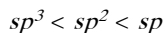
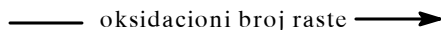
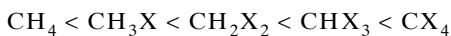


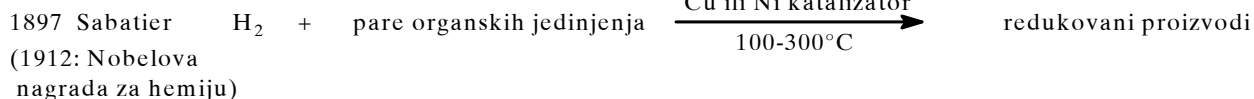
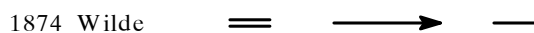
REDUKCIJE

* Definicija, oksidacioni broj



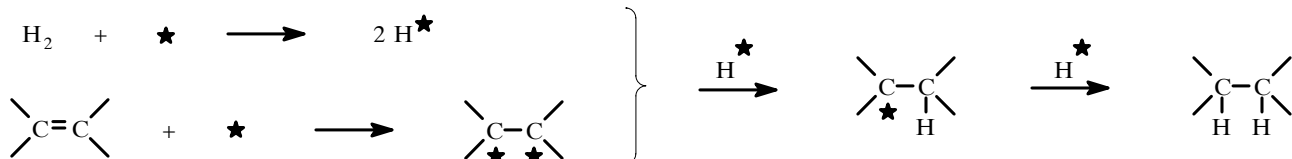
- * Podela: 1) Katalitičke hidrogenizacije
- 2) Redukcije metalnim hidridima
- 3) Redukcije rastvornim metalima
- 4) Redukcije nemetalnim reagensima

1) KATALITIČKE HIDROGENIZACIJE



* Podela: heterogene i homogene katalitičke hidrogenizacije

Heterogene katalitičke hidrogenizacije



* Katalizatori: Pt, Pd, Rh, Ni-Raney, CuCr_2O_4 , Ru

* Nosači: C, SiO_2 , Al_2O_3 , BaSO_4 , CaCO_3 , SrCO_3

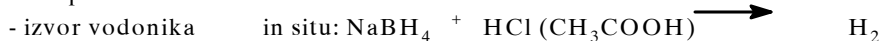
* Katalitički otrovi: S_8 , hinolin, $\text{Pb}(\text{OAc})_2, \dots$

* Tehnika izvođenja hidrogenizacije

- na nižim, srednjim i visokim pritiscima

- temperatura

- izvor vodonika

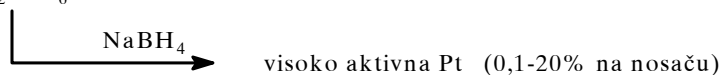
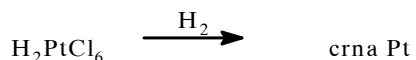
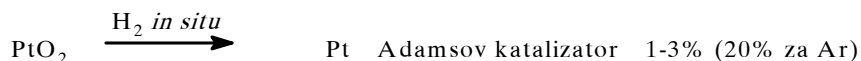


* Rastvarači

* Katalitički transfer H_2 (Pt, Pd, Ni-Raney / HCOOH , H_2NNH_2 , Et_3SiH , cikloheksadien, tetralin, itd.)

Katalizatori

Pt koloidna platina, platinski sunder - više se ne koriste

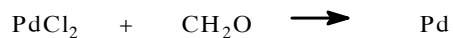
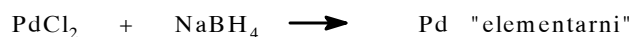
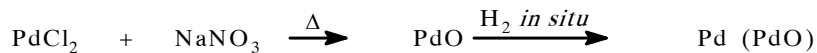


* SnCl_2 , FeCl_3 : aktivatori

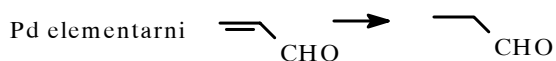
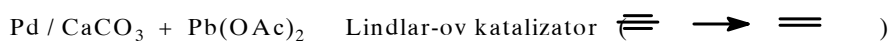
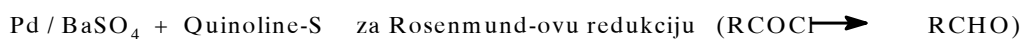
* univerzalni katalizator, izuzev za hidrogenolize i $-\text{CO}_2\text{H}(\text{R}) \longrightarrow -\text{CH}_2\text{OH}$

* veoma aktivni katalizatori, obično piroforni

Pd



* Uticaj nosača - modifikovanje reaktivnosti

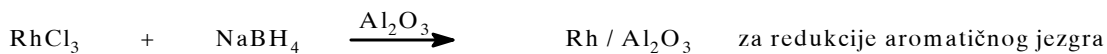


* Koristi se i u kiselim i u baznim uslovima

* Pogodan za hidrogenolize

* ne redukuje COOH

Rh



Raney-Ni (Ni^{R})



Prednosti: + za sve redukcije, uključujući COOH, COOR

+ nije podložan trovanju \Rightarrow desulfurizacije

+ ne koristi se na nosaču

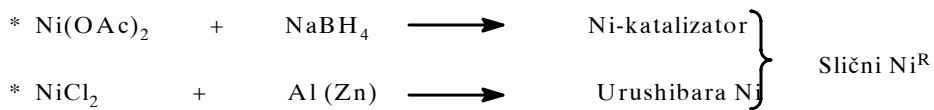
Nedostaci: - veća količina katalizatora

-feromagnetičan

- ponekad zahteva energične reakcione uslove

- piroforan

- teško se odmerava



CuCr₂O₄ (kupri-hromitni katalizator)



Veoma energični uslovi za hidrogenizacije



* Namena katalizatora i uobičajeni reakcioni uslovi: TABLICA

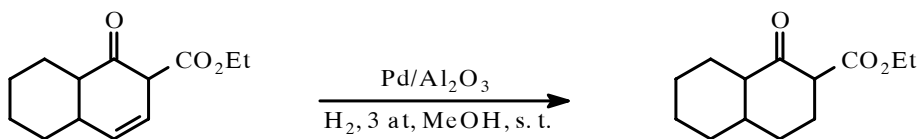
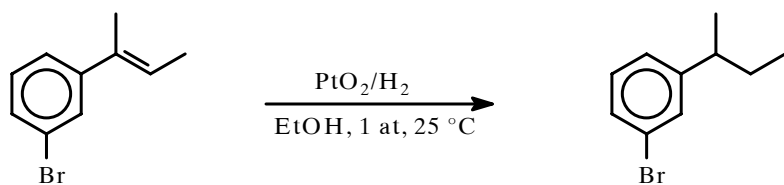
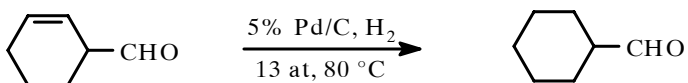
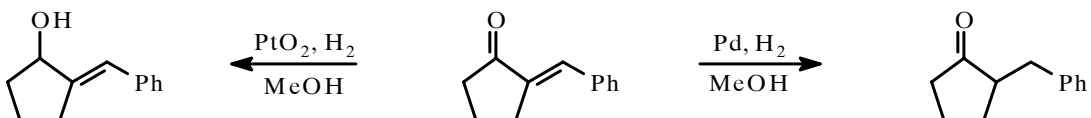
* Za redukcije C=O i CO₂R u prisustvu C=C bolji su metalni hidridi

