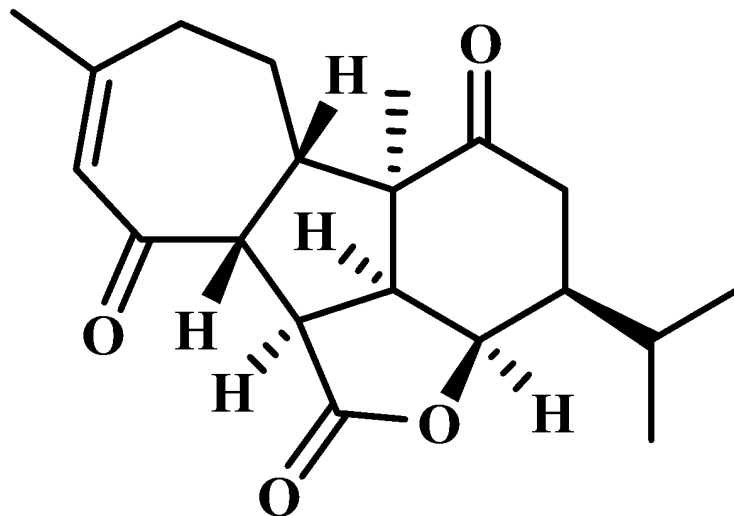


# Enantioselective Total Synthesis of (–)-Pavidolide B

Peng-Peng Zhang, Zhi-Ming Yan, Yuan-He Li, Jian-Xian Gong, and Zhen Yang

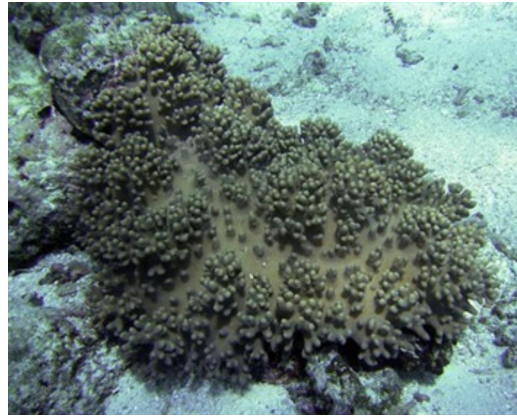
*J. Am. Chem. Soc.*, 2017, 139, 13989–13992



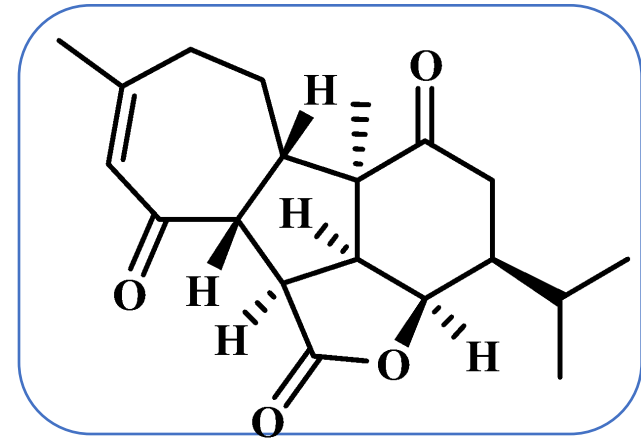
аспирант ИОХ РАН  
Радулов П.С.



