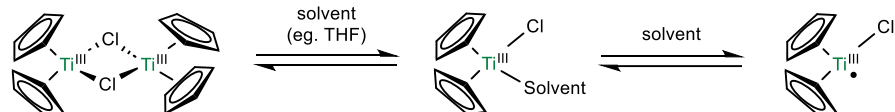
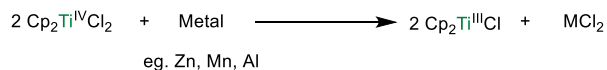
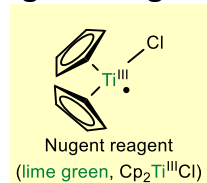
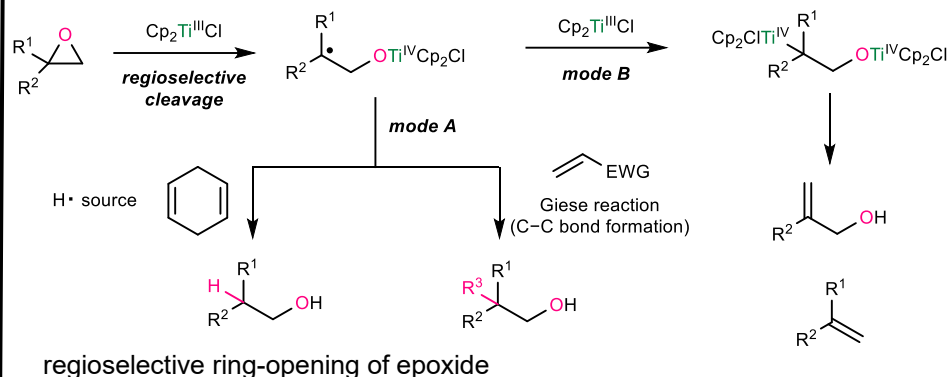


## Nugent reagent

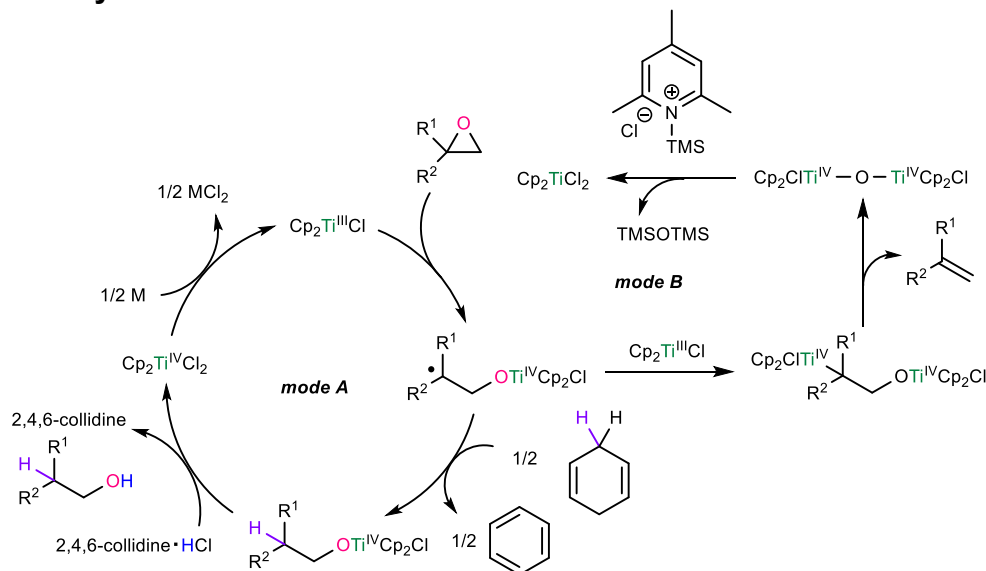


1. a mild SET reagent (unpaired *d* electron, E<sub>o</sub> = -0.8 V vs Fc<sup>+</sup>/Fc)
2. has a vacant site, allowing to inner-sphere electron transfer
3. in situ preparation from metal reductant and Cp<sub>2</sub>TiCl<sub>2</sub>