HIDROGENIZACIJA FUNKCIONALNIH GRUPA

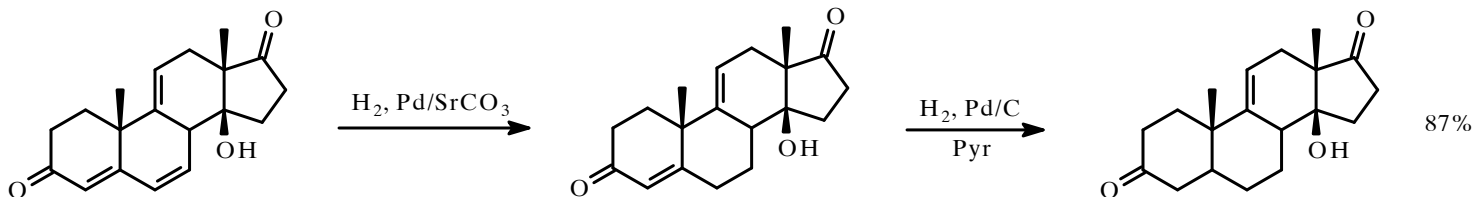
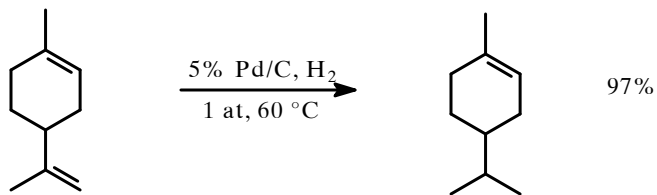
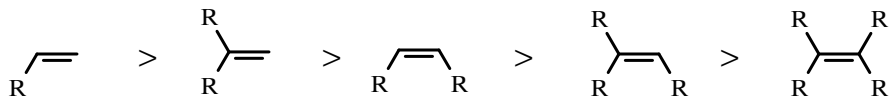
* Redosled reaktivnosti: Pt: C=O > C=C > Hidrogenoliza > Ar

Pd: C=C > Hidrogenoliza > C=O > Ar

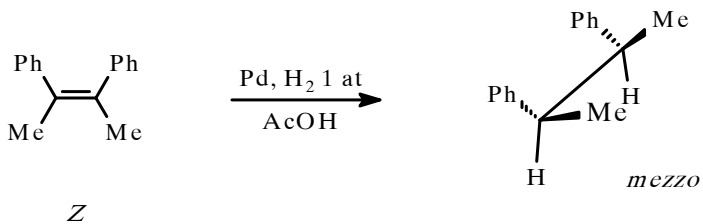
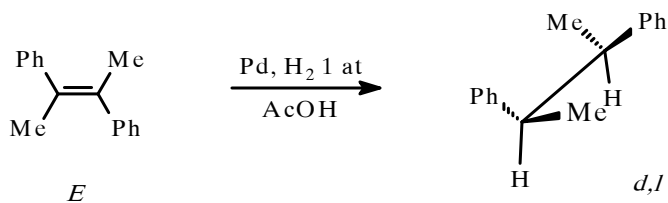
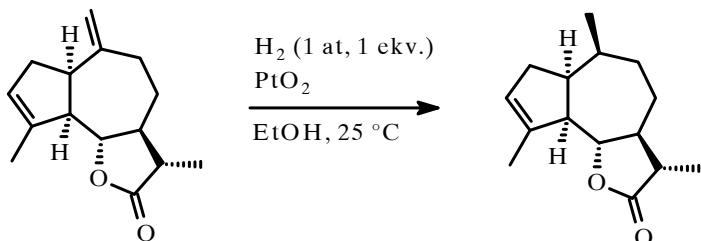
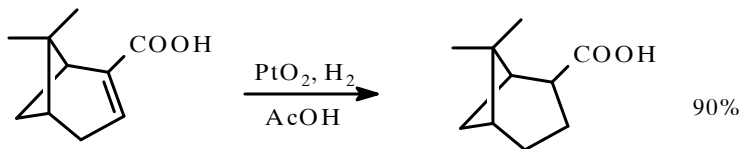
ALKENI lako se hidrogenizuju, nizak pritisak H₂, blagi reakcioni uslovi



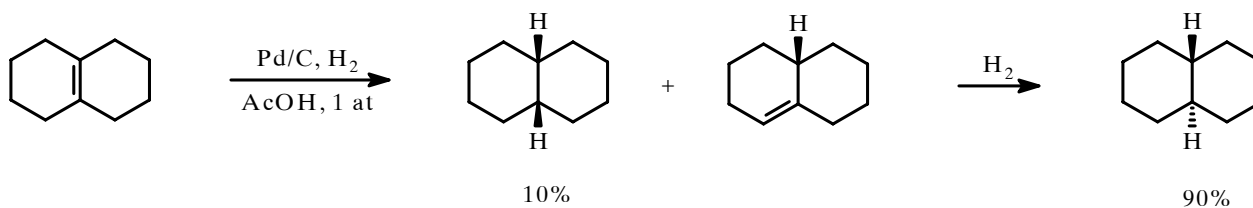
* Sterni efekti - redosled reaktivnosti



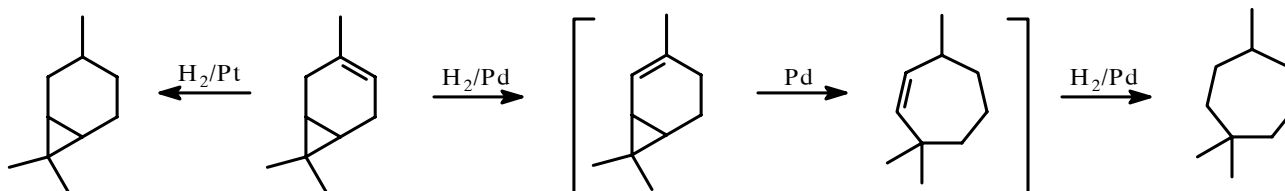
* Stereoselektivnost: *cis*-adicija, napad sa sterno manje zaštićene strane



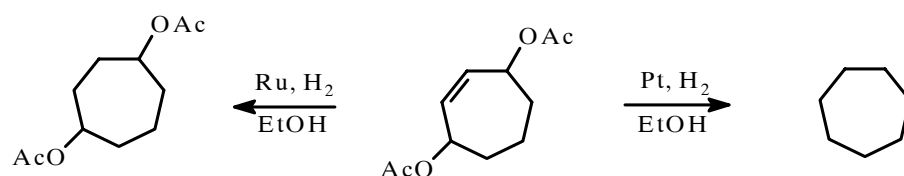
Ako nije *cis* \Rightarrow izomerizacija / hidrogenizacija



