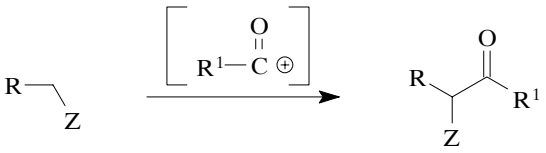
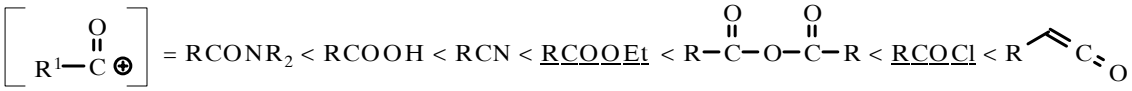
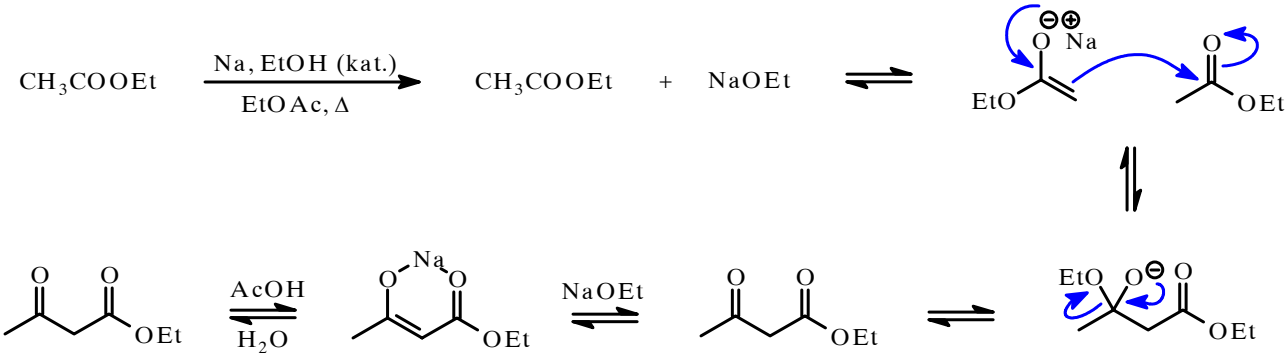
ACILOVANJE AKTIVNIH METILENSKIH JEDINJENJA



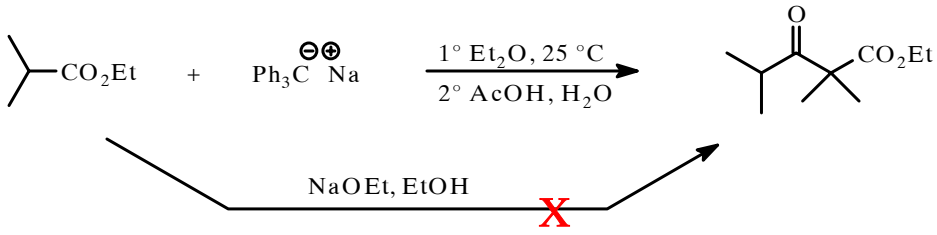


Intermolekulske reakcije

* Claisen-ova kondenzacija



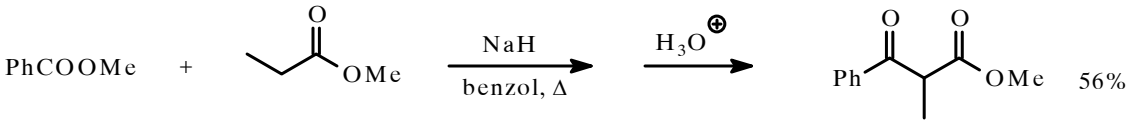
29%

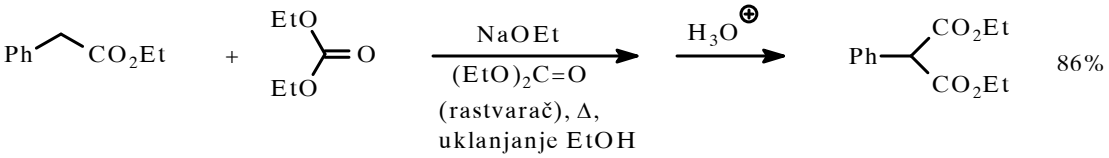


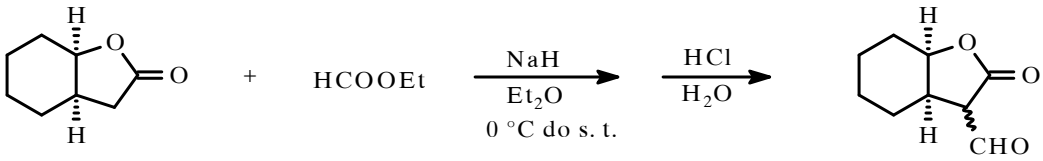
* Najbolja baza: NaH + ROH (kat.)
* Druge baze: Ph_3CNa, KH, $Na^+ {}^-CH_2S(O)CH_3$

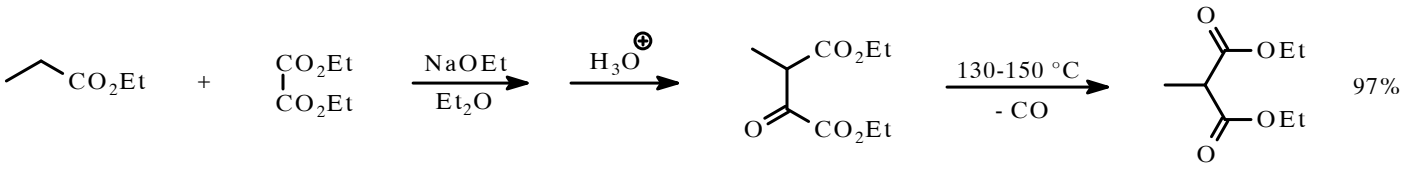
* Ukrštene kondenzacije: jedan estar bez α-H atoma

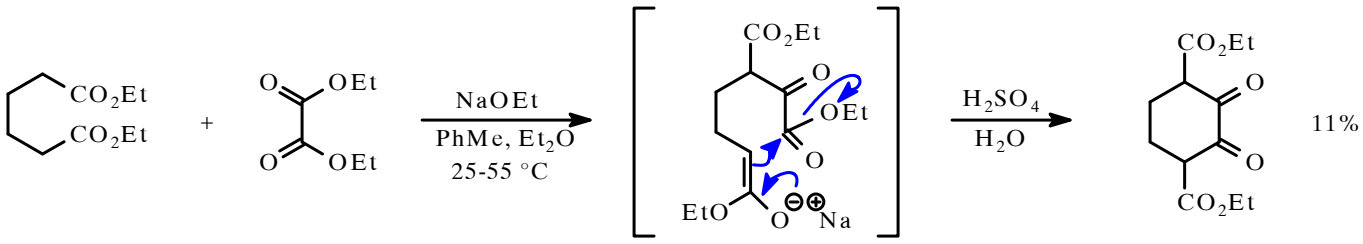
ArCOOR, HCOOR, $(EtO)_2C=O$, $(COOEt)_2$