**Leen van Ofwegen**

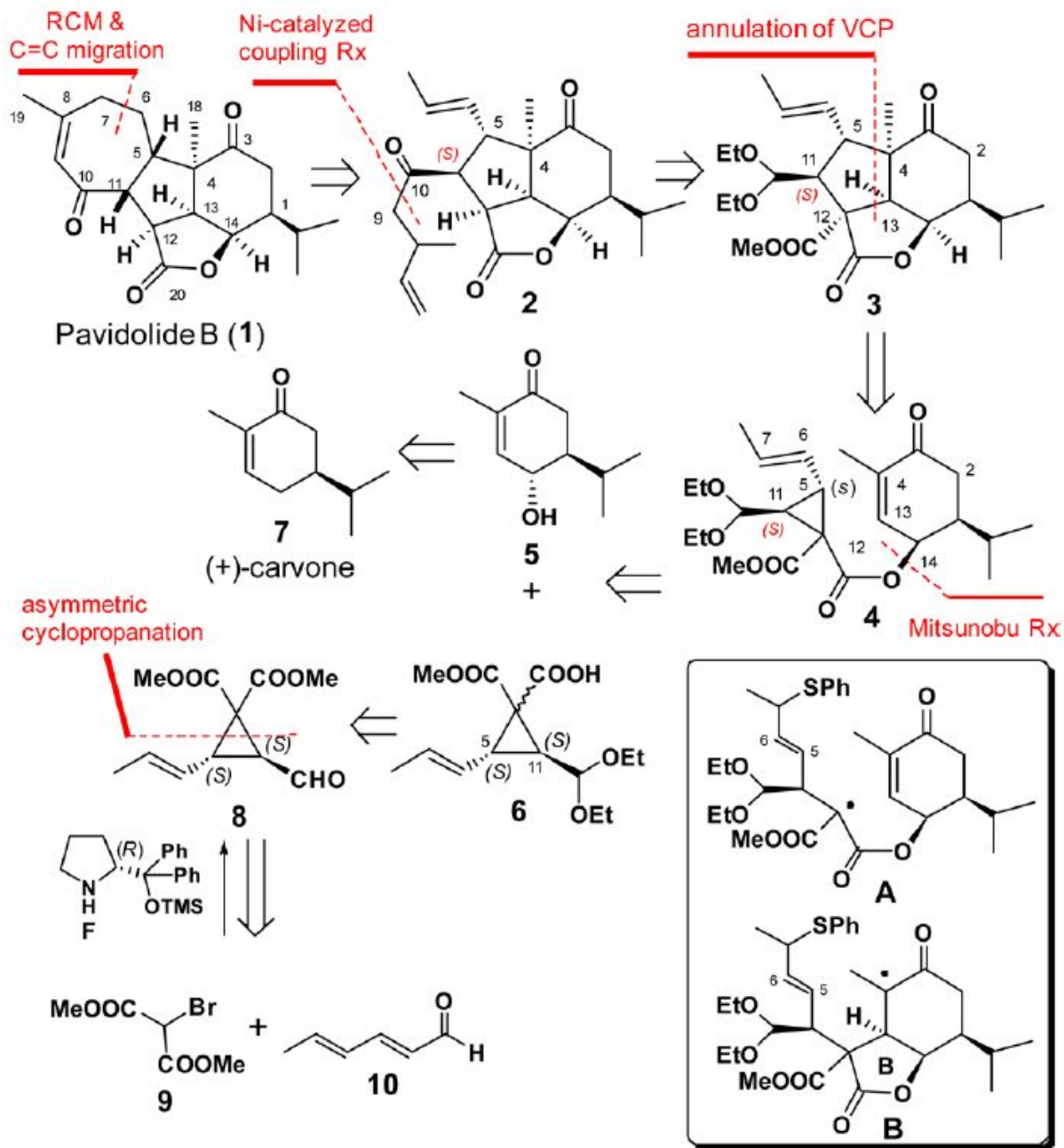


*Sinularia pavidia*

