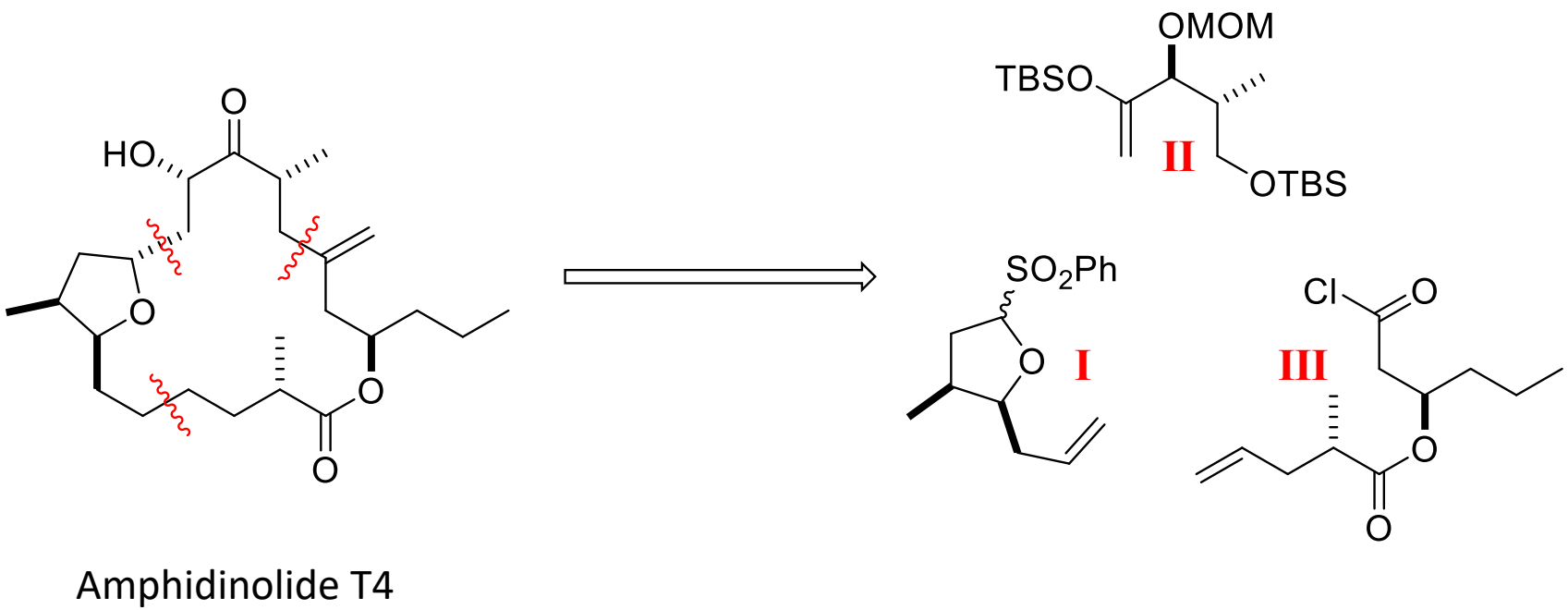
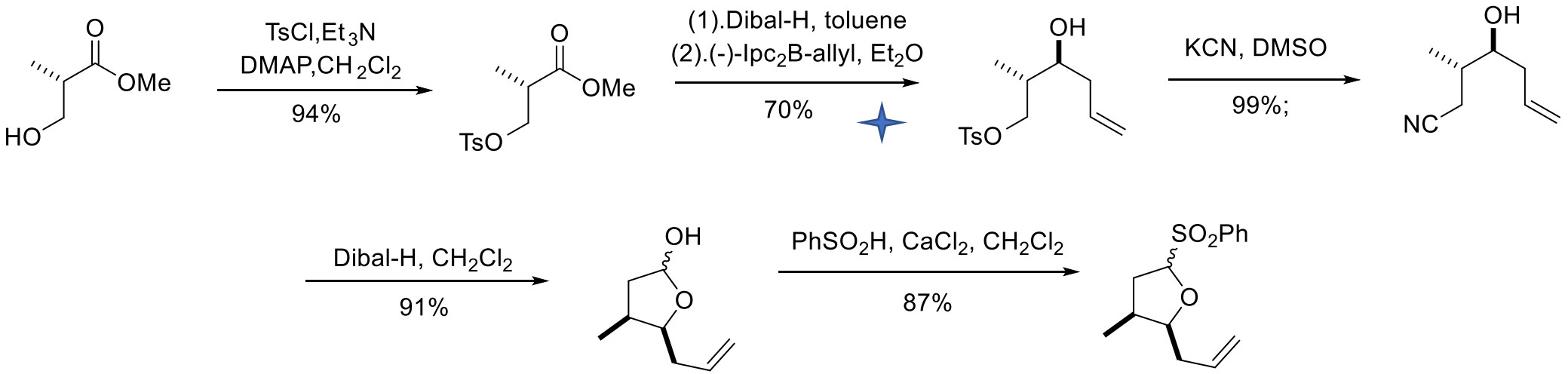
Total Synthesis of Amphidinolide T4



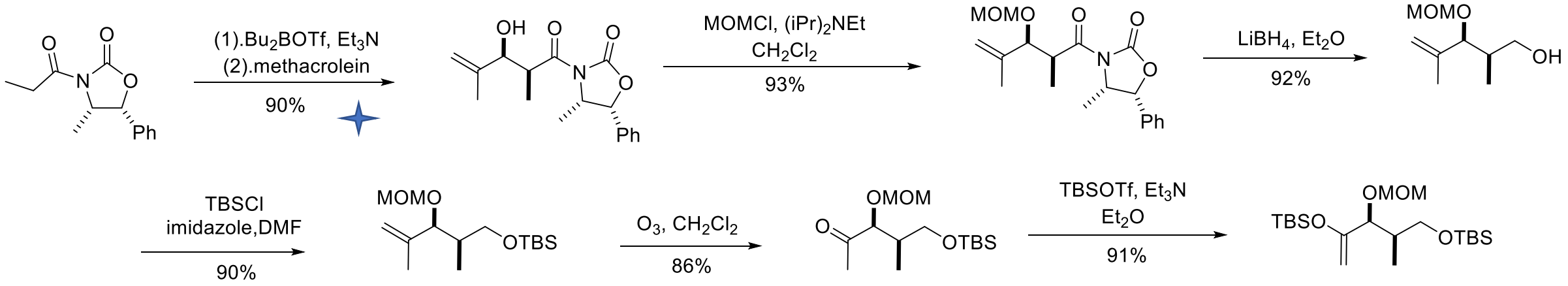
Amphidinolide T4

Fürstner A, Aïssa C, Riveiros R, et al. Total synthesis of amphidinolide T4[J]. Angewandte Chemie International Edition, 2002, 41(24): 4763-4766.

