

# ALDOLNA REAKCIJA

\* U PROTIČNIM USLOVIMA

\* Katalizovane bazama

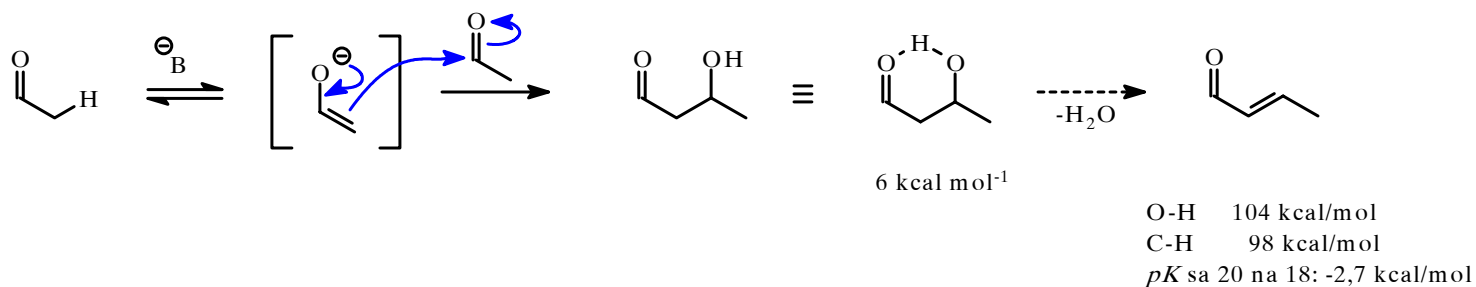
\* Katalizovane kiselinama

\* U APROTIČNIM USLOVIMA (Reakcije preformiranih enolata ili dirigovane adicije)

\* U baznim uslovima

\* U kiselim uslovima

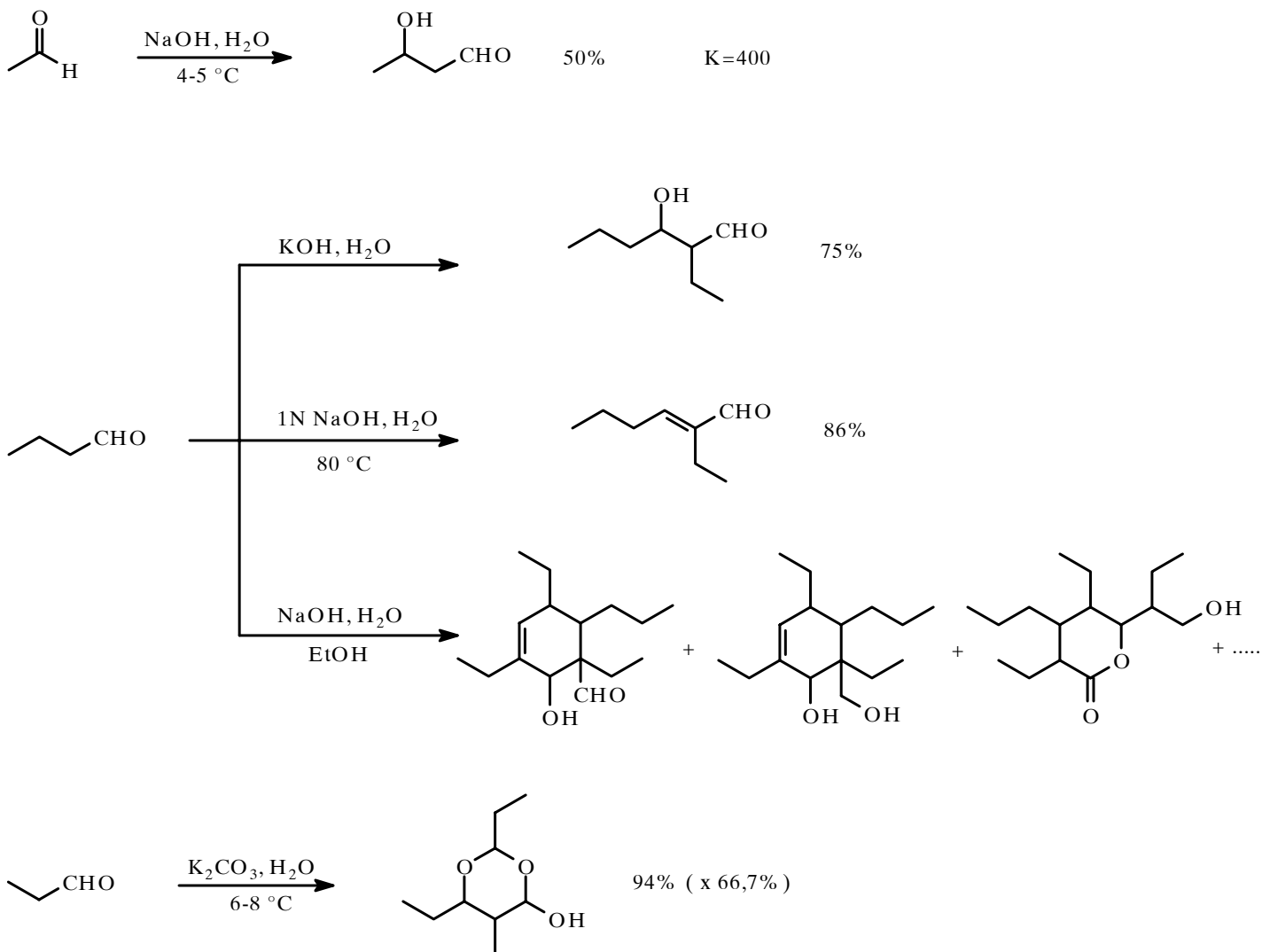
## ALDOLNA REAKCIJA U PROTIČNIM USLOVIMA (INTERMOLEKULSKA)

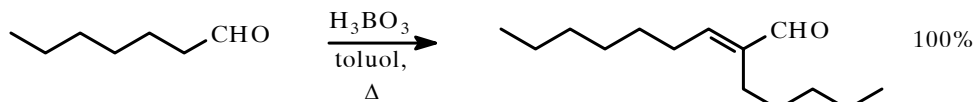


\* Samokondenzacije aldehida

NaOH, H<sub>2</sub>O, EtOH: za aldehide do 6 C-atoma

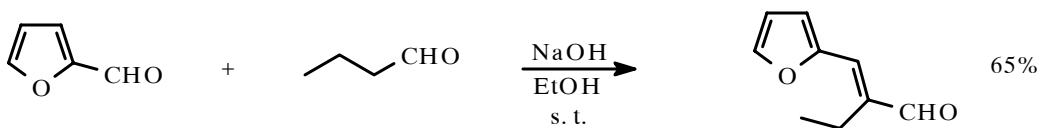
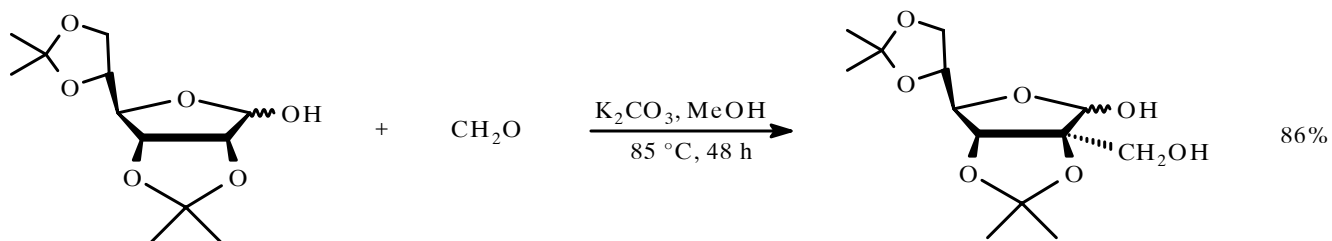
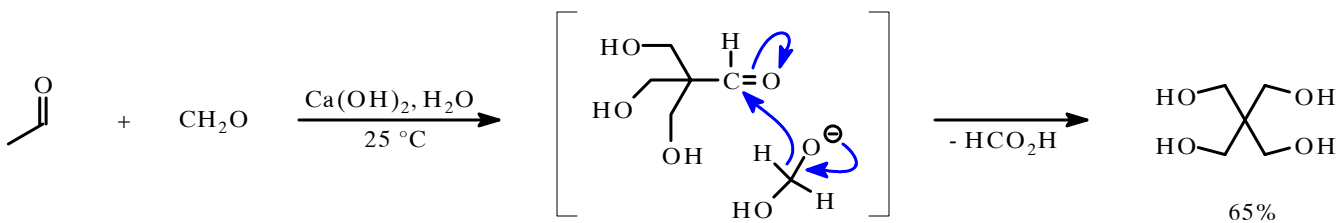
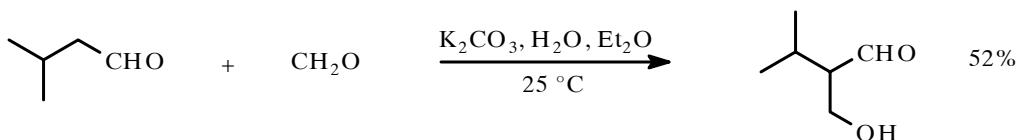
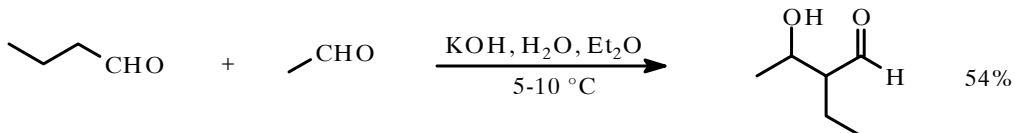
>6 C-atoma: dehidratacija





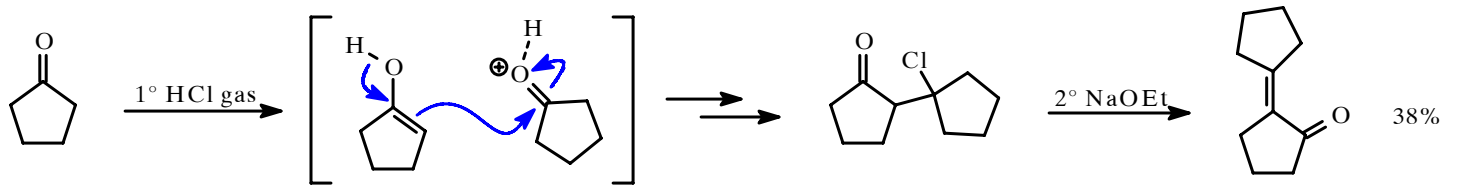
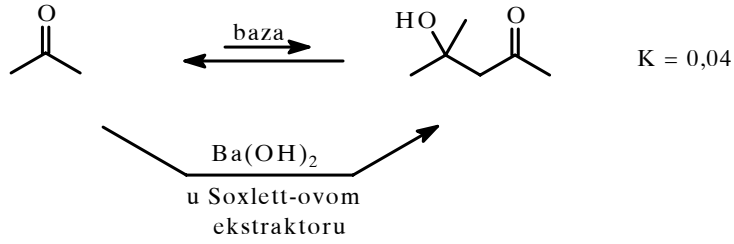
\* Ukrštene adicije aldehida

\* Akceptor: **sterno manje zaštićena CHO** grupa



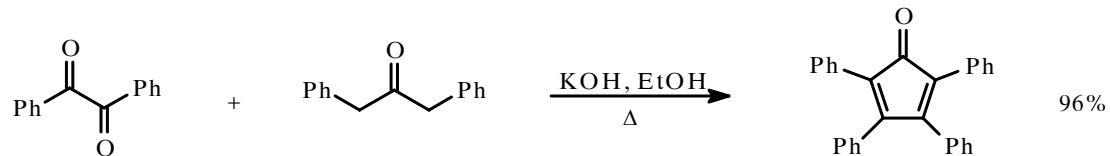
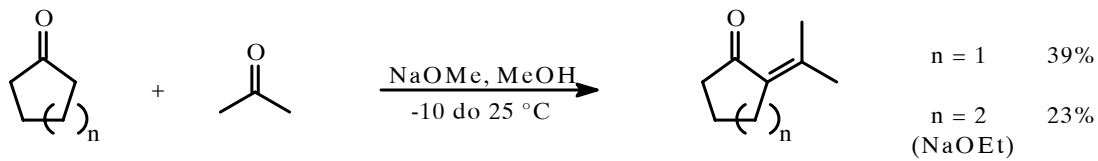
## \* Samokondenzacije ketona

- Nepovoljnija ravnoteža nego kod aldehida
- Ketoli su skloni dehidraciji



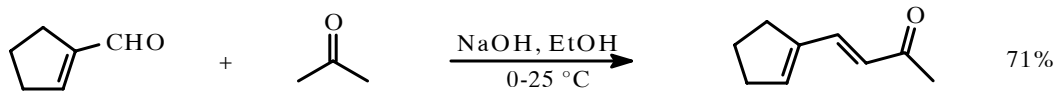
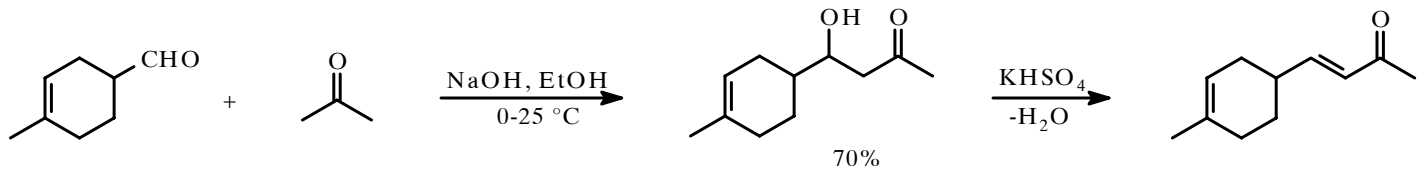
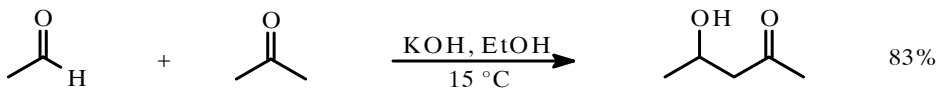
## \* Ukrštene reakcije ketona

4 moguća proizvoda  $\Rightarrow$  mali preparativni značaj



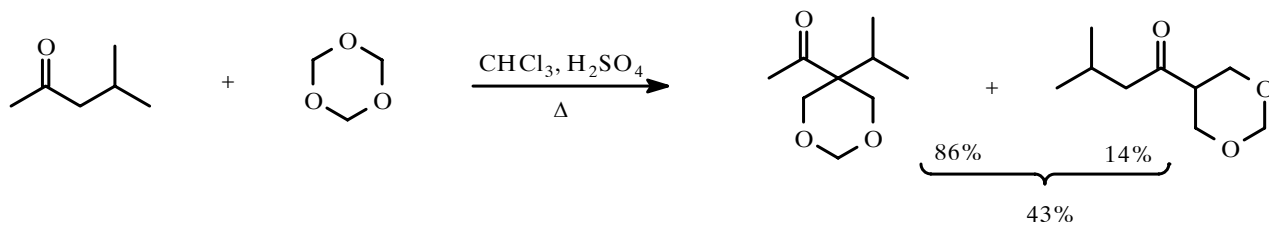
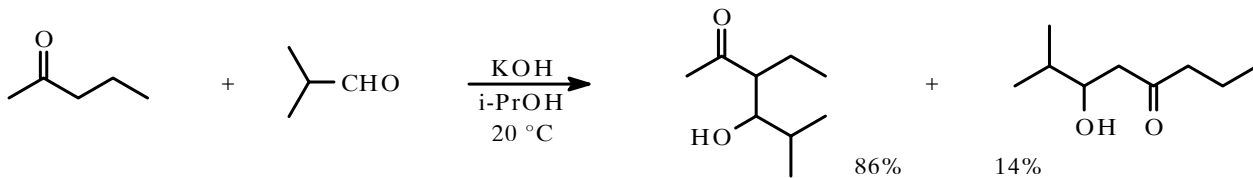
\* Reakcije ketona sa aldehydima