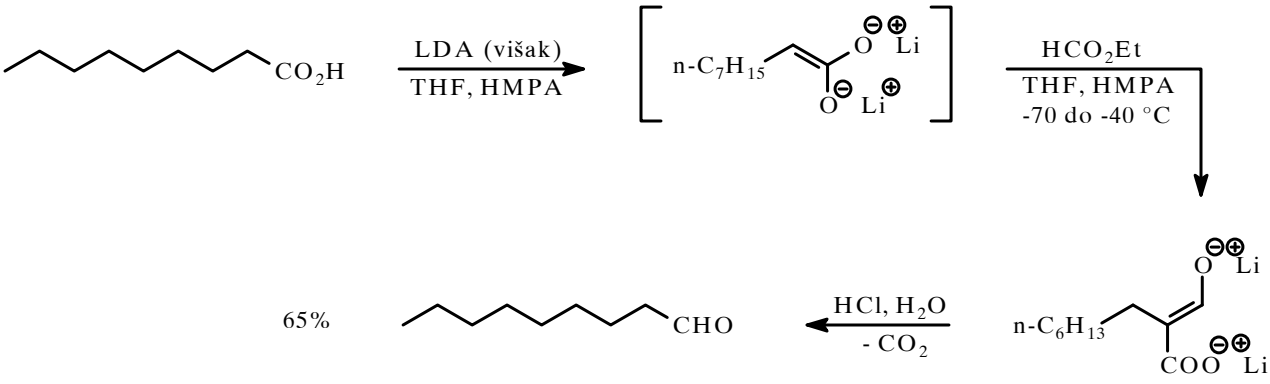


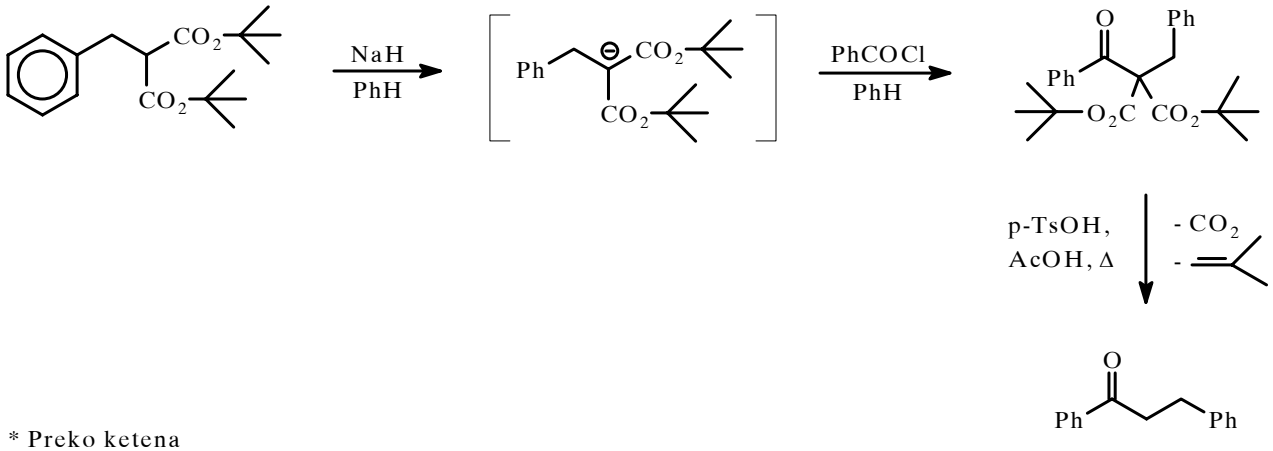




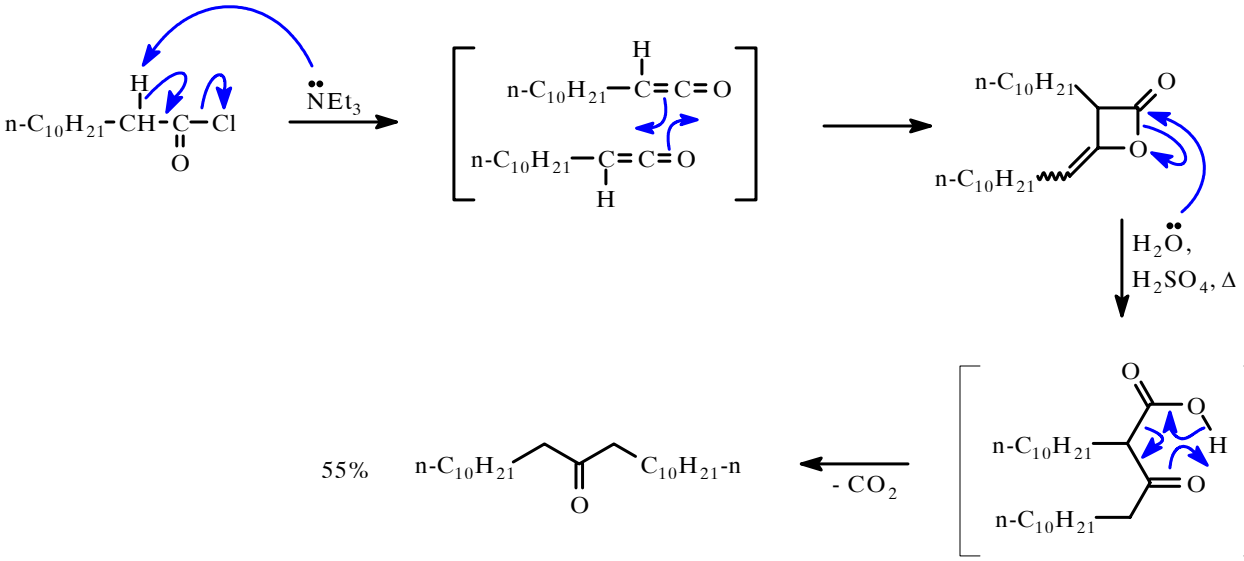


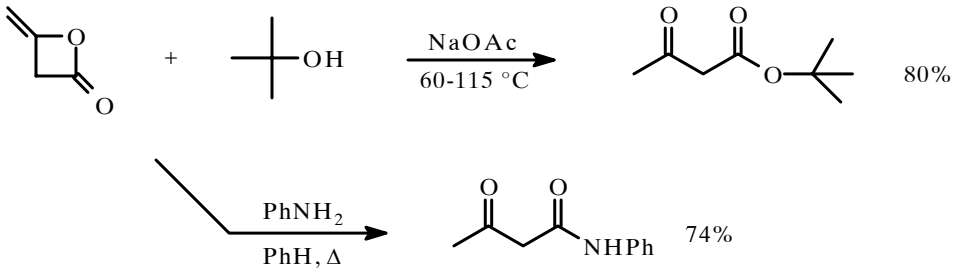




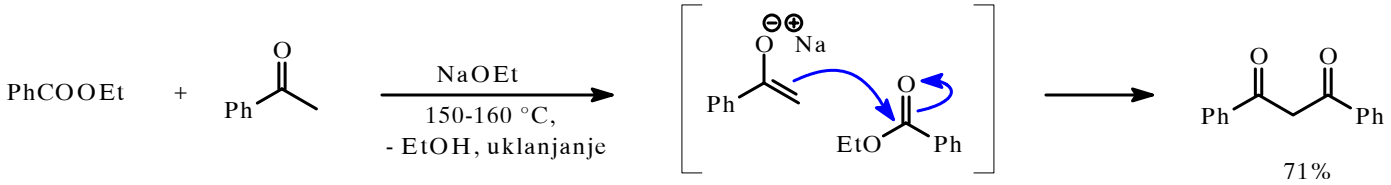


* Preko ketena

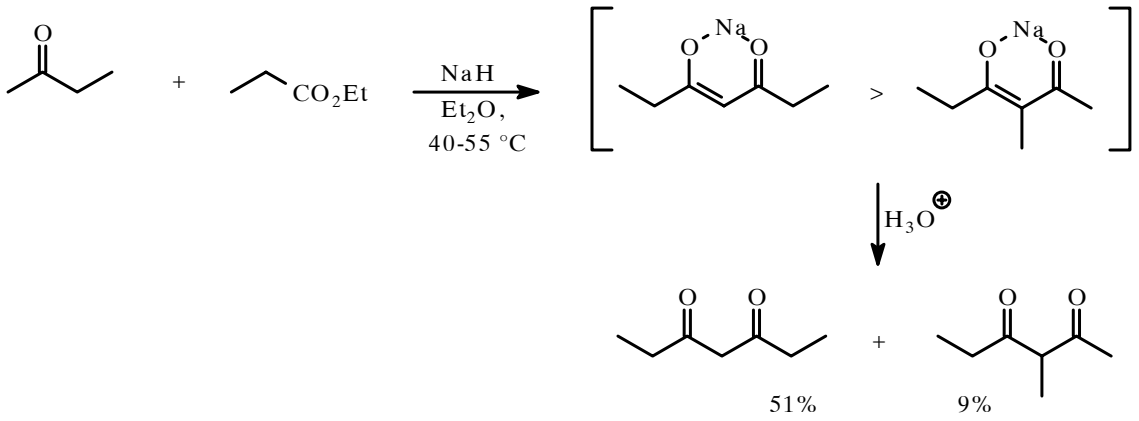


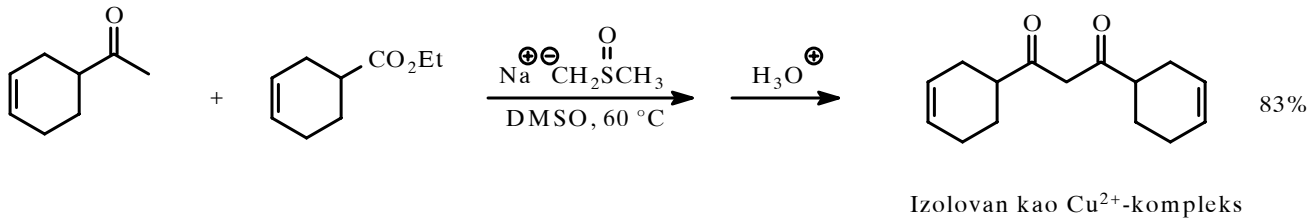


* Acilovanje ketona i nitrila

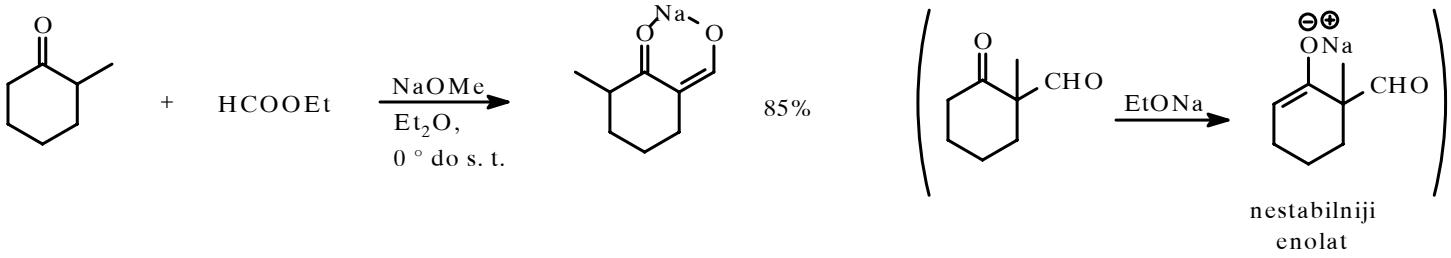


* Nesimetrični ketoni reaguju na manje supstituisanom kraju (stabilnost krajnjeg enolata)