Izomerizaciona sposobnost: Pd > Ni >> Pt



Sprečavanje hidrogenolize

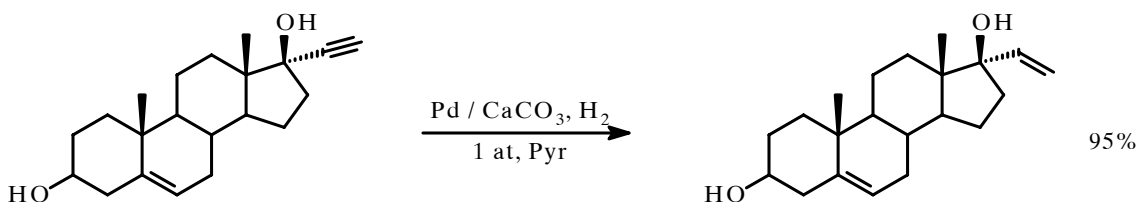
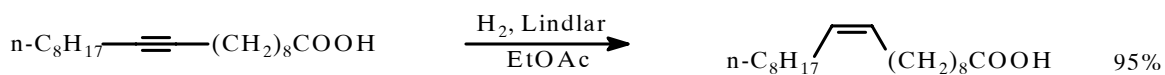
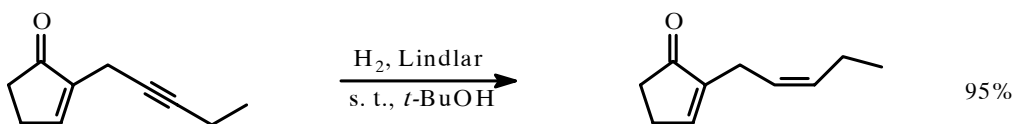


ALKINI Jače se adsorbuju na površinu katalizatora \Rightarrow mogućnost selektivne redukcije

Da bi se ostvarila hemoselektivna hidrogenizacija neophodno je:

1. Koristiti Lindlar-ov katalizator: 5% Pd / CaCO₃ + Pb(OAc)₂ (ili hinolin)
2. Atmosferski pritisak H₂ (1 at), merenje utrošenog H₂

* *cis*-hidrogenizacija \Rightarrow Z-alkeni

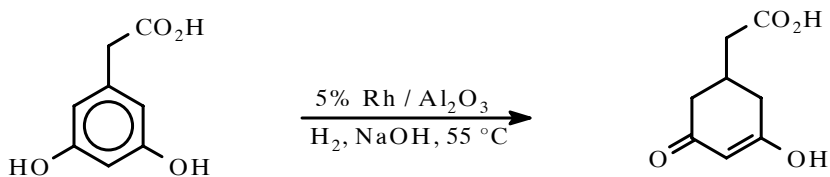
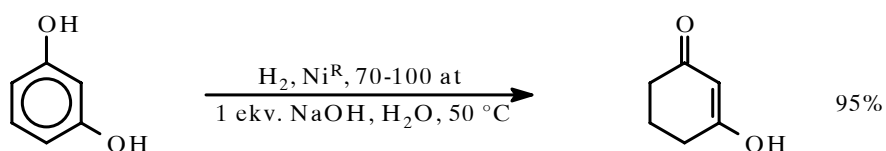
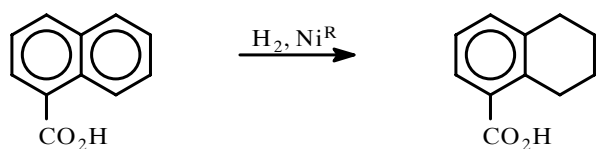
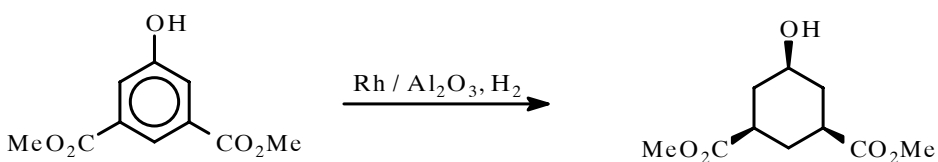
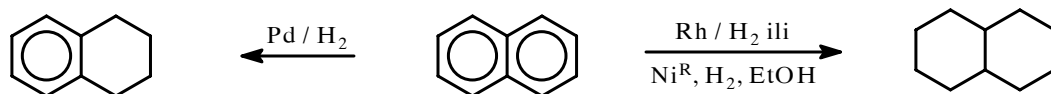
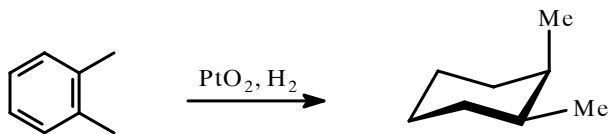


AROMATIČNA JEZGRA

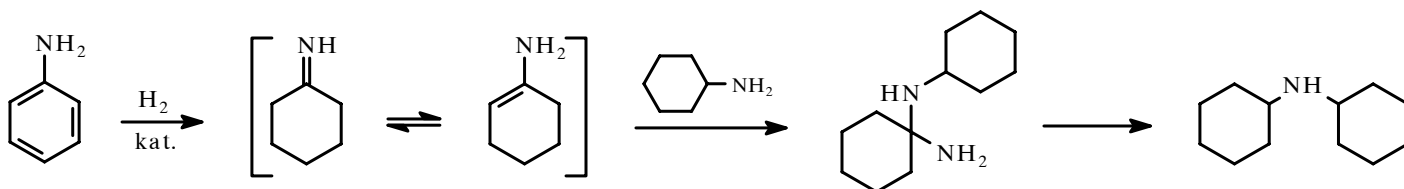
Ni^R: Ph-OH > PhH > Ph-NH₂ > Ph-COONa

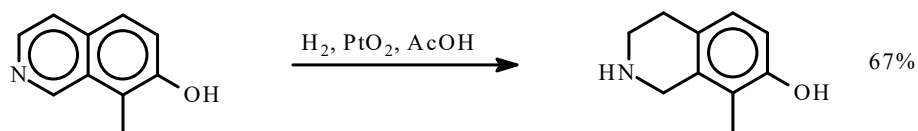
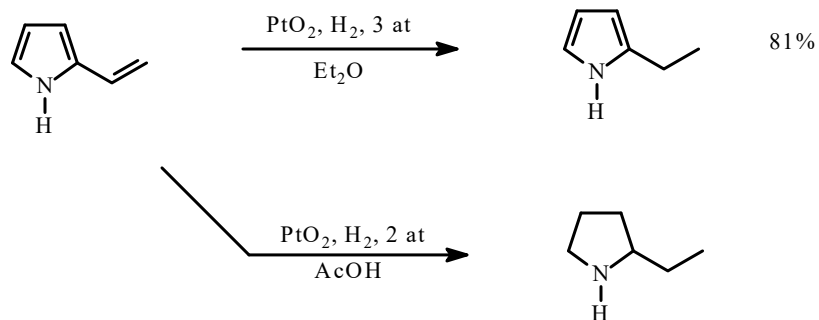
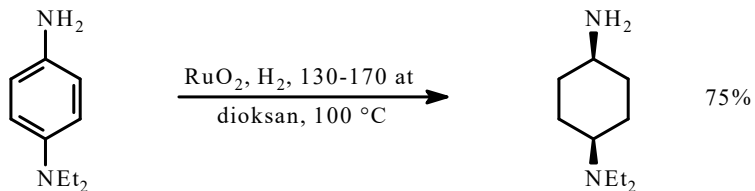
Pt : Ph-OH > Ph-NH₂ > PhH > Ph-COOH > Ph-CH₃ (H[⊕])