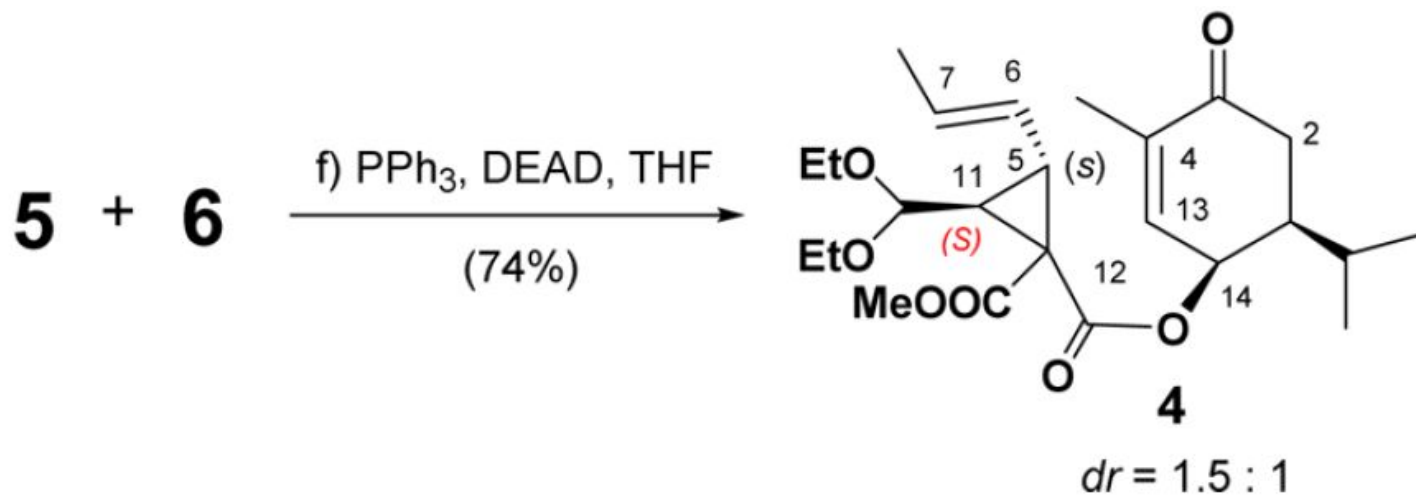
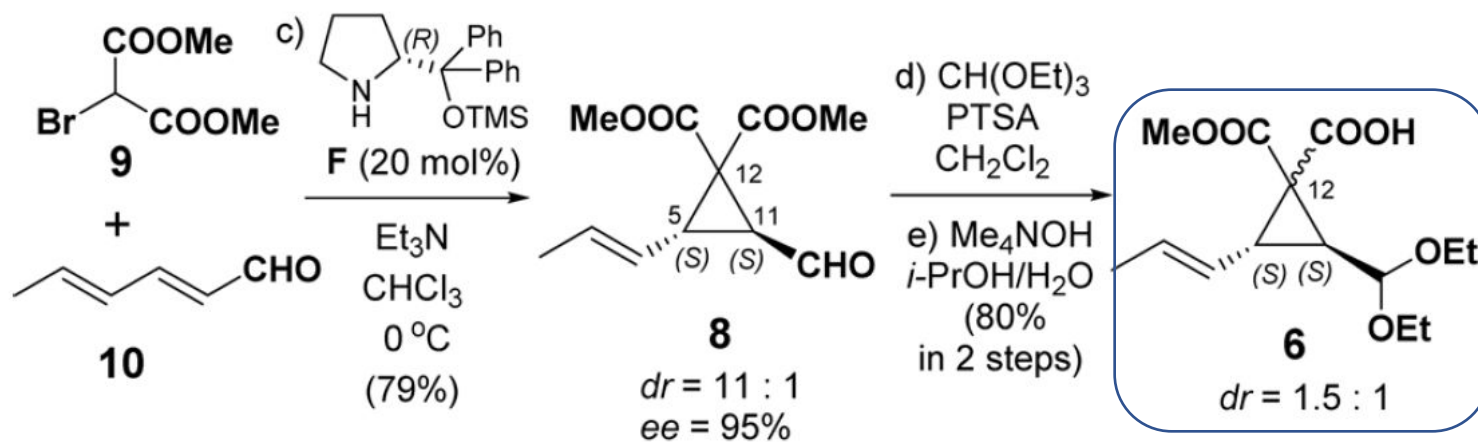
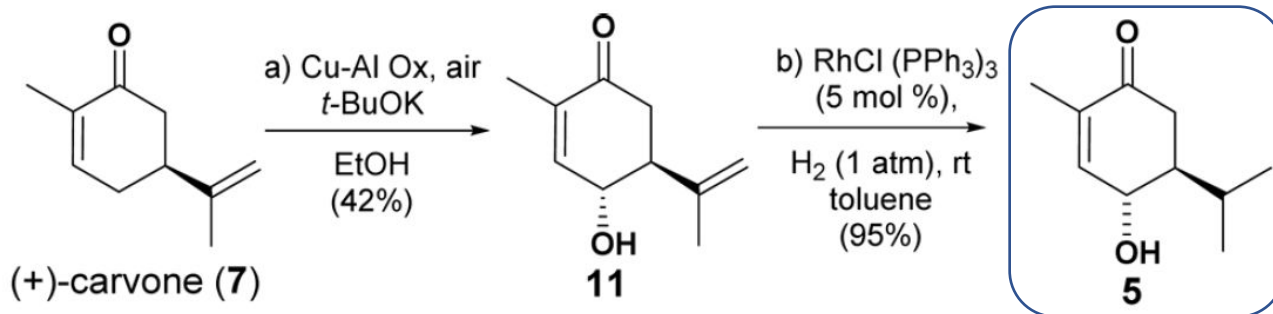