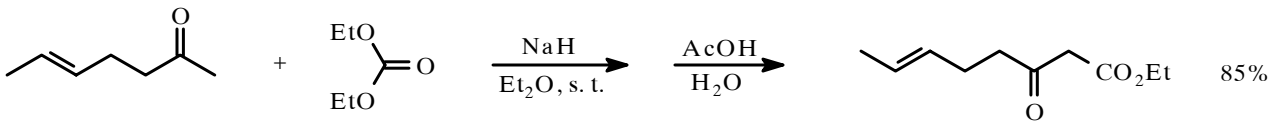


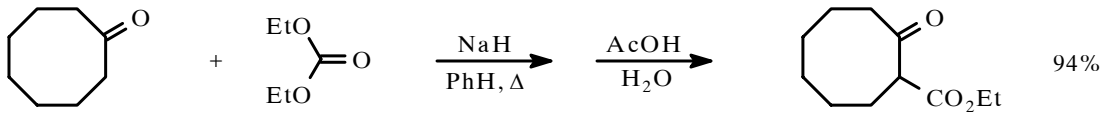


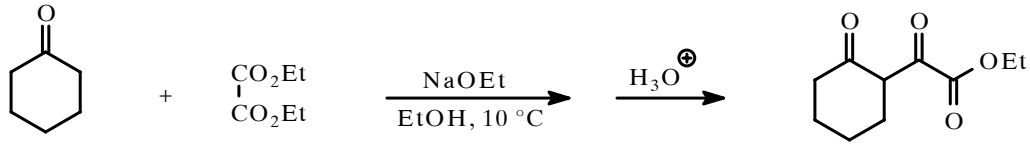
Izolovan kao Cu^{2+}-kompleks

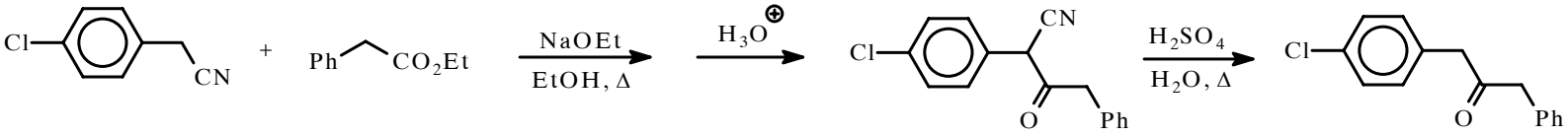


nestabilniji enolat



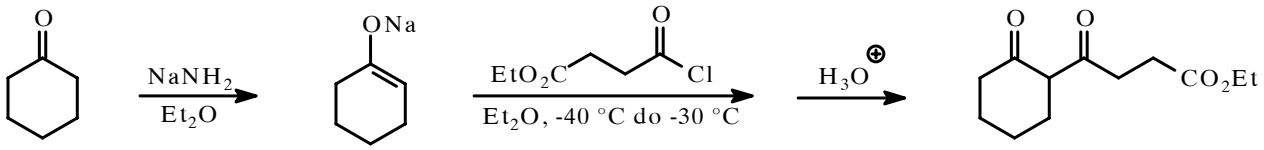




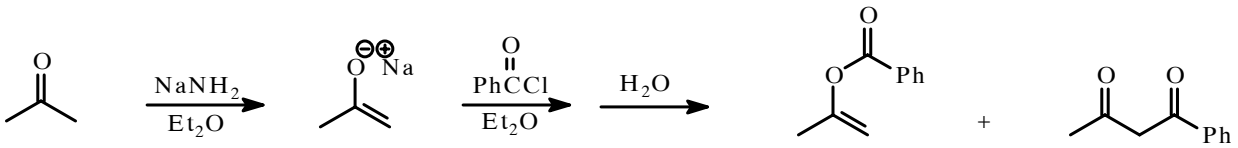


75%

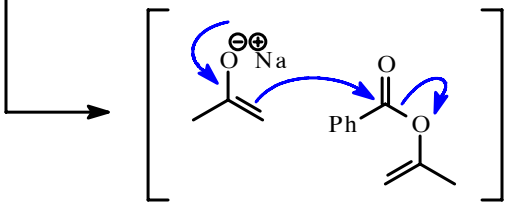
* Preformirani enolati; *O*- i *C*-acilovanje



