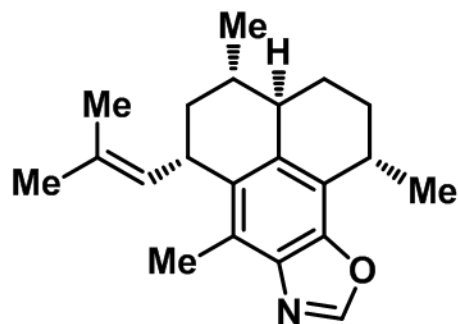


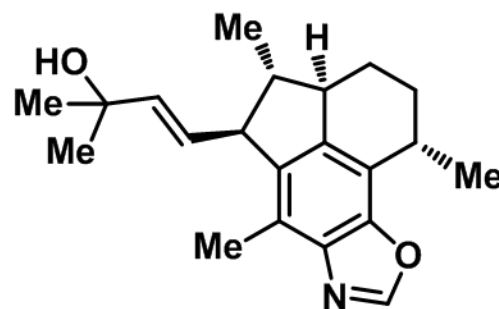
**Natural Product Synthesis**

International Edition: DOI: 10.1002/anie.201901651

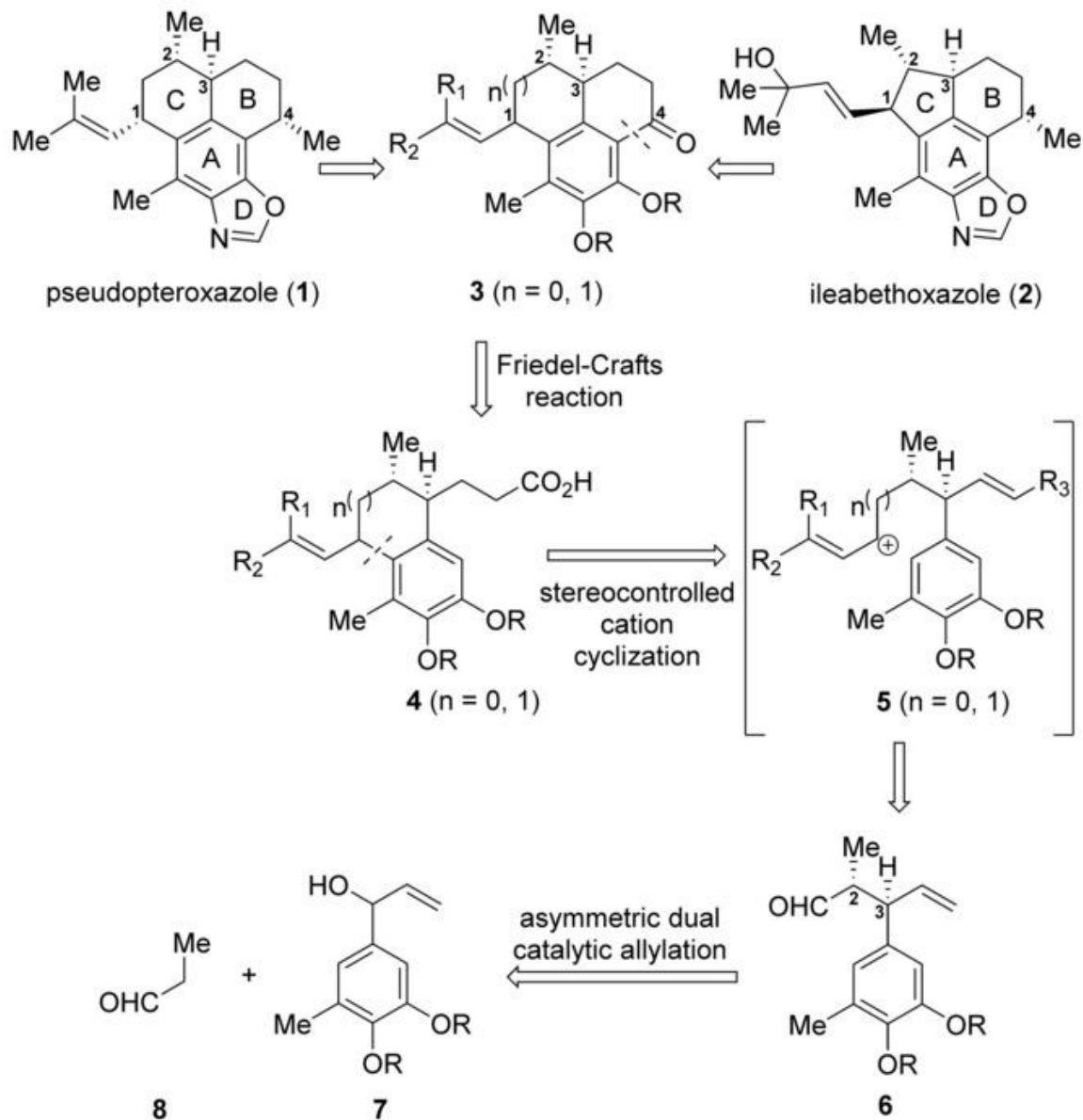
German Edition: DOI: 10.1002/ange.201901651