**(-)-Pavidolide B**

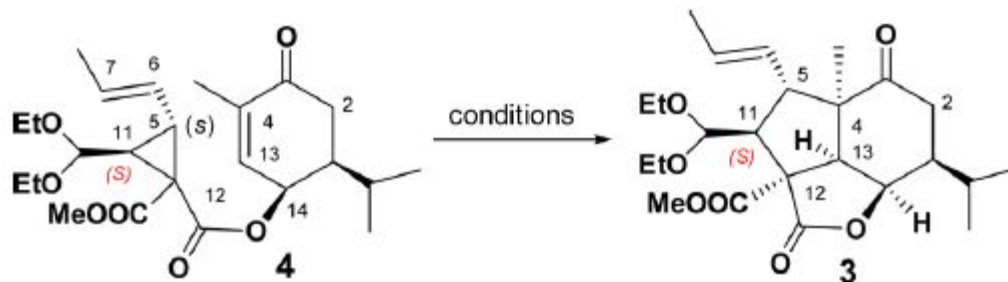
# Retrosynthetic analysis of pavidolide B



# Asymmetric Synthesis of Precursor 4

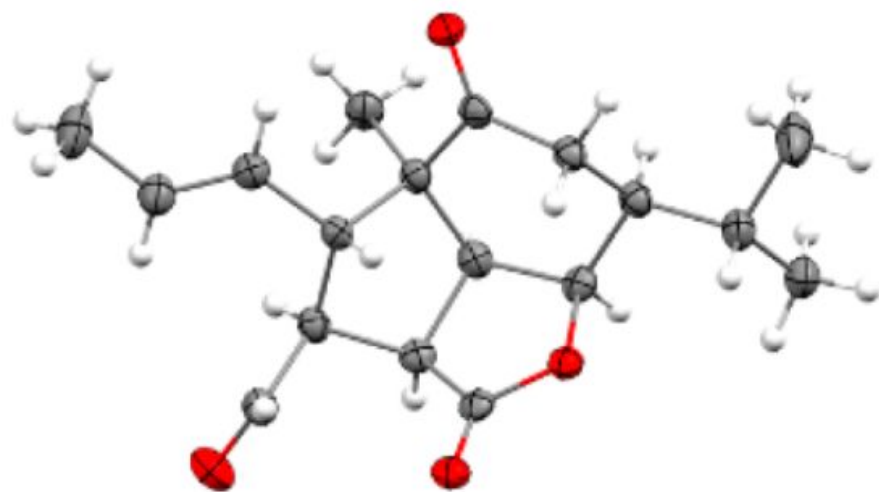
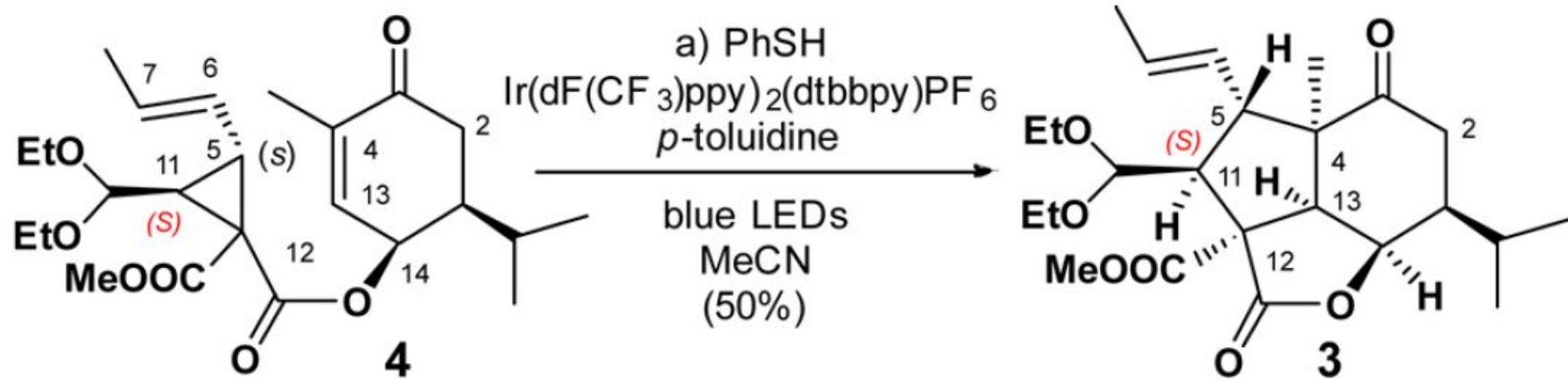