Aldehidi - akceptori; ketoni - donori

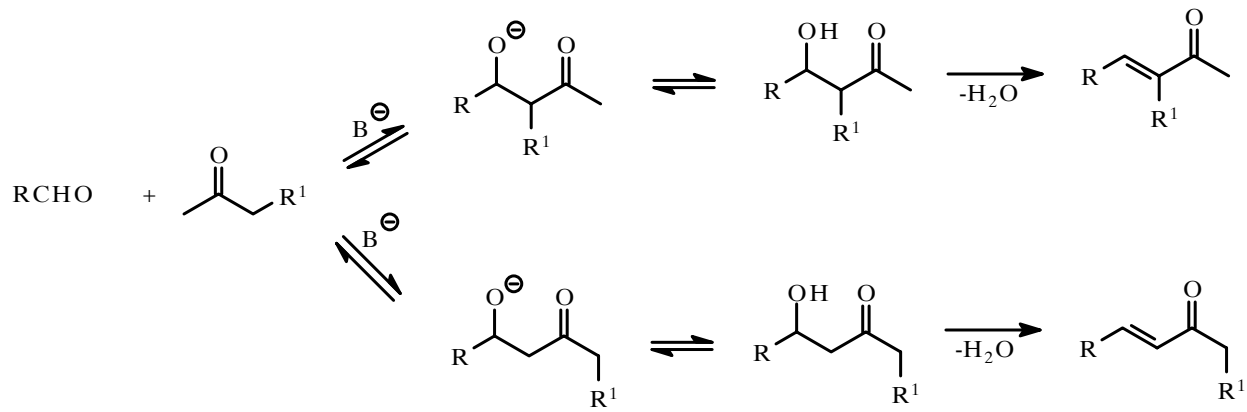
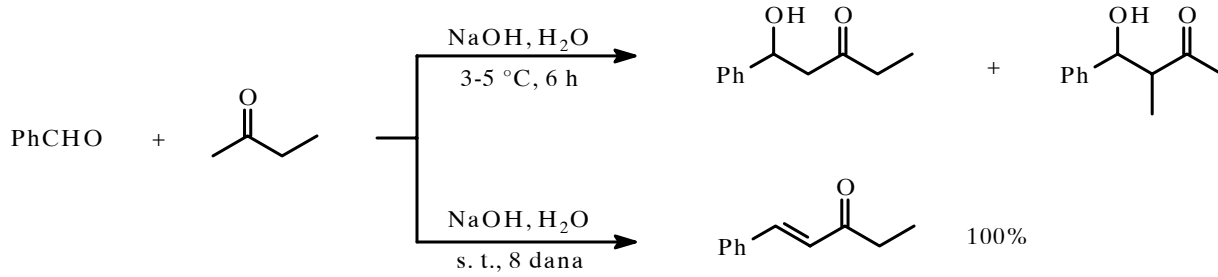
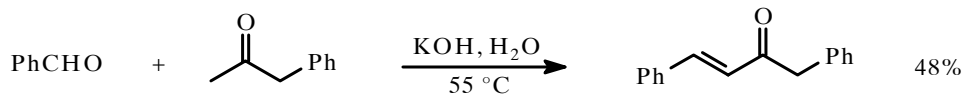
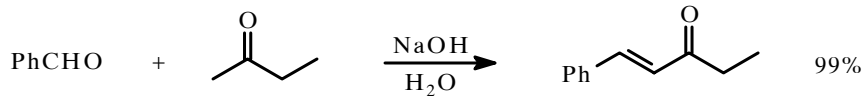


\* Nesimetrični ketoni

adicija: C-3

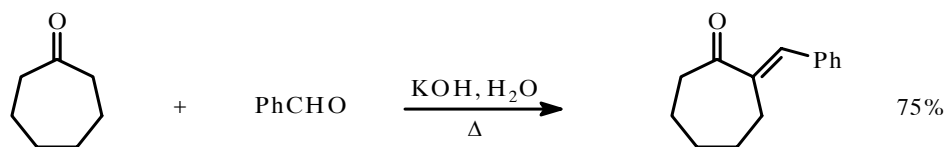
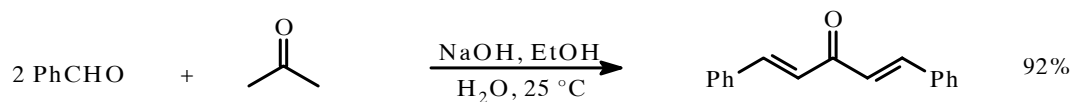
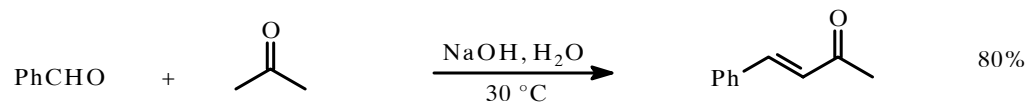
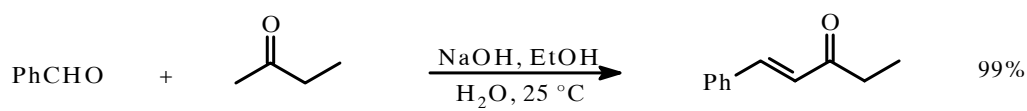
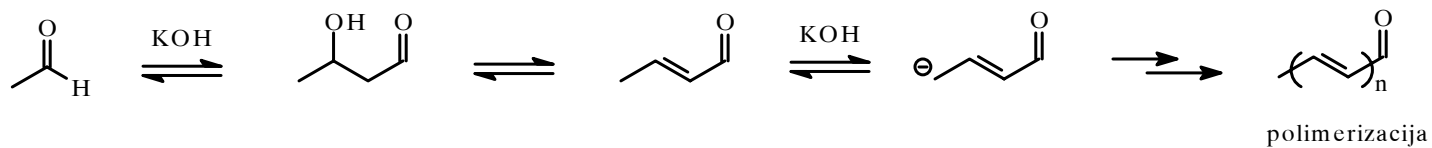


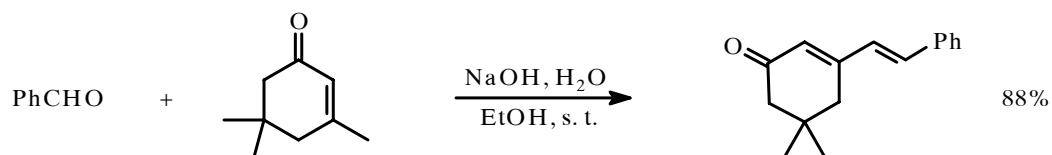
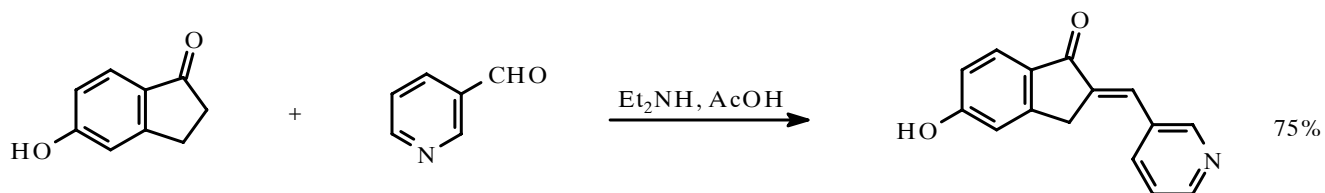
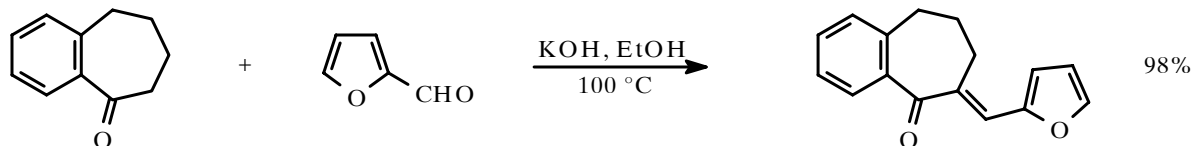
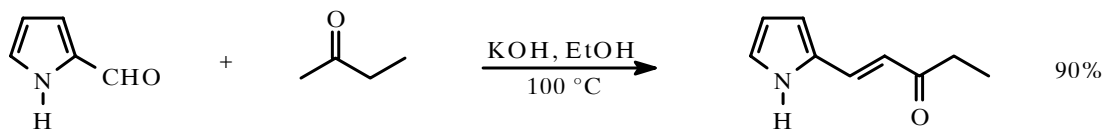
Kondenzacija: C-1



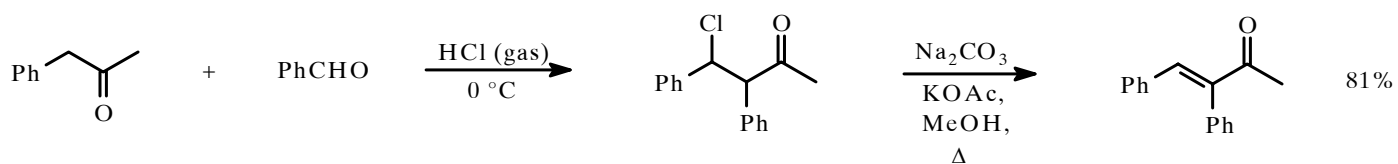
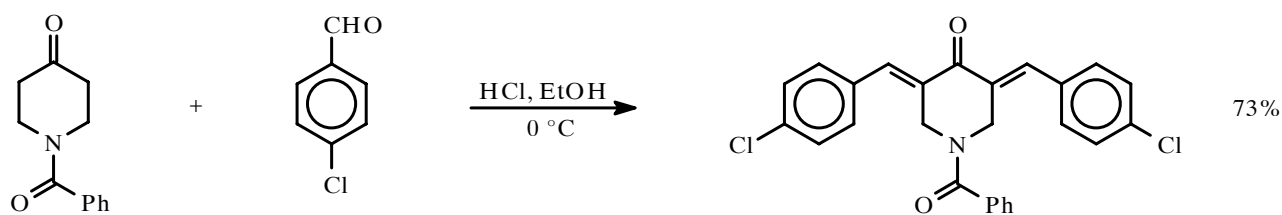
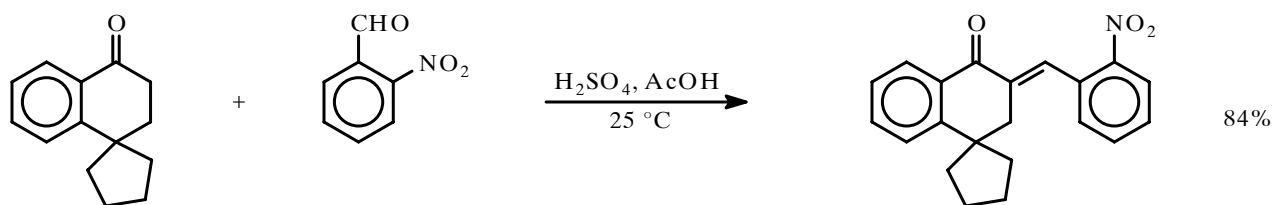
\* ALDOLNE KONDENZACIJE

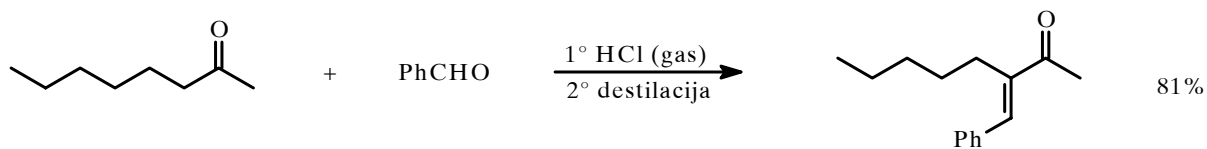
Claisen-Schmidt-ova kondenzacija (Ar-CHO)



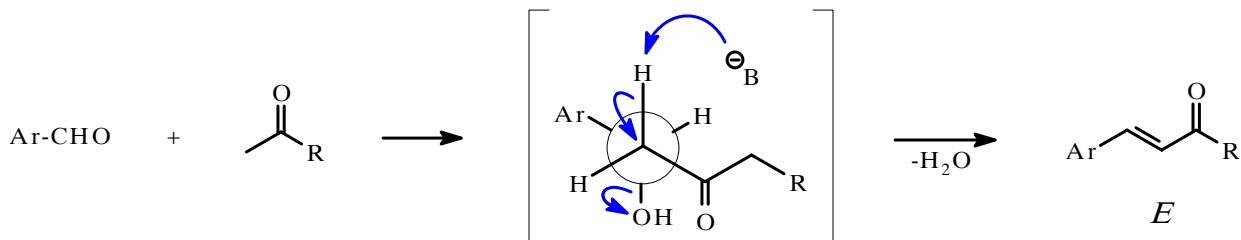


\* Kiselo katalizovana

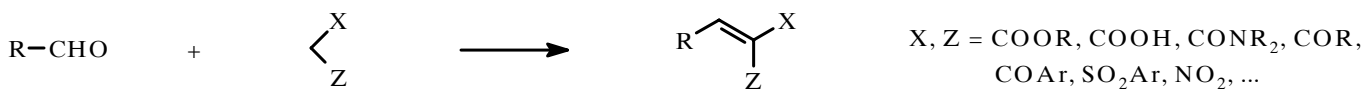




\* Stereohemija dehidratacije



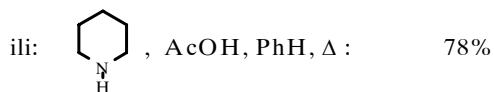
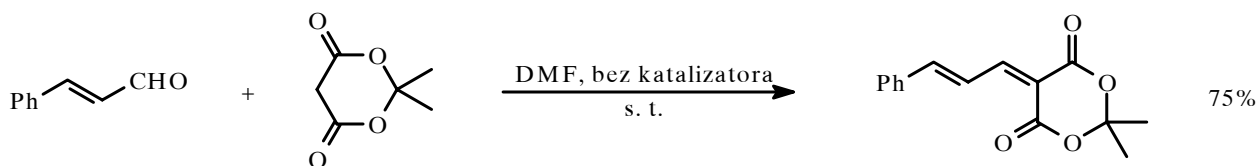
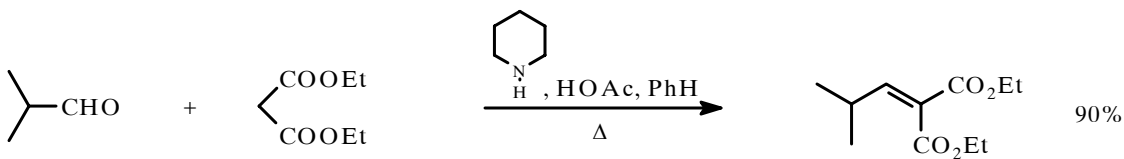
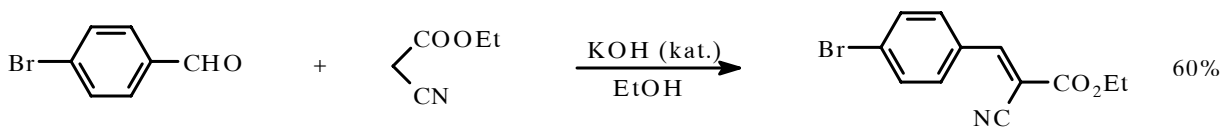
Knoevenagel-ova reakcija



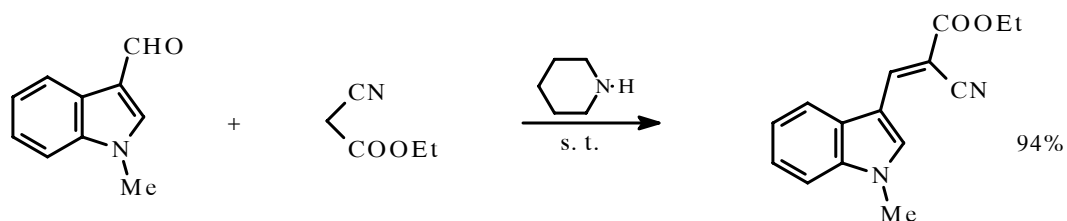
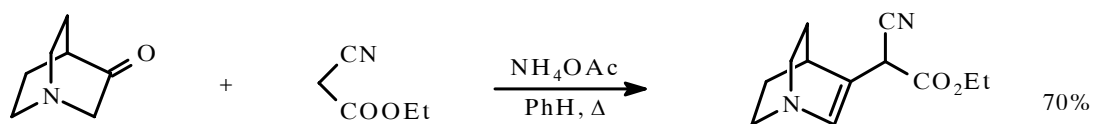
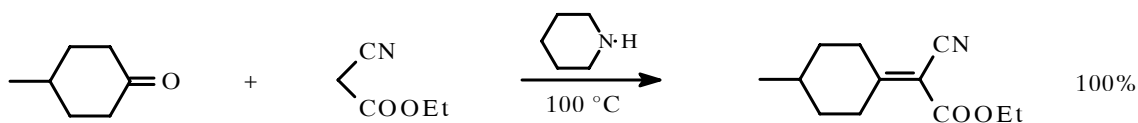
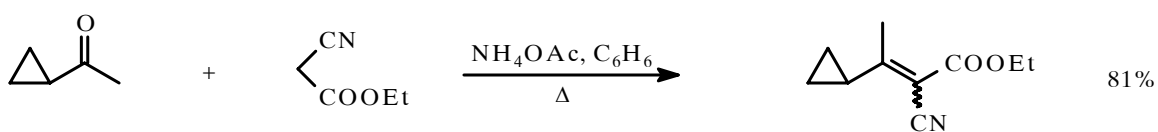
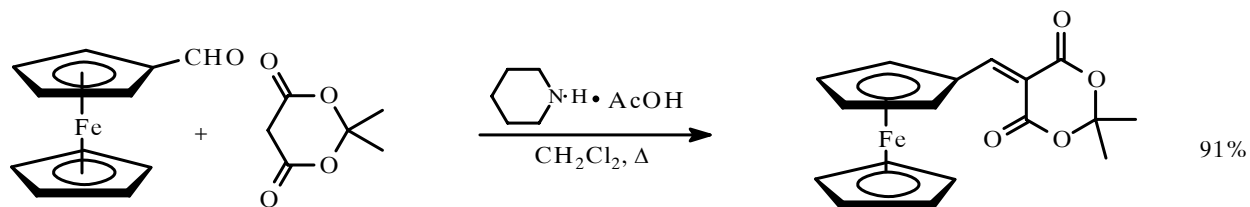
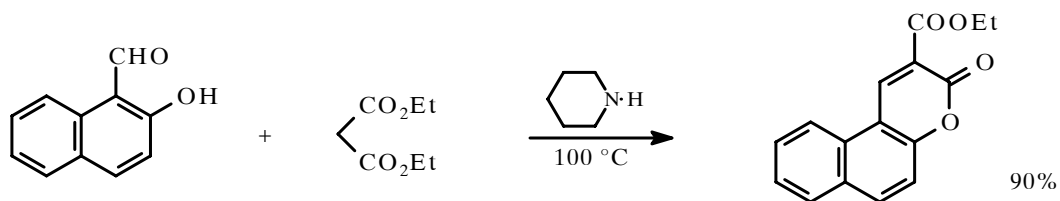
Baze: NH<sub>3</sub>, NH<sub>4</sub>OAc, Piperidin, Pyr, KOH, PhNH<sub>2</sub>, Amin+AcOH

Kiseli katalizatori: ZnCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>+AcOH, TiCl<sub>4</sub>, BF<sub>3</sub>, ...