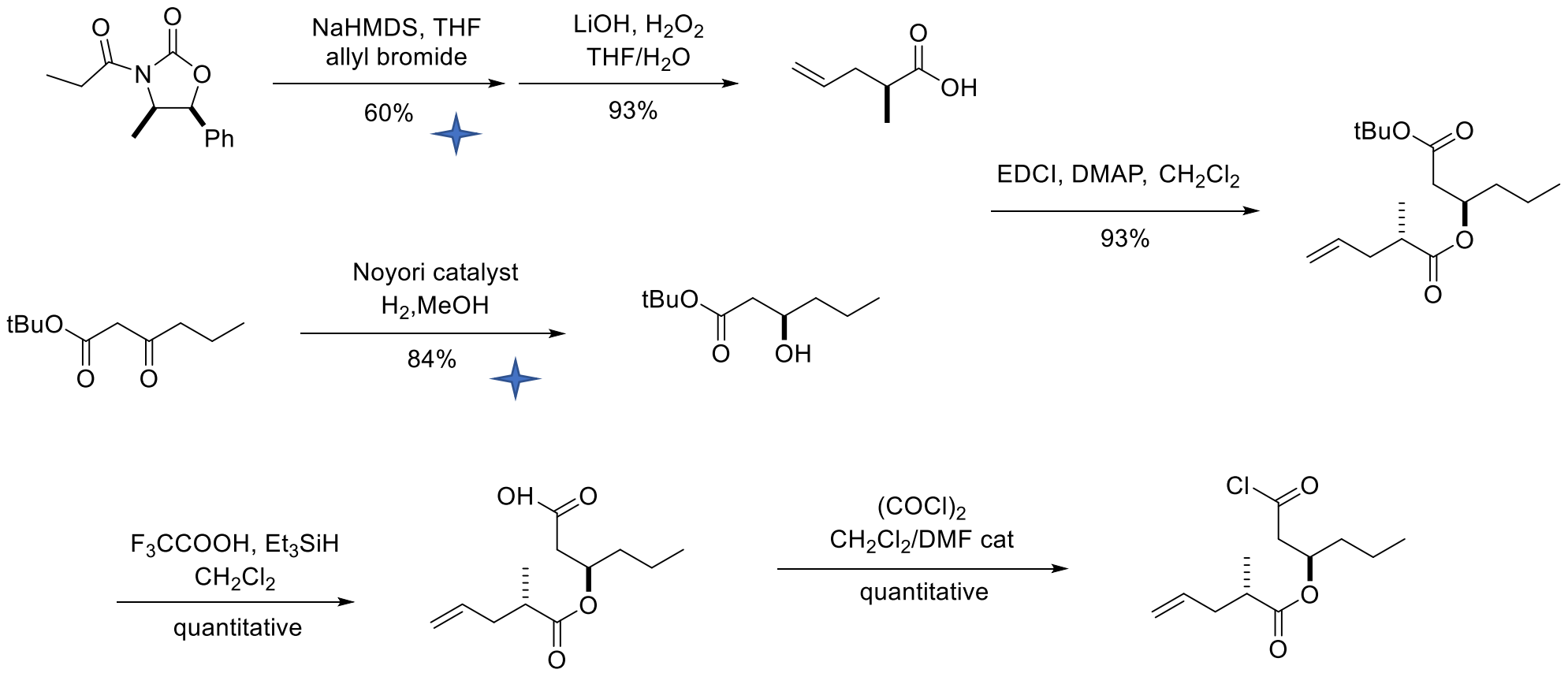
Synthesis of segment I



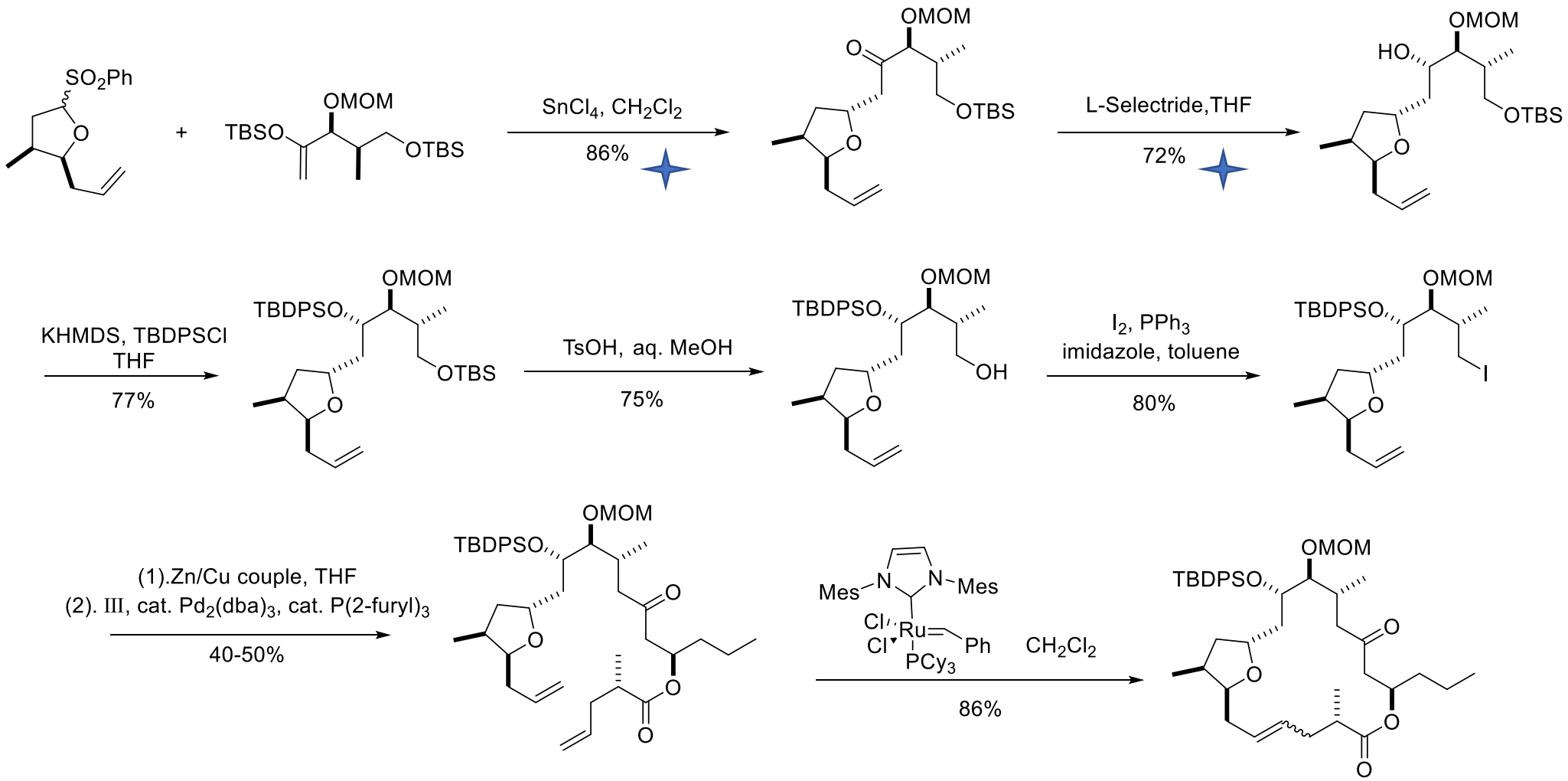
Synthesis of segment II



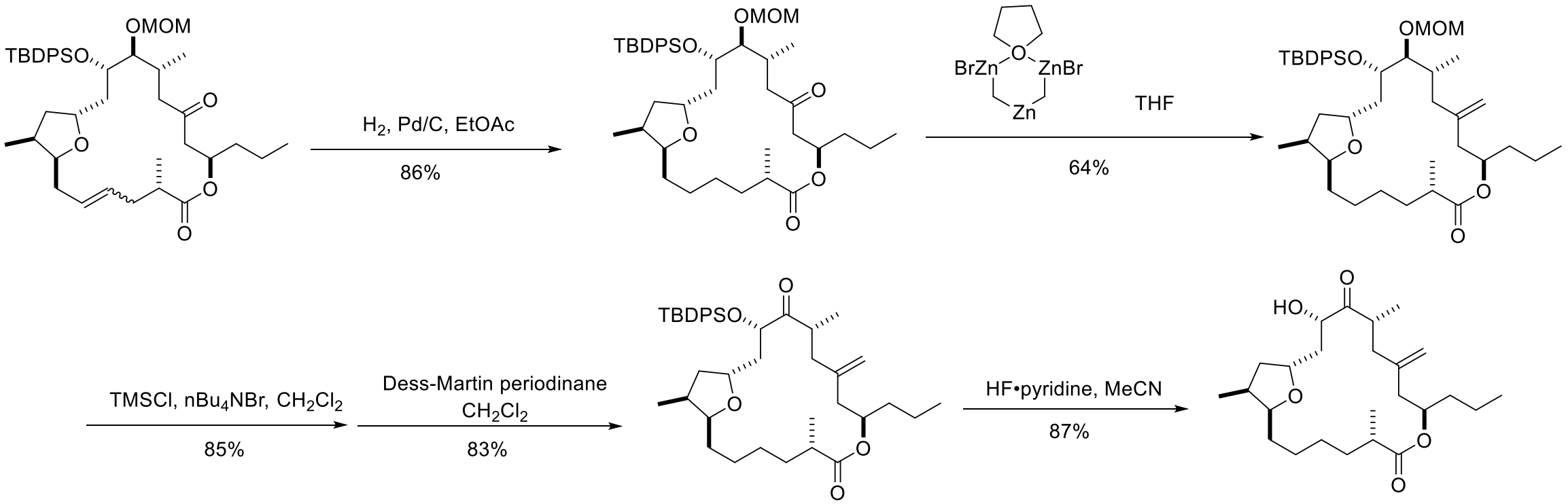
Synthesis of segment III



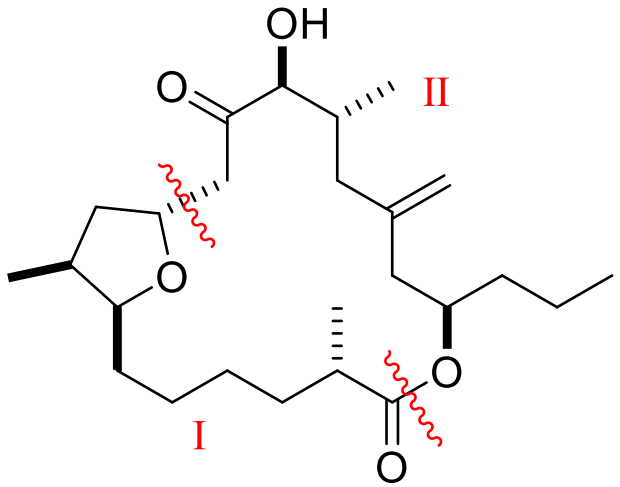
Fragment coupling & Completion of the total synthesis



