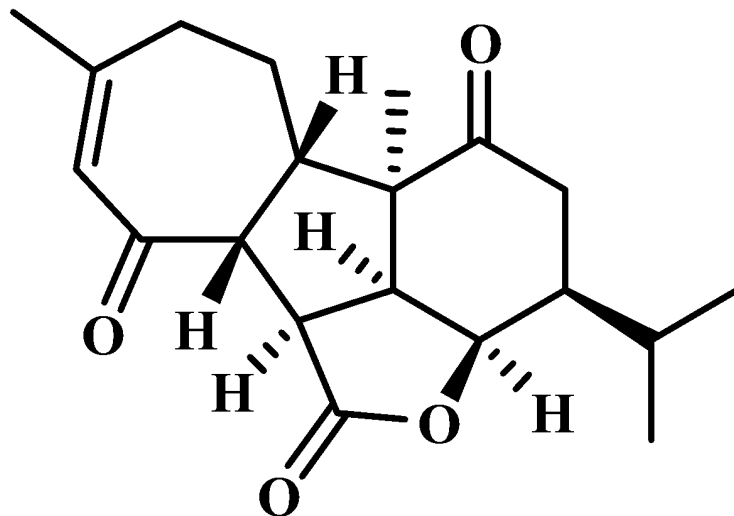


Enantioselective Total Synthesis of (–)-Pavidolide B

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

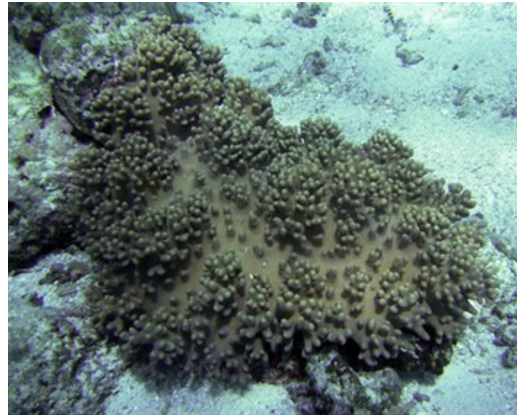
J. Am. Chem. Soc., 2017, 139, 13989–13992



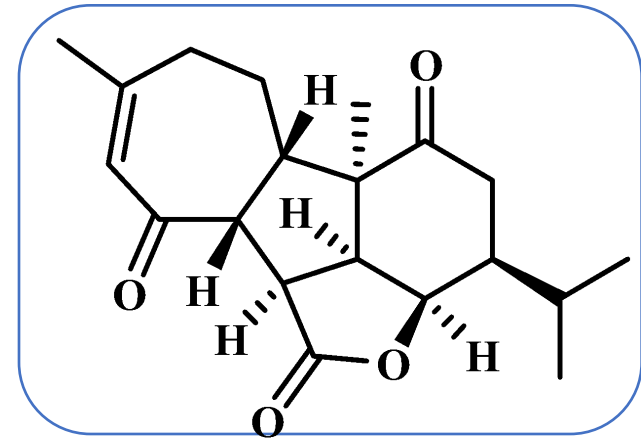
аспирант ИОХ РАН
Радулов П.С.