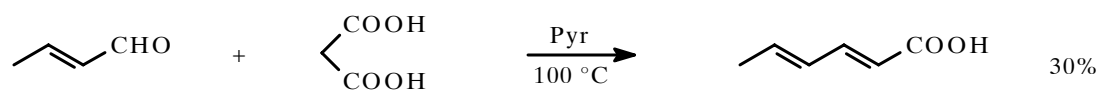
Rastvarači: PhH, PhMe, EtOH, n-BuOH, dioksan, Pyr

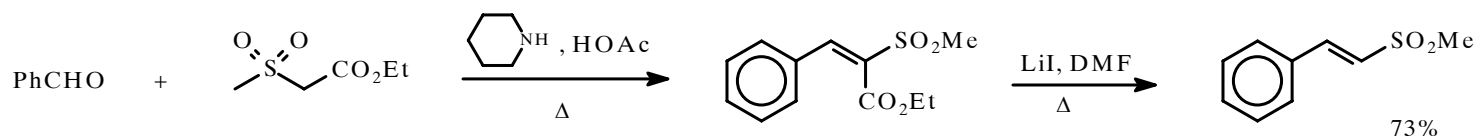
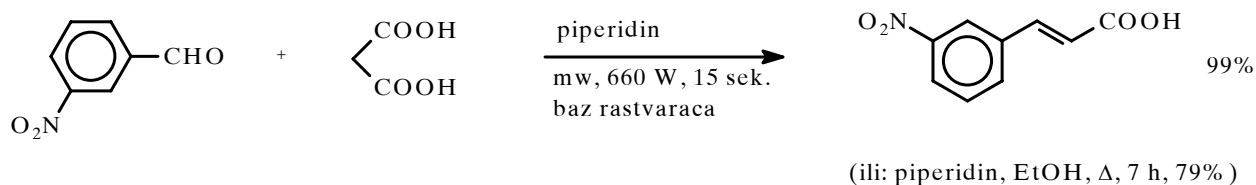
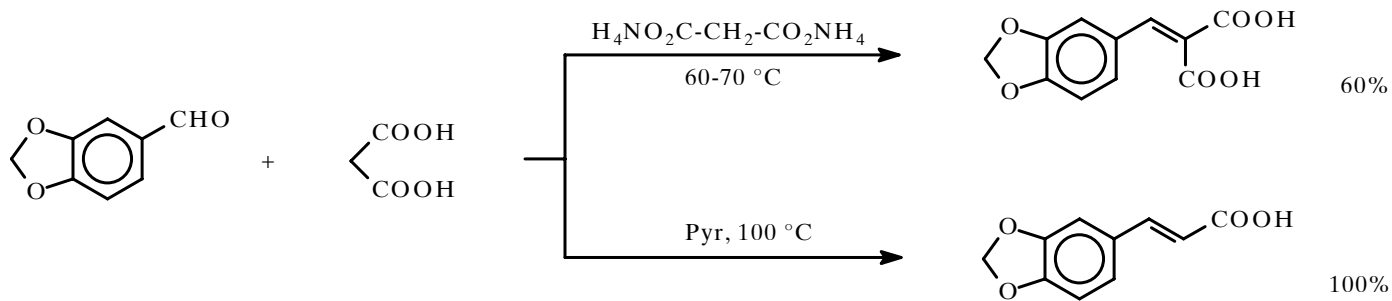




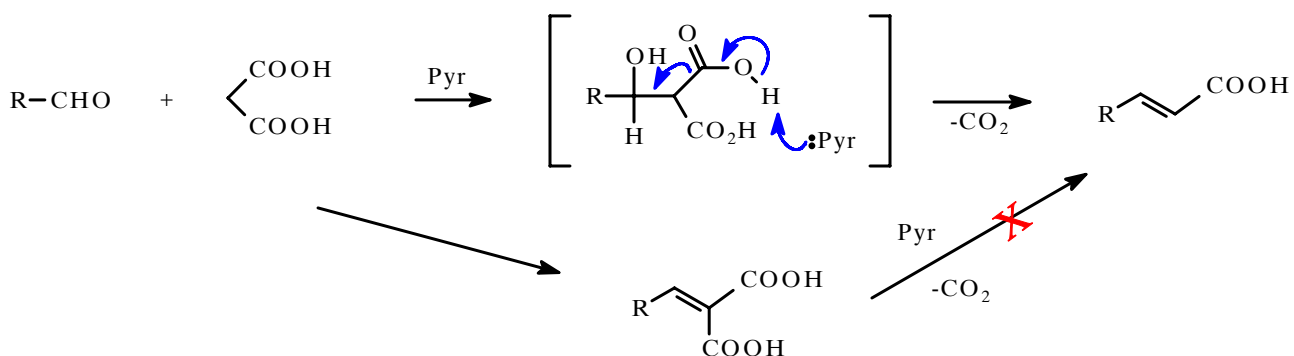
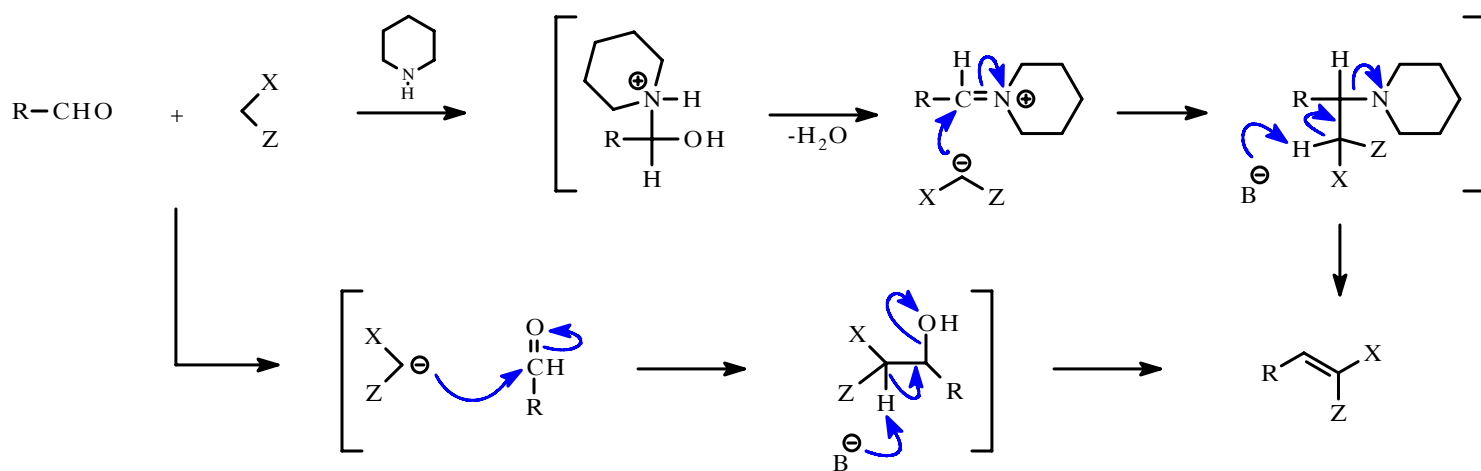


Doebner-ova modifikacija Knoevenagel-ove kondenzacije:

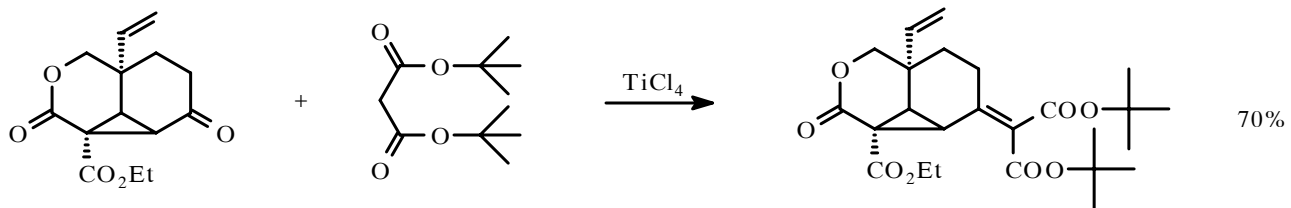
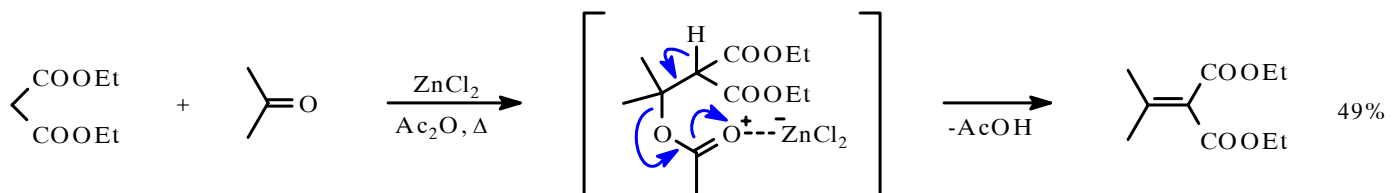
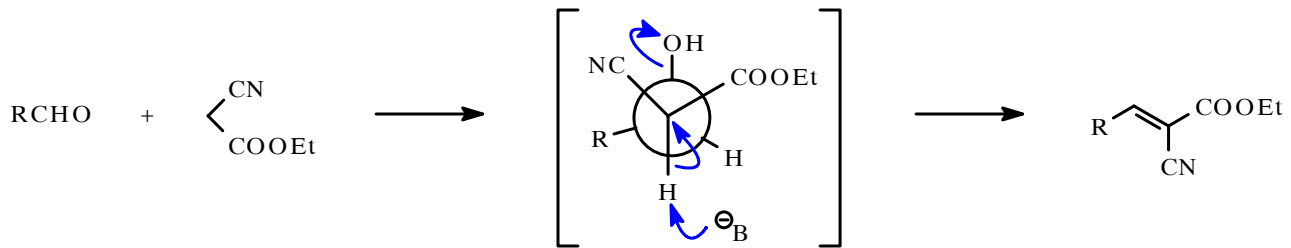




\* Mehanizam

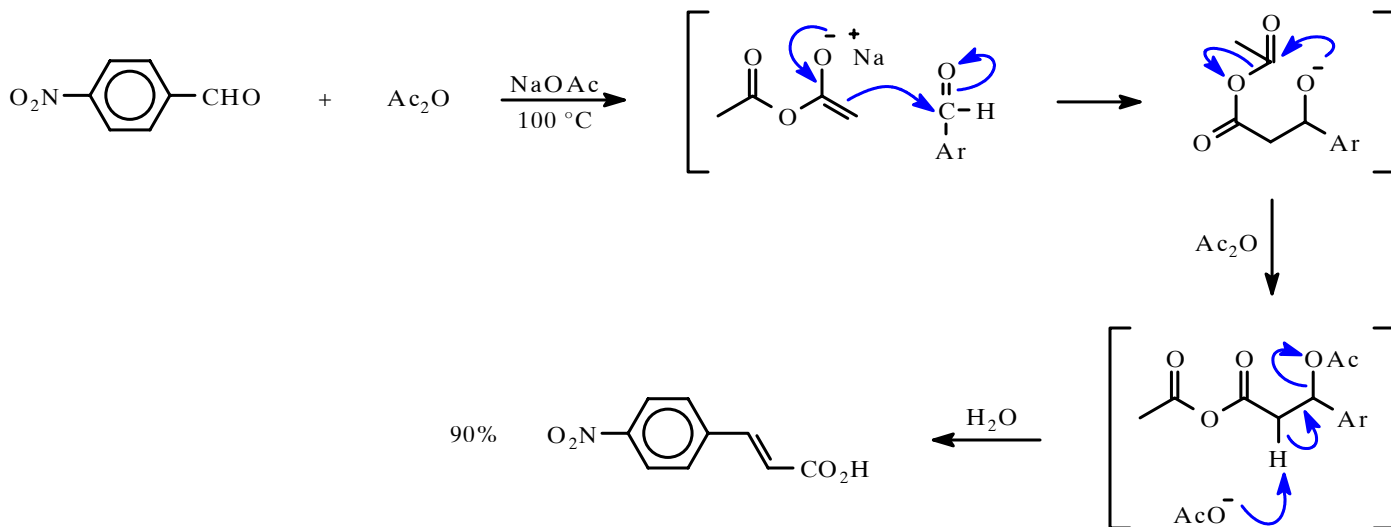
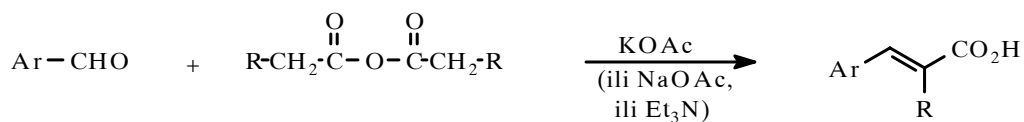