## Screening of the Reaction Conditions



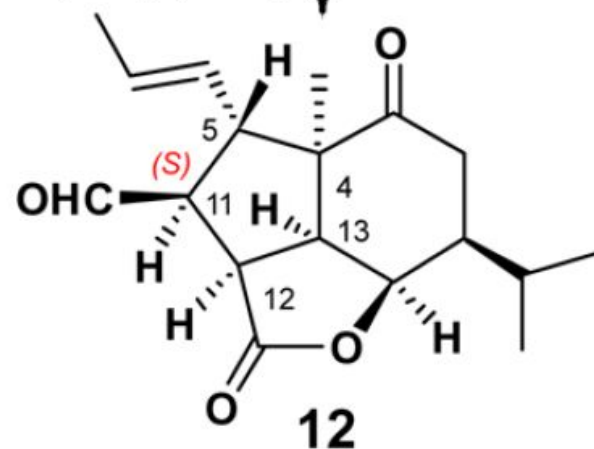
entry	conditions	solvent	temp (°C)	time (h)	yield <sup>a</sup>
1	PhSH, AIBN	toluene	60	9	trace
2	PhSH, AIBN	toluene	80	6	32%
3	PhSH, AIBN	toluene	100	3	31%
4	PhSH, AIBN	toluene	120	3	35%
5	PhSSPh, AIBN, UV (250 W)	toluene	25	5	32%
6	PhSSPh, AIBN, UV (250 W), AlMe <sub>3</sub>	toluene	25	3	40–48%
7	PhSSPh, BPO, <sup>b</sup> UV(250 W)	toluene	25	5	23%
8	PhSH, Ru(bpy) <sub>3</sub> Cl <sub>2</sub> , <i>p</i> -toluidine, blue LEDs	MeCN	25	4	30%
9	PhSH, Ir(ppy) <sub>2</sub> (dtbbpy)PF <sub>6</sub> , <i>p</i> -toluidine, blue LEDs	MeCN	25	5	47%
10	PhSH, <i>p</i> -toluidine, Ir(dF(CF <sub>3</sub> ) ppy) <sub>2</sub> (dtbbpy)PF <sub>6</sub> , blue LEDs	MeCN	25	2	50% <sup>c</sup>
11	benzyl mercaptan, <i>p</i> -toluidine, Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy)PF <sub>6</sub> , blue LEDs	MeCN	25	5	23%
12	methyl thioglycolate, <i>p</i> -toluidine, blue LEDs, Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy)PF <sub>6</sub>	MeCN	25	2	25%