Fragment coupling & Completion of the total synthesis

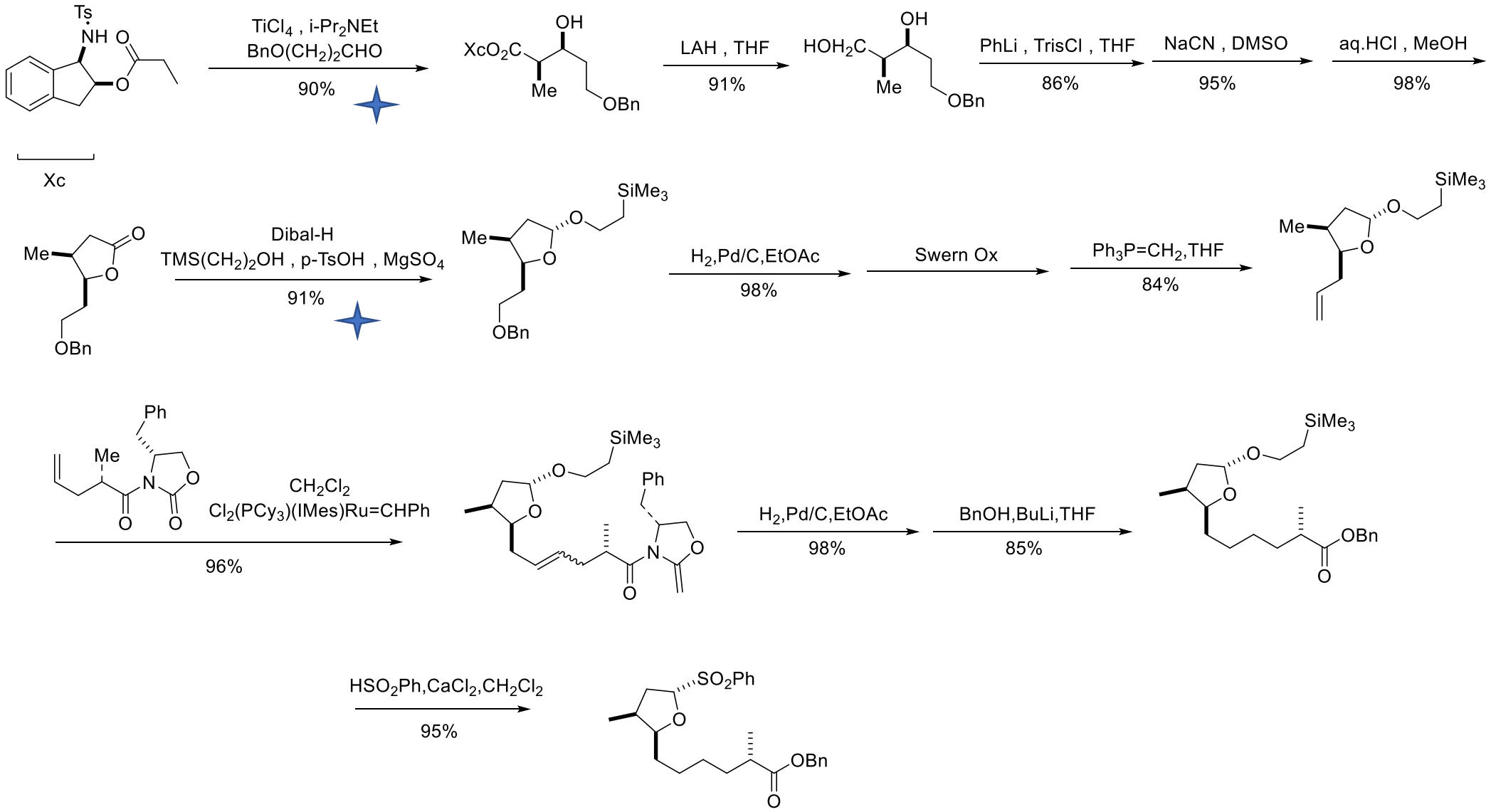


Enantioselective Total Synthesis of (+)-Amphidinolide T1

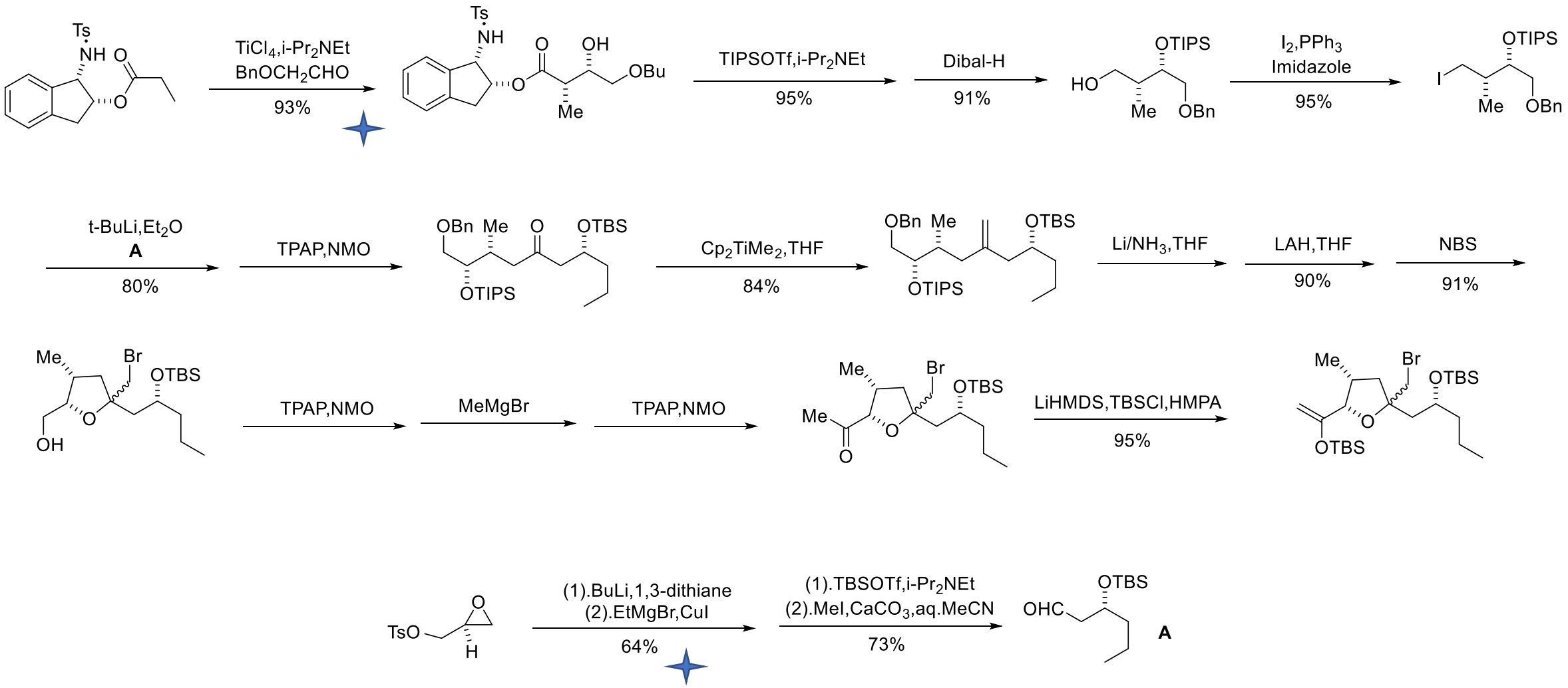


Ghosh A K, Liu C. Enantioselective total synthesis of (+)-amphidinolide T1[J]. Journal of the American Chemical Society, 2003, 125(9): 2374-2375.

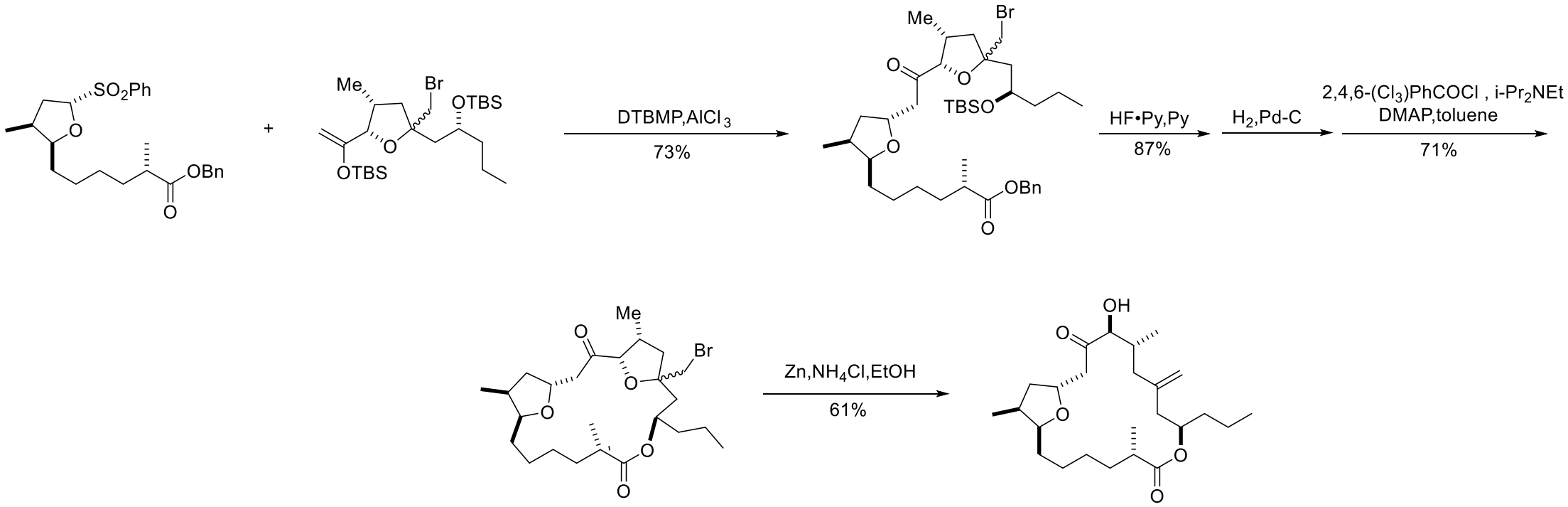
Synthesis of segment I



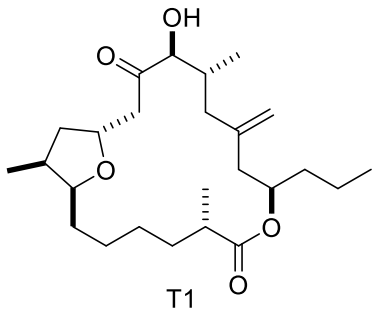
Synthesis of segment II

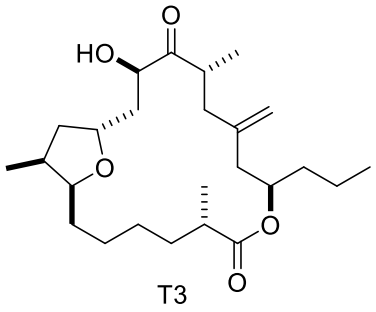


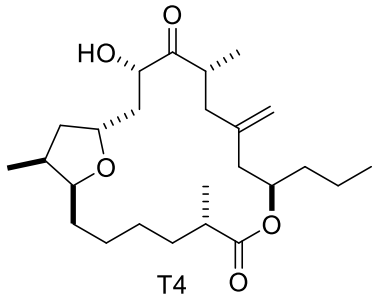
Fragment coupling & Completion of the total synthesis

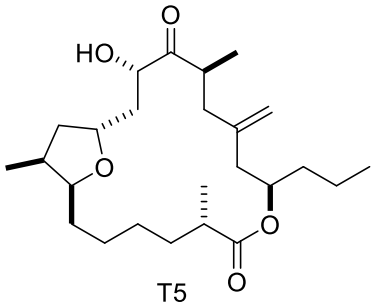


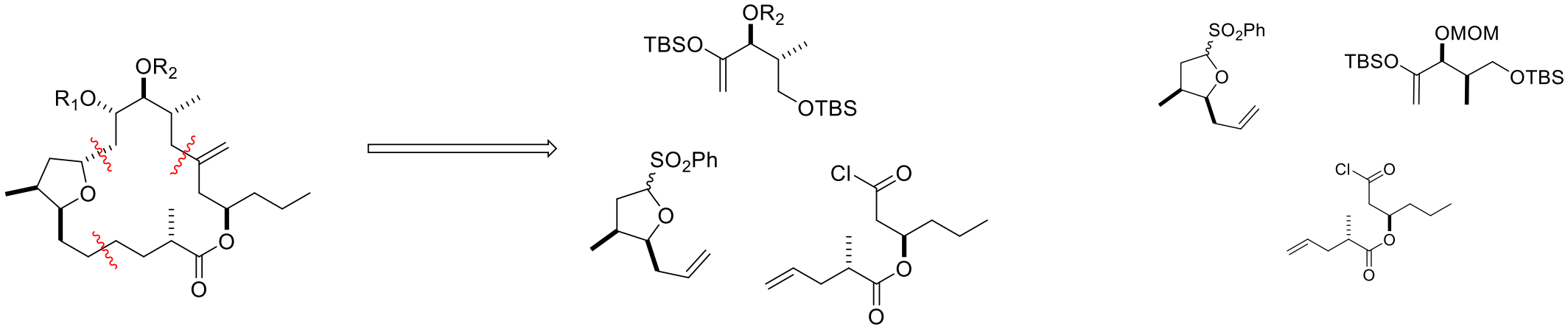
Total Syntheses of Amphidinolide T1, T3, T4, and T5