\* Stereohemija

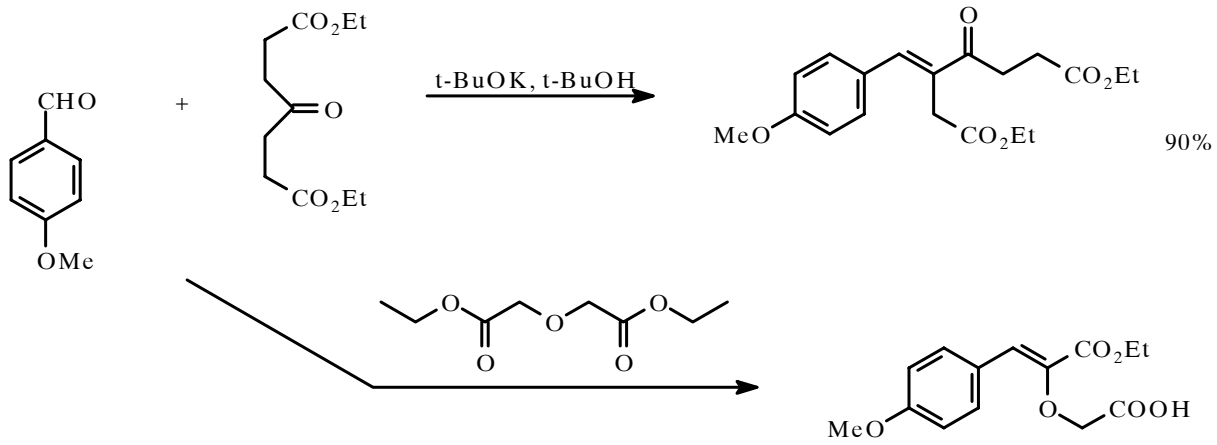
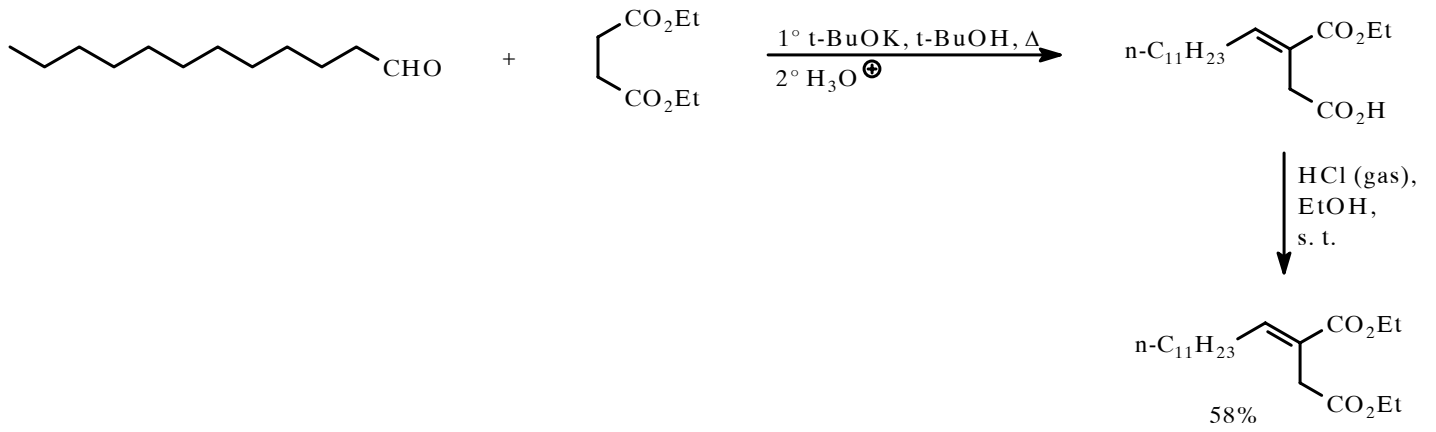


\* Aldolne kondenzacije potpomognute ciklizacijom: Perkin-ova, Stobbe-ova i Darzens-ova reakcija

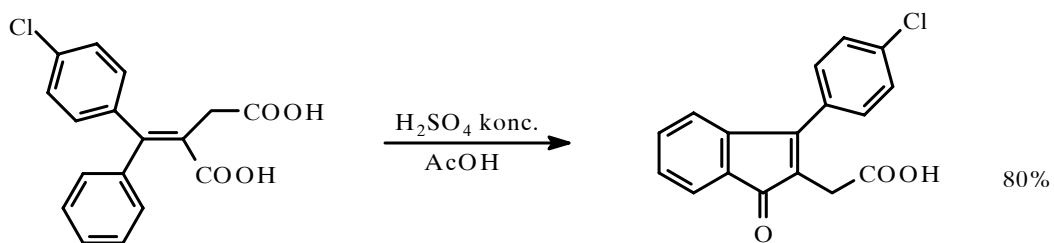
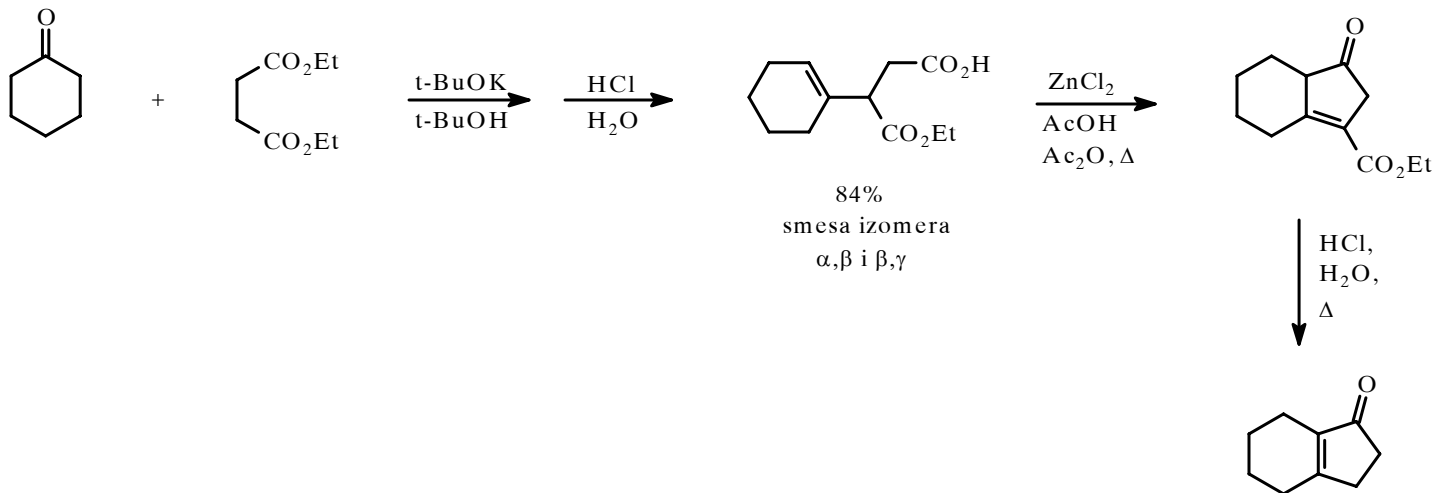
\* Perkin-ova reakcija

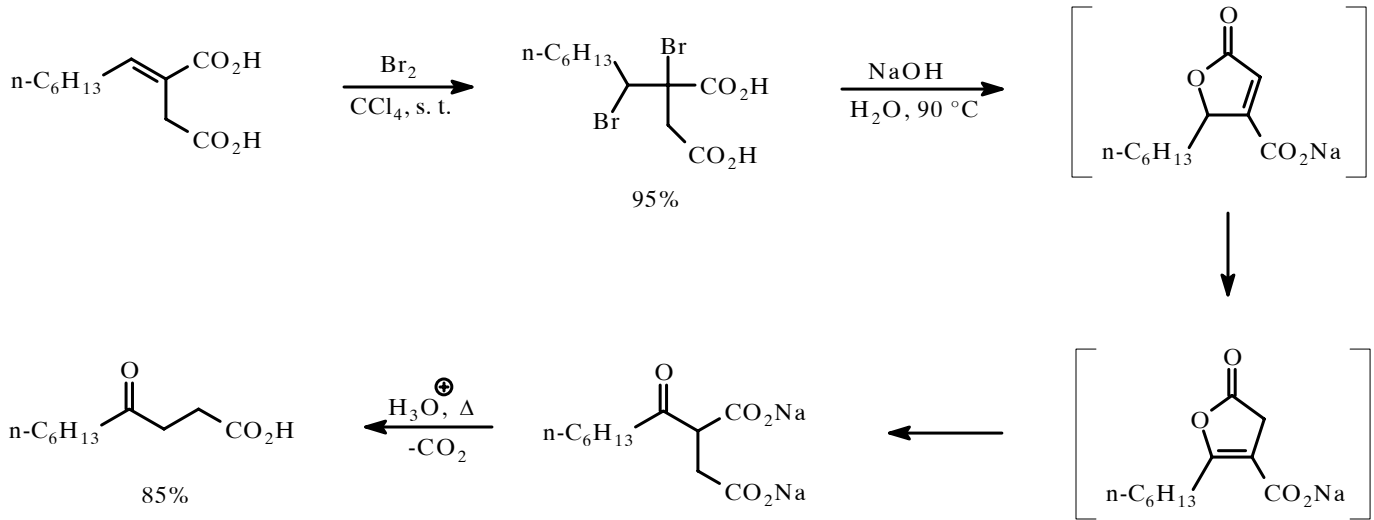




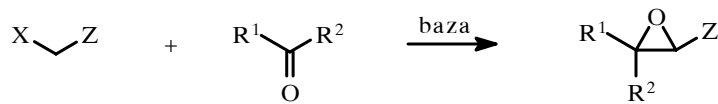


\* Transformacije proizvoda





\* Darzens-ova kondenzacija (glicidno-estarska kondenzacija)

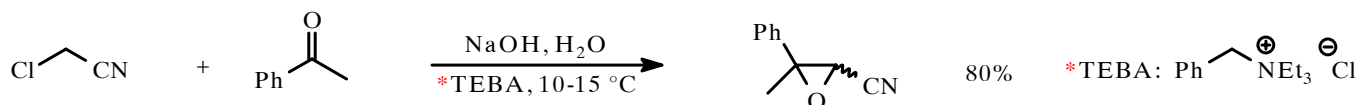
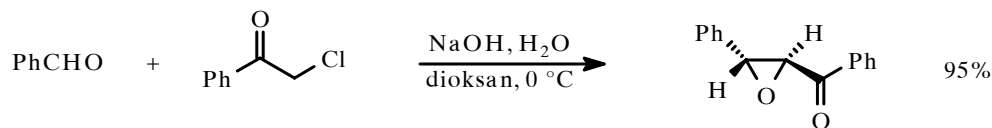
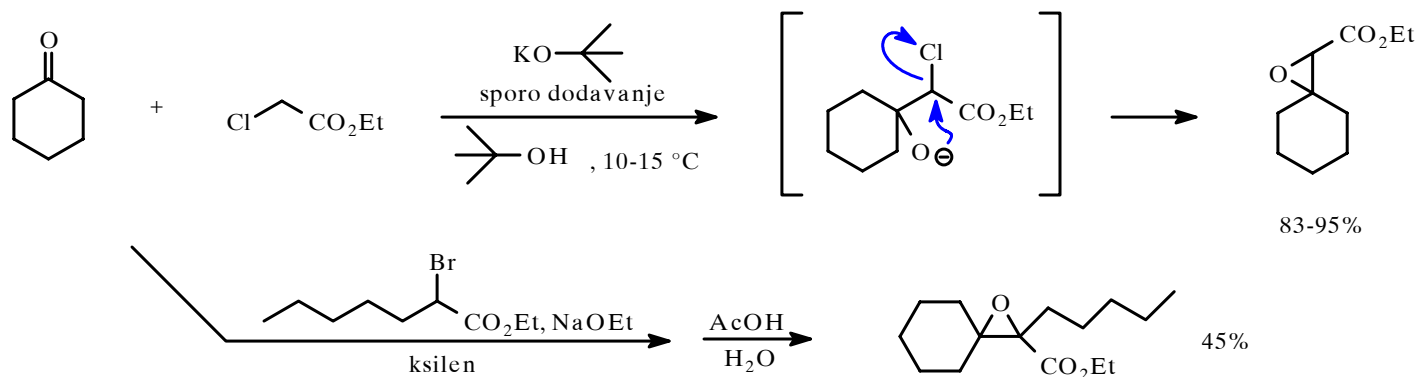


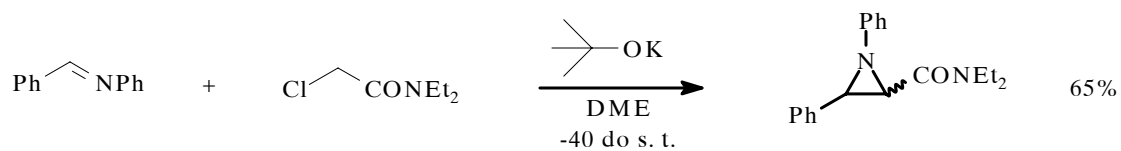
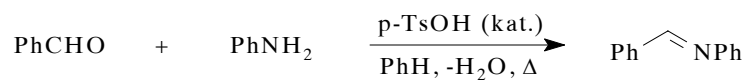
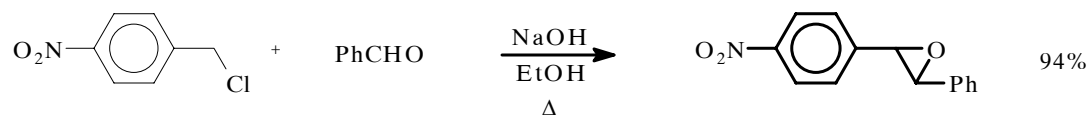
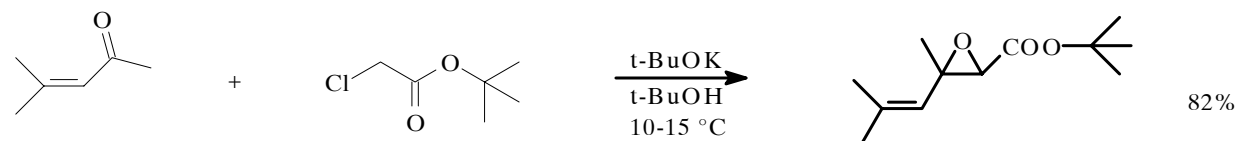
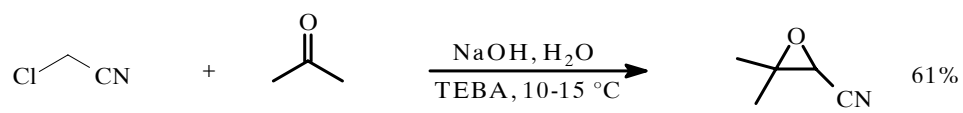
X = Br, Cl

Z = COOR, CN, COR, COAr, ...

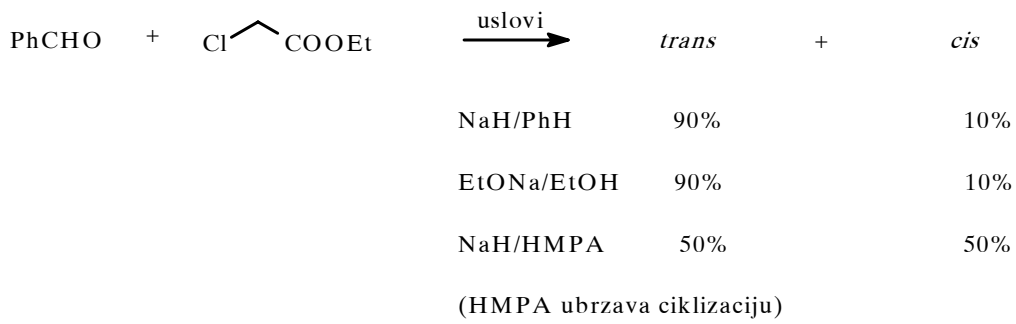
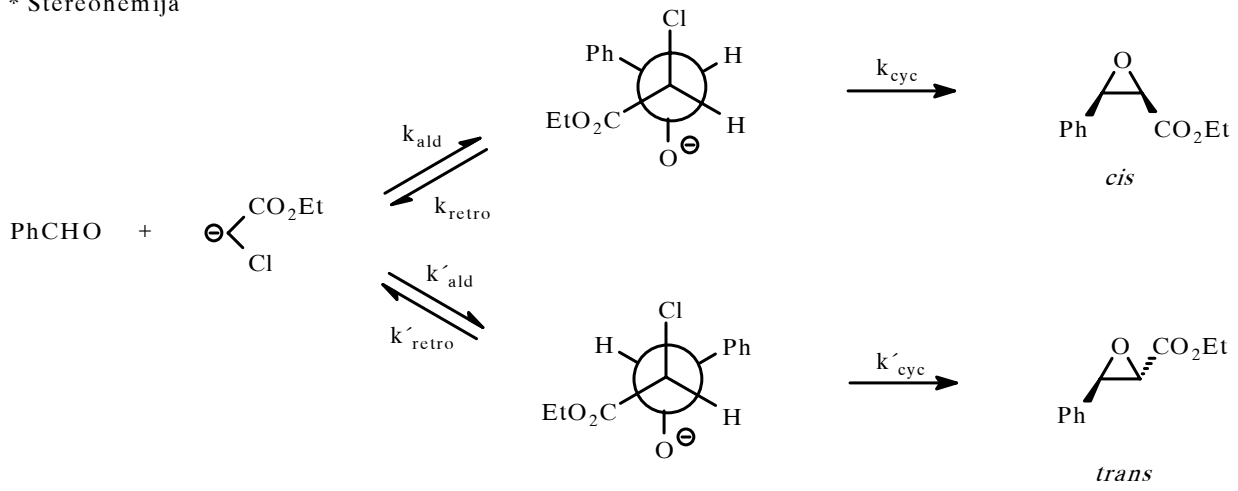
Baze: t-BuOK, NaOEt, NaOH

