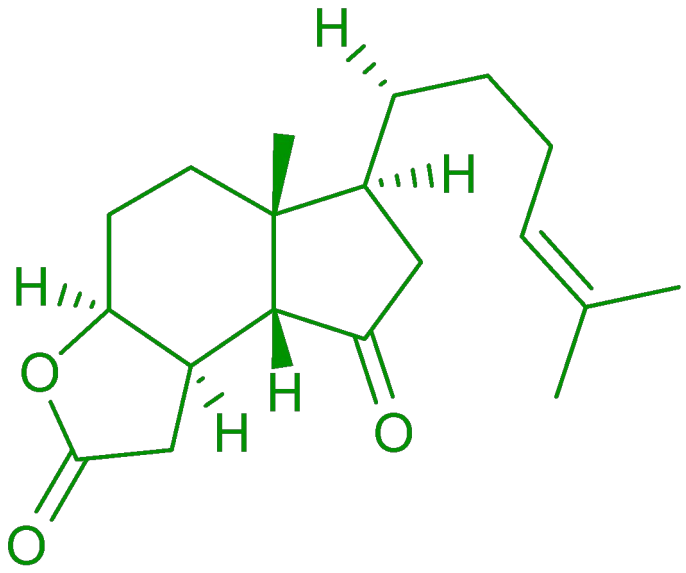
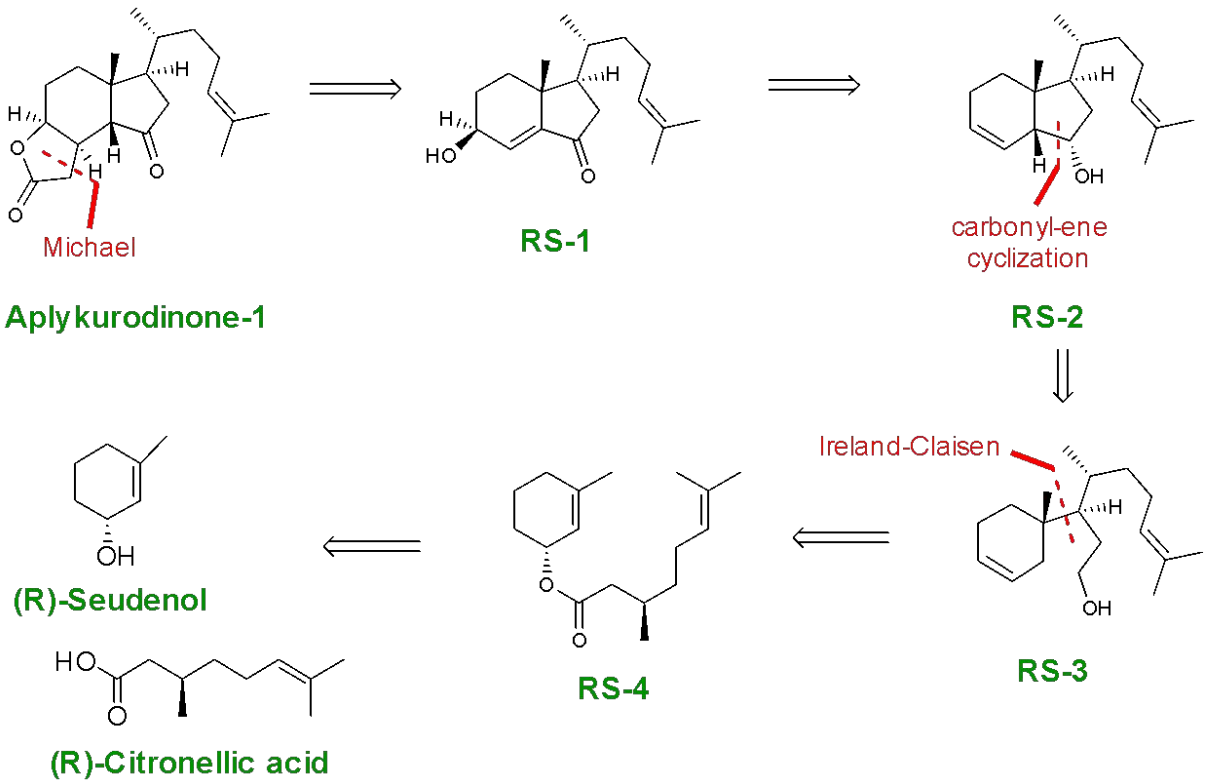