**Enantioselective Total Synthesis of Pseudopteroxazole and Ilebethoxazole***Xuan Zhang<sup>+</sup>, Xianhe Fang<sup>+</sup>, Miao Xu, Yibo Lei, Zibo Wu, and Xiangdong Hu\**

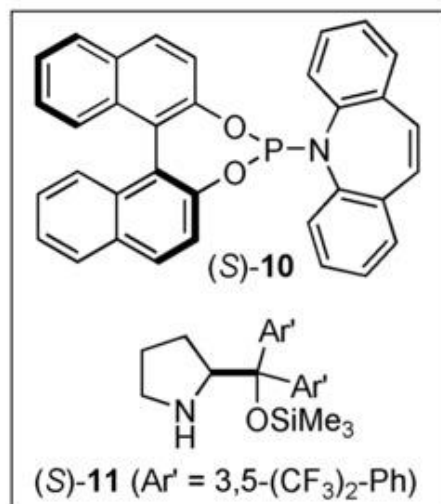
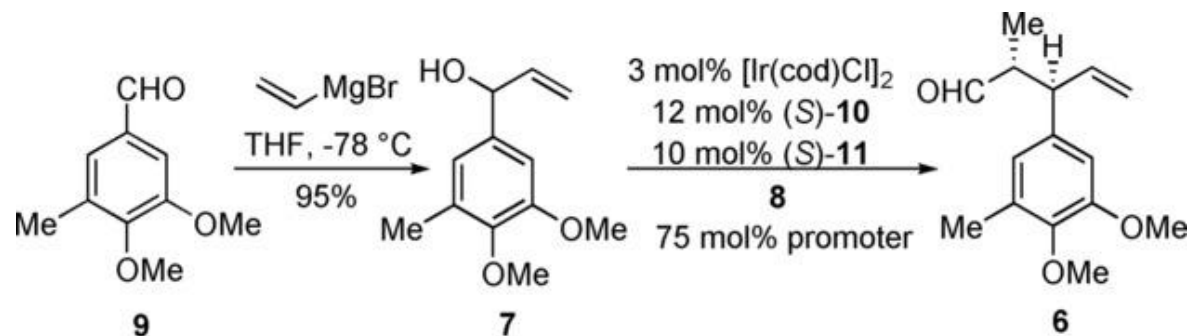
pseudopteroxazole (1)



ilebethoxazole (2)



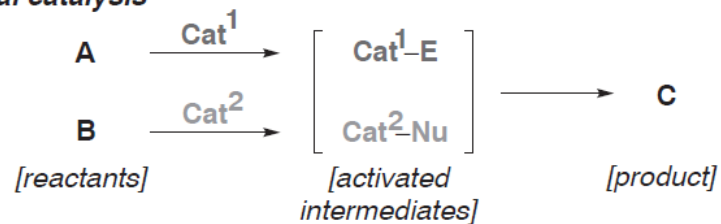
**Scheme 1.** Retrosynthetic analysis of pseudopteroxazole (1) and ileabethoxazole (2).