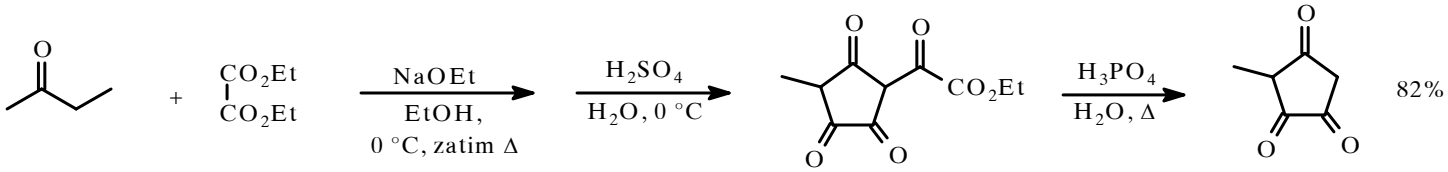
44%



1 ekv. PhCOCl dodat u 2 ekv. enolata:	9%	33%
1 ekv. enolata dodat u 1 ekv. PhCOCl:	41%	6%



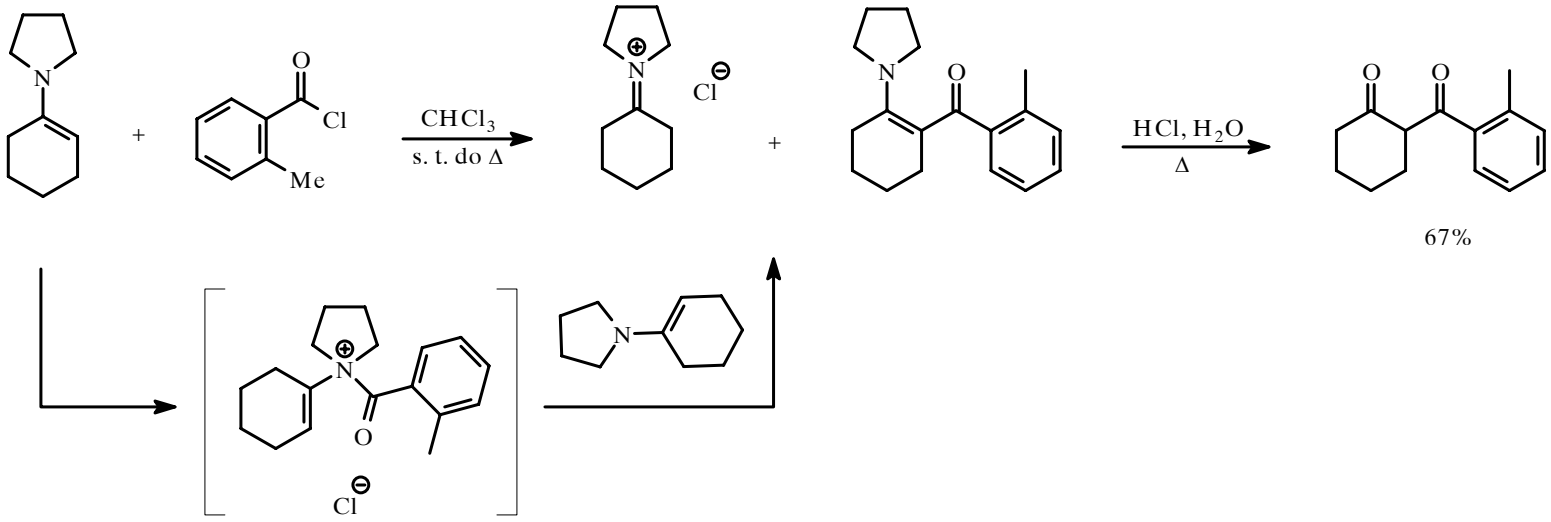
* Domino-reakcije

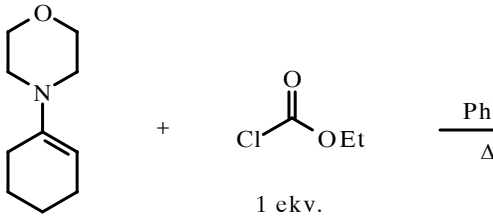


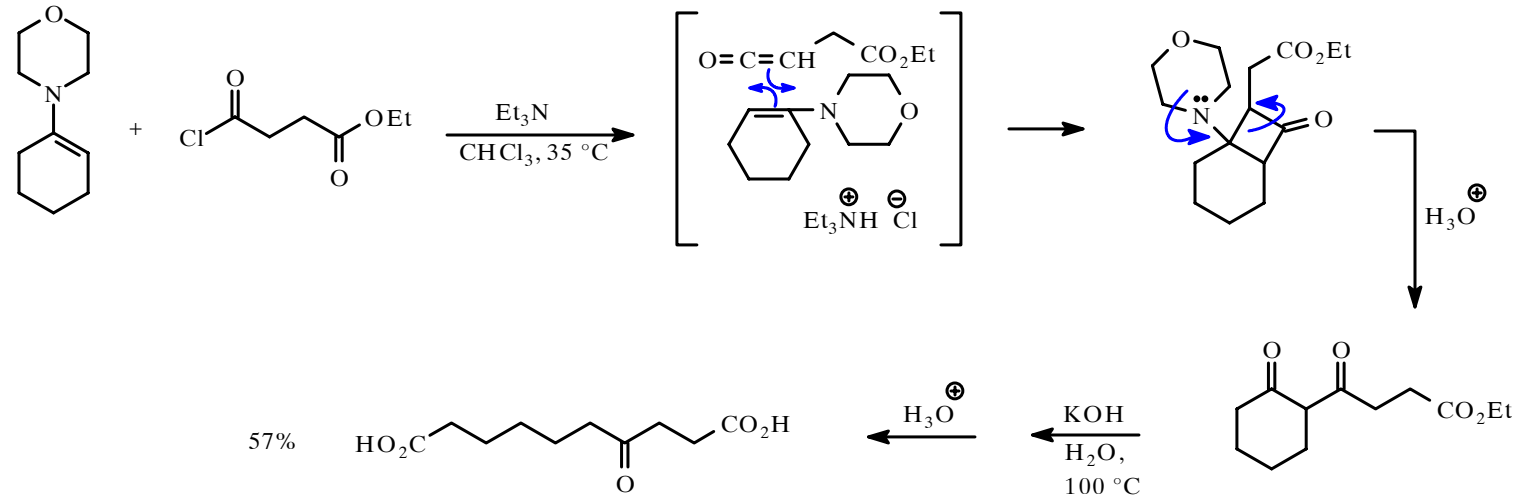
82%

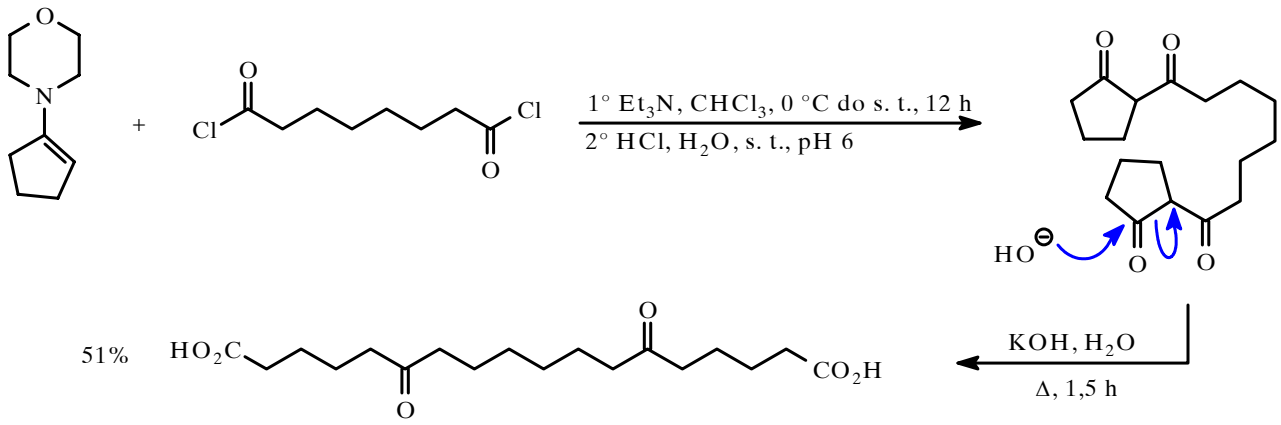