СИНТЕЗ (+)-APLYKURODINONE-1

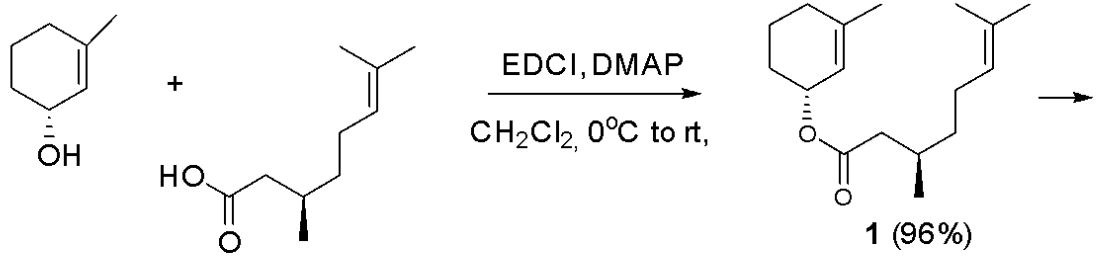
Вера Дорохова
ВХК РАН, А-41

SIPHONOTA GEOGRAPHICA

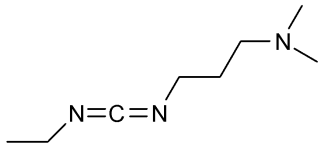
РЕТРОСИНТЕТИЧЕСКИЙ АНАЛИЗ



СИНТЕЗ



EDCI

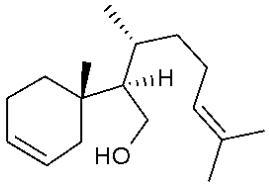


1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide

1) LDA, TBSCl
THF/HMPA,
-78°C to rt

2) toluene, 80°C, 20 h
3) DIBAL-H, -78°C, 1 h

enolization + Ireland-Claisen + reduction of the silyl ester

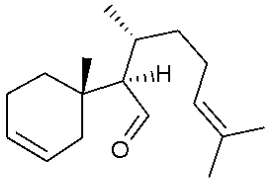


2 (60%, d.r. 11:1)

DMP

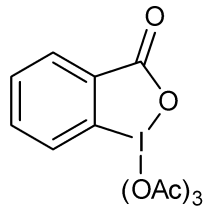
CH_2Cl_2, 0°C, 1 h

Dess-Martin oxidation



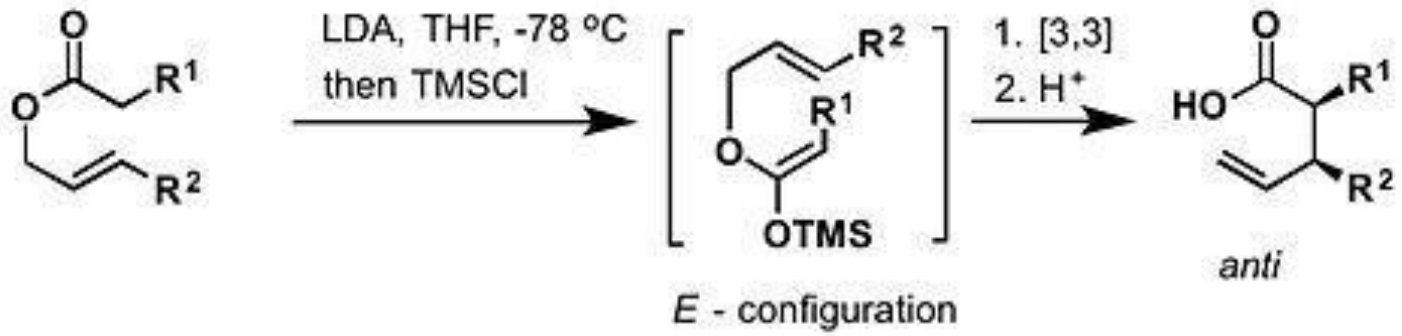
3 (95%)