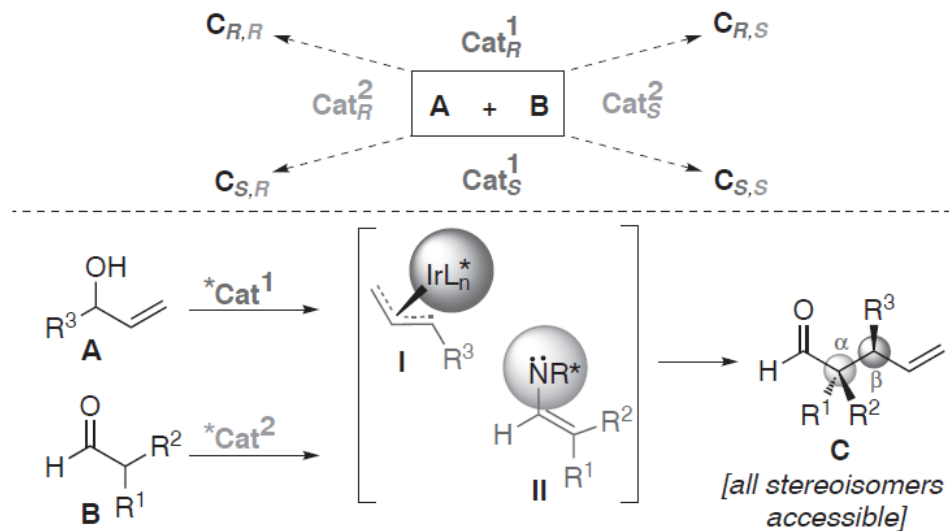
promoter	d.r.	yields
$\text{Sc}(\text{OTf})_3$	-	-
$\text{Zn}(\text{OTf})_2$	-	-
$\text{CH}(\text{CO}_2\text{H})_2$	3.6:1	61%
$(\text{MeO})_2\text{P}(\text{O})\text{OH}$	6.6:1	63%
$\text{Cl}_3\text{CO}_2\text{H}$	7:1	41%
$\text{F}_3\text{CCO}_2\text{H}$	5:1	40%
$\text{Cl}_2\text{CHCO}_2\text{H}$	6.3:1	81%
$\text{F}_2\text{CHCO}_2\text{H}$	10:1	83% (94%ee)