* Acilovanje enamina

* višak enamina ili dodatak Et_3N



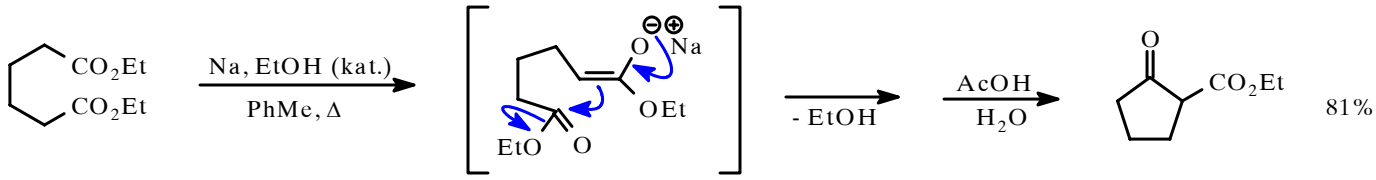


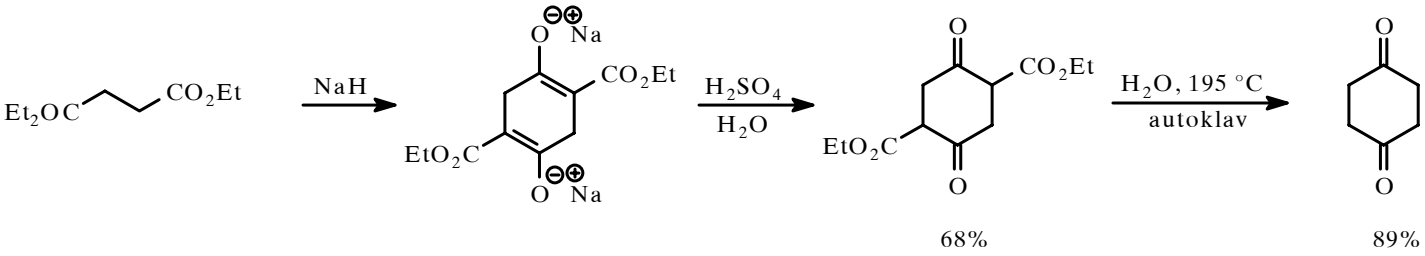




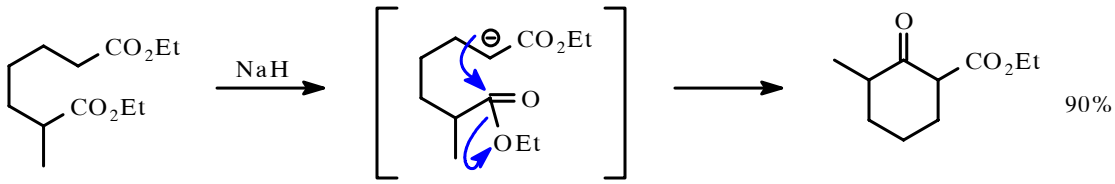
Intramolekulsko acilovanje

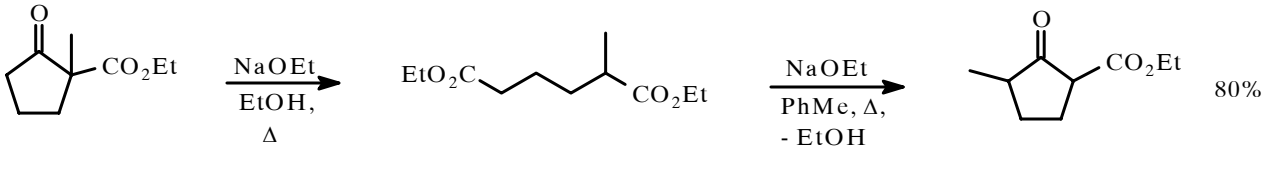
* Dieckmann-ova kondenzacija

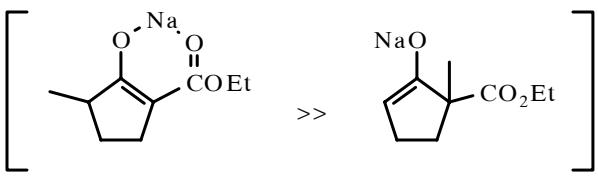


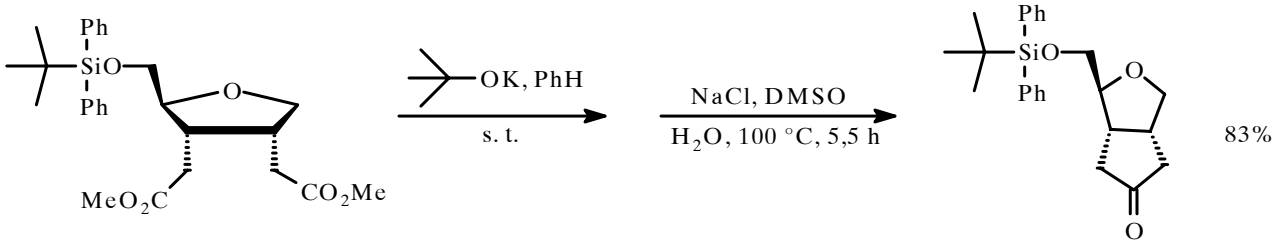