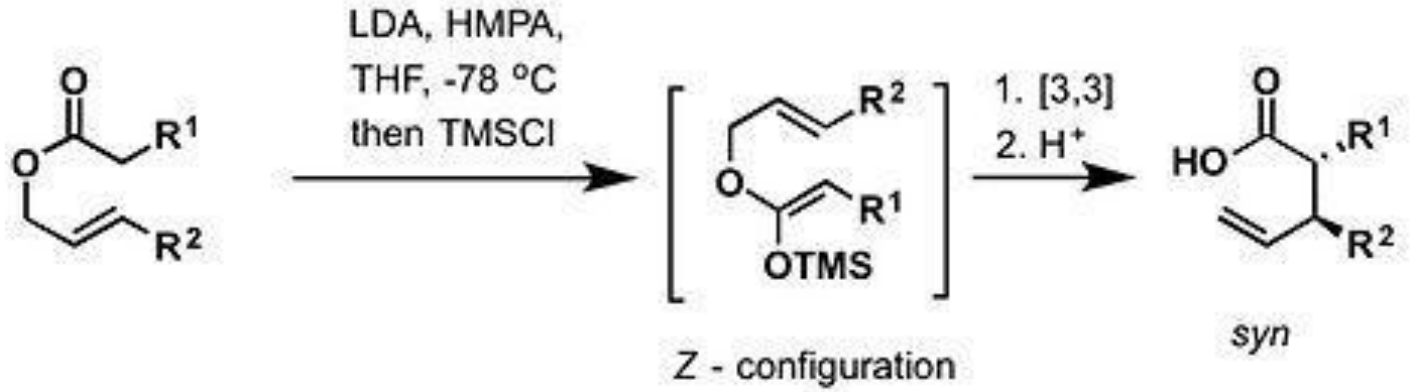
DMP



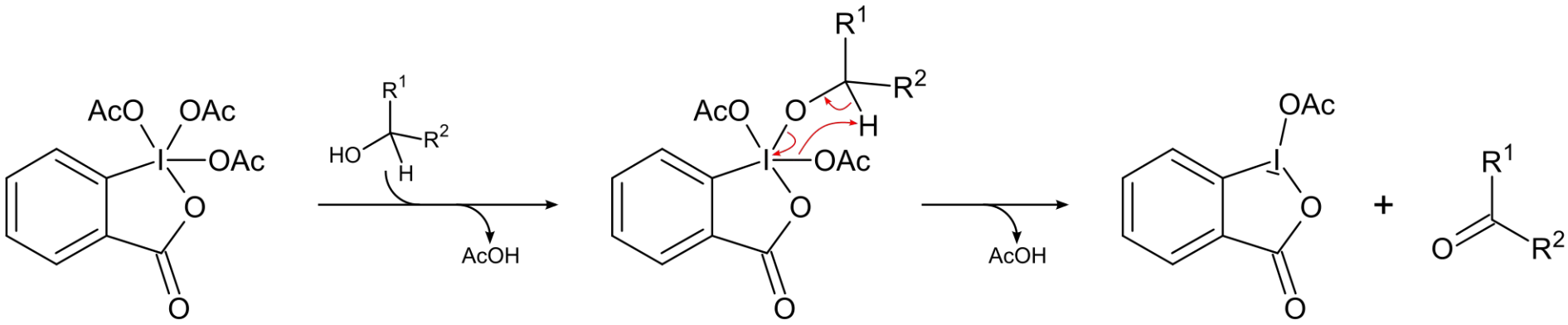
Dess-Martin periodinane

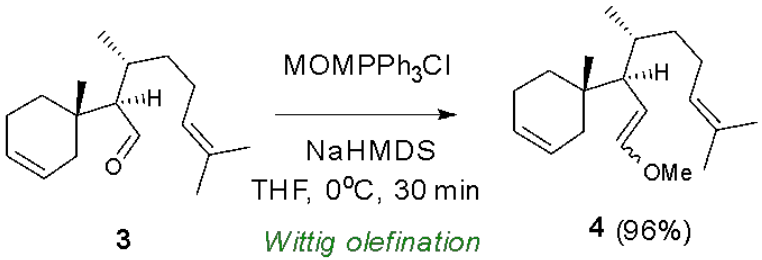