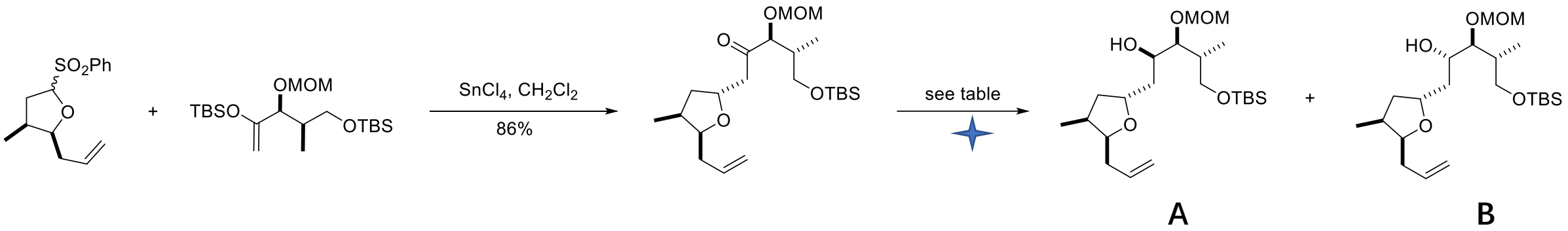






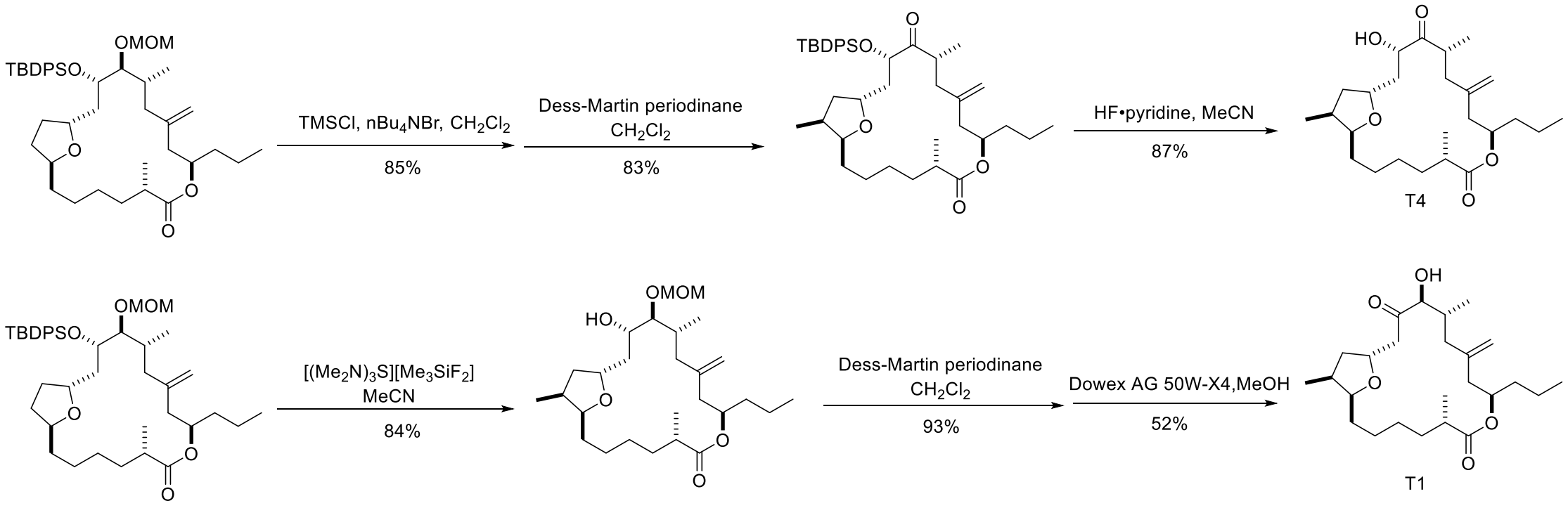
Aïssa C, Riveiros R, Ragot J, et al. Total syntheses of amphidinolide T1, T3, T4, and T5[J]. Journal of the American Chemical Society, 2003, 125(50): 15512-15520.

Fragment coupling

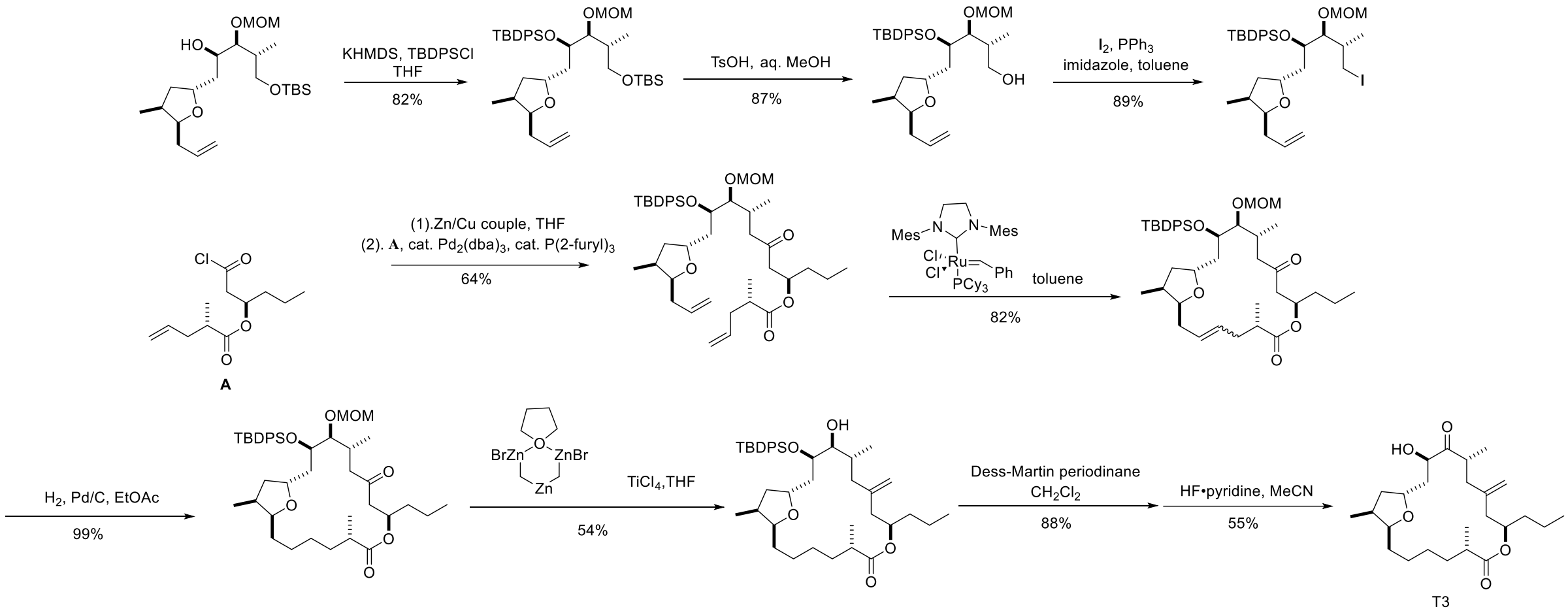


entry	Reducing agent	T/℃	A yield/%	B yield/%
1	L-Selectride	-78	3	72
2	$LiHBEt_3$	-78 to rt	32	19
3	$LiAlH_4$ (5 equiv.)+LiI (10 equiv.)	-100	70	11