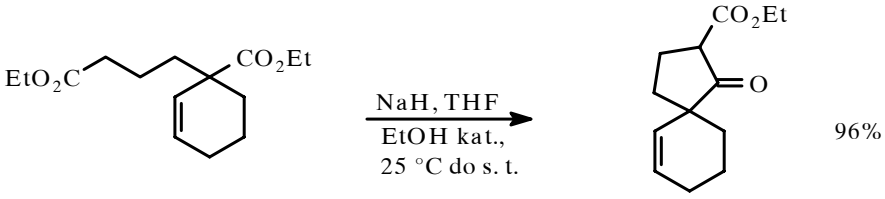
* Nesimetrični estri

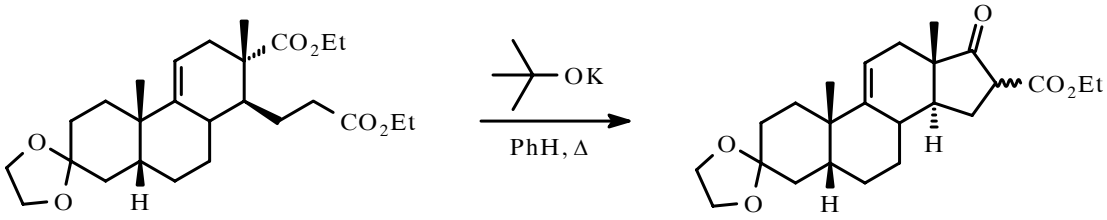


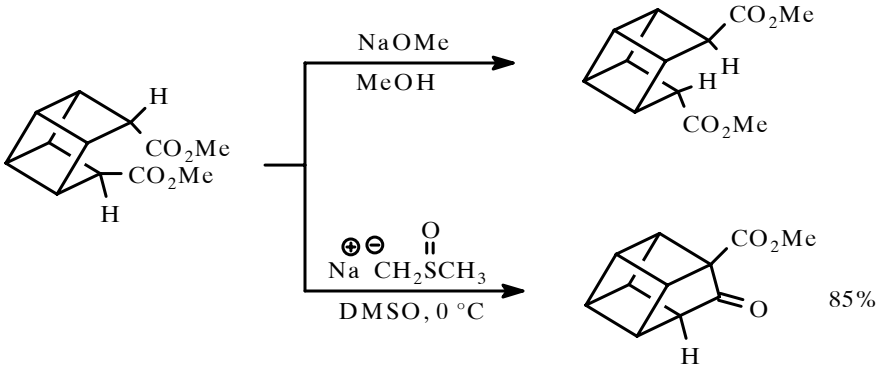


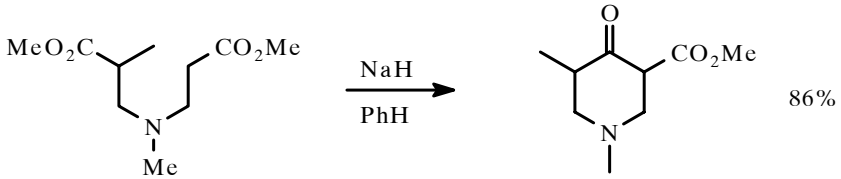


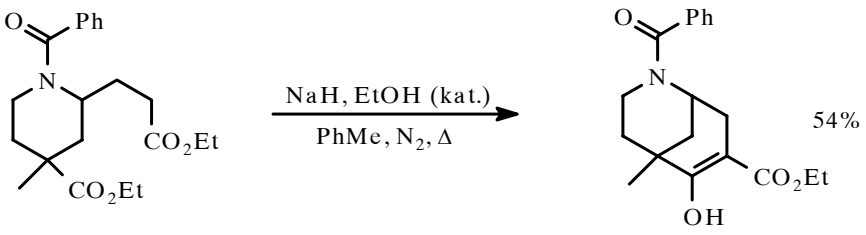

Ph
SiO
Ph
O
MeO2C
CO2Me
OK, PhH
s. t.
NaCl, DMSO
H2O, 100 °C, 5,5 h
Ph
SiO
Ph
O
O
83%