IRELAND-CLAISEN REARRANGEMENT





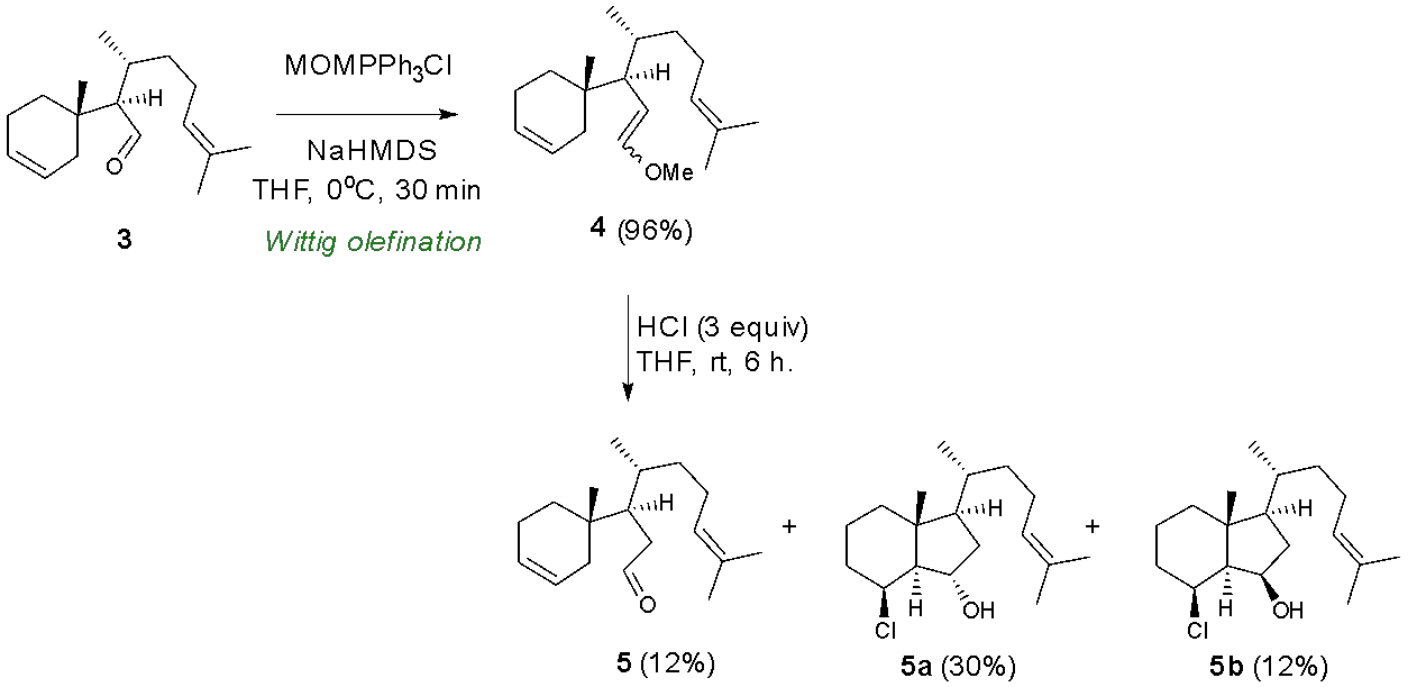
DESS-MARTIN OXIDATION





3

4 (96%)