* *cis*-adicija H₂

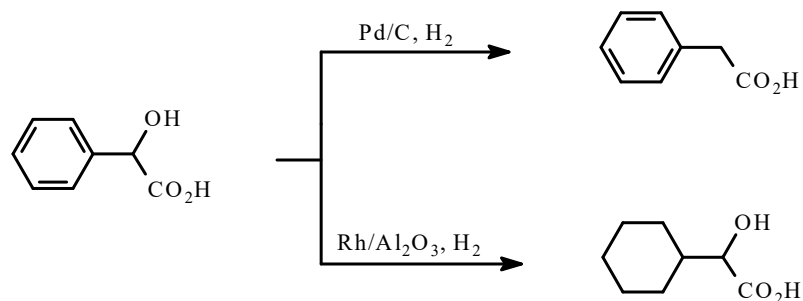


Sa aminima: moguće sporedne reakcije (izbor katalizatora)

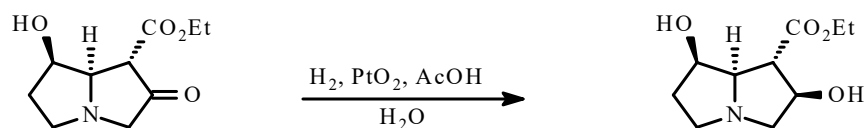
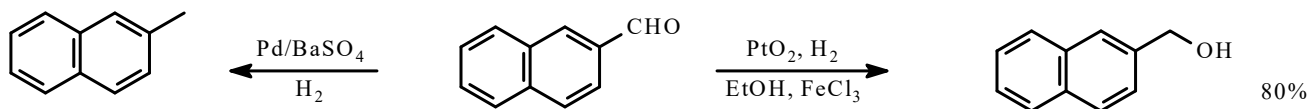
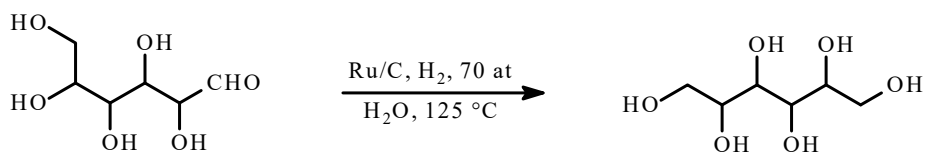




Protiv hidrogenolize: Rh



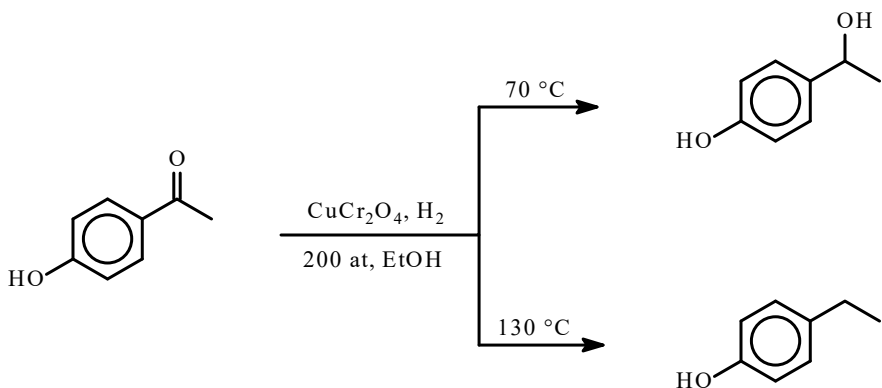
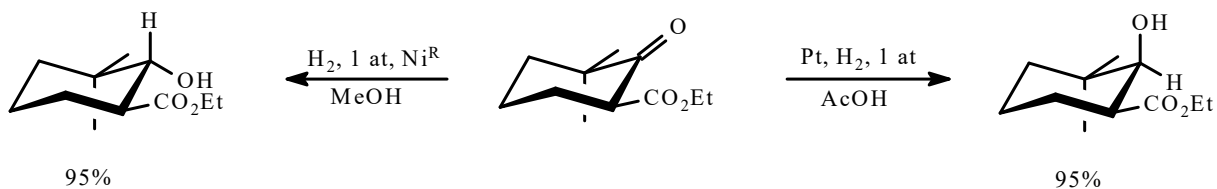
C=O Pt > Pd, Ni^R, Ru > CuCr₂O₄



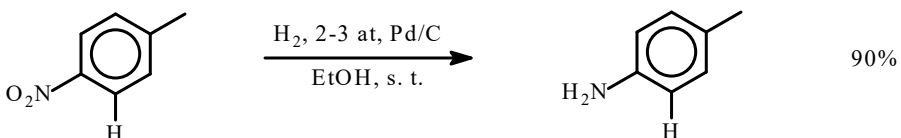
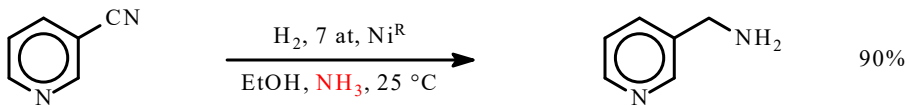
* Stereoselektivnost pri redukcijama cikličnih sistema

1) Napad sa stereo manje za {ti}ene strane

2) pH < 7: aksijalni alkoholi; pH > 7: ekvatorijalni alkoholi (termodinamički stabilniji)

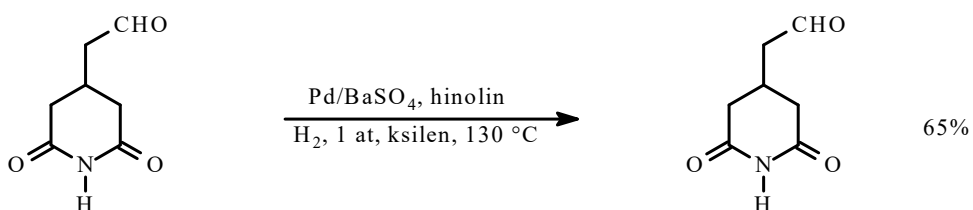
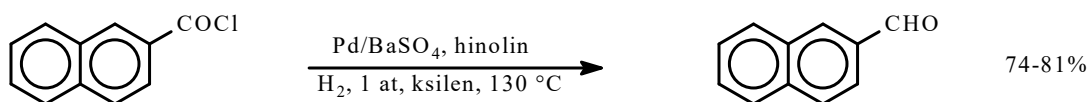