Leen van Ofwegen

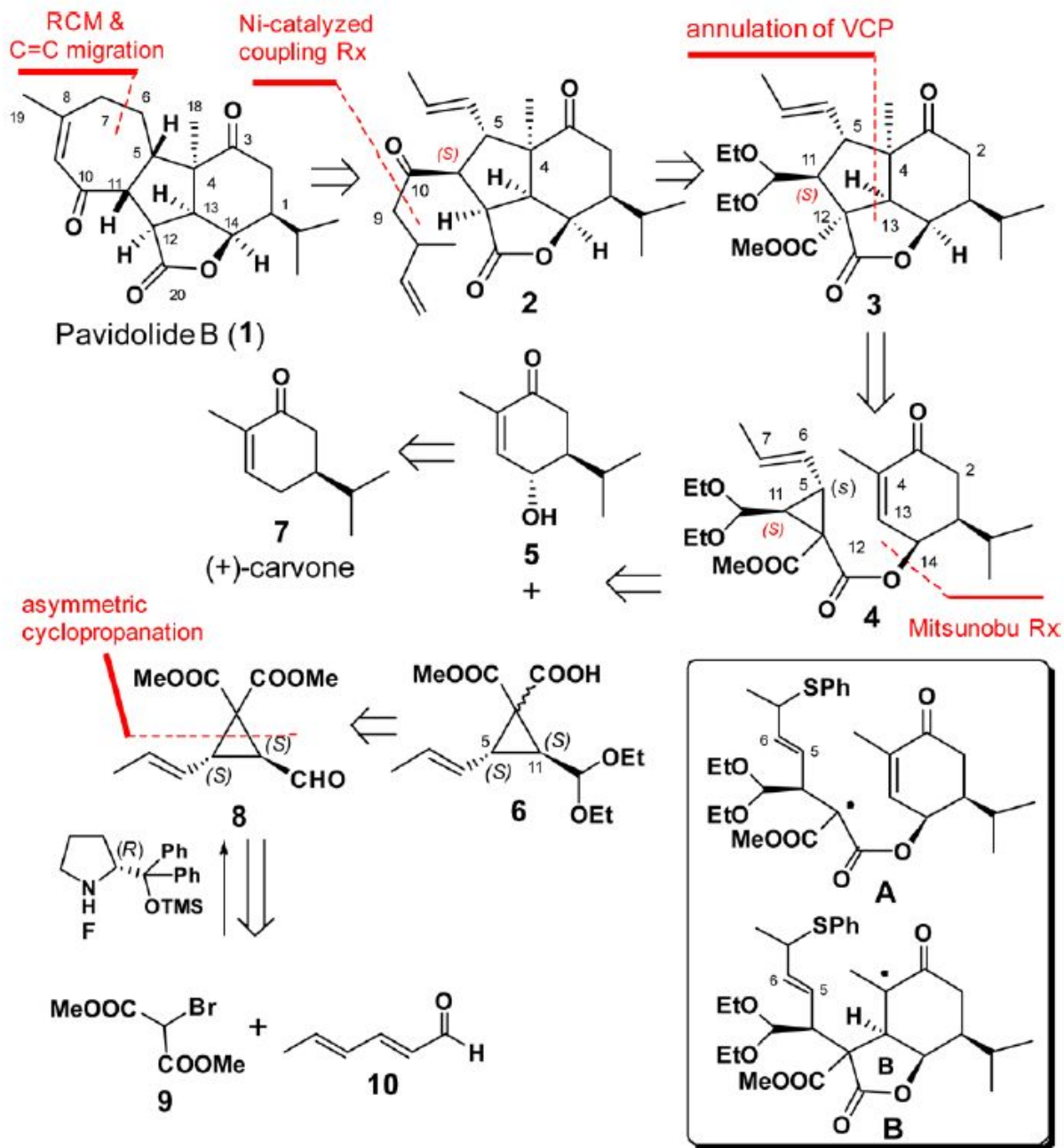


Sinularia pavidia

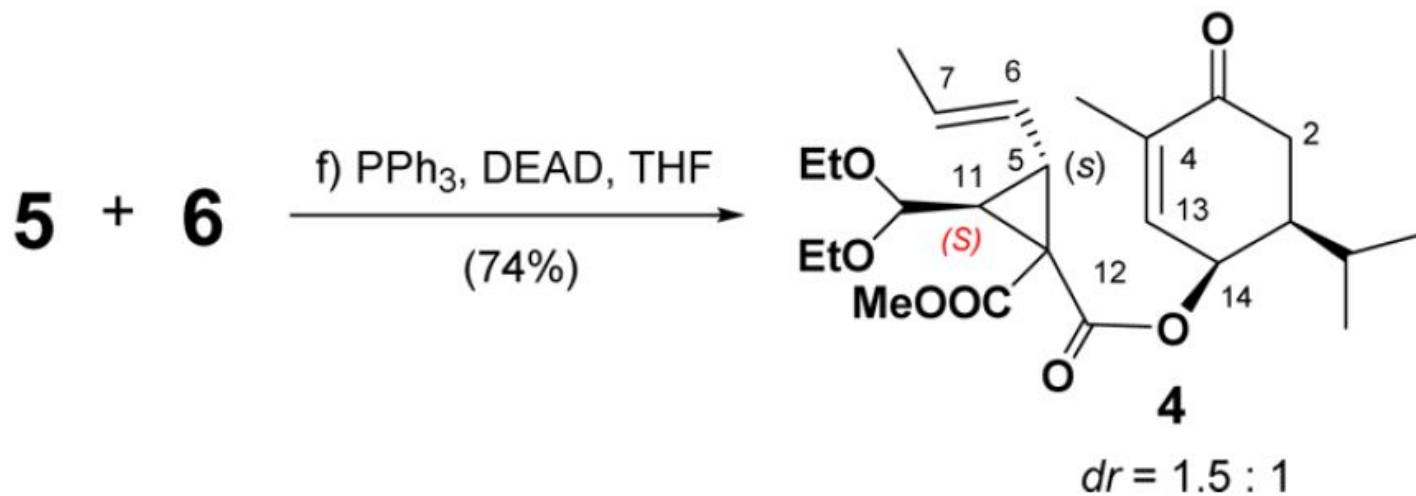