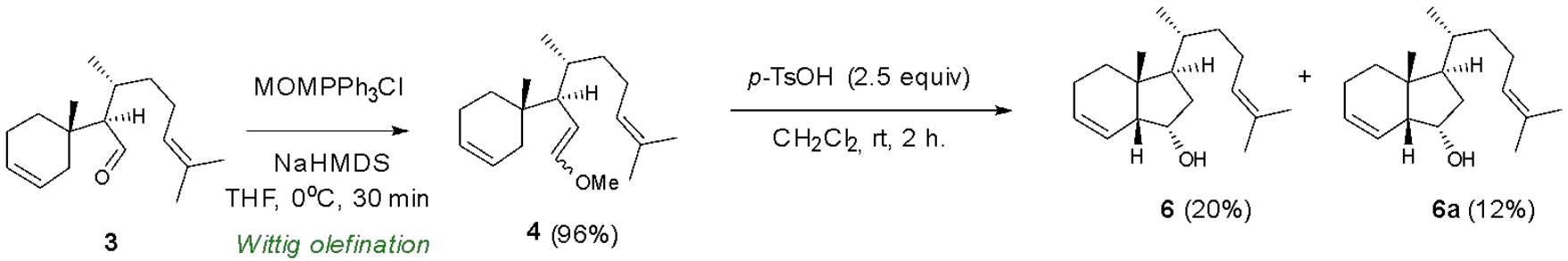
3

4 (96%)

5 (12%)

5a (30%)

5b (12%)

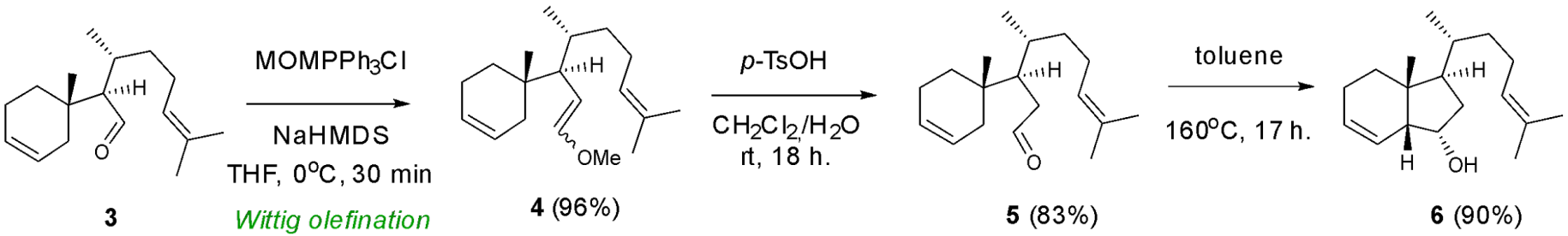


3

4 (96%)

6 (20%)

6a (12%)