OSTALE FUNKCIONALNE GRUPE

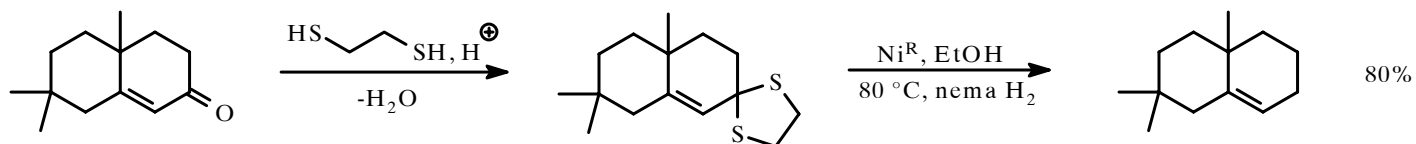


HIDROGENOLIZE

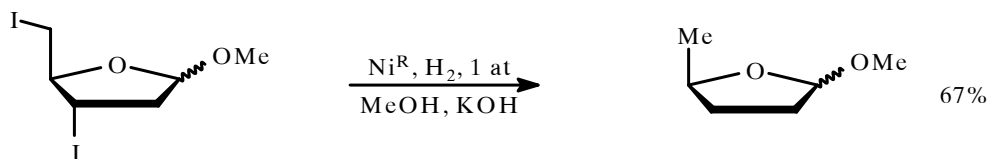
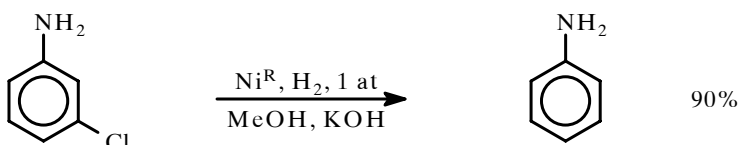
* Rosenmund-ova redukcija $R-COCl \longrightarrow R-CHO$



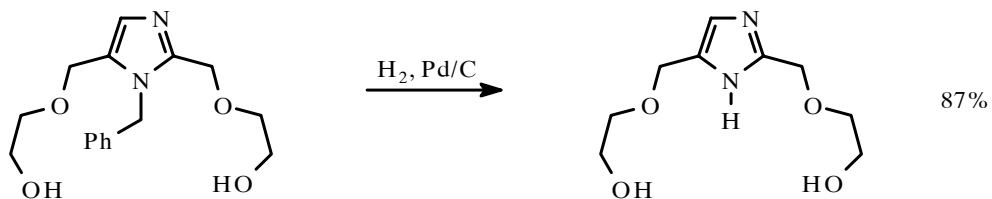
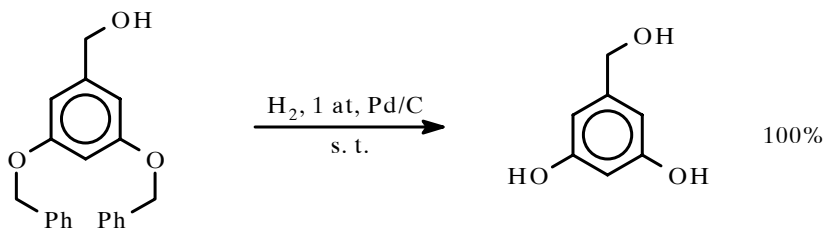
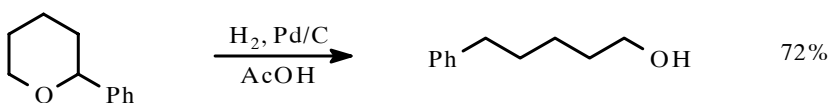
* Deoksigenacije ketona (Ni^R)



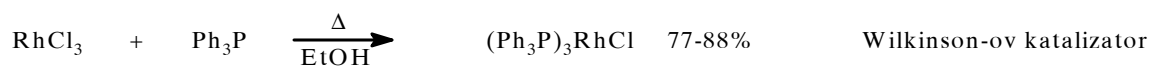
* Dehalogenovanje



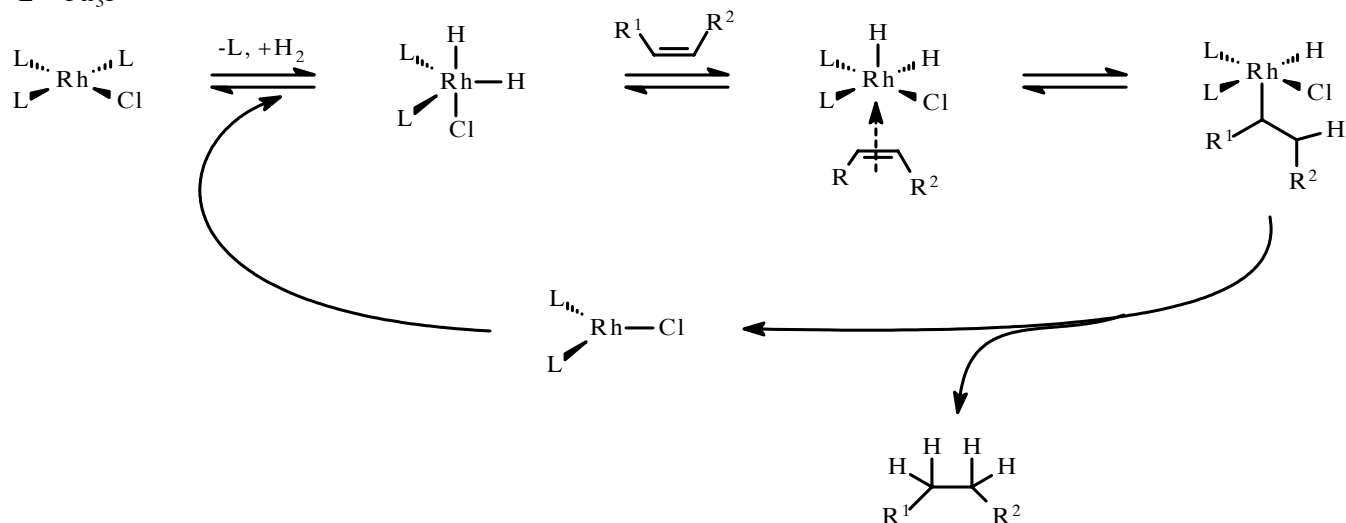
* Deprotekcija PhCH₂-X derivata (X = O, N)



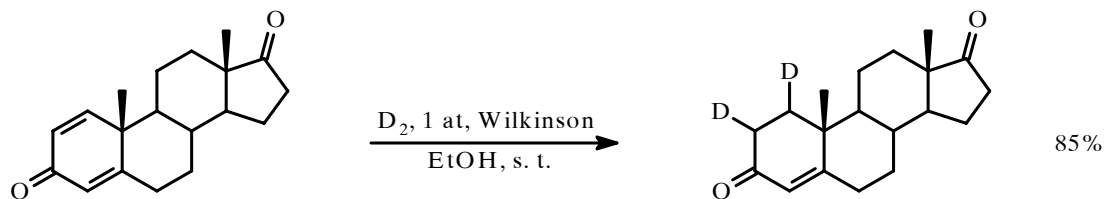
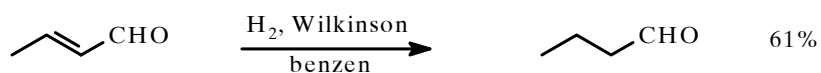
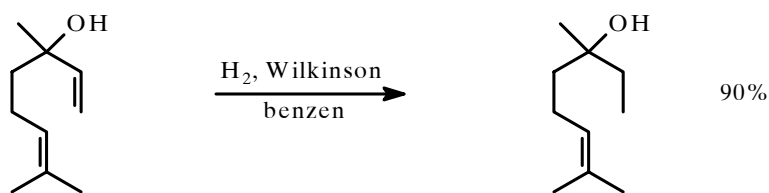
HOMOGENE KATALITIČKE HIDROGENIZACIJE