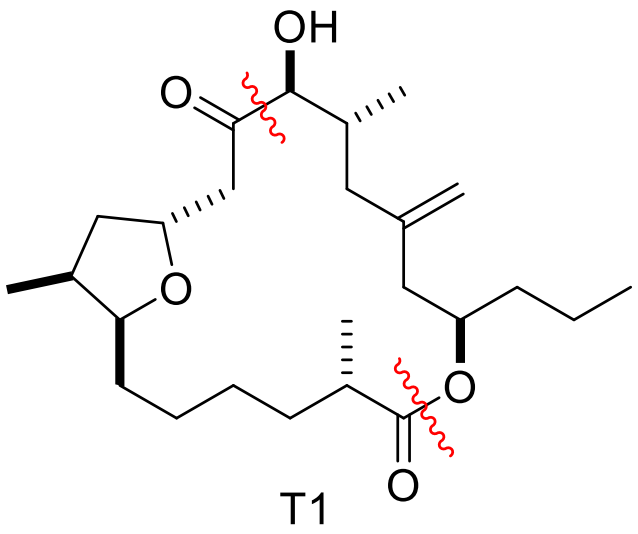
Completion of the total synthesis



Completion of the total synthesis



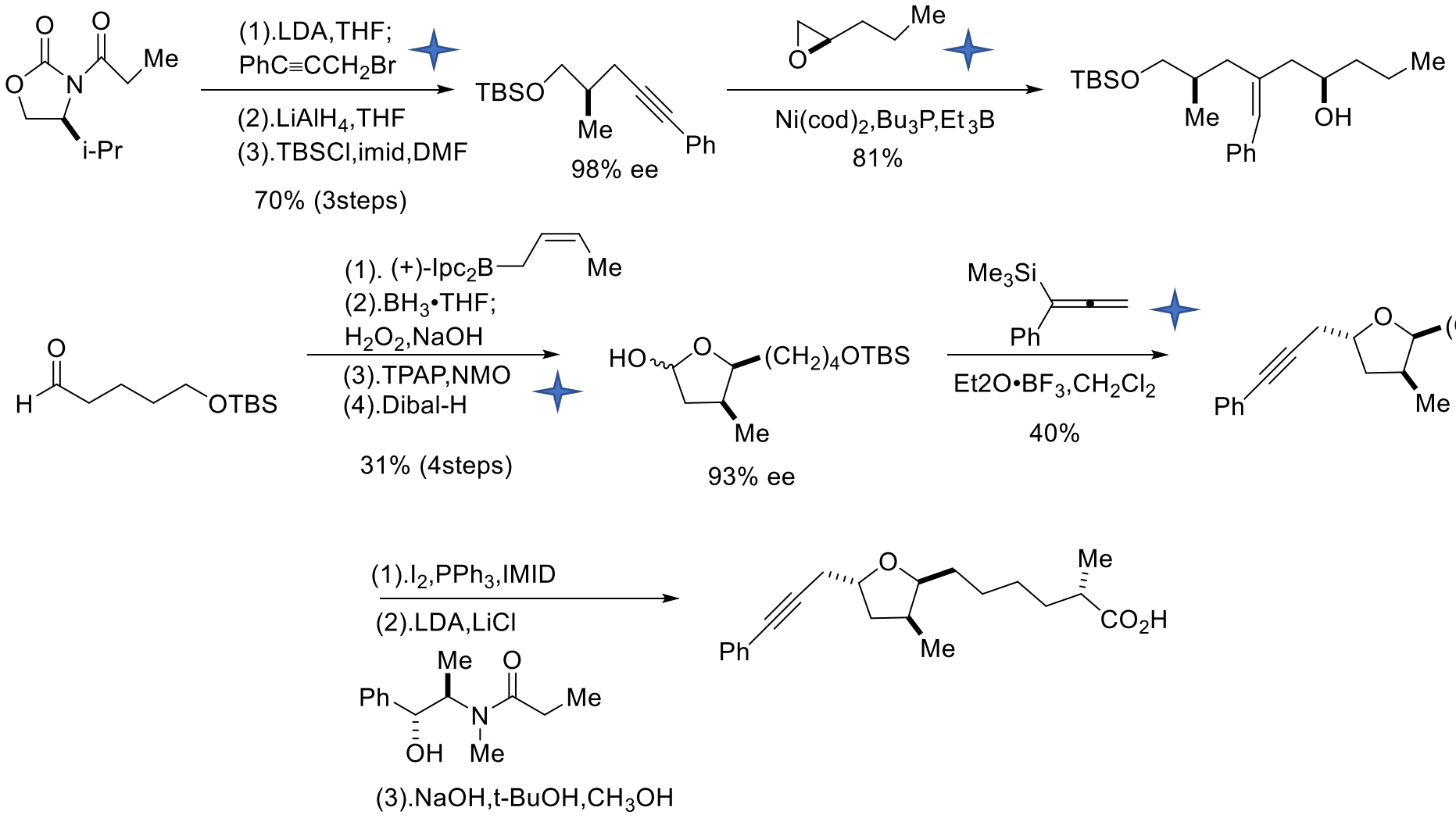
Synthesis of Amphidinolide T1 via Catalytic, Stereoselective Macrocyclization



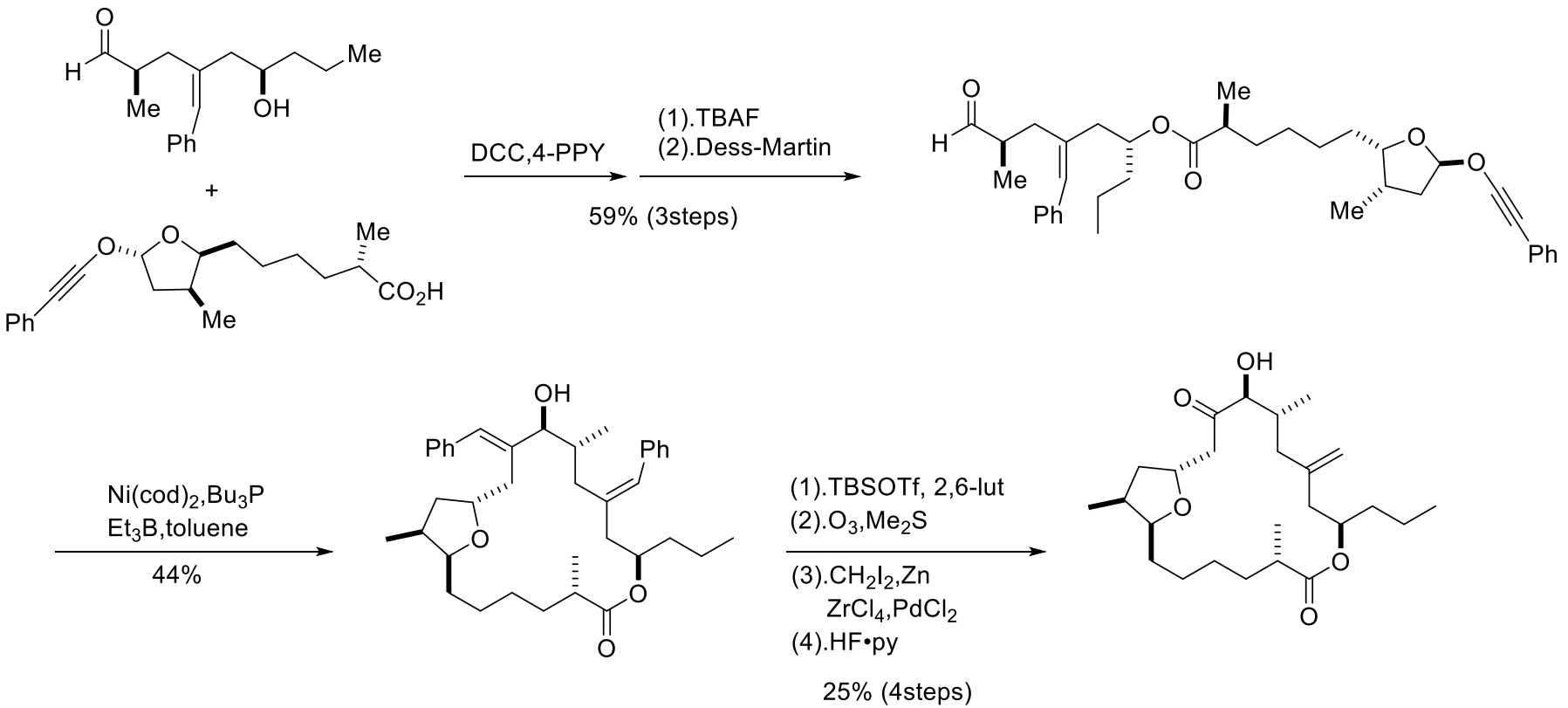
T1

Colby E A, O'Brie K C, Jamison T F. Synthesis of amphidinolide T1 via catalytic, stereoselective macrocyclization[J]. Journal of the American Chemical Society, 2004, 126(4): 998-999.

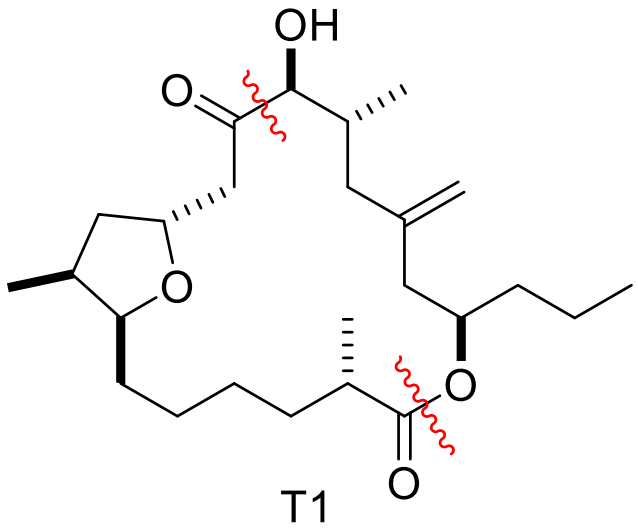
Synthesis of segment



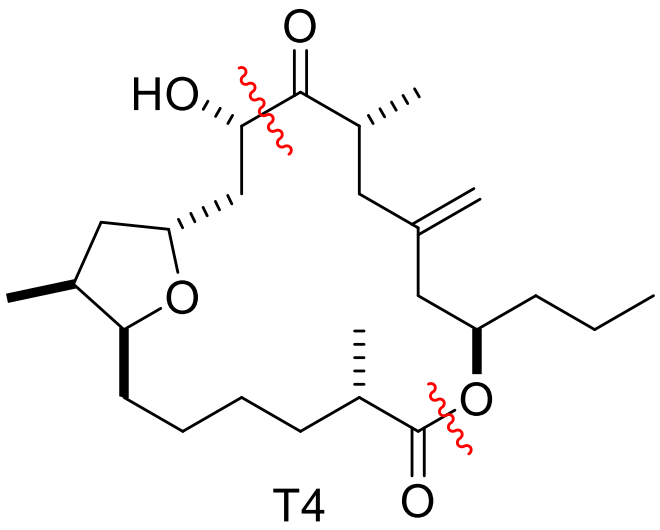
Fragment coupling & Completion of the total synthesis



Total Syntheses of Amphidinolides T1 and T4 via Catalytic, Stereoselective, Reductive Macrocyclizations