Rastvarači: t-BuOH, H<sub>2</sub>O, DME, THF, ArH

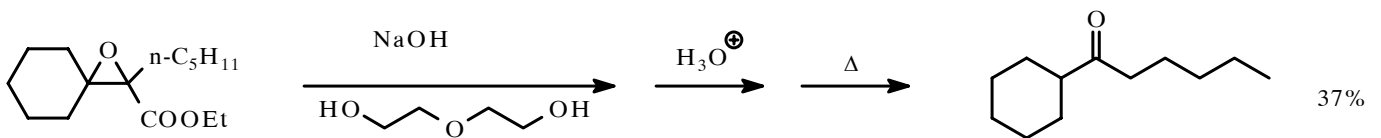
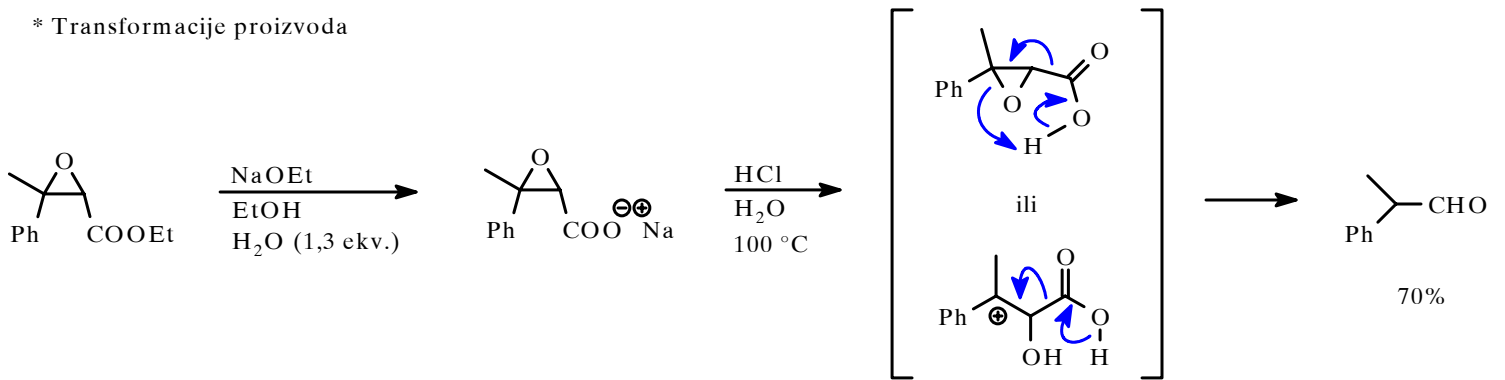




\* Stereohemija



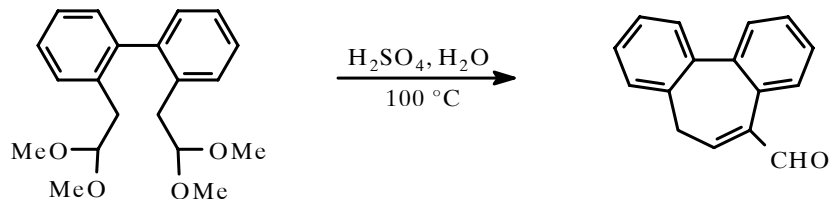
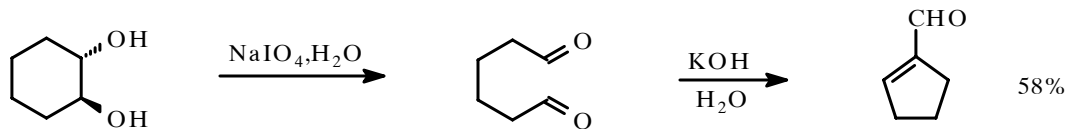
\* Transformacije proizvoda



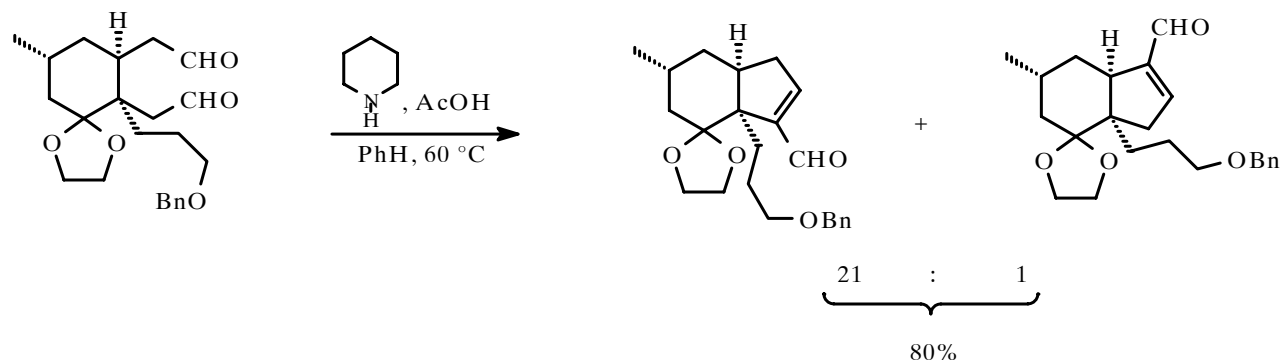


## 2. INTRAMOLEKULSKE ADICIJE I KONDENZACIJE

### \* Dialdehidi

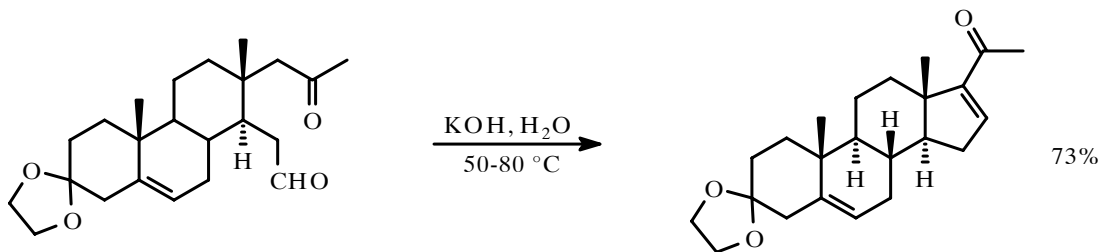
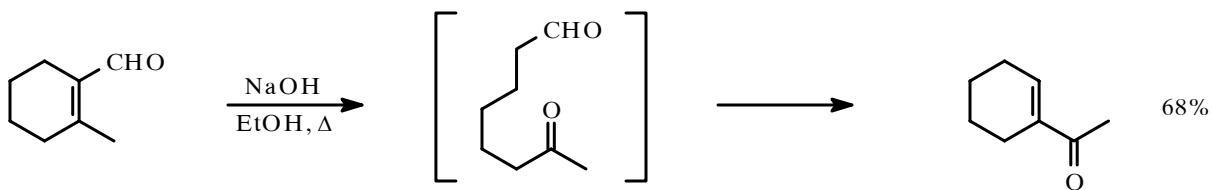


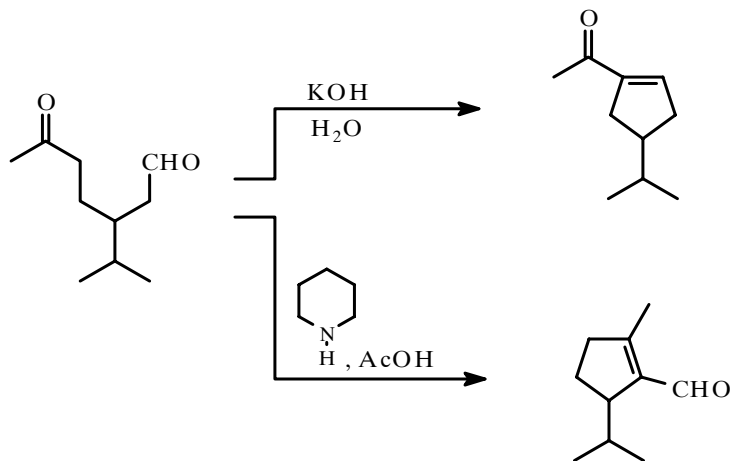
### \* Nesimetrični aldehidi: stereo manje zaštićena CHO grupa obično je akceptor



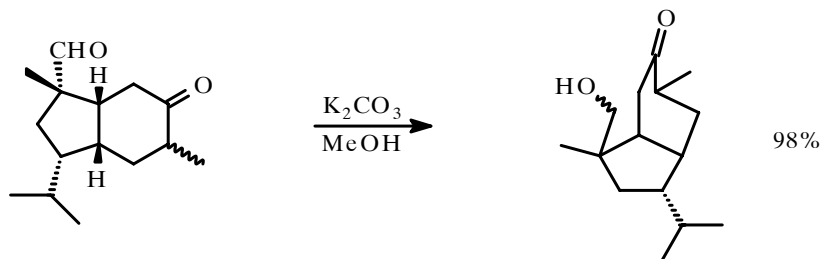
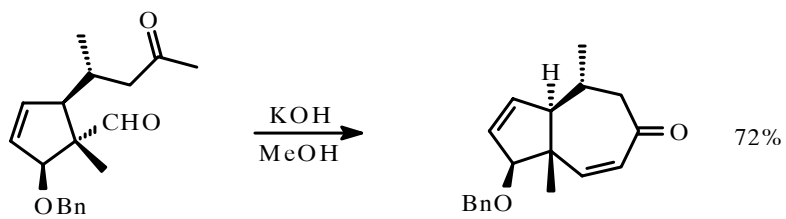
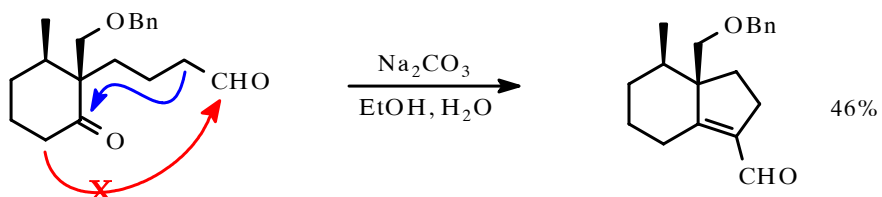
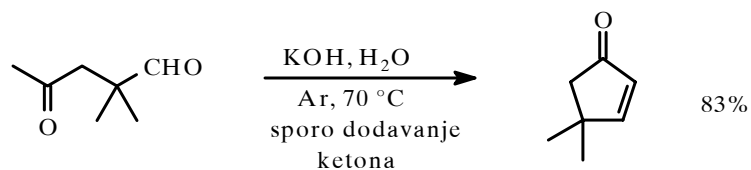
### \* Ketoaldehidi

Pod termodinamičkim uslovima: **enon >> enal**

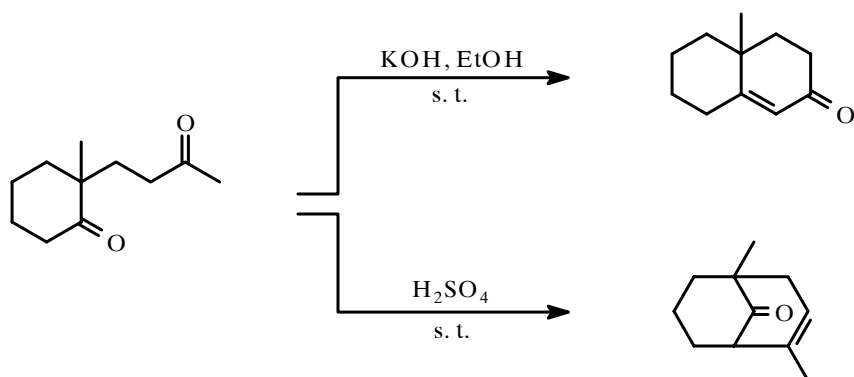
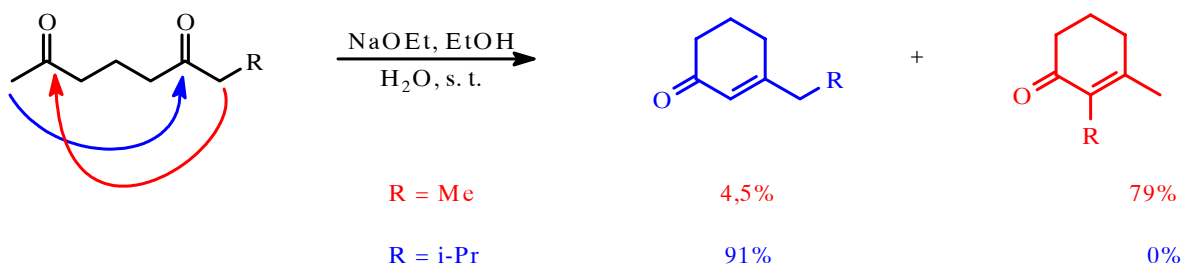
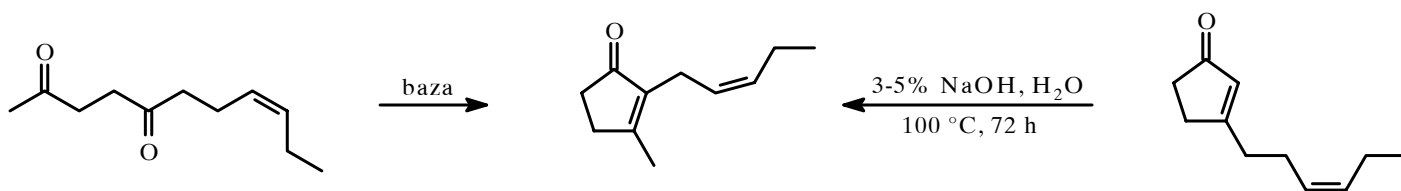
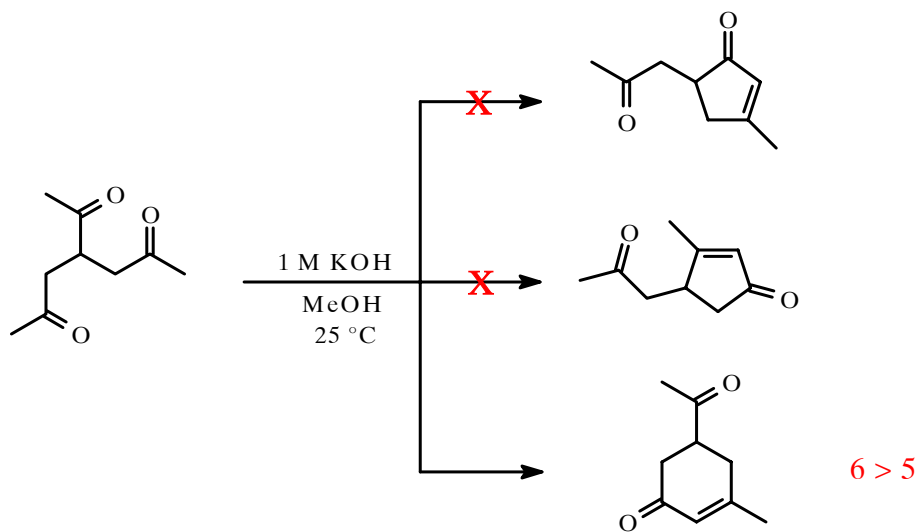