**Figure 1.** Synthesis of **6** through asymmetric dual catalytic allylation.

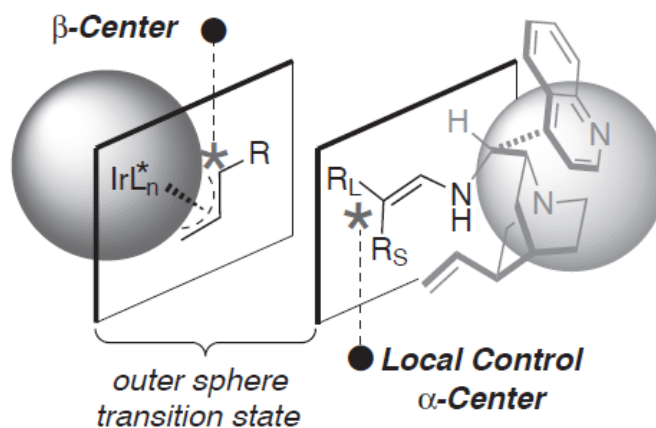
### A dual catalysis

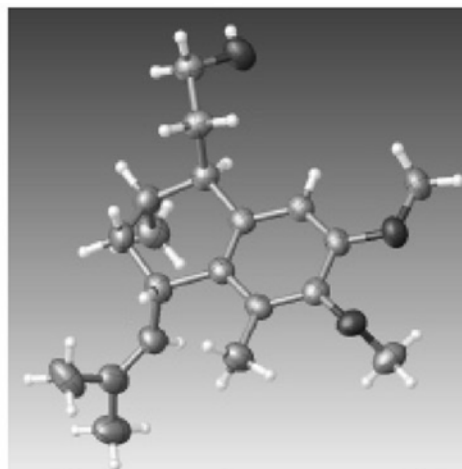


### B stereodivergent dual catalysis (this work)

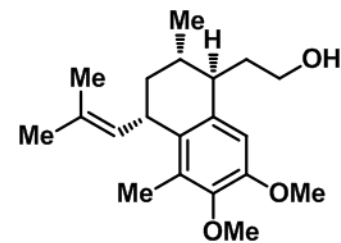


### Local Control



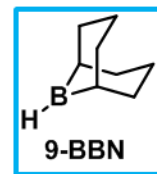


X-ray crystal structure of **15**

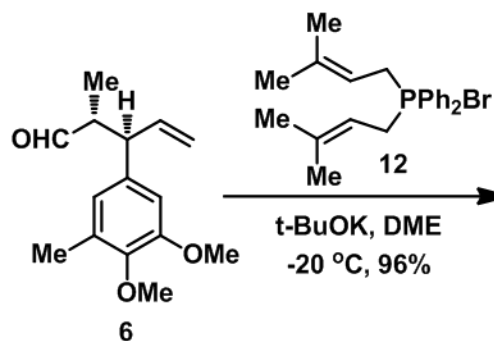


**15**

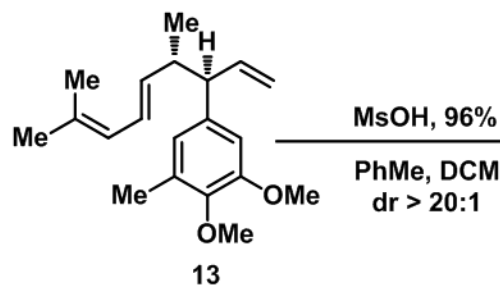
9-BBN  
H<sub>2</sub>O<sub>2</sub>, NaOH  
72%



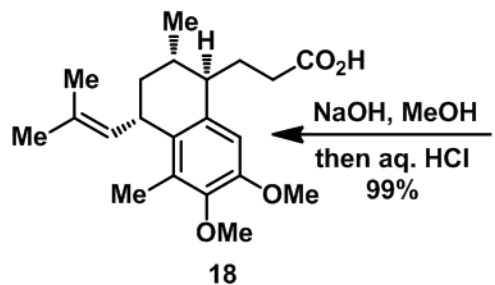
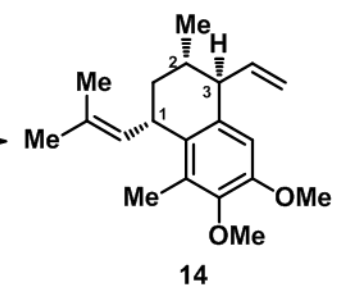
9-BBN



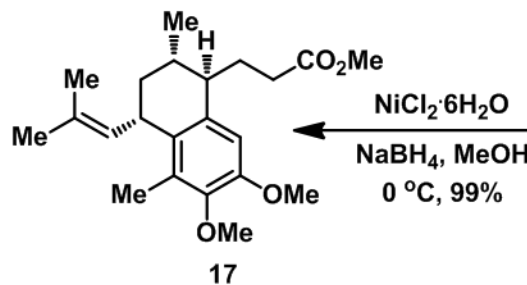
**Wittig-Vedejs E-selective olefination**