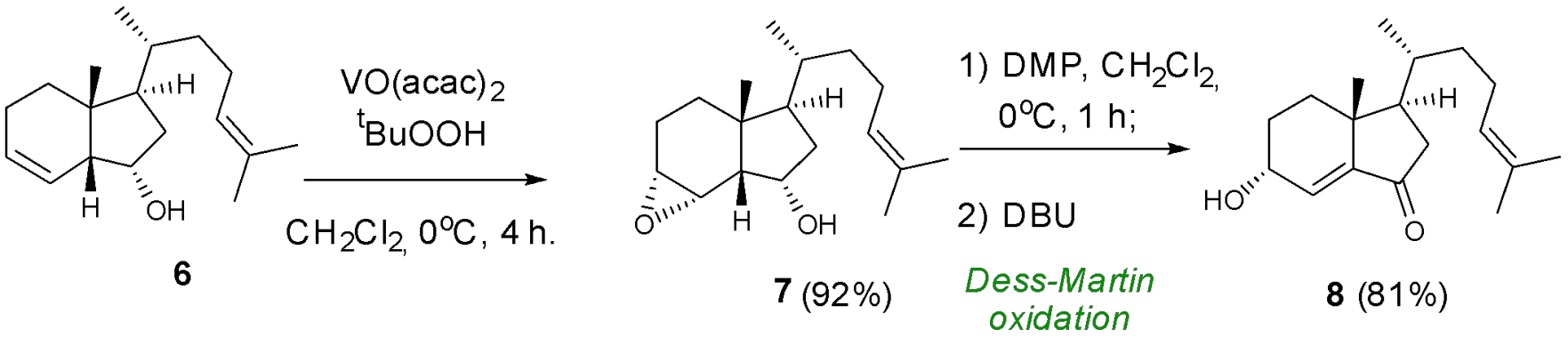

MOMPPh3Cl
NaHMDS
THF, 0°C, 30 min
Wittig olefination
p-TsOH
CH2Cl2/H2O
rt, 18 h.
toluene
160°C, 17 h.
OMe
OH
H
O

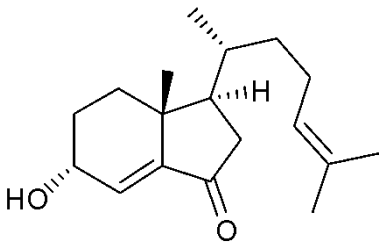
3

4 (96%)

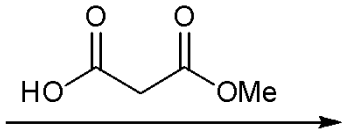
5 (83%)

6 (90%)


VO(acac)2
tBuOOH
CH2Cl2, 0°C, 4 h.
6
7 (92%)
1) DMP, CH2Cl2,
0°C, 1 h;
2) DBU
Dess-Martin
oxidation
8 (81%)

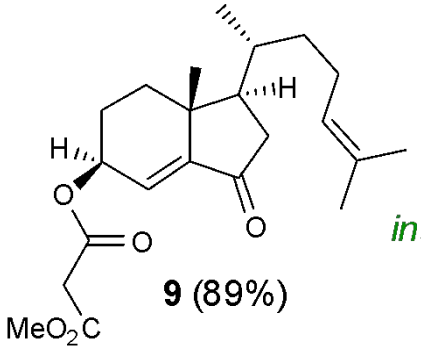


8



PPh_3, DIAD,
THF, 0°C, 20 min

Mitsunobu esterefication

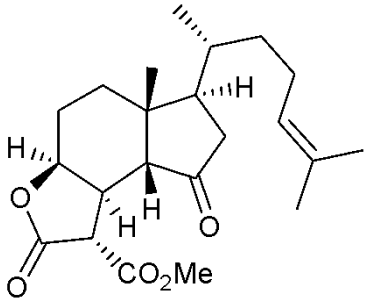


9 (89%)