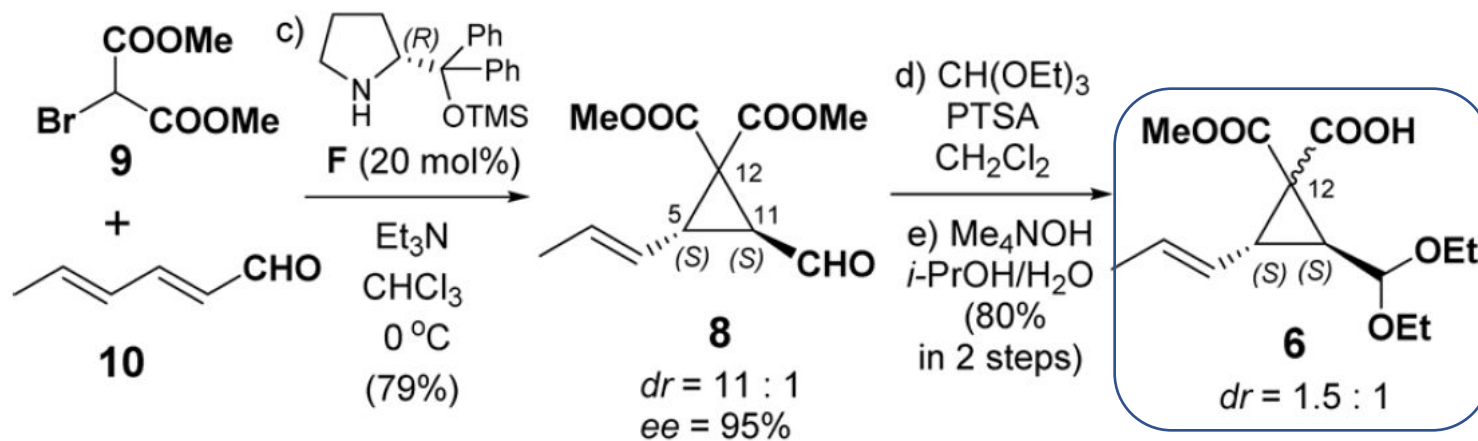
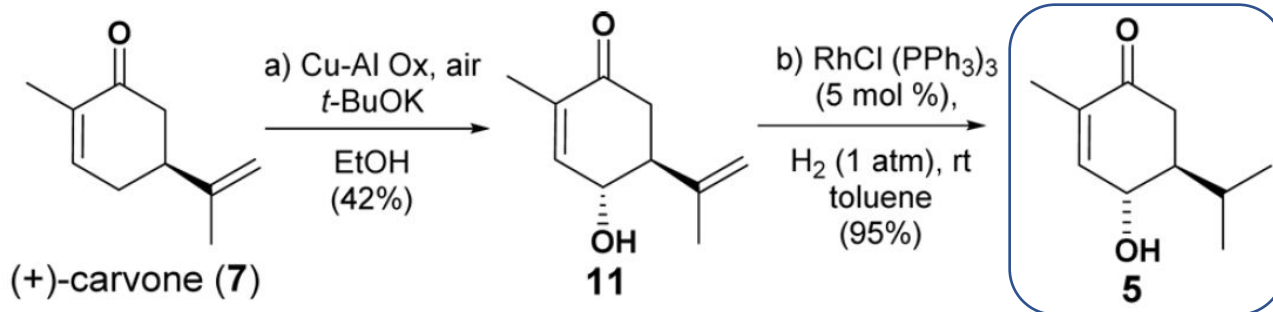