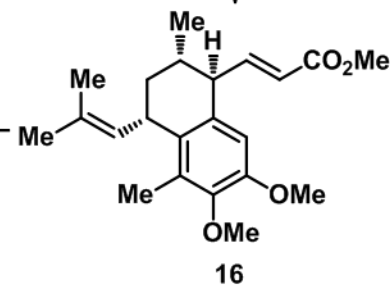
**Alkene (olefin) metathesis (P10)**



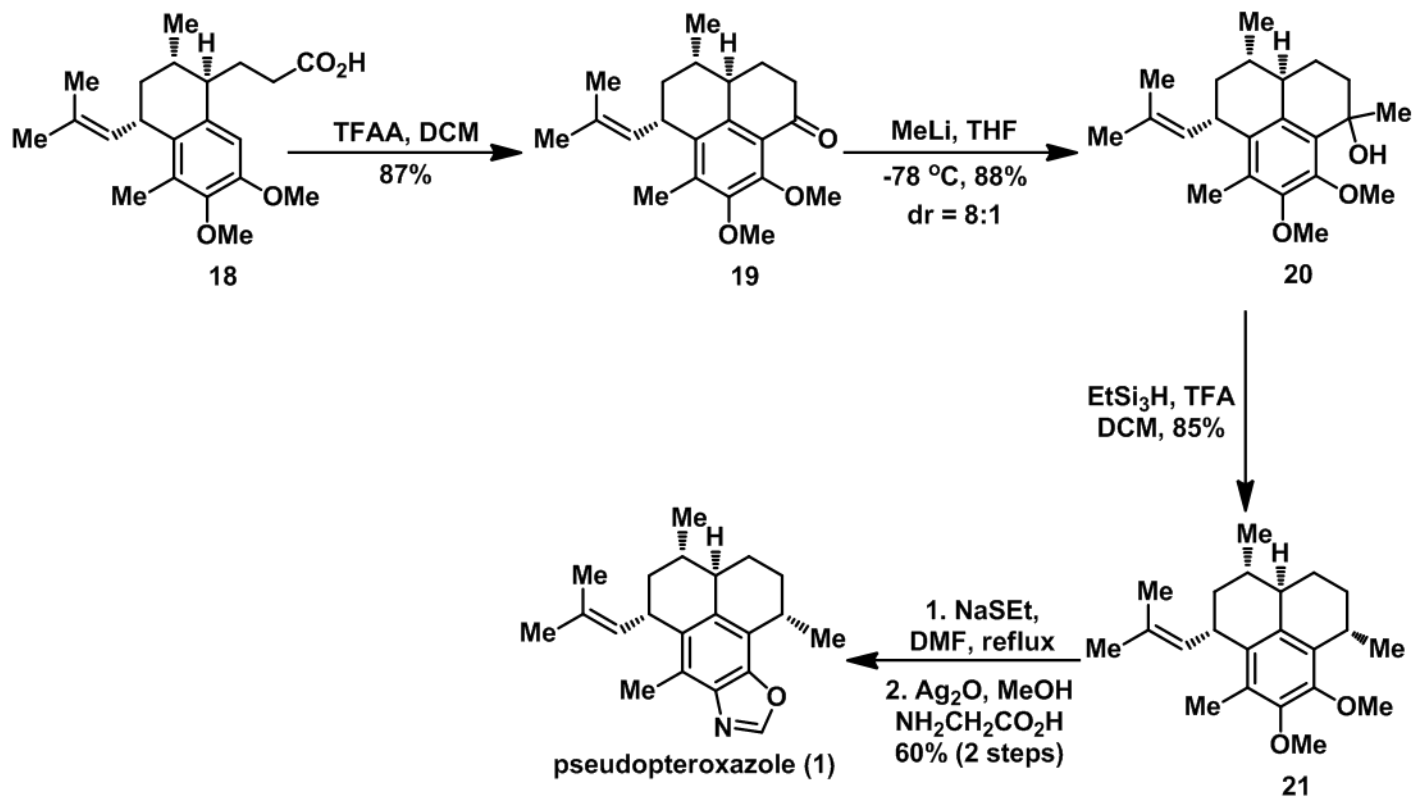