Cs_2CO_3

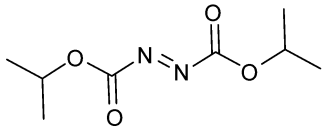
MeCN,
60°C, 20 min

intramolecular Michael addition



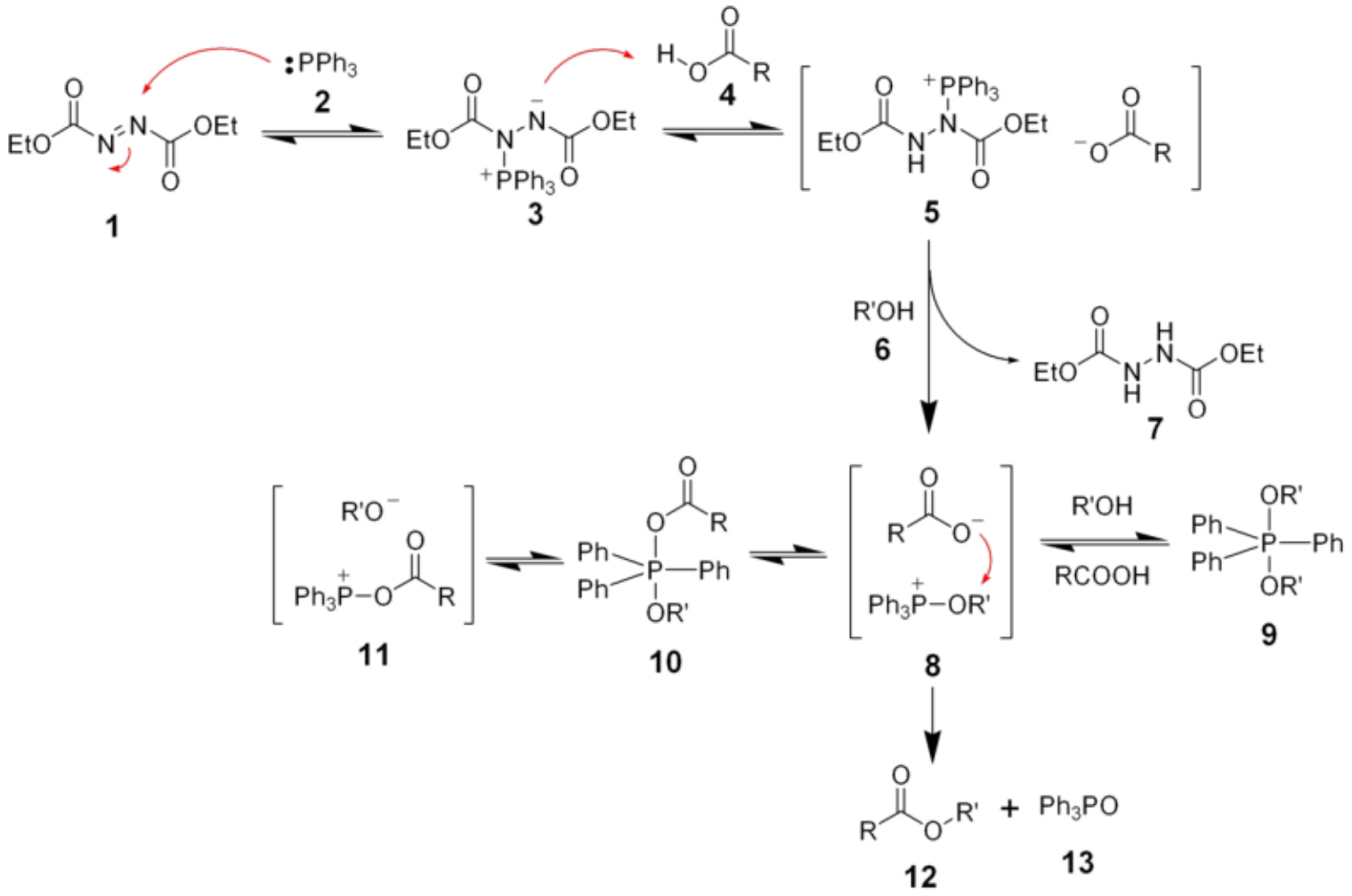
10 (87%)