## Reaction mode -stoichiometric Ti species-



## Catalytic modification

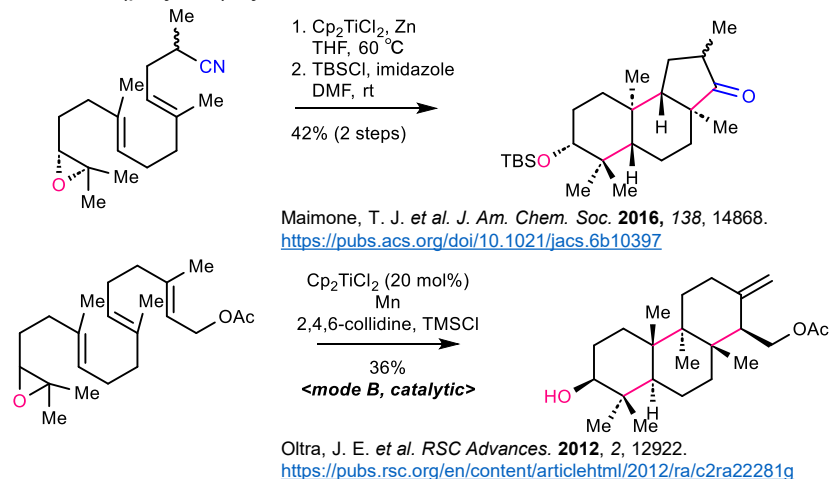


1. metal reductant/2,4,6-collidine · HCl system for **mode A**
2. metal reductant/2,4,6-collidine/TMSCl for **mode B**

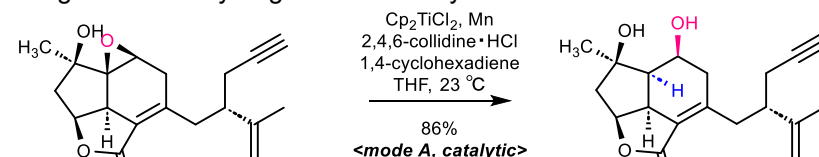
Gansauer, A et al. *J. Am. Chem. Soc.* **1998**, *120*, 12849. <https://pubs.acs.org/doi/10.1021/ja981635p>  
For a review, see: Oltra, J. E. et al. *Eur J. Org. Chem.* **2015**, *2015*, 4567.  
<https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/ejoc.201500292>

## Classical application in total syntheses

### 1. radical (polyene) cyclization

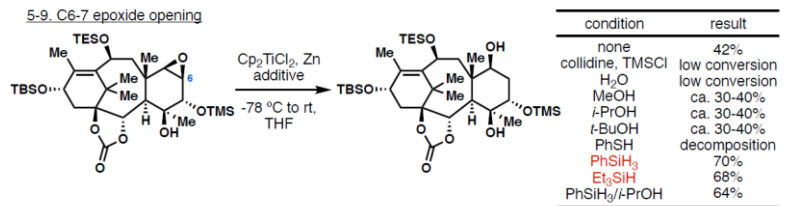


### 2. regioselective hydrogenation –catalytic version-



Stoltz, B. M. et al. *J. Am. Chem. Soc.* **2020**, *142*, 8585.  
<https://pubs.acs.org/doi/10.1021/jacs.0c02513>

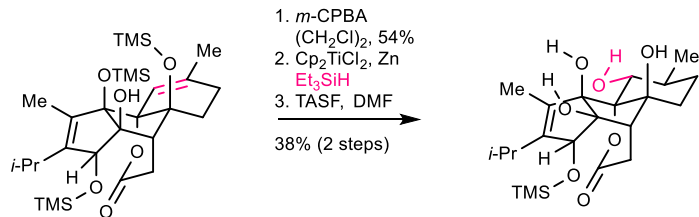
## Triethylsilane as an alternative reductant



- epoxide reduction in presence of carbonate, TMS, *t*-OH
- hypothesized slow C6 radical quenching lead to decomposition
- Et<sub>3</sub>SiH gave the cleanest TLC and was employed as the final condition

*Tetrahedron*. **2002**, 58, (35), 7017.  
*Angew. Chem. Int. Ed.* **2006**, 45, (33), 5522.  
*J. Am. Chem. Soc.* **2016**, 138 (14), 4962.

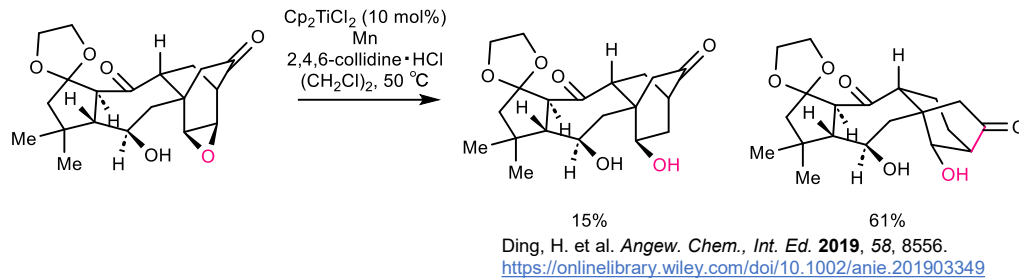
Baran, P. S. et al. *J. Am. Chem. Soc.* **2020**, 142, 10526.  
<https://pubs.acs.org/doi/10.1021/jacs.0c03592>