# Asymmetric Total Synthesis of Pavidolide B



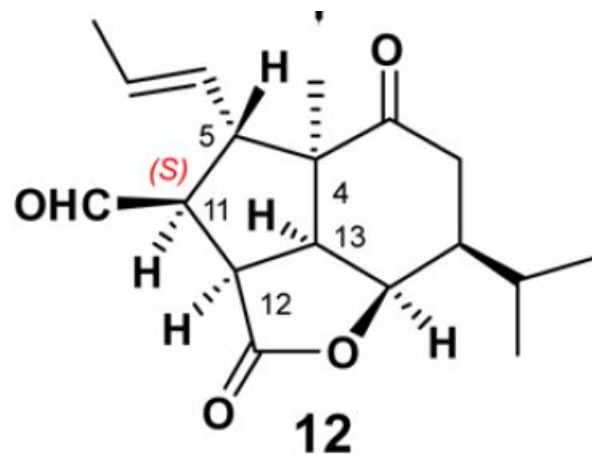
ORTEP of **12**

b)  $\text{Me}_4\text{NOH}$ , *i*-PrOH/ $\text{H}_2\text{O}$ , rt, 12 h;  
120 °C, toluene, 4 h;  
then HCl (2 M) (90%)

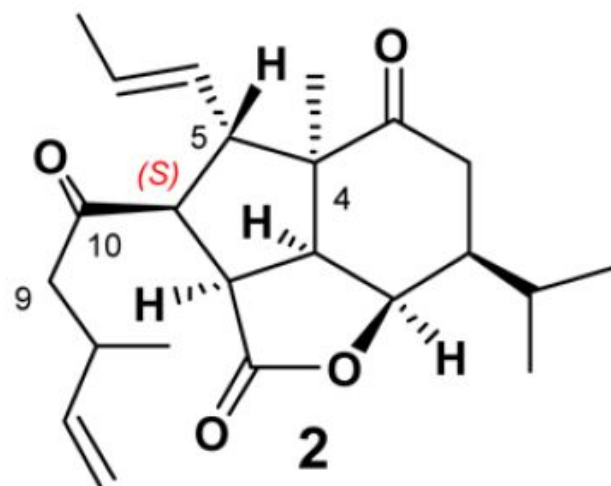


c)  $\text{Ni}(\text{acac})_2$ ,  $\text{Et}_2\text{Zn}$ , isoprene  
d) DMP,  $\text{NaHCO}_3$ ,  $\text{CH}_2\text{Cl}_2$   
(94% in 2 steps)

# Asymmetric Total Synthesis of Pavidolide B

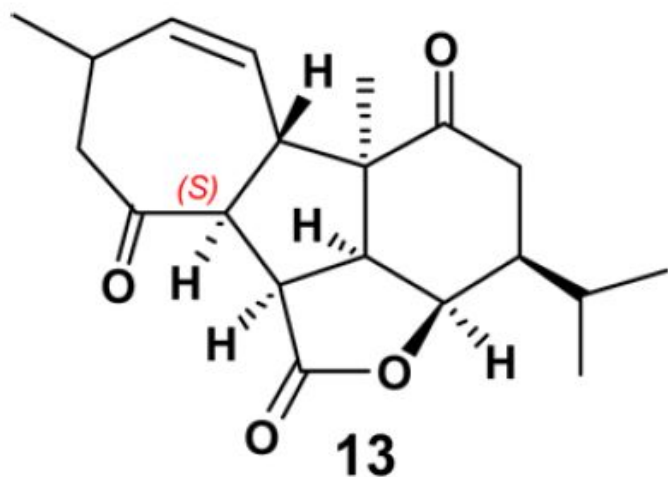


c)  $\text{Ni}(\text{acac})_2$ ,  $\text{Et}_2\text{Zn}$ , isoprene  
d) DMP,  $\text{NaHCO}_3$ ,  $\text{CH}_2\text{Cl}_2$   
(94% in 2 steps)