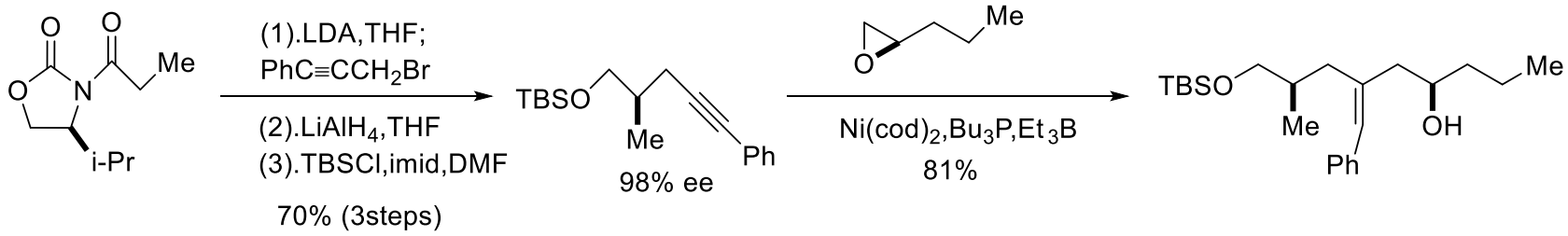
T1

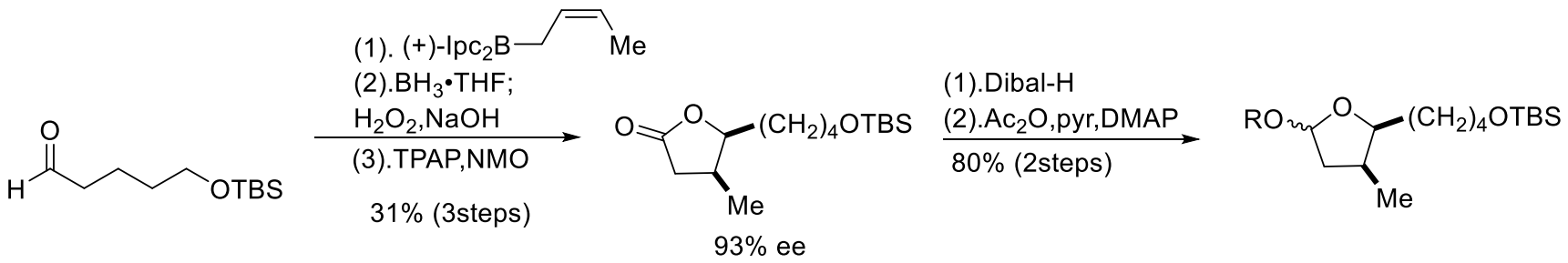


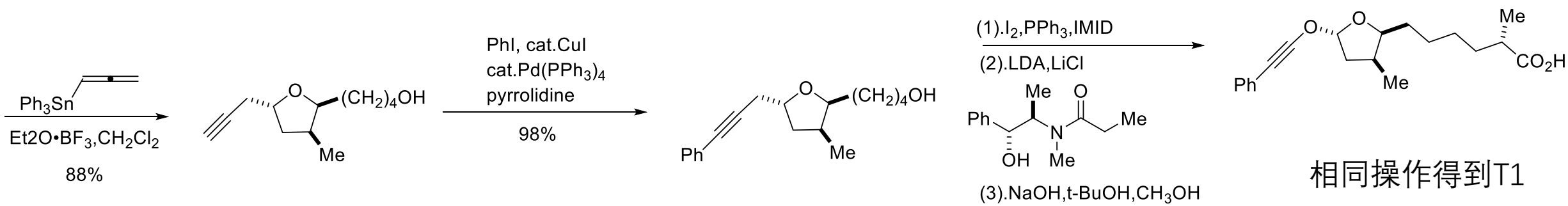
T4

Colby E A, O'Brie K C, Jamison T F. Total syntheses of amphidinolides T1 and T4 via catalytic, stereoselective, reductive macrocyclizations[J]. Journal of the American Chemical Society, 2005, 127(12): 4297-4307.

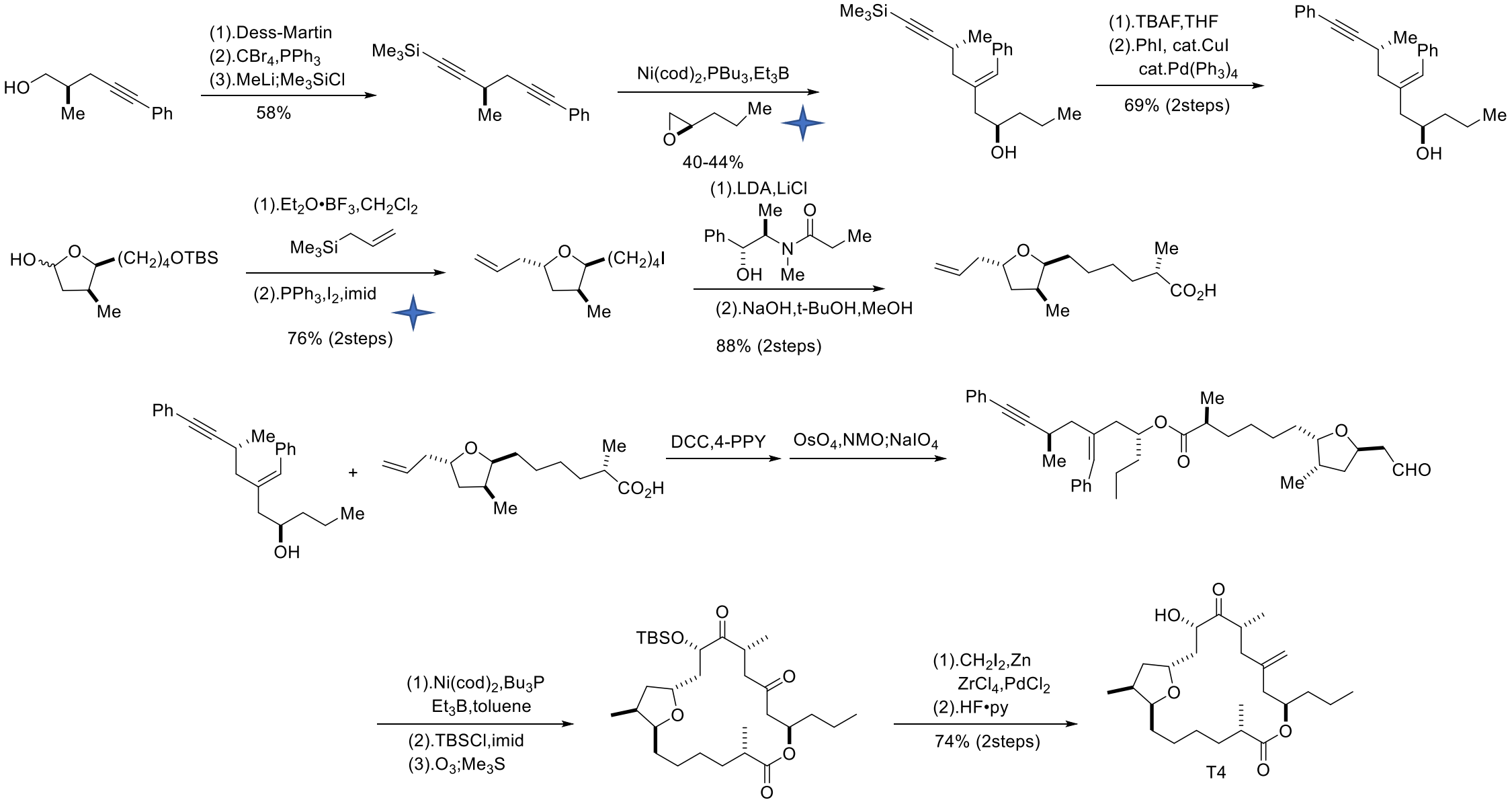
Synthesis of segment



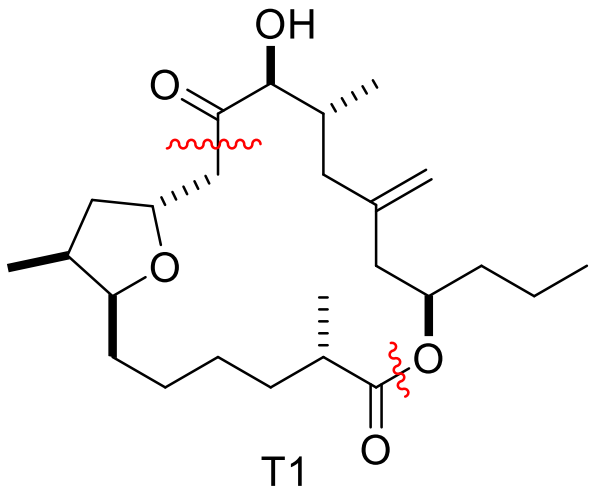




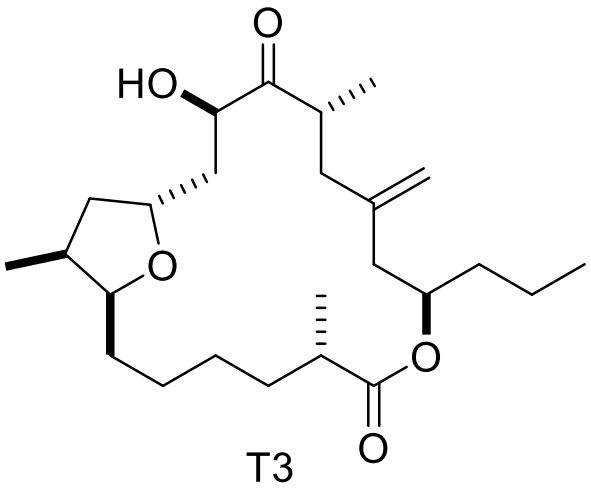
Fragment coupling & Completion of the total synthesis



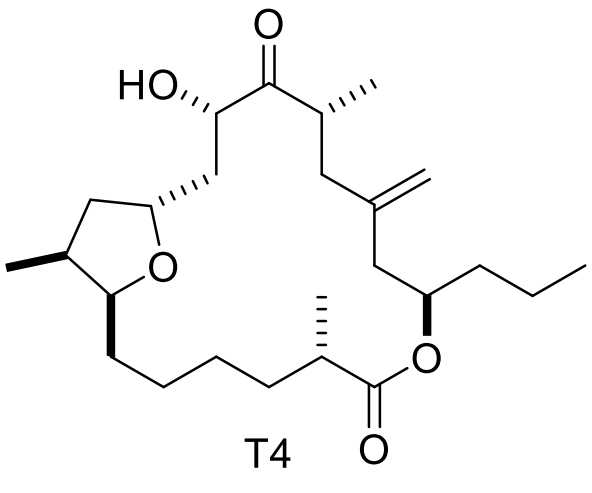
Total Syntheses of Amphidinolides T1, T3, and T4