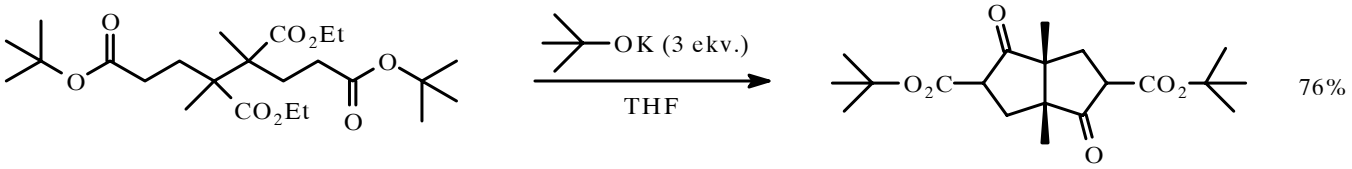

EtO2C
CO2Et
NaH, THF
EtOH kat.,
25 °C do s. t.
CO2Et
O
96%

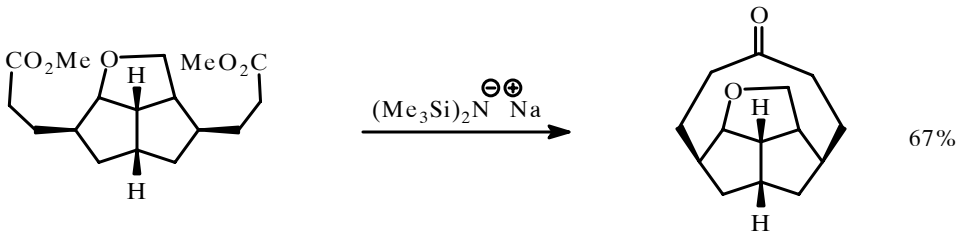

CO2Et
CO2Et
O
O
H
OK
PhH, Δ
O
CO2Et
O
O
H
H

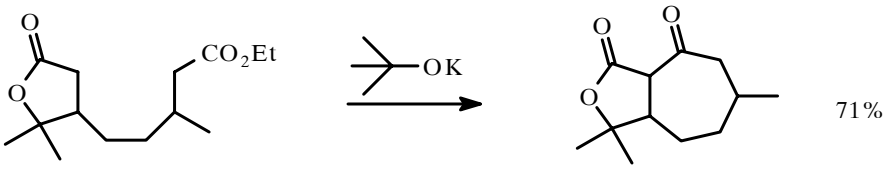

H
CO2Me
CO2Me
H
NaOMe
MeOH
CO2Me
H
H
CO2Me
Na CH2SCH3
O
DMSO, 0 °C
CO2Me
O
H
85%


MeO2C
CO2Me
N
Me
NaH
PhH
O
CO2Me
N
86%

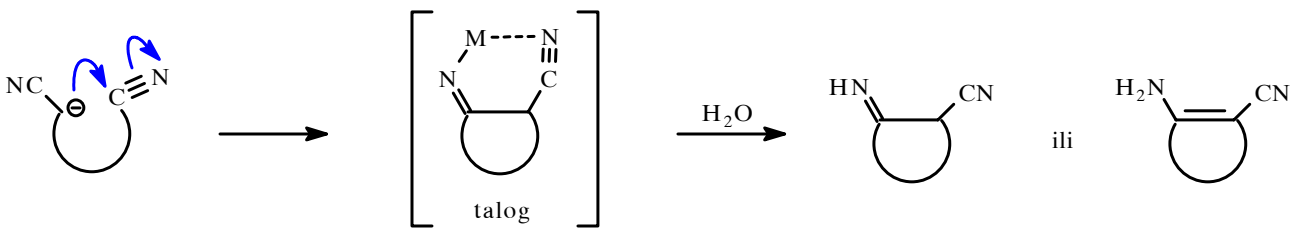

O
Ph
N
CO2Et
CO2Et
NaH, EtOH (kat.)
PhMe, N2, Δ
O
Ph
N
CO2Et
OH
54%

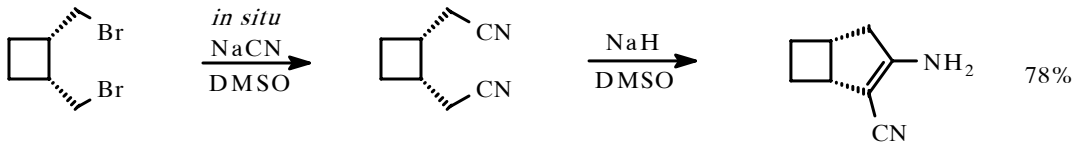


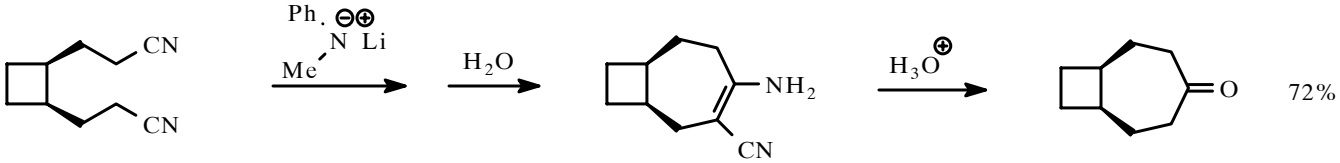


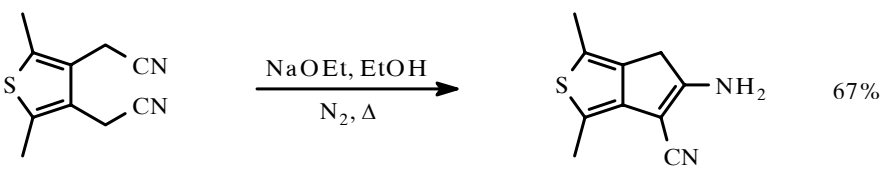


* Thorpe-Ziegler-ova kondenzacija

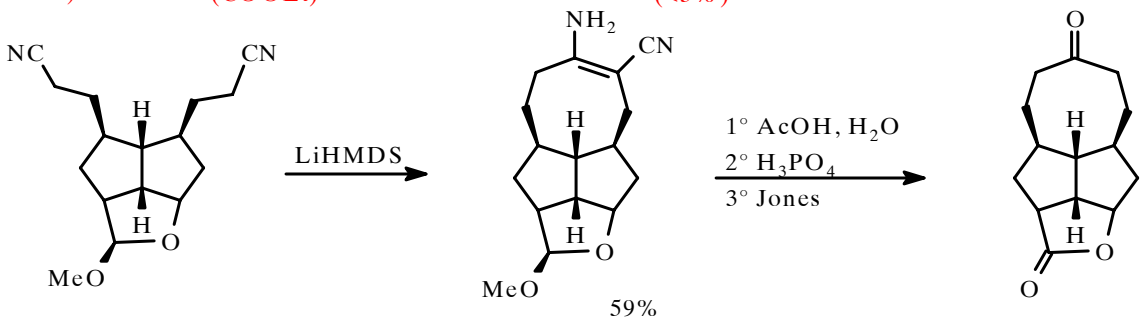




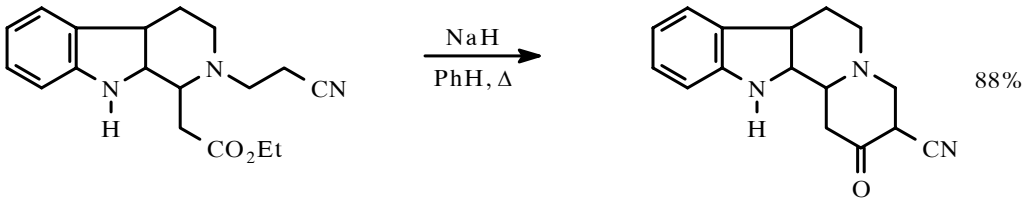


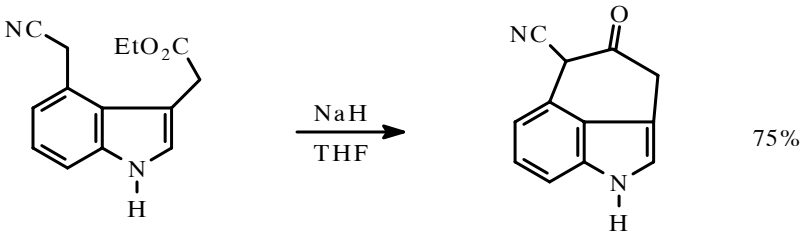


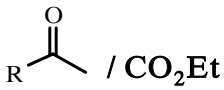
(COOEt) (COOEt) (<5%)