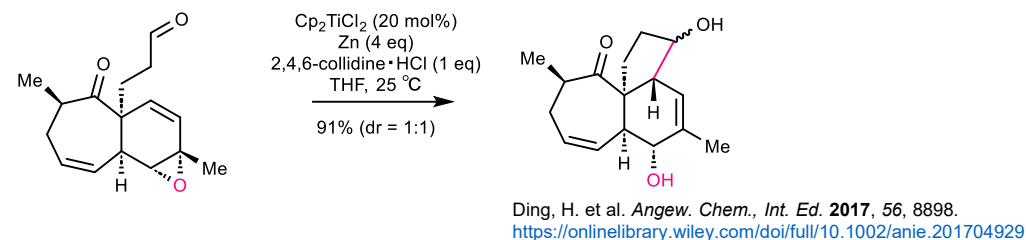
Micarizio, G. M. et al. *J. Am. Chem. Soc.* **2020**, 142, 12937.  
<https://pubs.acs.org/doi/10.1021/jacs.0c05766>

## Combination of other chemistry -reports from Hanfeng Ding group-

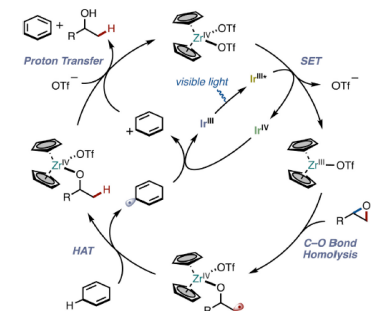
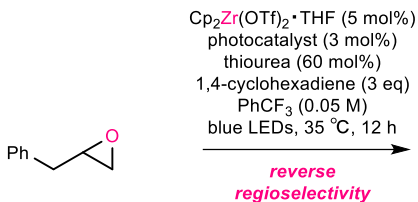
### 1. Dowd-Beckwith reaction –Total synthesis of Rhodomollenin XX-



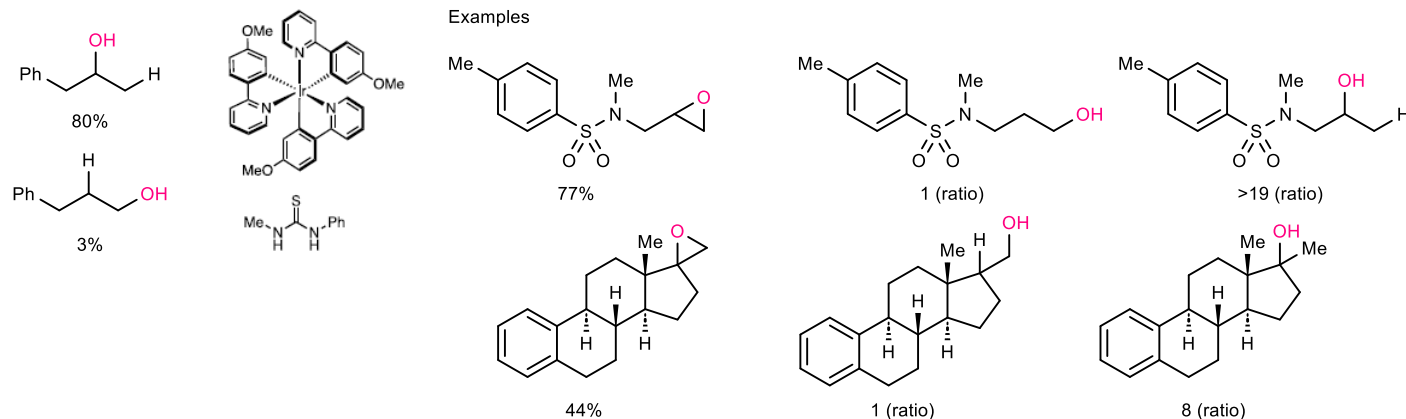
### 2. Barbier-type reaction –Total synthesis of Pepulanol-



## Zirconocene-mediated regioselective opening of epoxides



- zirconocene catalyst changed the regioselectivity
- the role of thiourea is still unclear



Yamaguchi, J. et al. *Chem.* **2022**, 8, 1762.  
<https://www.sciencedirect.com/science/article/pii/S245192942200208X>