(-)-Pavidolide B

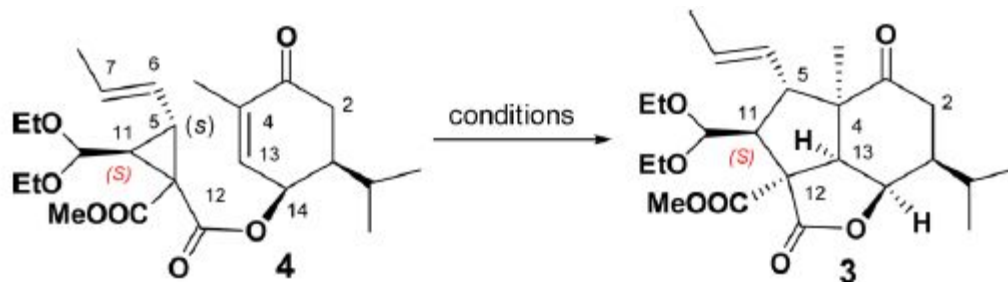
Retrosynthetic analysis of pavidolide B



Asymmetric Synthesis of Precursor 4

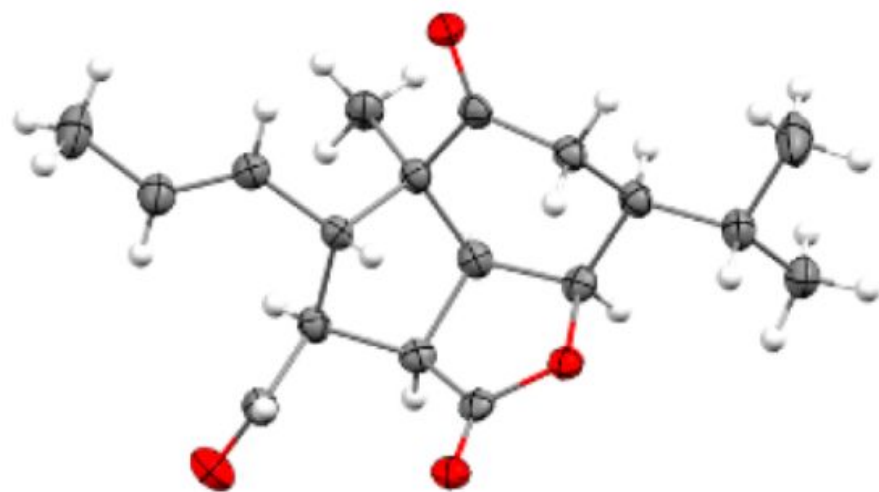
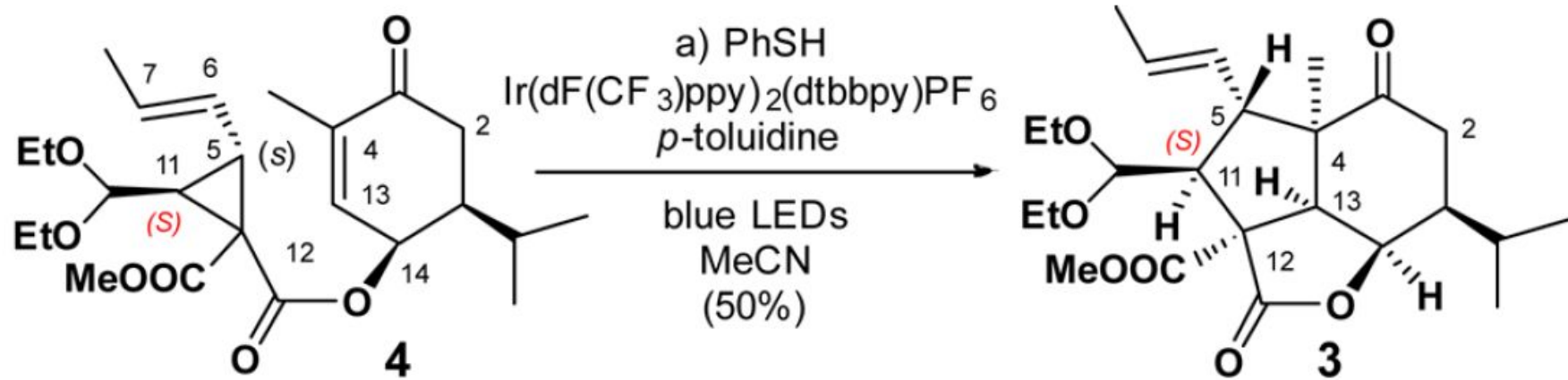