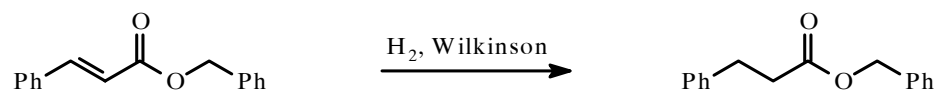
L = Ph₃P



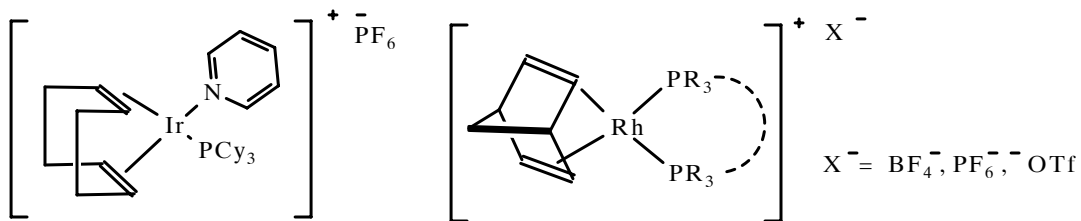
* Selektivan za C=C i C≡C veze



* Nema hidrogenolize



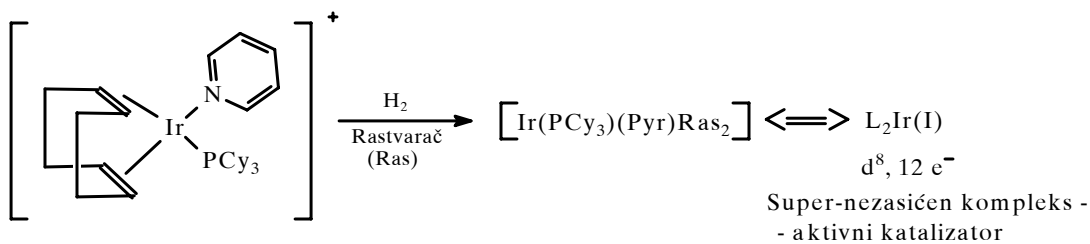
Crabtree-jev i Schrock-Osborn-ov katalizator:
visoko-reaktivni katjonski kompleksi



Crabtree-jev katalizator

Schrock-Osborn-ov katalizator

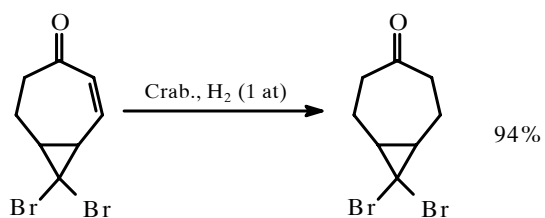
Iz inicijalnog kompleksa aktivne katalitičke vrste nastaju *in situ* redukcijom:



Relativne brzine redukcije različito supstituisanih alkena
pomocu Crabtree-jevog katalizatora

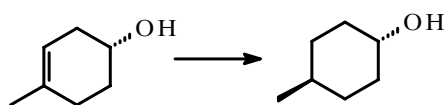
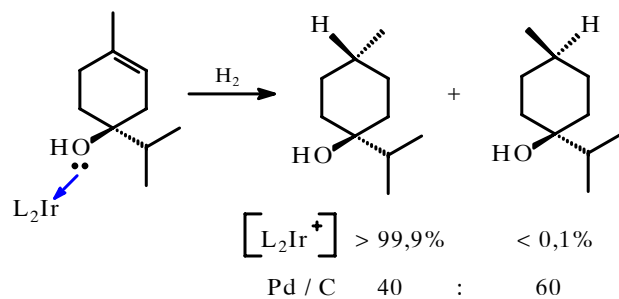
Supstrat				
Relativna reaktivnost Crabtree-jevog katalizatora	1,6	1,1	0,95	1

Crabtree-jev katalizator selektivno katalizuje reakcije samo na olefinskoj vezi



Diastereoselektivne hidrogenizacije

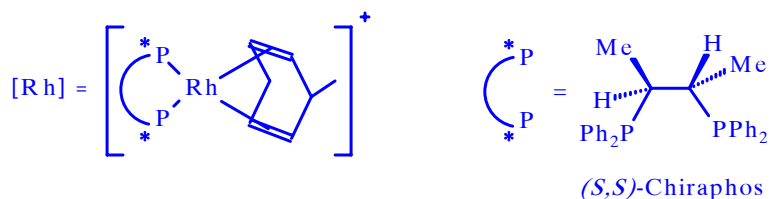
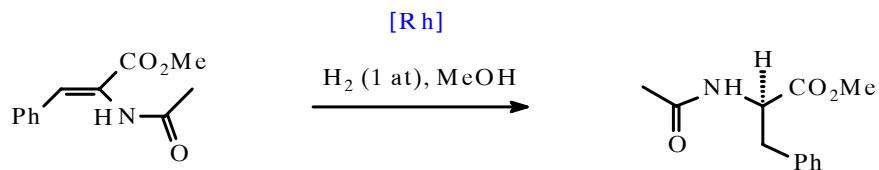
Dirigovane hidrogenizacije: napad se vrši sa strane sa koje se nalazi grupa koja može da koordinira katjonski kompleks



