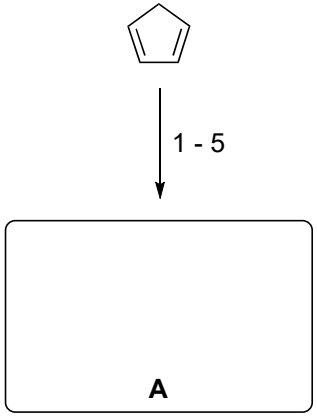
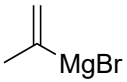
Concise Enantioselective Total Synthesis of (+)-Punctaporonin U

P. Gri, Q. Wang and J. Zhu

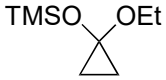
J. Am. Chem. Soc. **2025**, *147,* 40106−40112

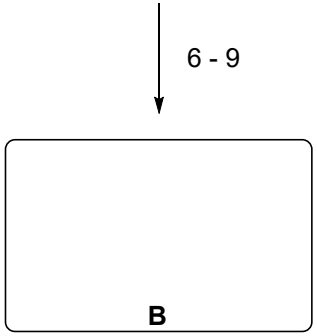


1) O_2, hν, Rose Bengal, Thiourea, MeOH
2) Vinyl acetate, Pancreatin lipase, NEt_3
3) TBSCl, Imidazole
4) K_2CO_3, MeOH
5) PCC



1

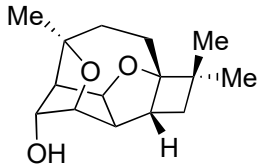




6) MeOH
7) MeMgBr, *then* **1**
8) 1 M HCl / Et_2O
9) KHMDS, TBSCl

2) Racemic resolution. >99% ee

8) Type of reaction?

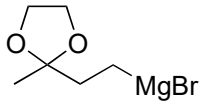


(+)-Punctaporonin U

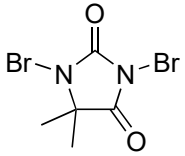
10-12

10) **A**, **B** (2.0 equiv), TESOTf, (2,6-*t*Bu)pyridine, CH_2Cl_2, –40 °C
11) **2**, $LaCl_3 \cdot 2LiCl$
12) TFAA, pyridine, *then* $TsOH \cdot H_2O$

10) *Hint: syn* addition. dr 4:1. Name of reaction?



2



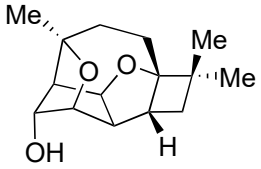
DBDMH

C

13-15

13) MeONa (2.5 equiv), *then* iPr_2SiCl_2, NEt_3, *then* DBDMH, *then* HF·pyridine. (50% yield)
14) $NMe_4BH(OAc)_3$
15) (2,6-*t*Bu)pyridine, 3 days

13) Draw a probable mechanism of the key step. *Hint:* a dianion intermediate is formed
14) Name of reaction?



(+)-Punctaporonin U