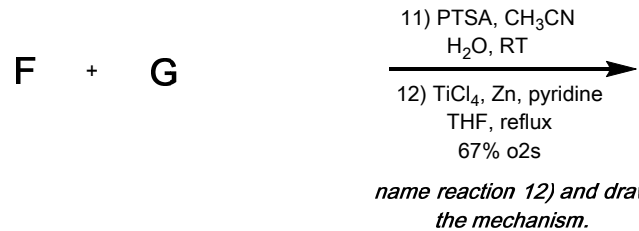
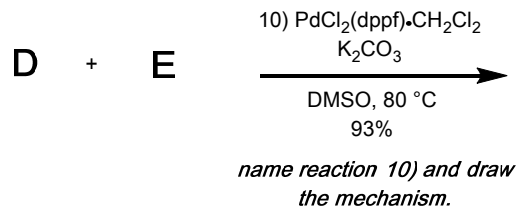
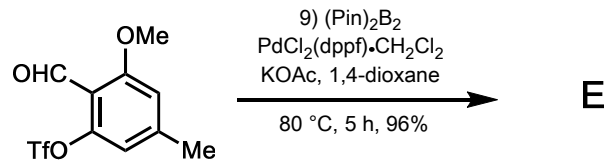
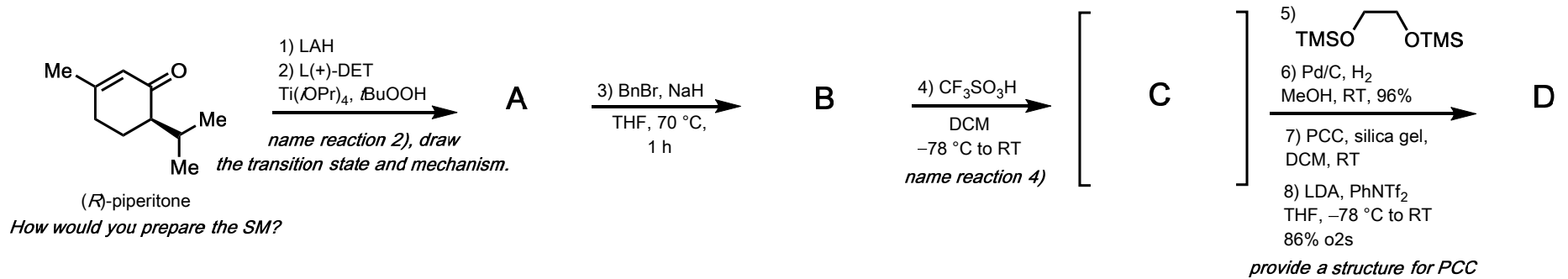


# Total Synthesis of the Hamigerans

Xiaojun Li, Shuanhu Gao *Angew. Chem.* 2016, 128, 10096-10100.



**M**

18) (COOH)<sub>2</sub>, (CH<sub>2</sub>OH)<sub>2</sub>  
 CH<sub>3</sub>CN, 78%  
 19) MeMgBr, THF, 0 °C

20) DMP, DCM, RT  
 21) PTSA, CH<sub>3</sub>CN/H<sub>2</sub>O  
 90% o3s

*name reaction 20) and draw  
 the mechanism. How would you  
 prepare DMP?*

**N**

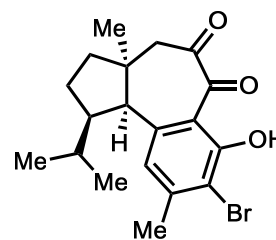
22) K<sub>2</sub>CO<sub>3</sub>  
 DMSO  
 d.r. = 5:1  
 at C<sub>14</sub>

**O**

23) PTSA  
 92%

**P**

24) 10% Pd/C, H<sub>2</sub>  
 EtOAc  
 25) BBr<sub>3</sub>, DCM  
 -78 °C  
 95% o2s

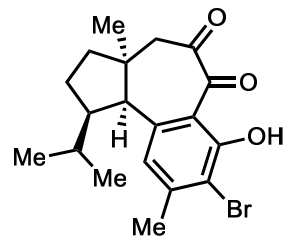
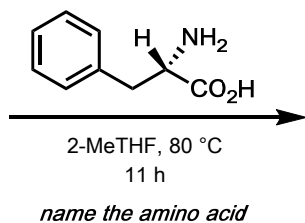
**Q****Hamigeran G**

26) py·HBr<sub>3</sub>, DCM  
 MeOH, RT

27) SeO<sub>2</sub>, 1,4-dioxane  
 H<sub>2</sub>O/AcOH, 100 °C  
 71% o2s

*name reaction 27) and draw  
 the mechanism.*

Biomimetic transformation of Hamigeran G into Hamigeran N:

**Hamigeran G**

**Hamigeran N** + *epi-isomer*