T1



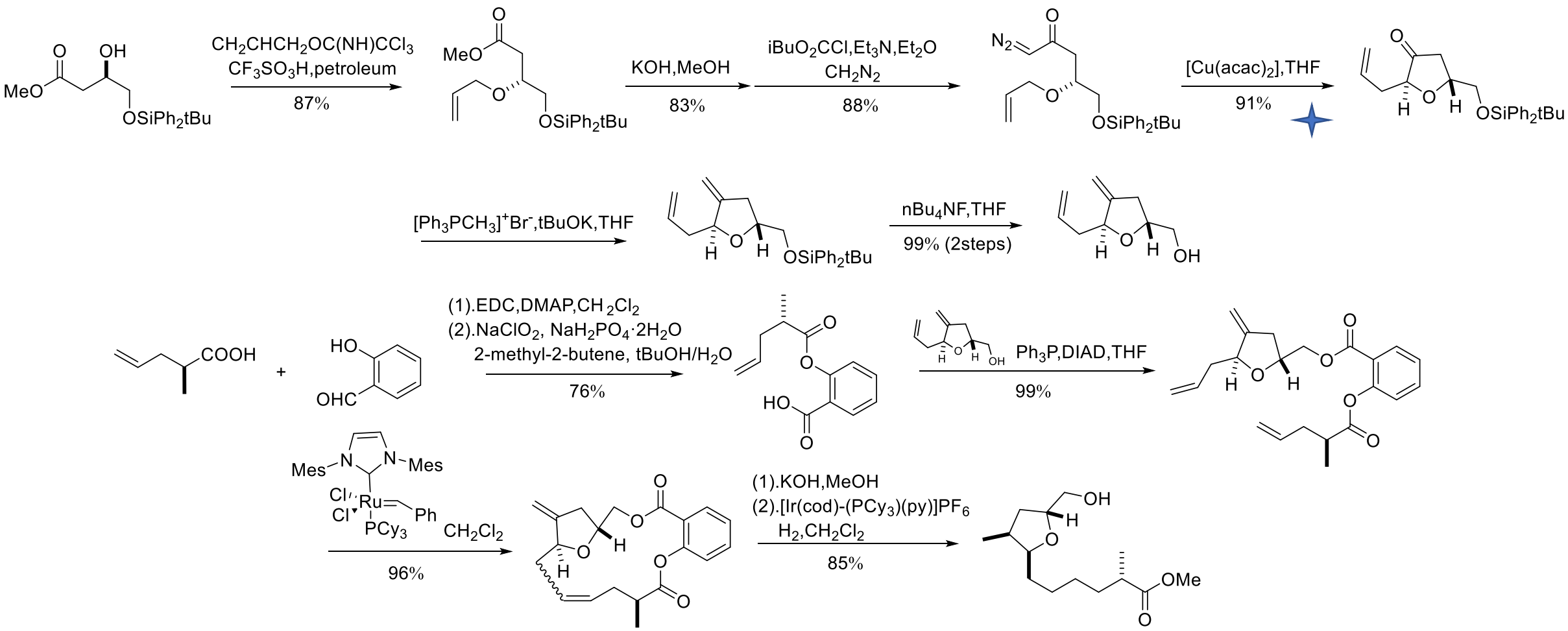
T3



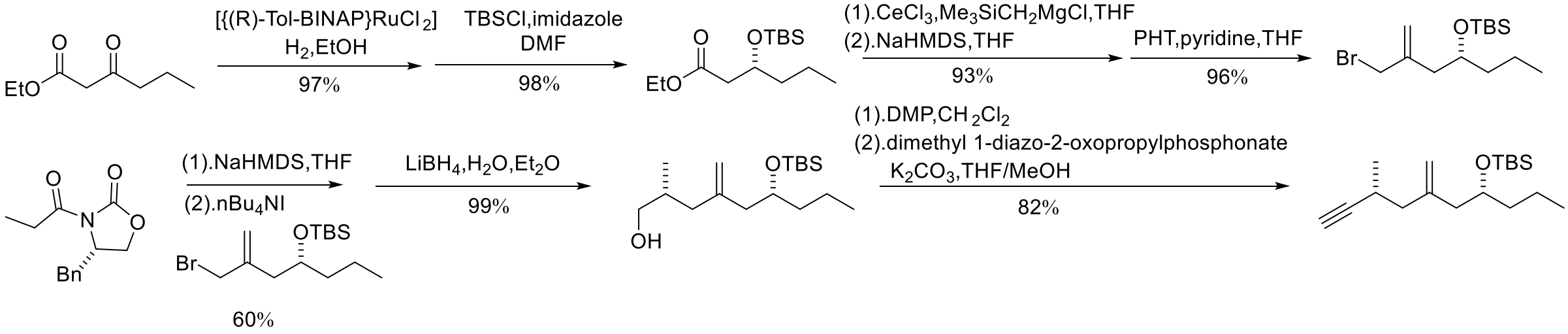
T4

Clark J S, Romiti F. Total syntheses of amphidinolides T1, T3, and T4[J]. Angewandte Chemie, 2013, 125(38): 10256-10259.

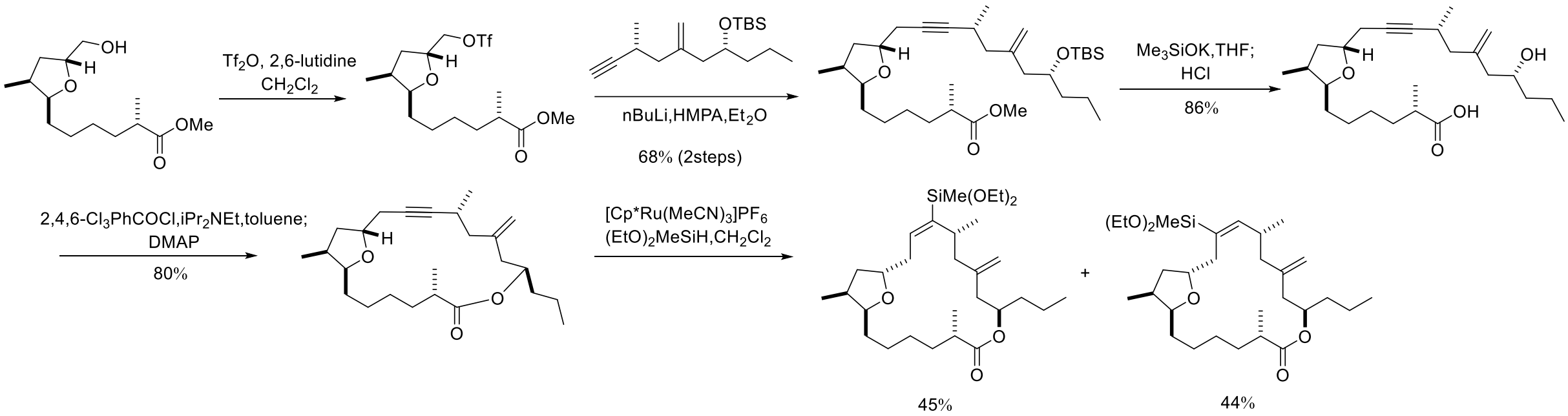
Synthesis of segment



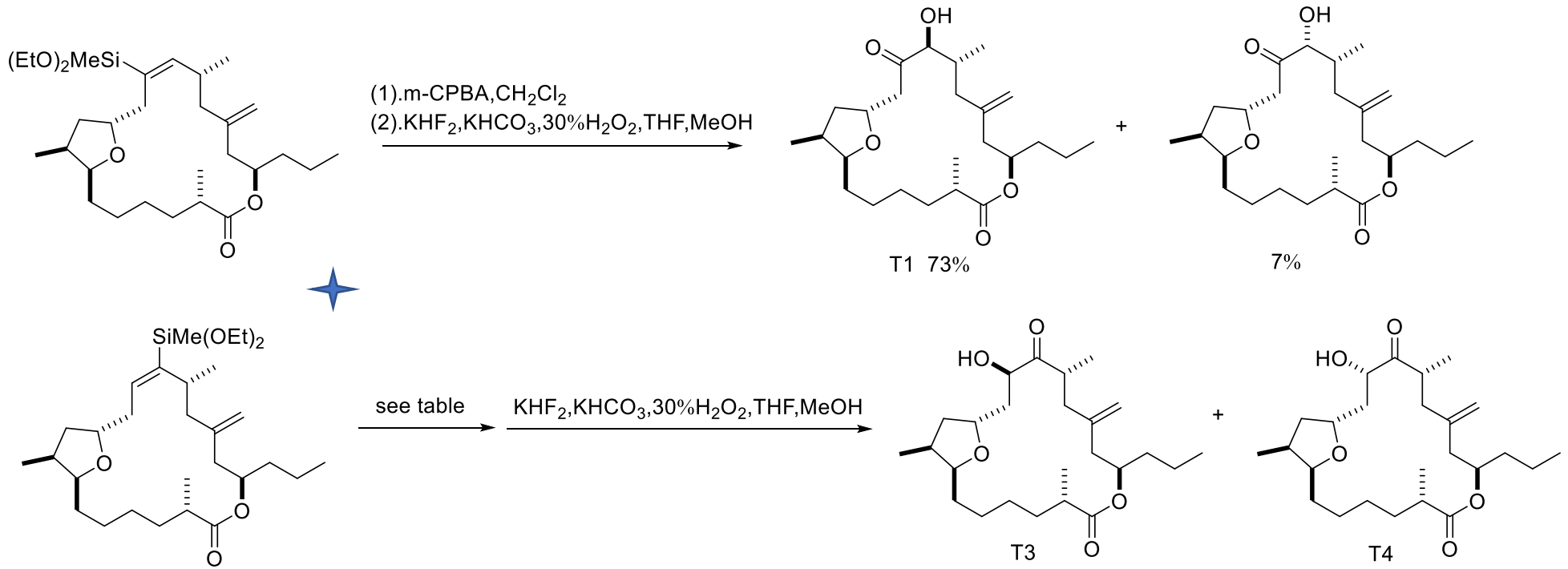
Synthesis of segment

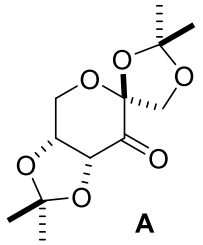


Fragment coupling & Completion of the total synthesis



Fragment coupling & Completion of the total synthesis



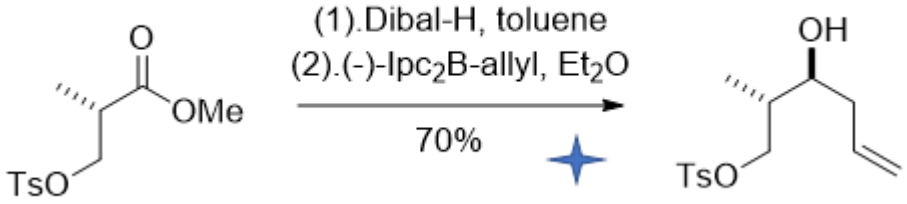


Epoxidation conditions	Oxidant	T3 Yield	T4 Yield
Ⅰ	m-CPBA	30%	49%
Ⅱ	A , Oxone	61%	--
Ⅱ	ent-A , Oxone	--	57%