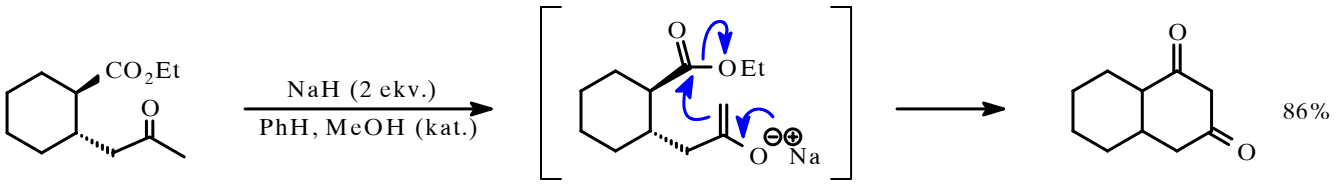


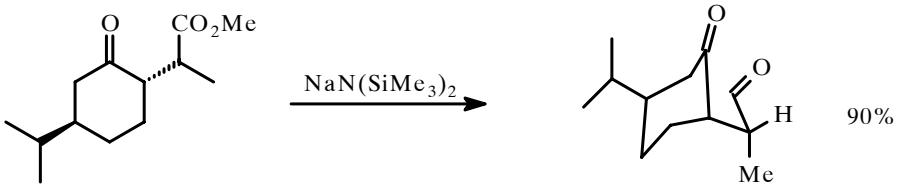
CN/COOR

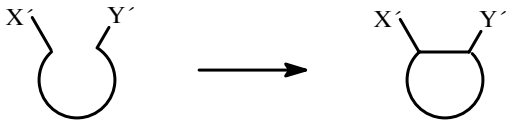








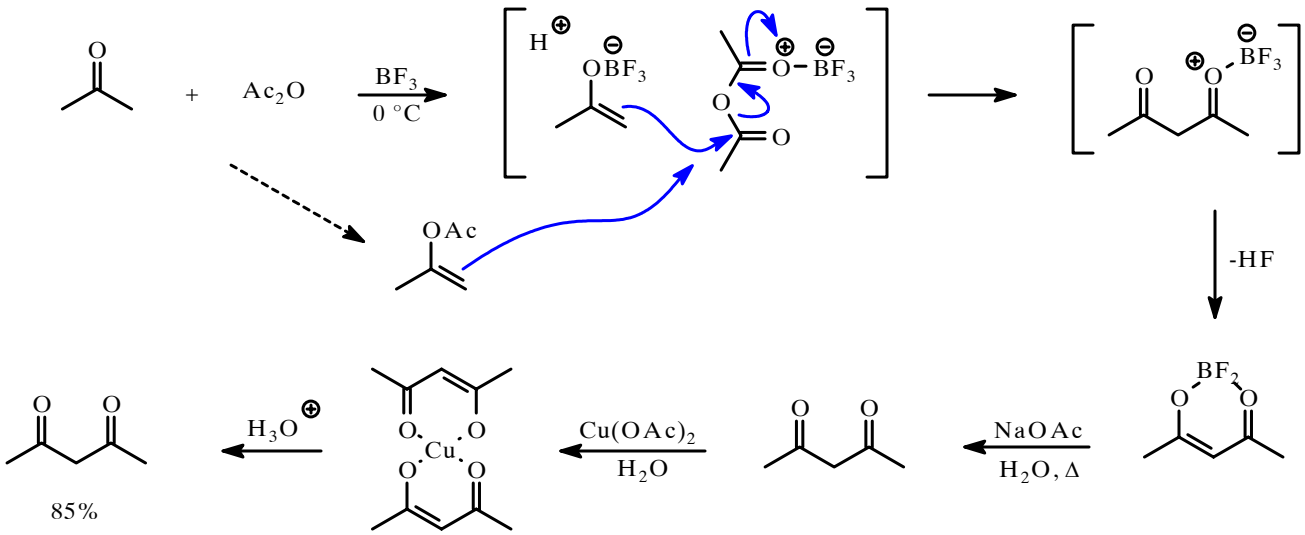


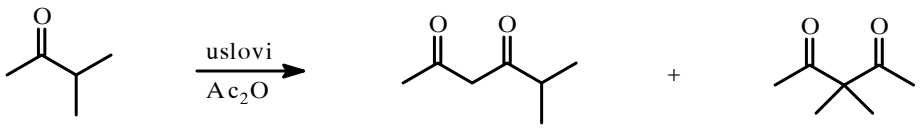


veličina prstena	METOD CIKLIZACIJE		
	Dieckmann	Thorpe-Ziegler	Aciloinska kond.
6	/	95%	58%
7	47	96	52
8	15	89	36
9	0	0	38
10	0	0	52
11	0,5	2	53
12	0,5	/	80
13	24	14	80
14	32	57	85

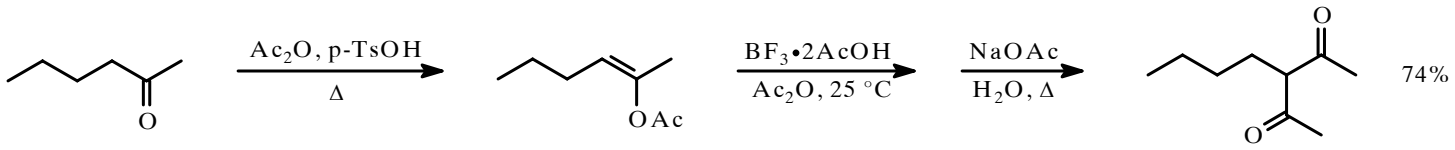
* Acilovanje u kiselim uslovima

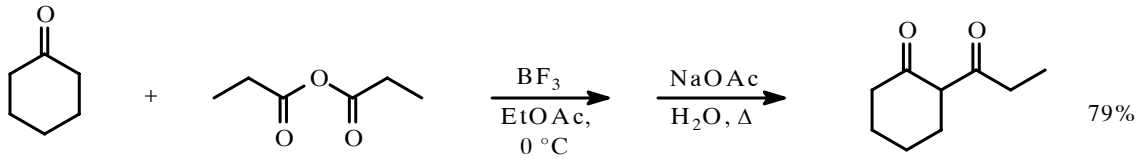
Katalizatori: BF_3, $AlCl_3$, H^+

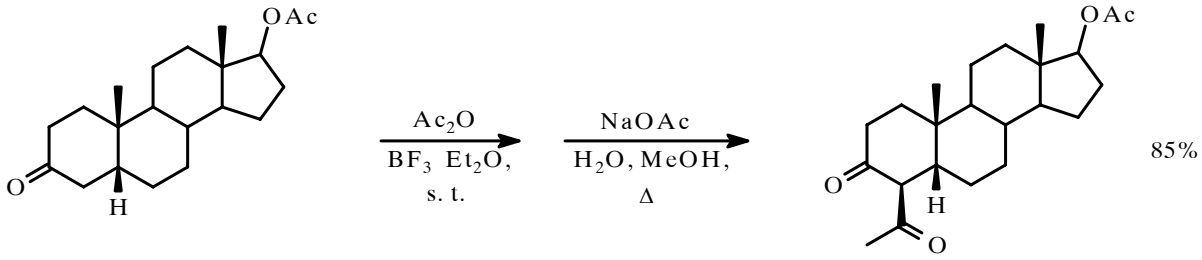


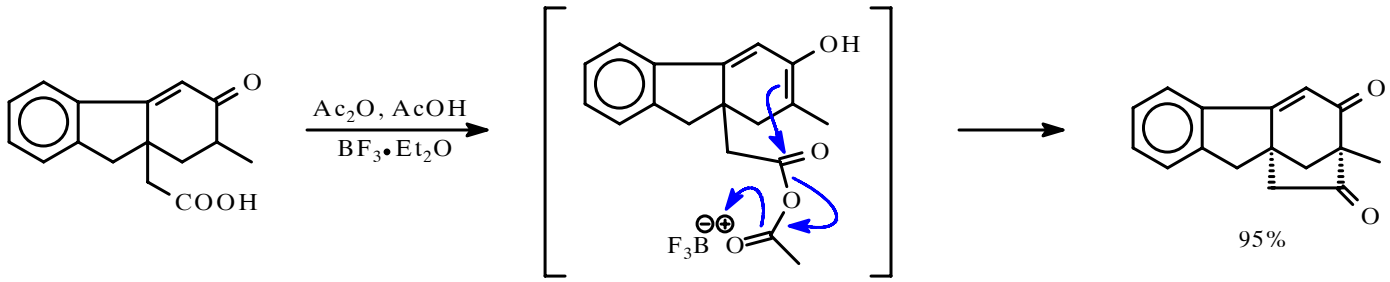


BF_3, 0°-10 °C	70%	30%
BF_3•2AcOH, p-TsOH (kat.), 25 °C	0%	100%


Ac2O, p-TsOH
Δ
OAc
BF3•2AcOH
Ac2O, 25 °C
NaOAc
H2O, Δ
74%


BF3
EtOAc,
0 °C
NaOAc
H2O, Δ
79%


OAc
Ac2O
BF3 Et2O,
s. t.
NaOAc
H2O, MeOH,
Δ
85%


COOH
Ac2O, AcOH
BF3•Et2O
OH
F3B
95%