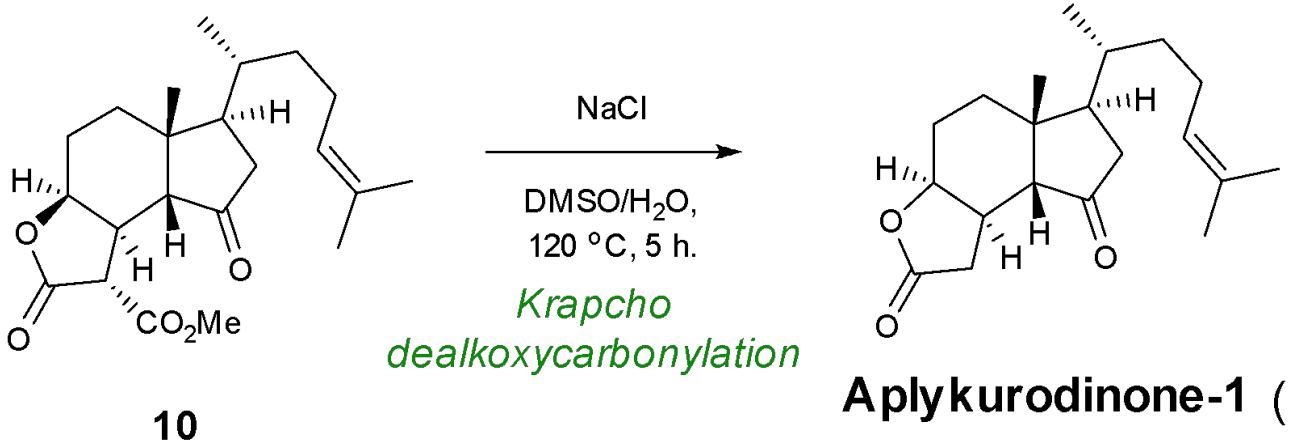
DIAD

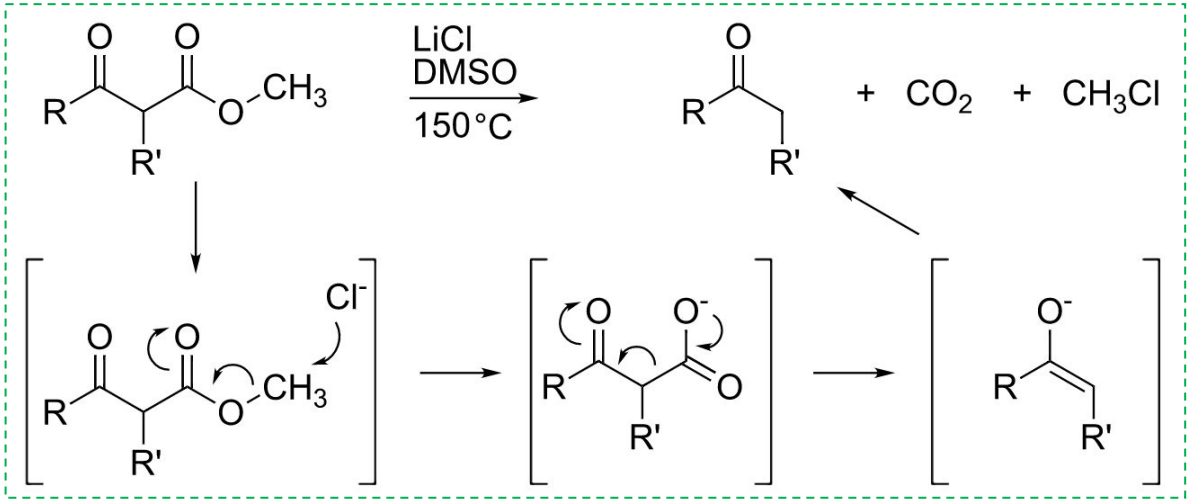


Diisopropyl azodicarboxylate

MITSUNOBU ESTEREFICATION







- ✔ 11 steps
- ✔ 19% overall yield
- ✔ Full stereochemical control
- ✔ No protecting groups

СПАСИБО ЗА ВНИМАНИЕ!