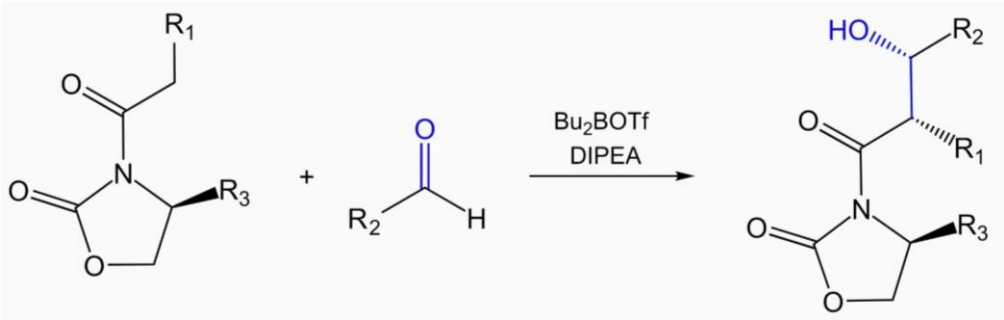
Ⅰ: oxidant, CH_2Cl_2

Ⅱ: oxidant, $Na_2B_4O_7 \cdot 10H_2O$, nBu_4NHSO_4, $KHCO_3$, Na_2EDTA, H_2O, MeCN, DMM

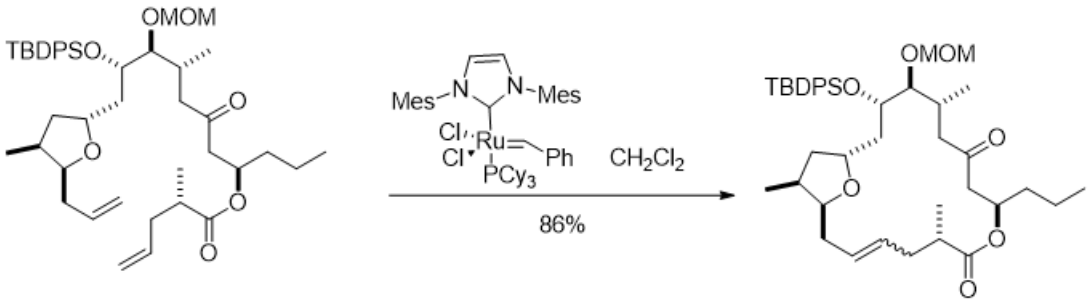
1.醛的烯丙基化



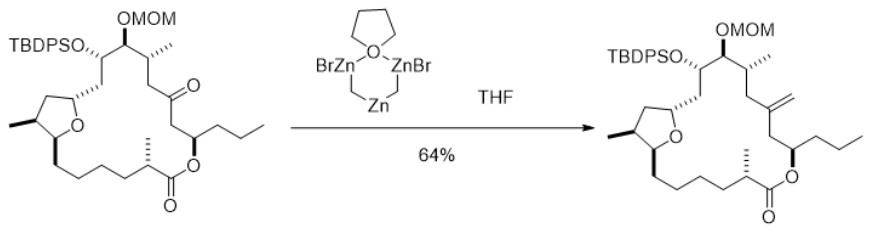
2.Evans Asymmetric Aldol Addition

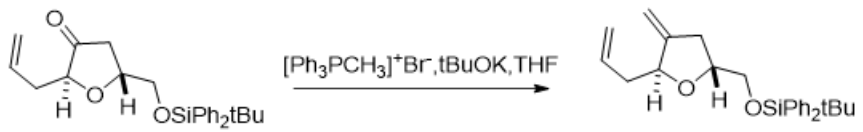


3.烯烃的复分解

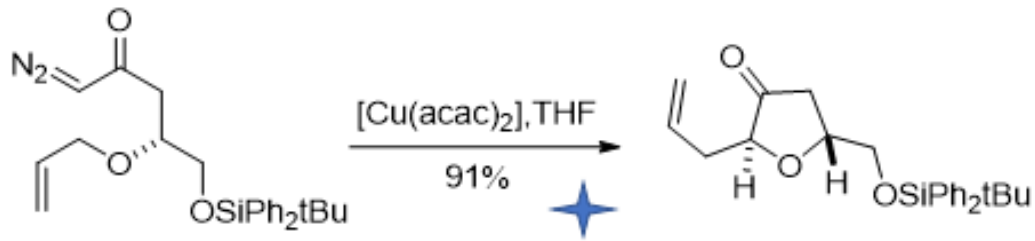


4.羰基的亚甲基化

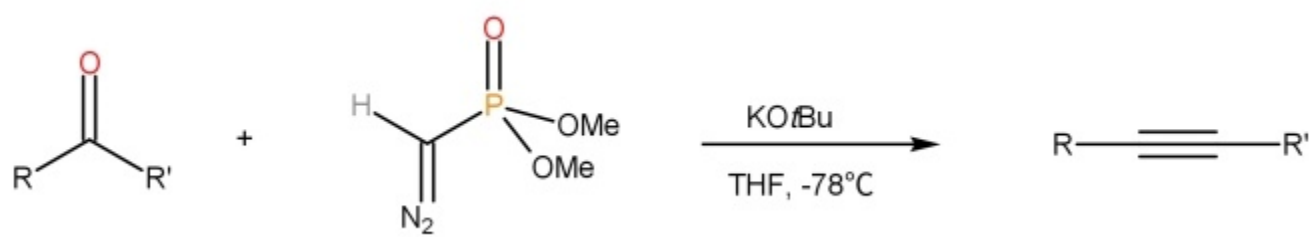


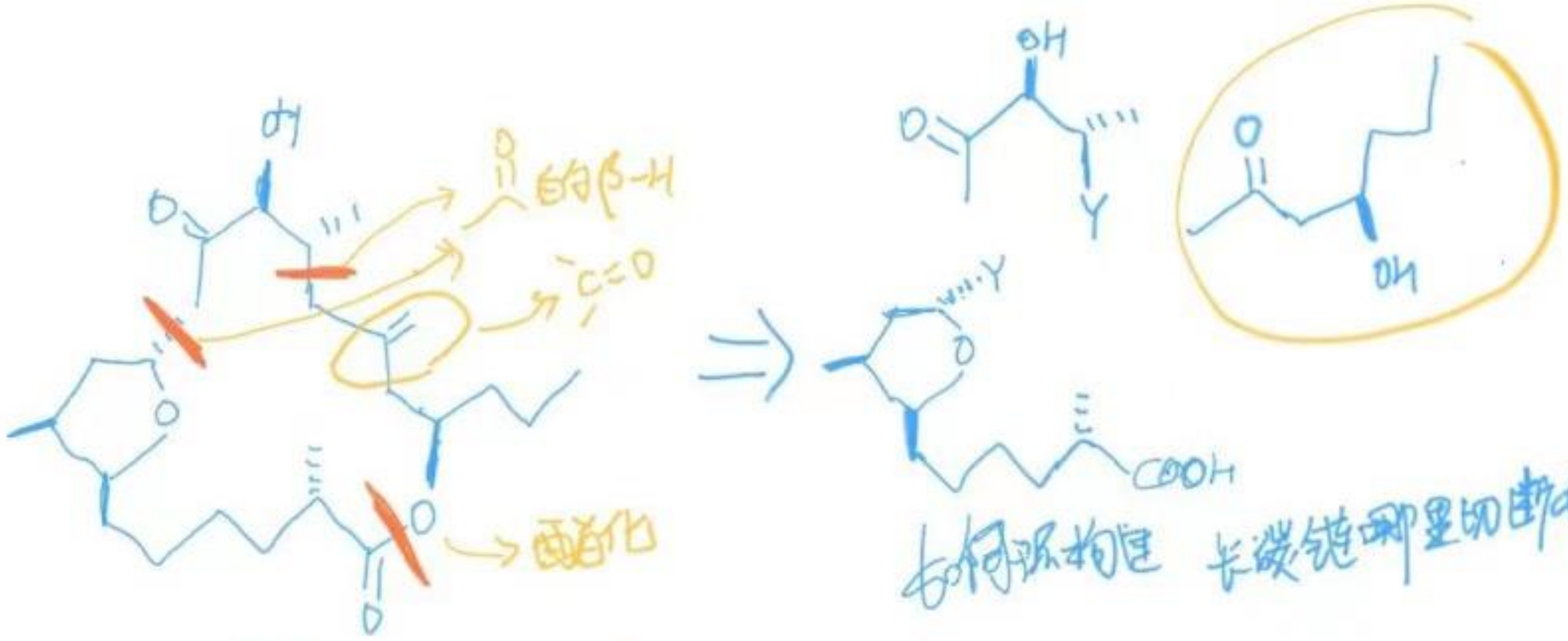


5.卡宾的插入



6. Seyferth-Gilbert增碳反应





如何调构型 长碳链哪里切断好