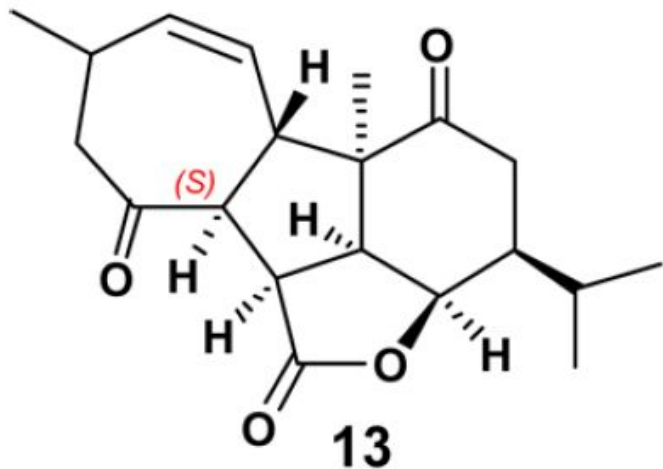


e) Grubbs II,  $\text{CH}_2\text{Cl}_2$

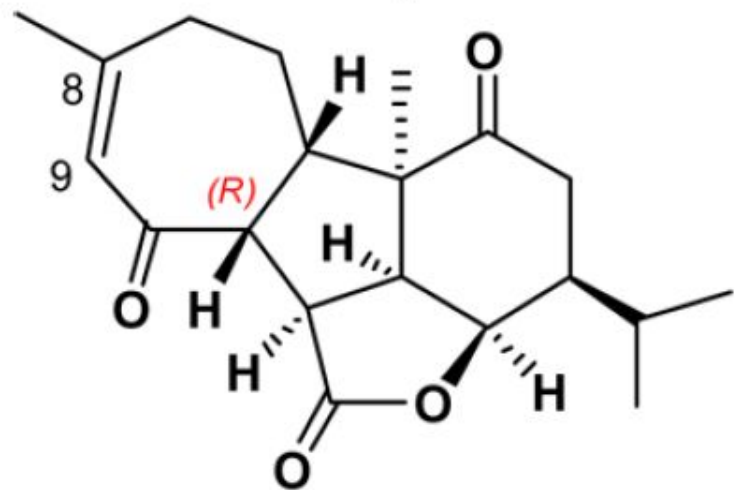
reflux  
(85%)



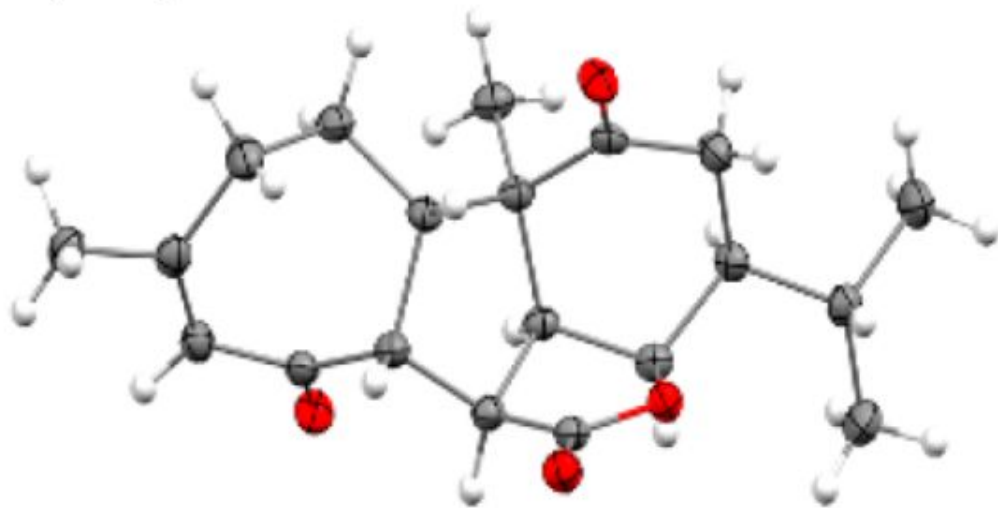
# Asymmetric Total Synthesis of Pavidolide B



f)  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , EtOH/ $\text{CH}_2\text{Cl}_2$   
100 °C, sealed tube (95%)



Pavidolide B (**1**)



ORTEP of **1**