Screening of the Reaction Conditions



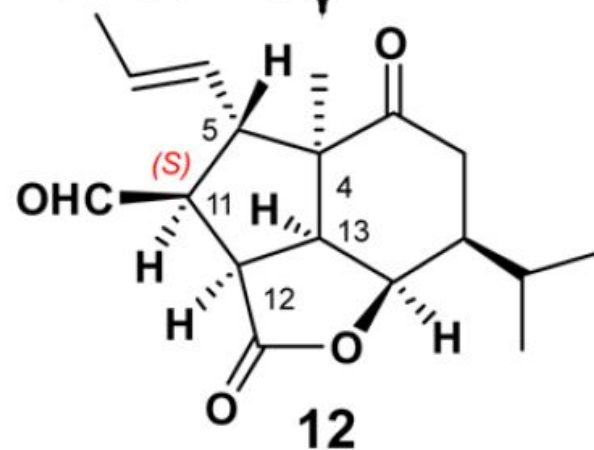
entry	conditions	solvent	temp (°C)	time (h)	yield ^a
1	PhSH, AIBN	toluene	60	9	trace
2	PhSH, AIBN	toluene	80	6	32%
3	PhSH, AIBN	toluene	100	3	31%
4	PhSH, AIBN	toluene	120	3	35%
5	PhSSPh, AIBN, UV (250 W)	toluene	25	5	32%
6	PhSSPh, AIBN, UV (250 W), AlMe ₃	toluene	25	3	40–48%
7	PhSSPh, BPO, ^b UV(250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

Asymmetric Total Synthesis of Pavidolide B



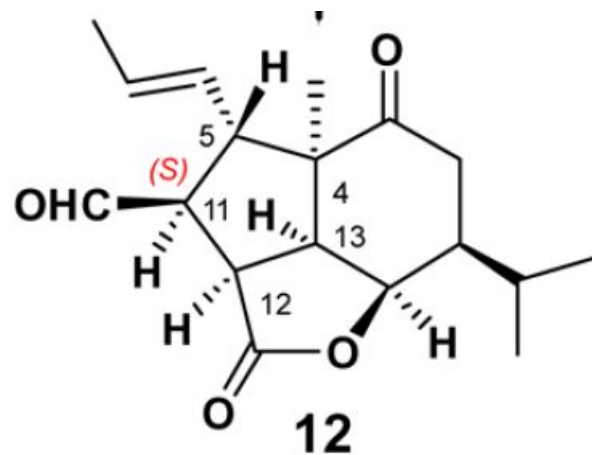
ORTEP of 12

b) Me_4NOH , *i*-PrOH/ H_2O , rt, 12 h;
120 °C, toluene, 4 h;
then HCl (2 M) (90%)

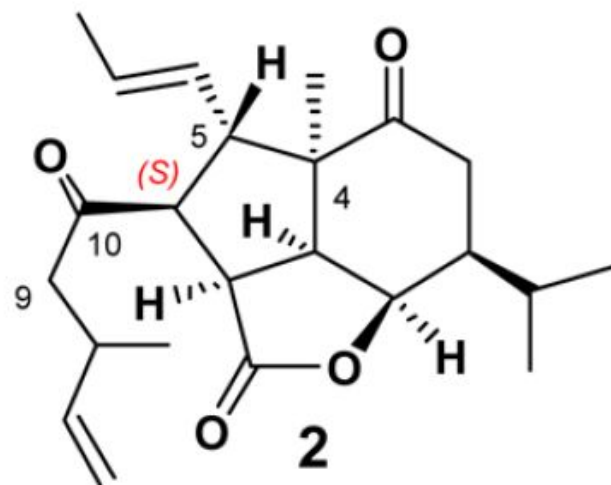


c) $\text{Ni}(\text{acac})_2$, Et_2Zn , isoprene
d) DMP, NaHCO_3 , CH_2Cl_2
(94% in 2 steps)

Asymmetric Total Synthesis of Pavidolide B

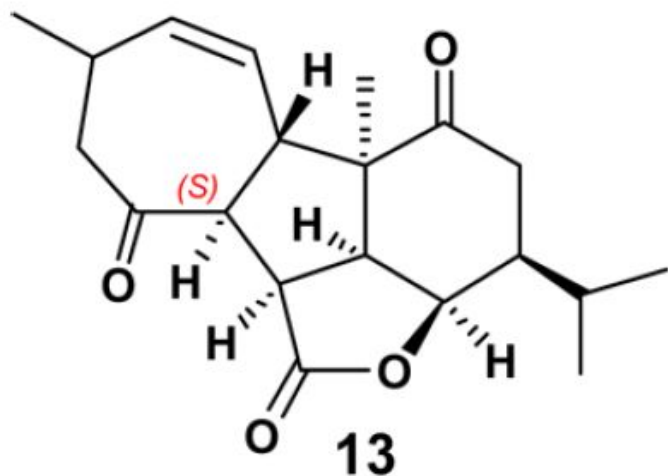


c) $\text{Ni}(\text{acac})_2$, Et_2Zn , isoprene
d) DMP, NaHCO_3 , CH_2Cl_2
(94% in 2 steps)