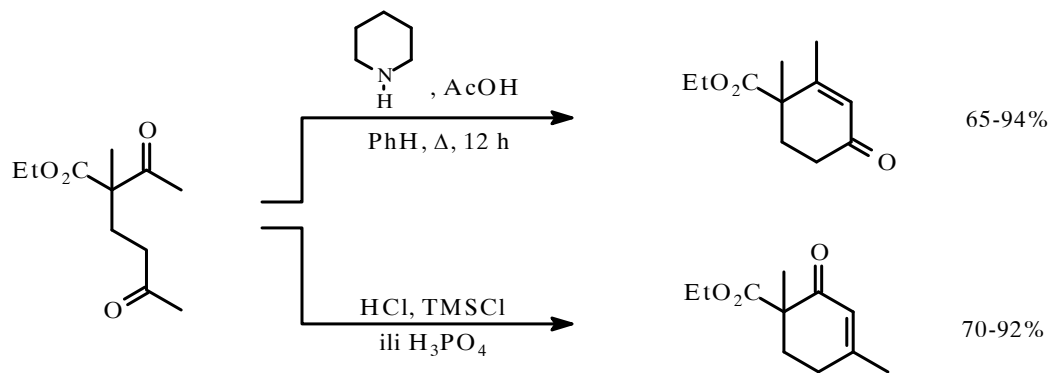


ne nastaje  
5 > 7

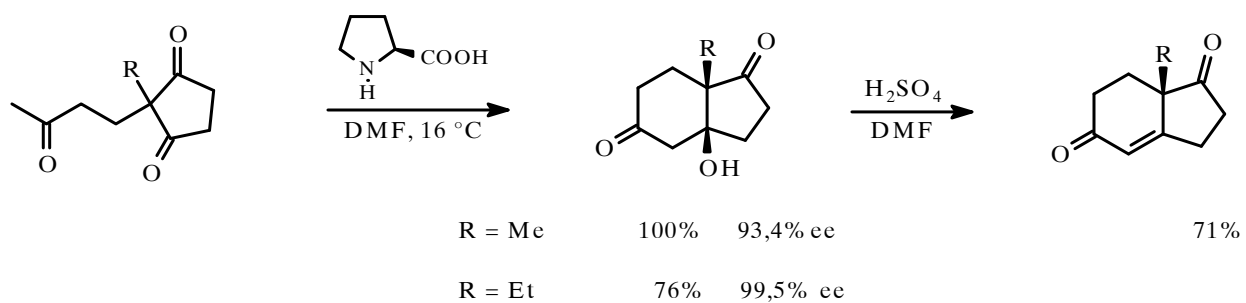


\* Diketoni





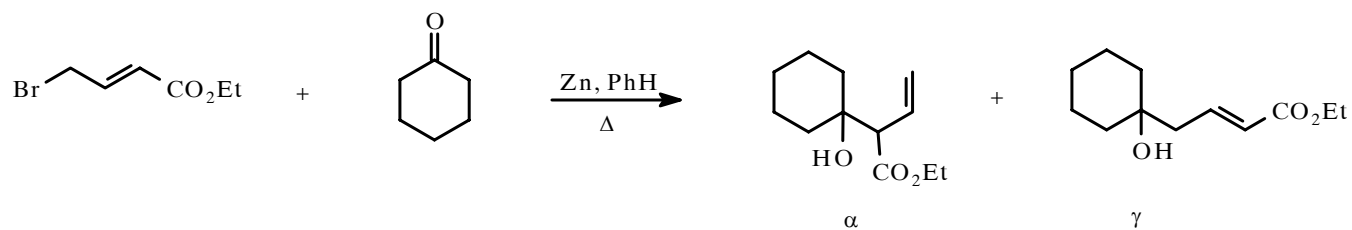
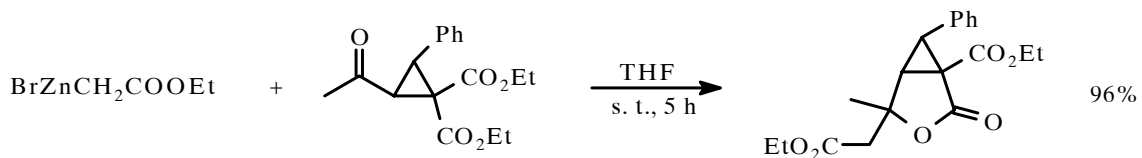
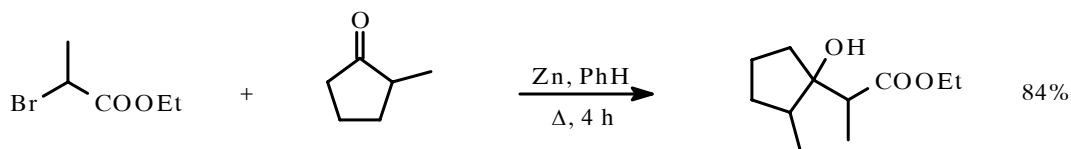
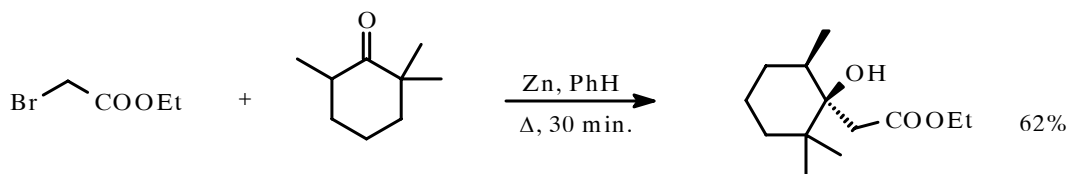
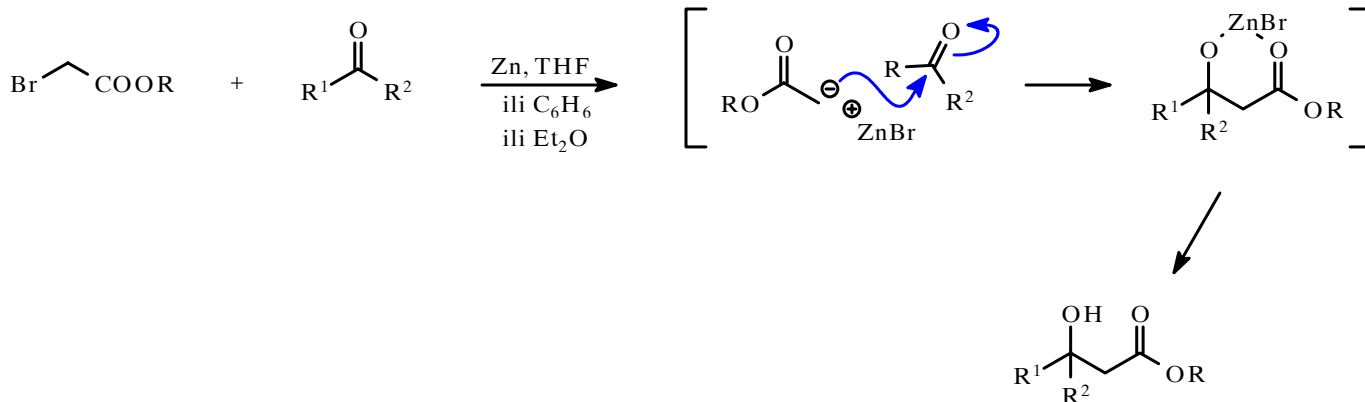
\* Asimetrična indukcija



### 3. ALDOLNE REAKCIJE U APROTIČNIM USLOVIMA (DIRIGOVANE)

\* U BAZNIM USLOVIMA

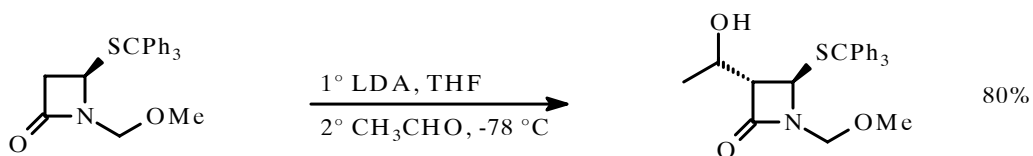
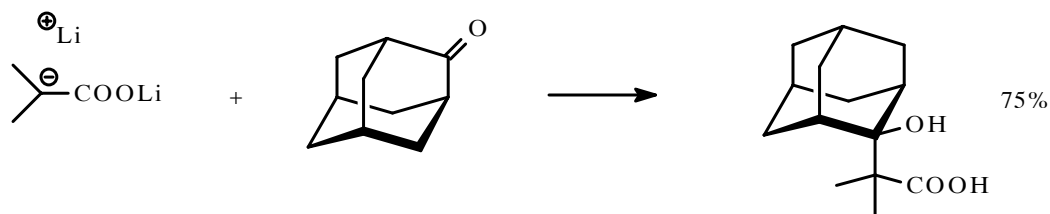
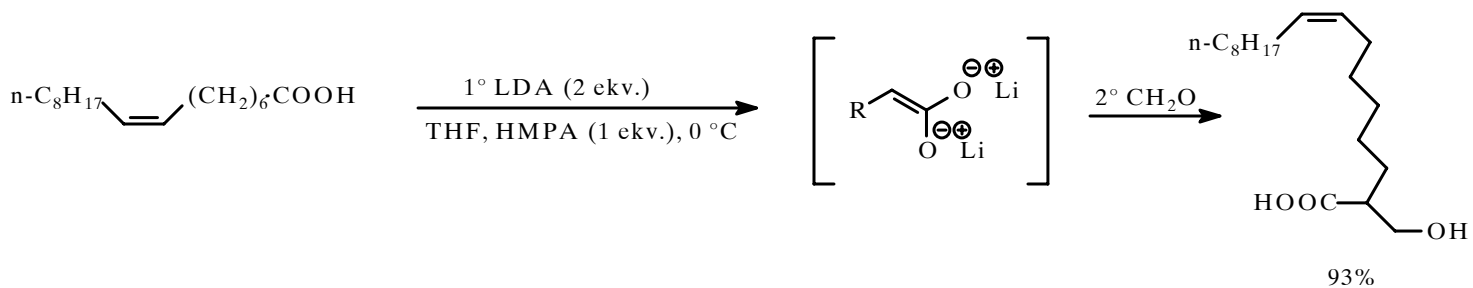
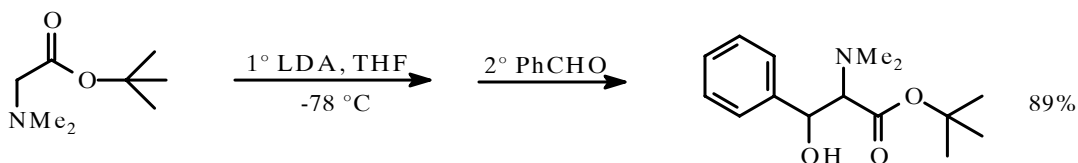
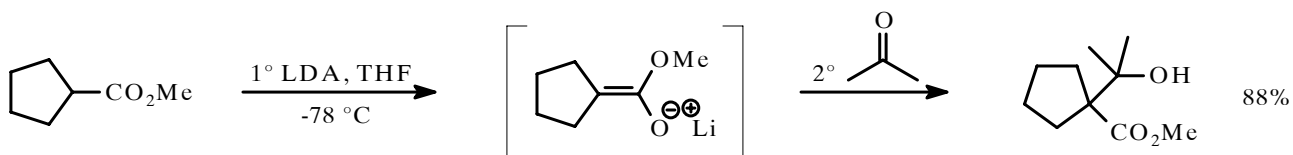
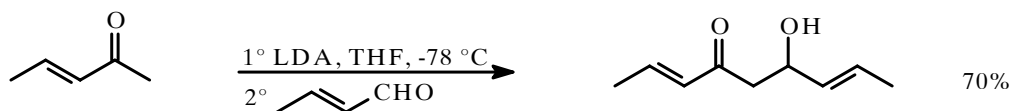
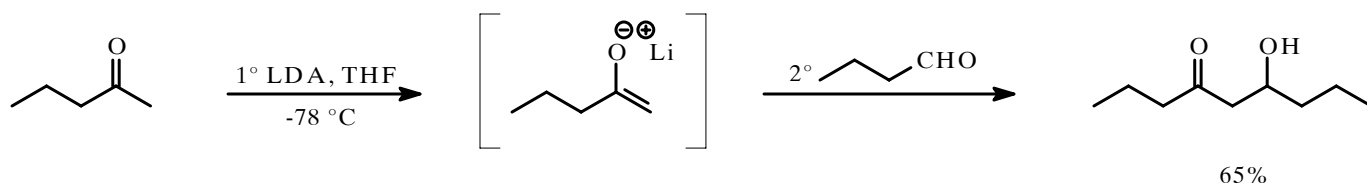
\* Reakcija po Reformatskom (Reformatsky)



Vreme reakcije

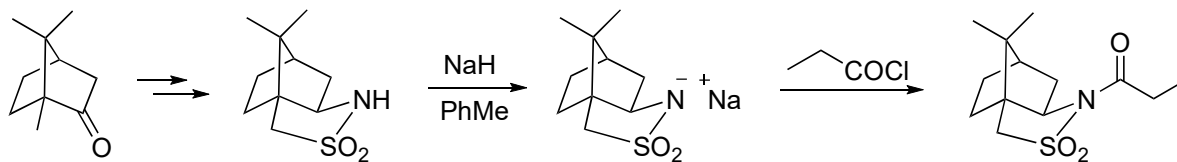
6 min.	60	:	40
45 min.	40	:	60
2 sata	0	:	100
-40 °C, 120 sati	100	:	0

\* Stvaranje preformiranih enolata pomoću baza

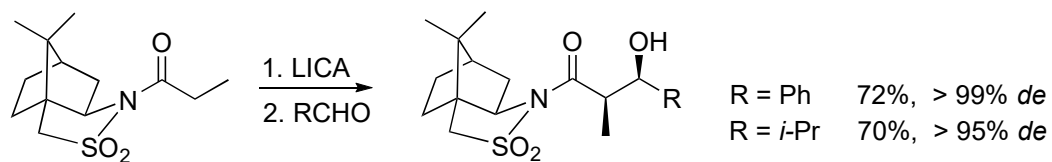


Asimetrične dirigovane aldolne adicije pomoću hiralnih induktora:

Oppolzer-ov sultam

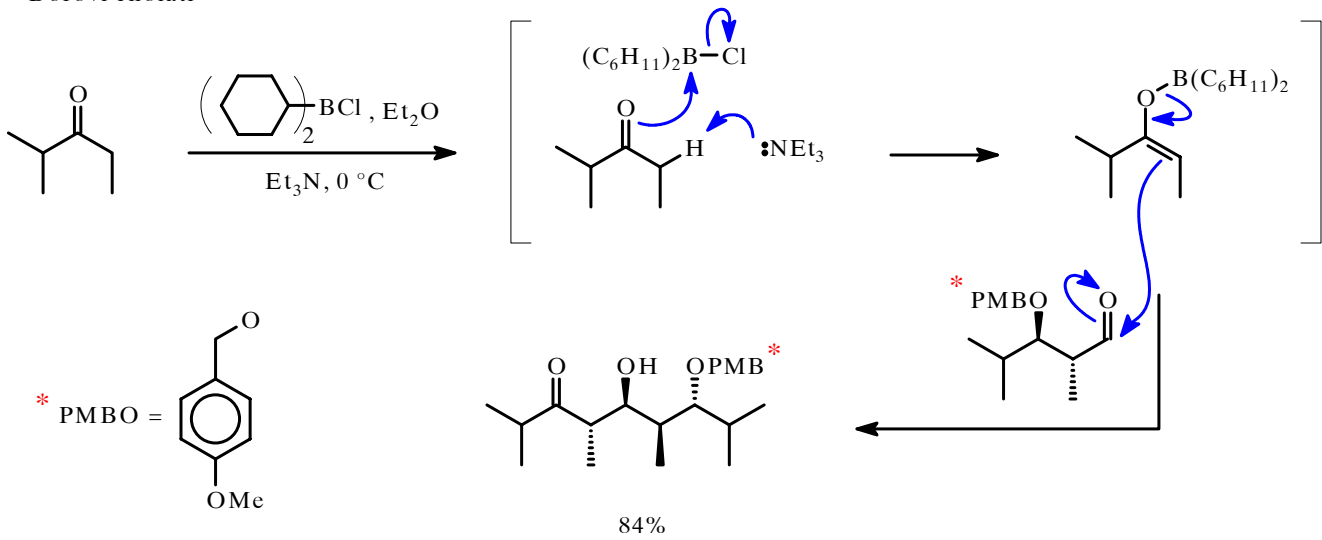


Org. Synth. Coll. Vol. VIII, 110



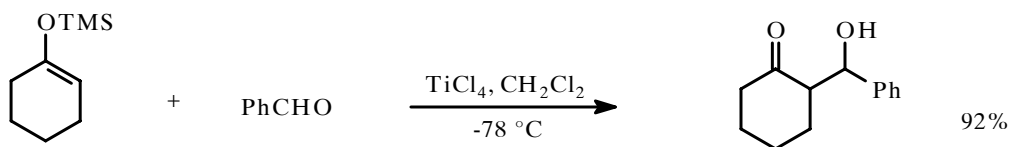
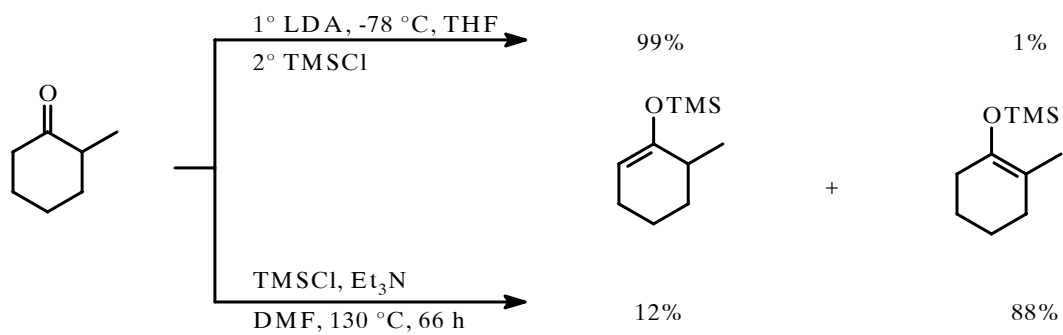
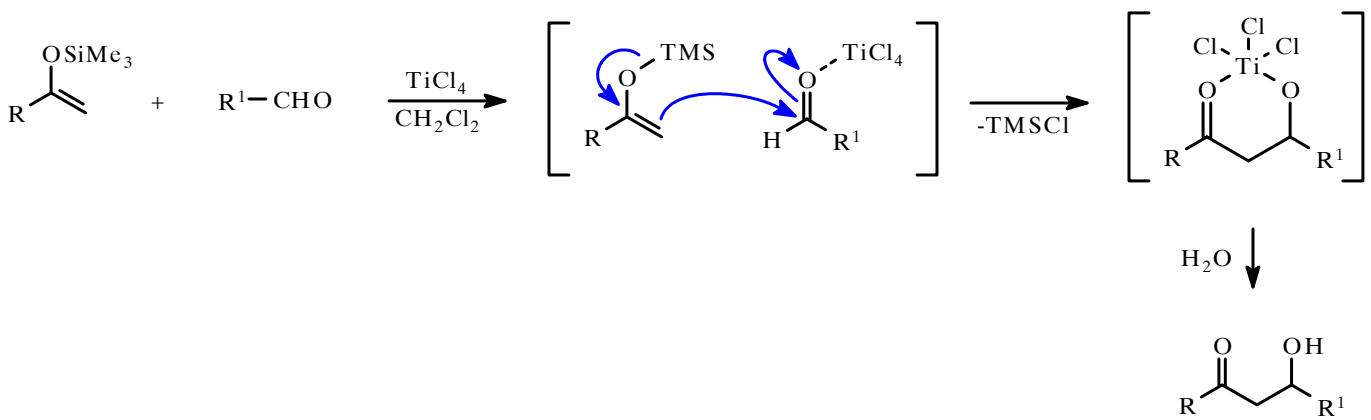
J. Am. Chem. Soc. 1990, 112, 2767