**18**

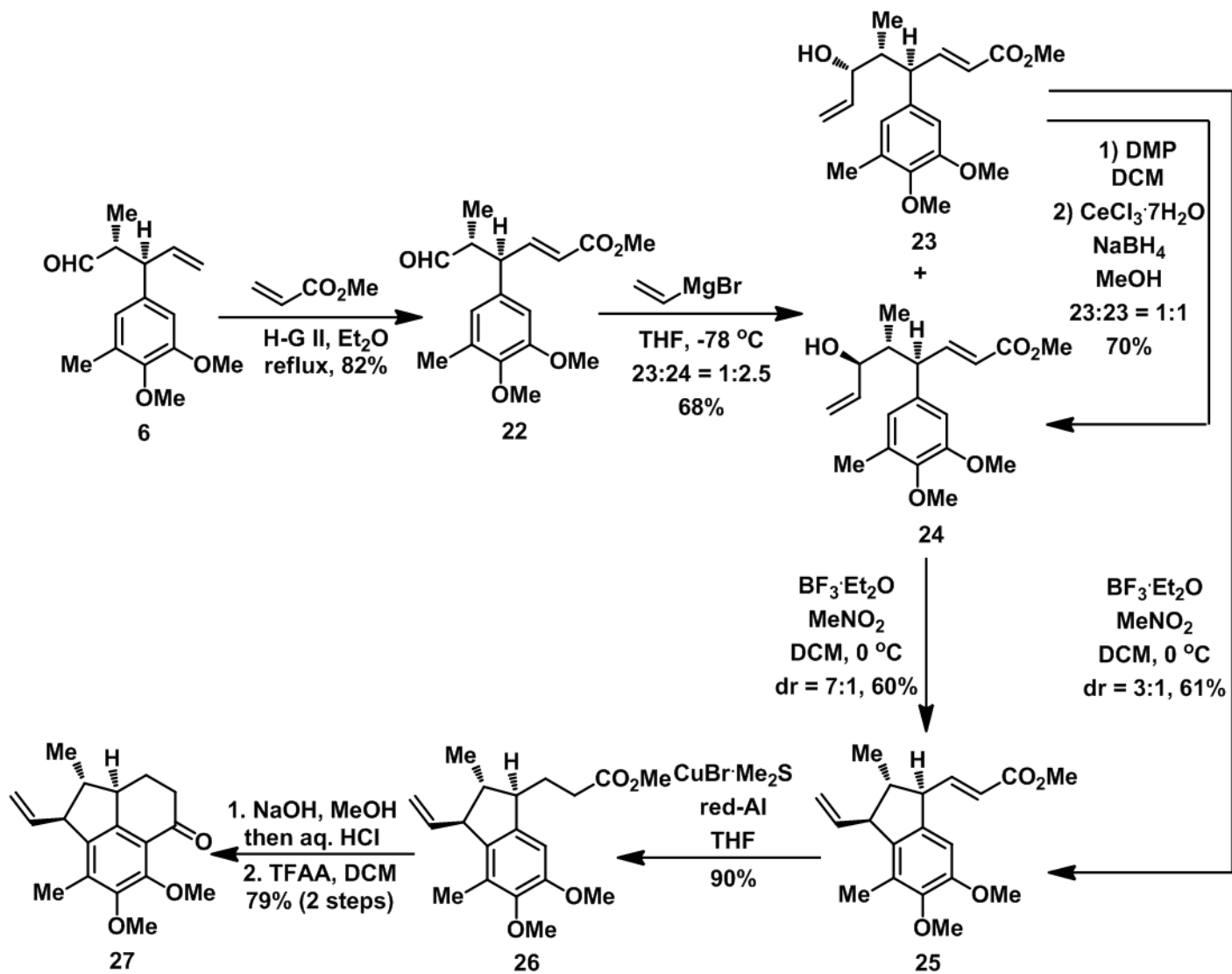


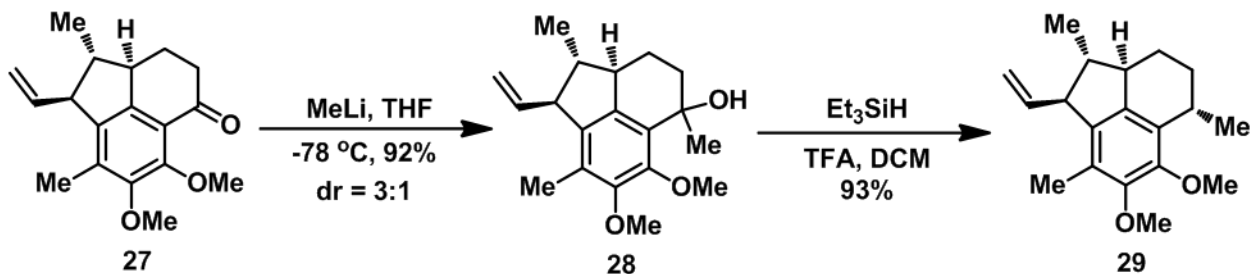
**17**



**16**







**Horner-Wadsworth-Emmons reaction (P212)**