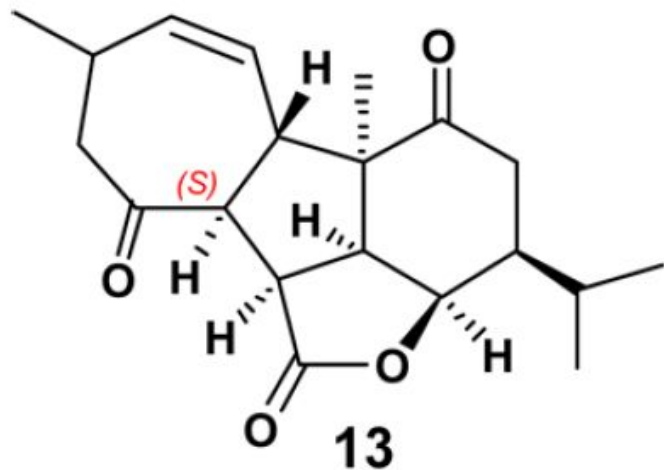


e) Grubbs II, CH_2Cl_2

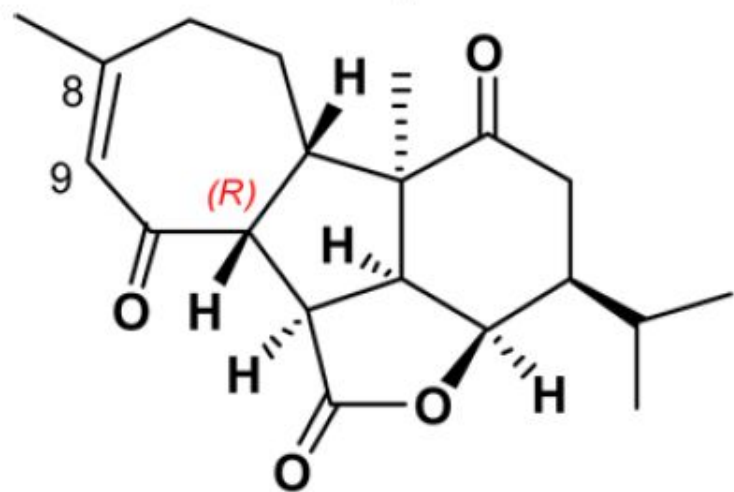
reflux
(85%)



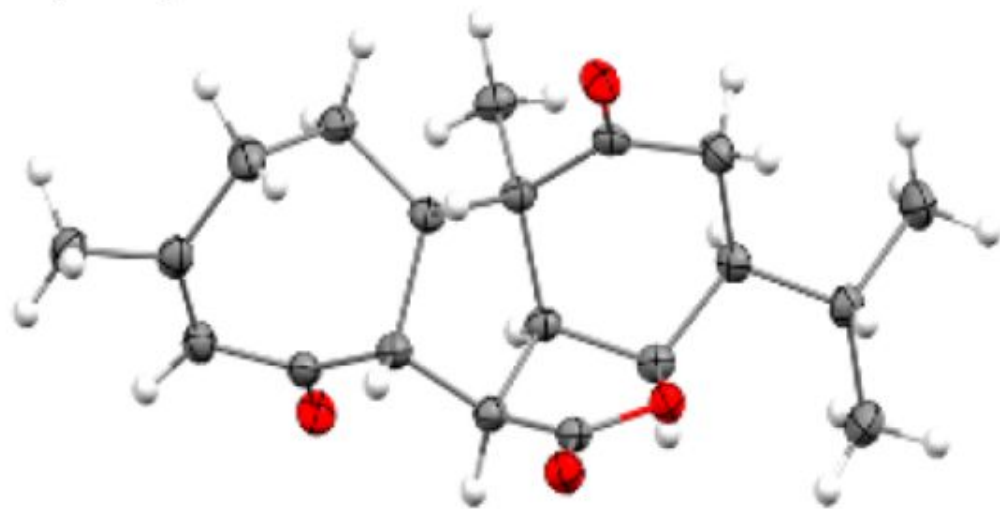
Asymmetric Total Synthesis of Pavidolide B



f) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, EtOH/ CH_2Cl_2
100 °C, sealed tube (95%)



Pavidolide B (**1**)



ORTEP of **1**