\* Borovi enolati

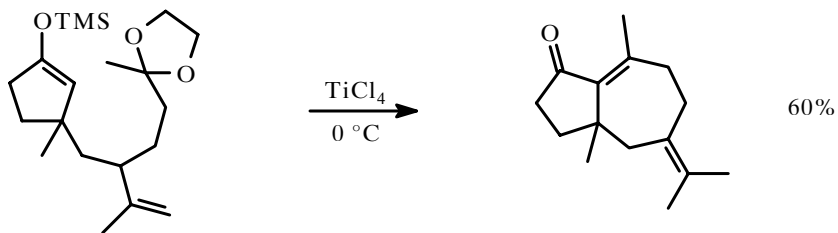
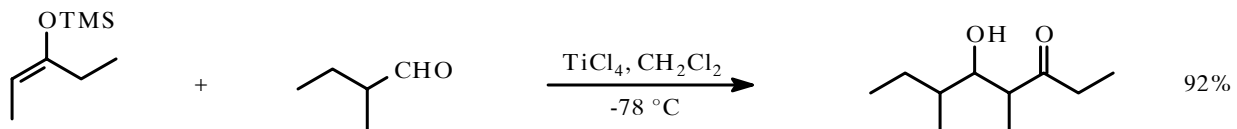
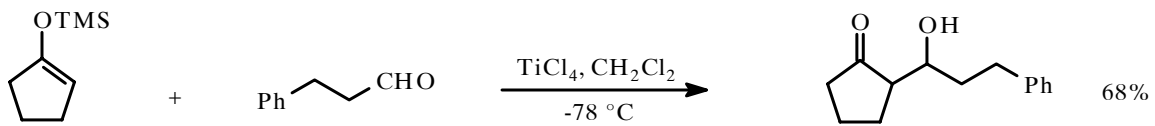


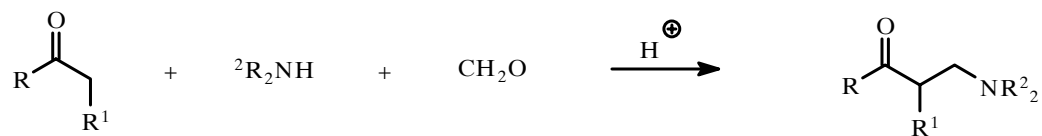
\* U KISELIM USLOVIMA

Mukaiyama-ina reakcija

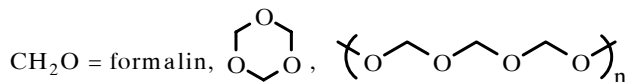
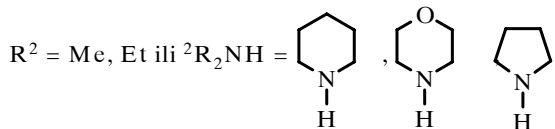




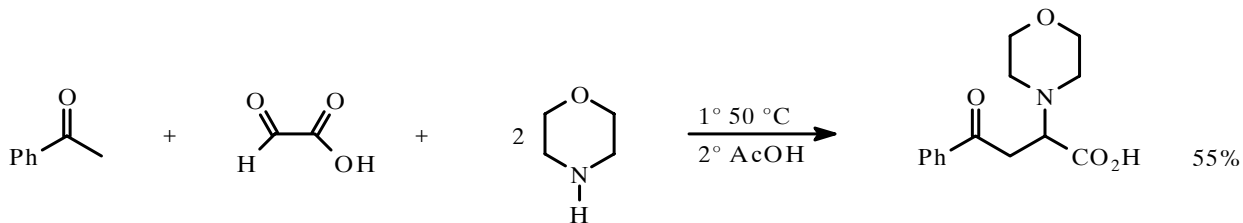
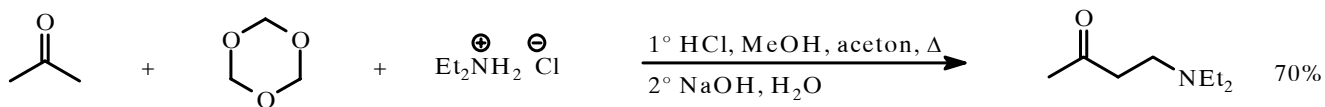
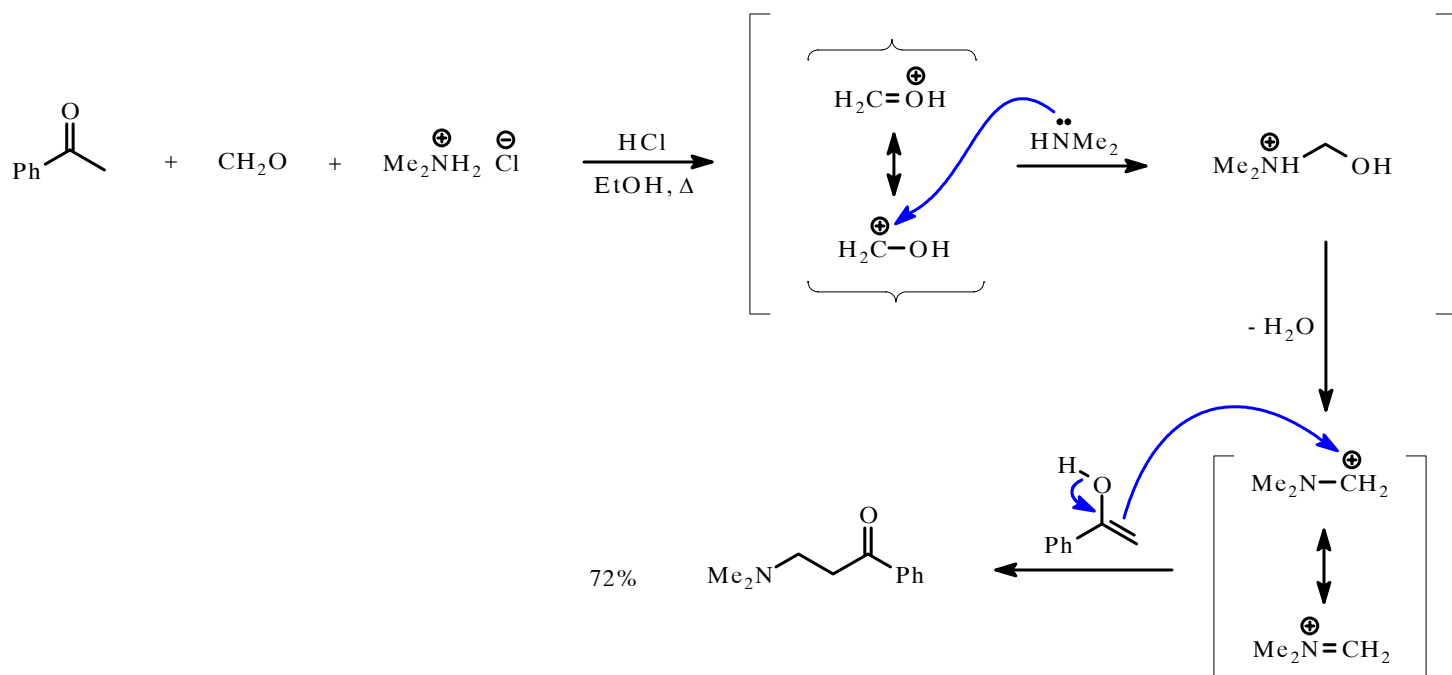




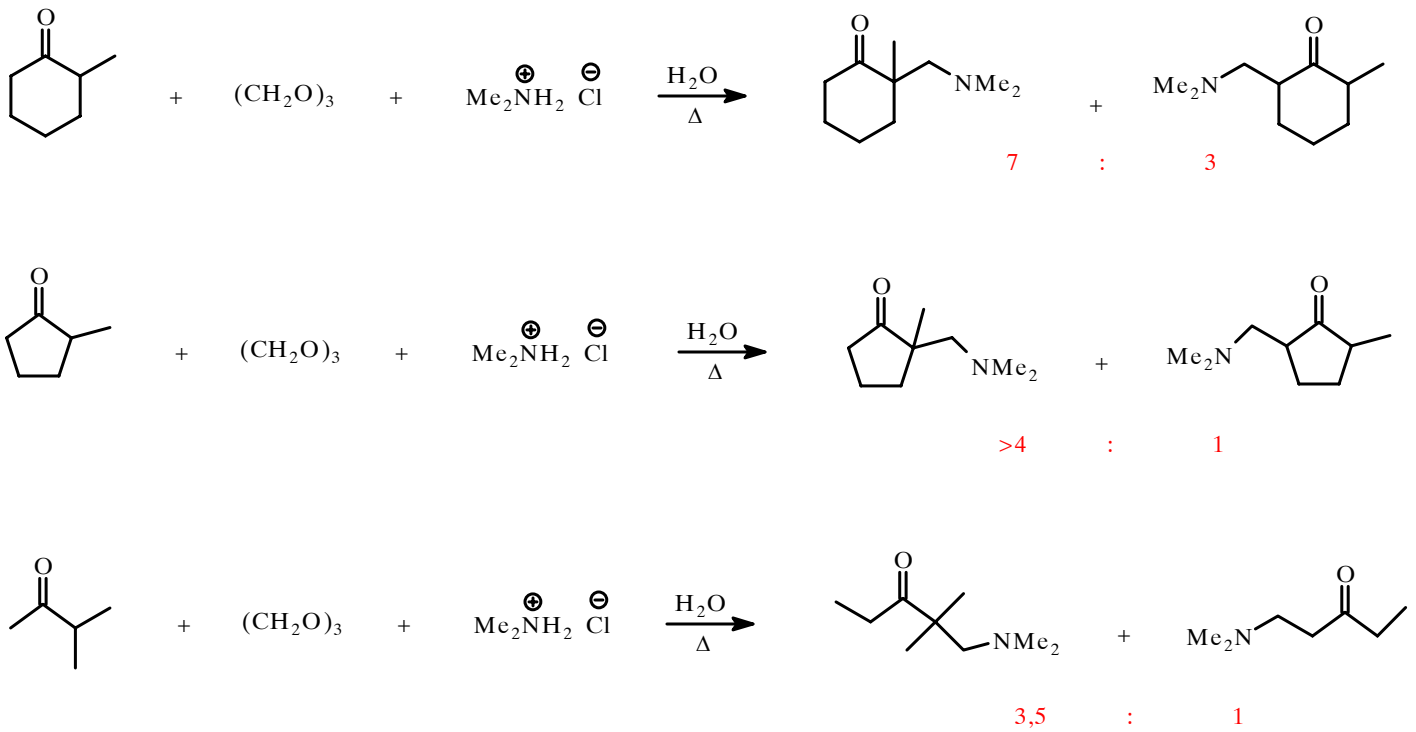
R = alkil, aril; R<sup>1</sup> = alkil, aril ili e-privlačna grupa



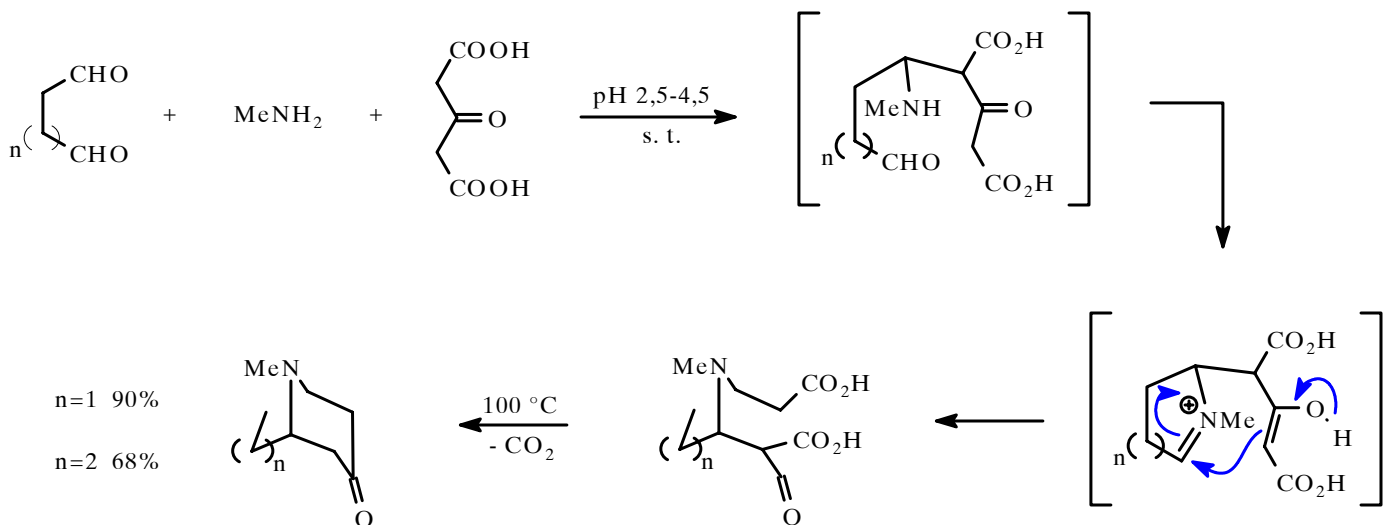
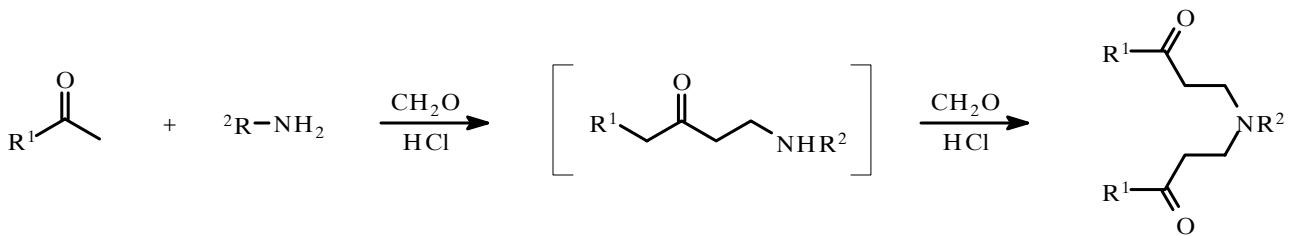
Rastvarač: H<sub>2</sub>O, MeOH, EtOH, AcOH,...