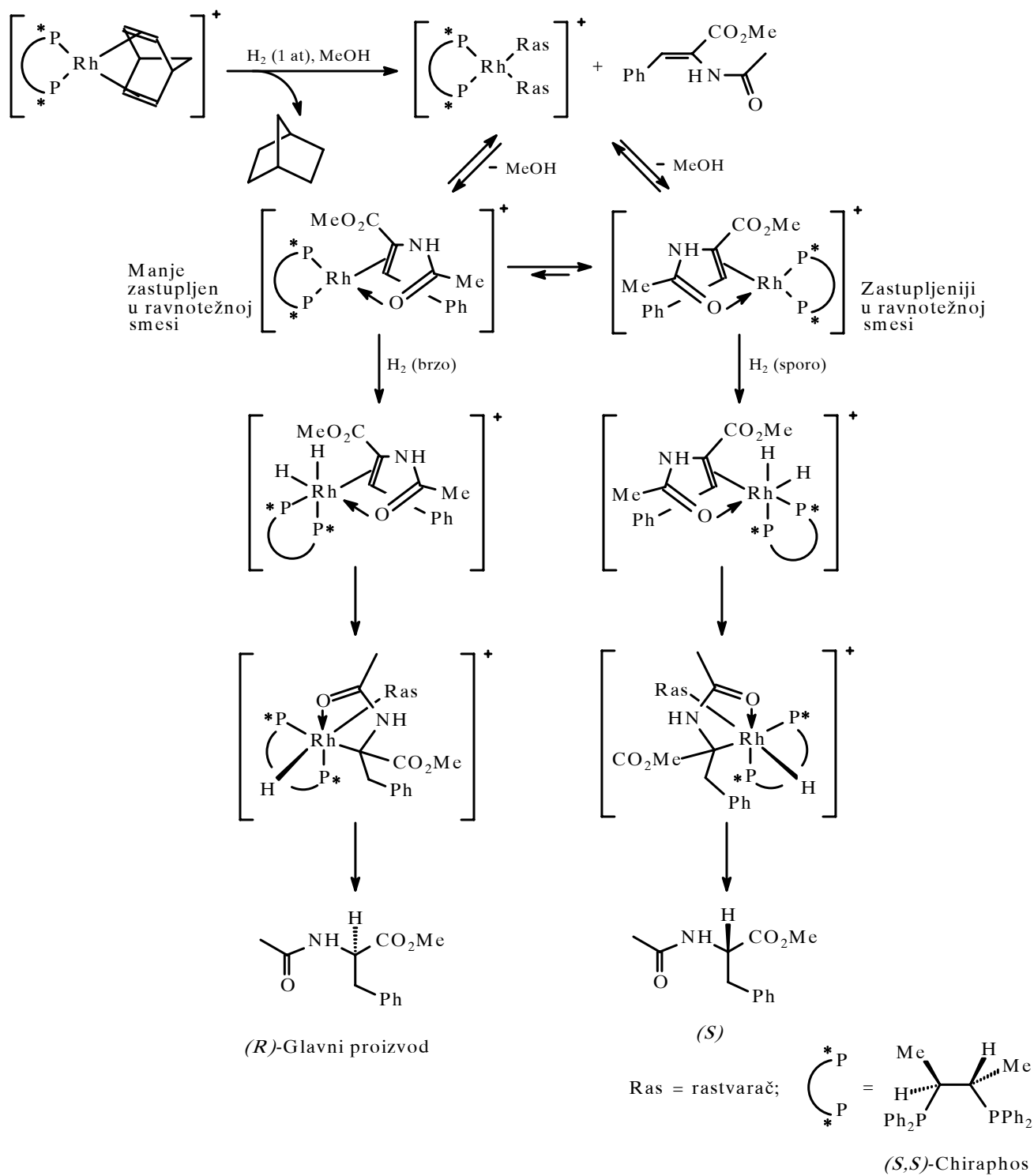
Crab. 1,5 mol% , 15 psi H₂ 52 : 1

Osb.-Sch. 10 mol% , 1000 psi H₂ 64 : 1

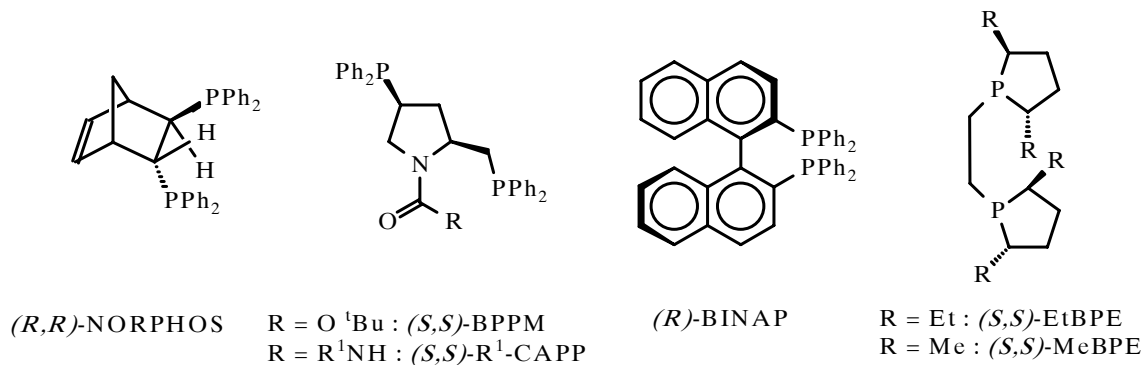
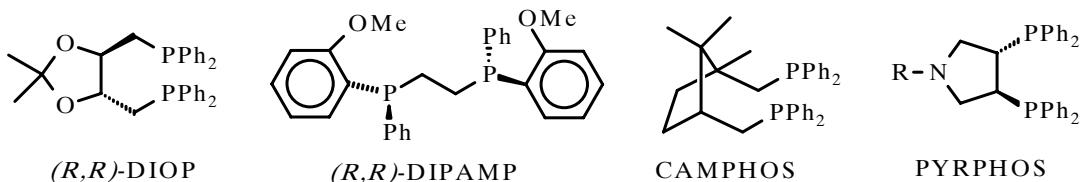
Enantioselektivne hidrogenizacije: Hiralni ligand u koordinacionoj sferi metalnog jona omogućava asimetričnu indukciju



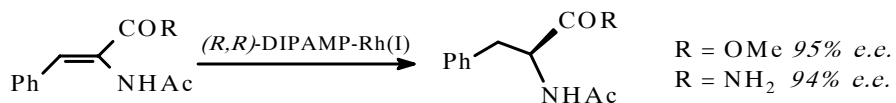
Mehanizam enantioselektivne hidrogenizacije



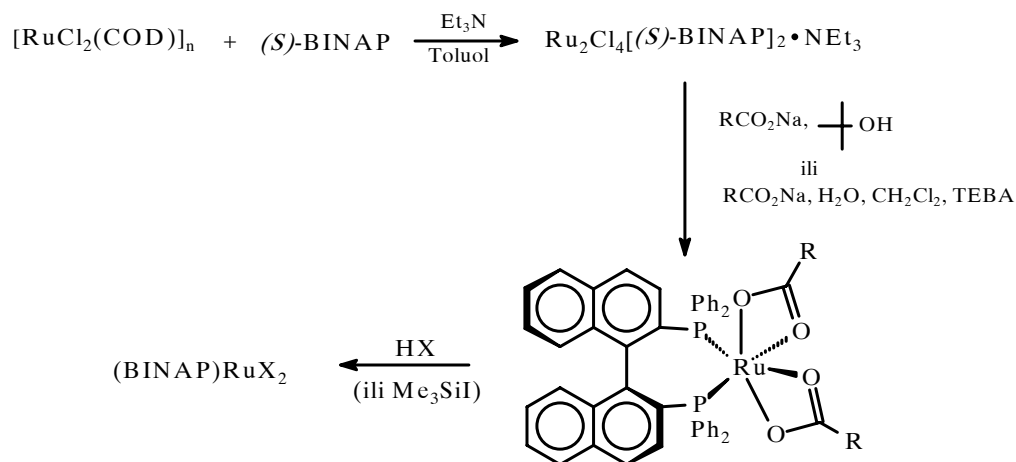
Hiralni ligandi za asimetrične hidrogenizacije