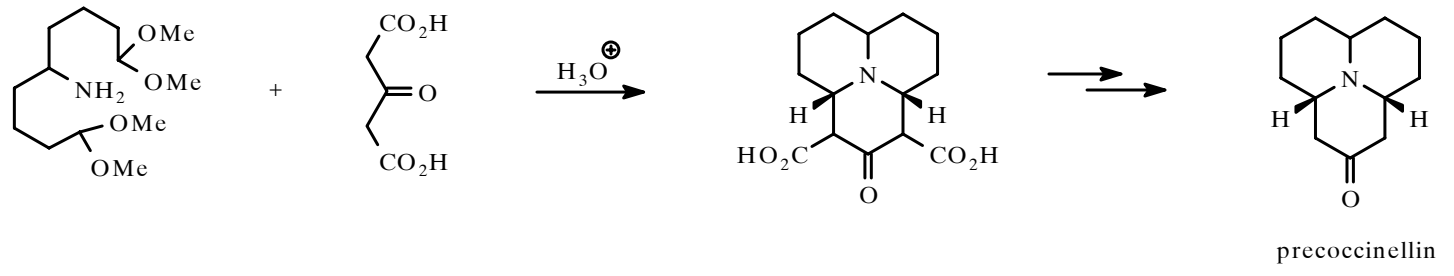
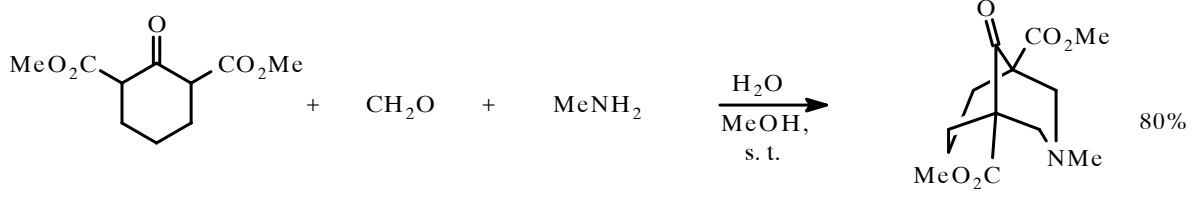


\* Nesimetrični ketoni: termodinamički proizvodi

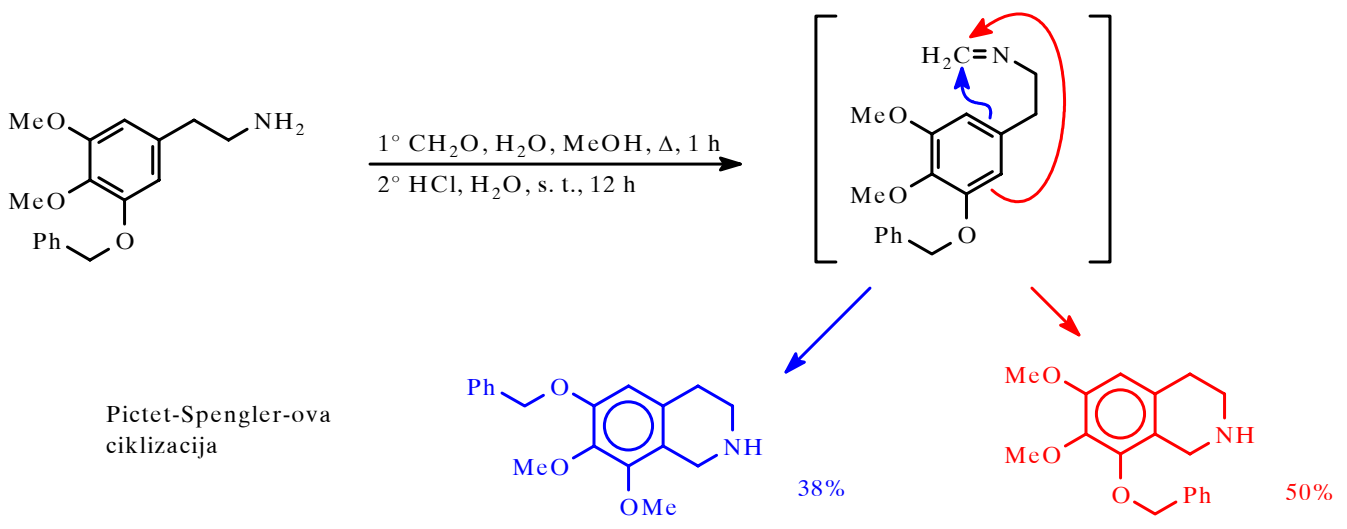
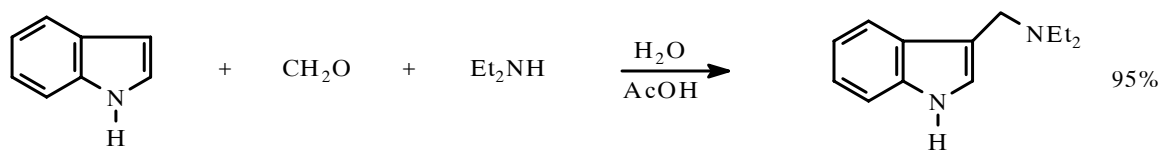
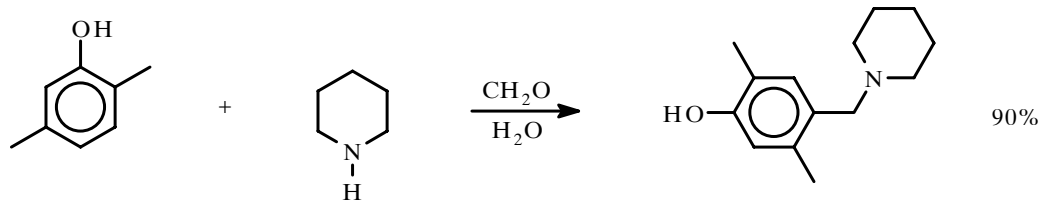
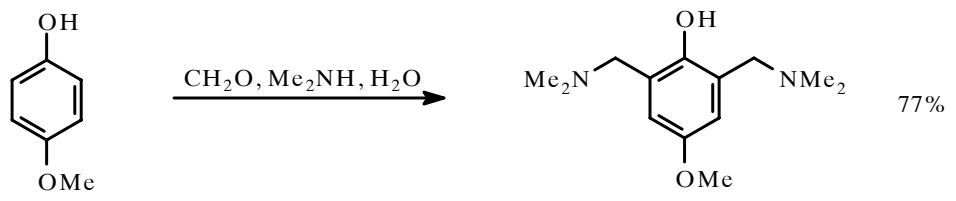


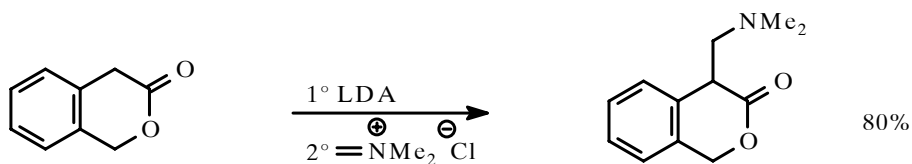
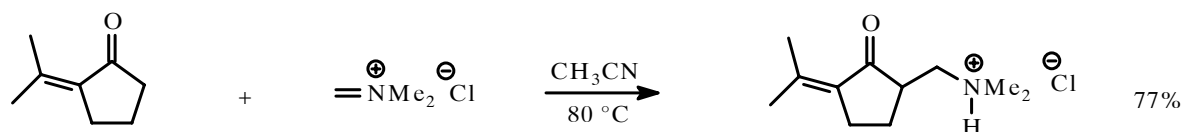
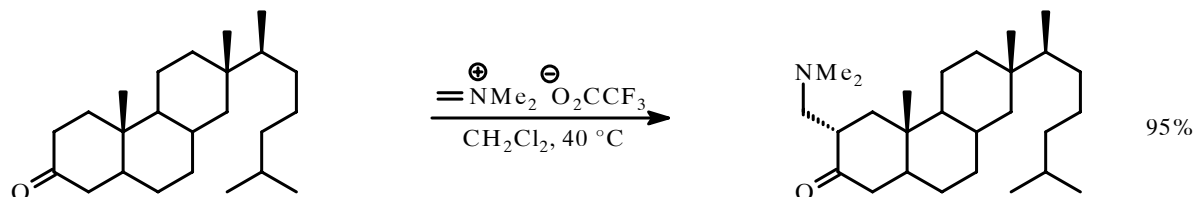
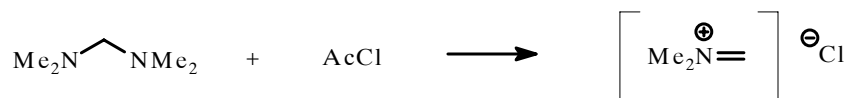
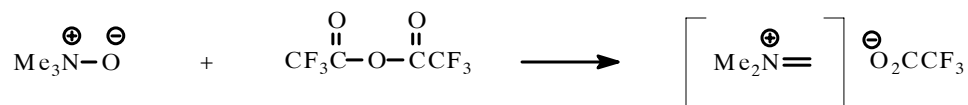
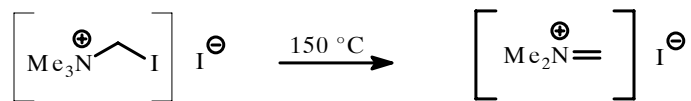
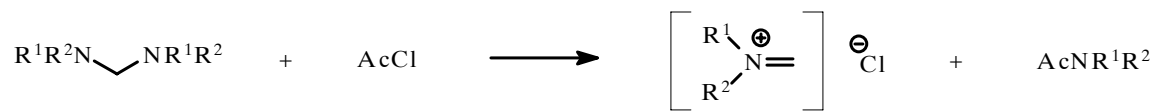
\* Primarni amini

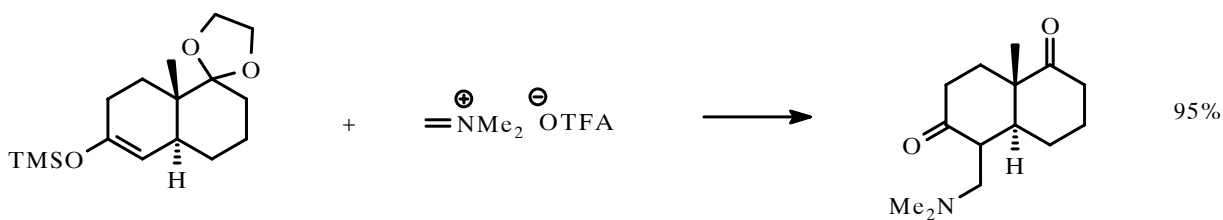
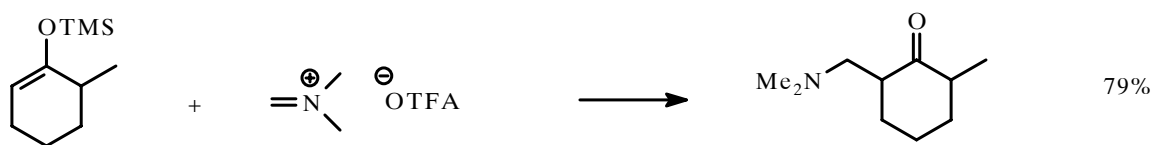
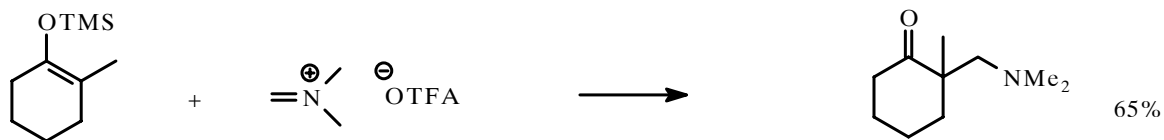
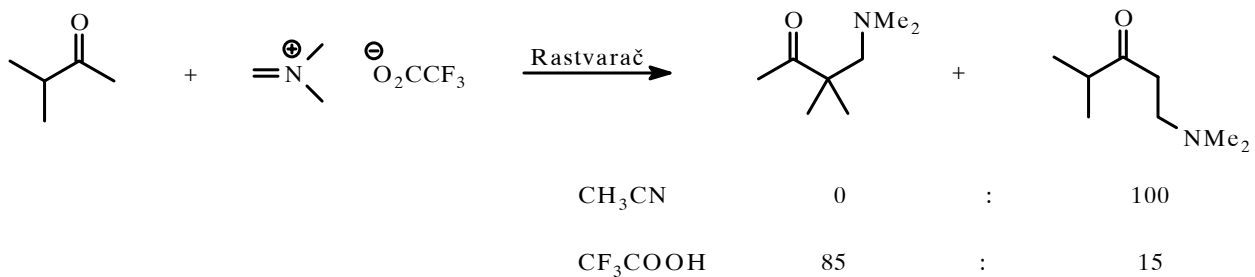




\* Ar - nukleofili

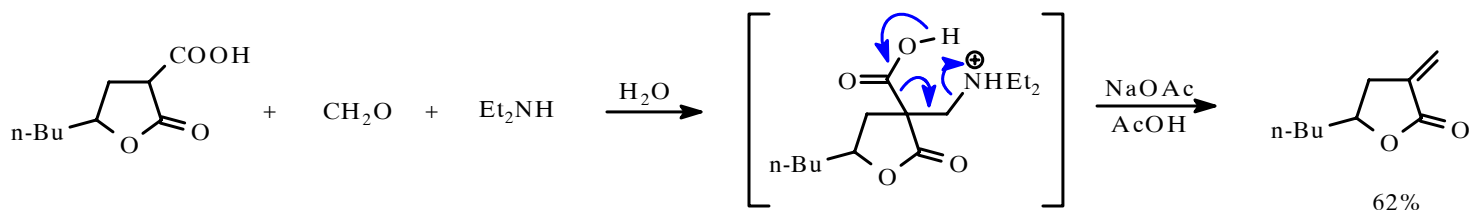
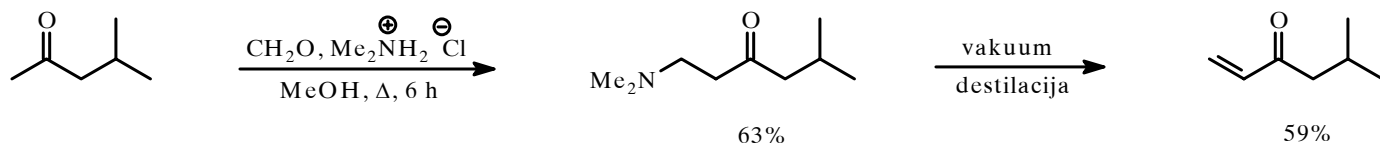


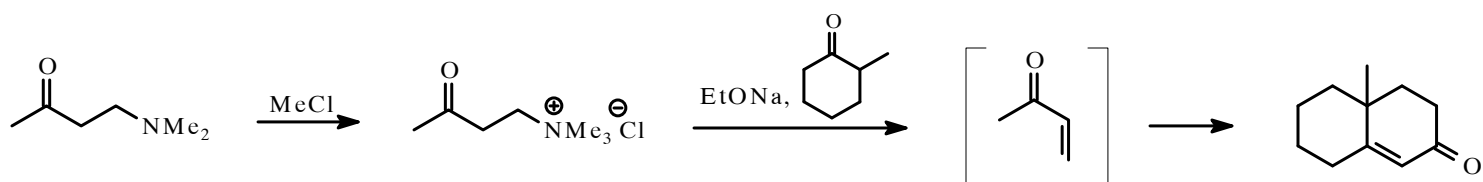
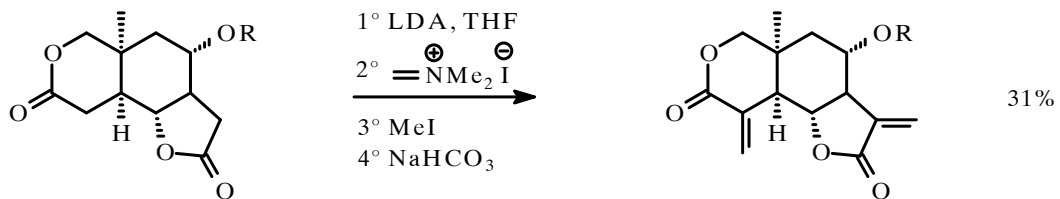
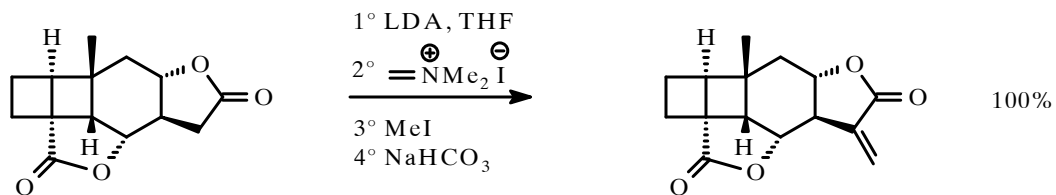




\* Transformacije Manich-ovih proizvoda

\* Eliminacija





\* Formalna supstitucija