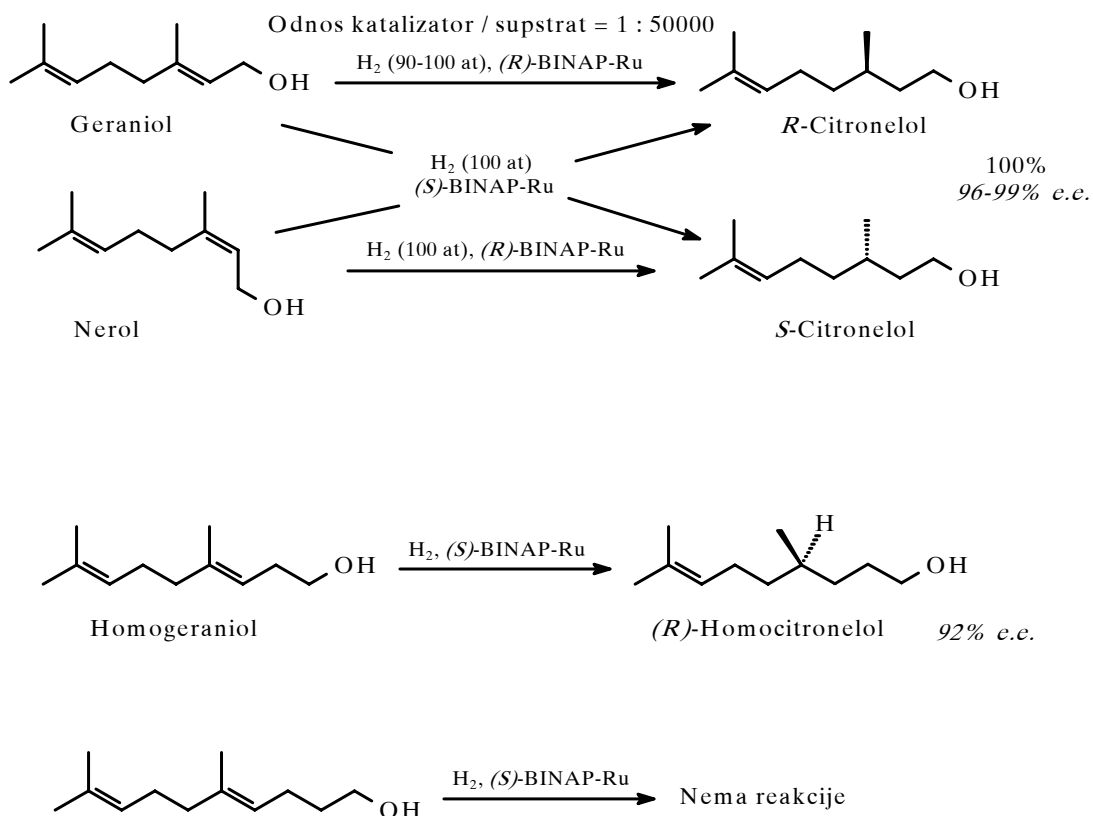
Primeri enantioselektivnih hidrogenizacij pomoću Rh-katalizatora:
 pored alkena, supstrat treba da poseduje još jednu grupu sposobnu da koordinira metalni jon



Redukcije pomoću Ru-katalizatora: najčešće korišćen ligand: BINAP

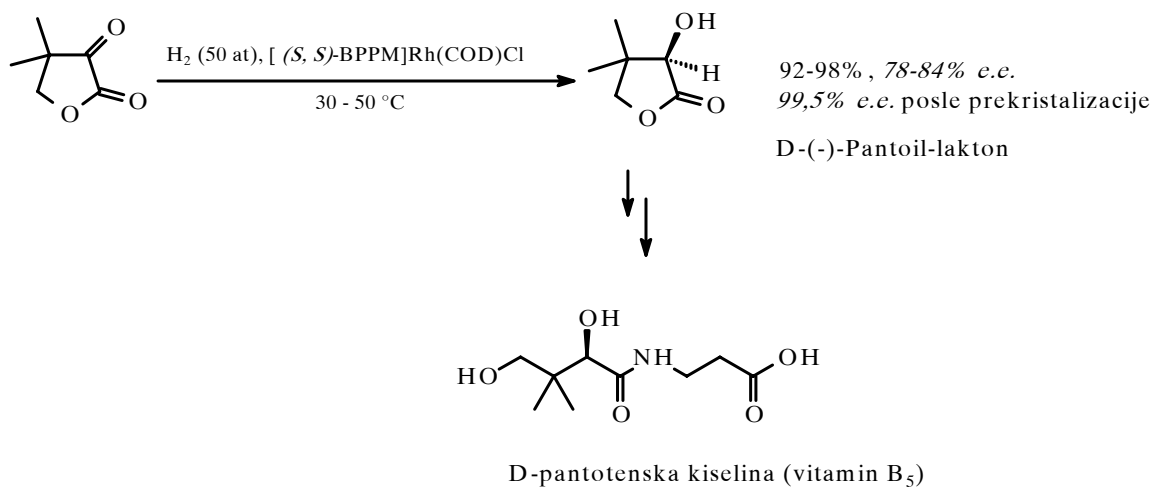


Slično reakcijama katalizovanim pomoću Rh-kompleksa: potrebno je da (u blizini alkena koji se redukuje) postoji još jedna grupa sposobna da koordinira metalni jon



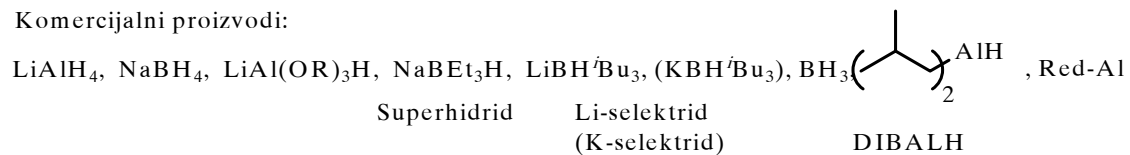
Enantioselektivna hidrogenizacija karbonilne grupe: primer pantoil-laktona

D-oblik vitamina B₅ je biološki aktivan, dok L-oblik poništava njegovo dejstvo

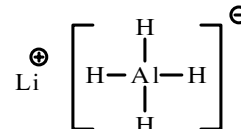
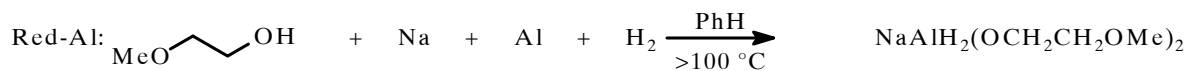
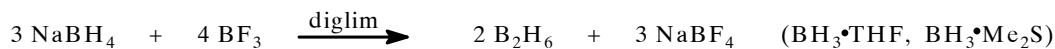
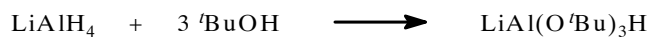
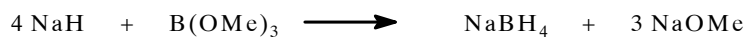
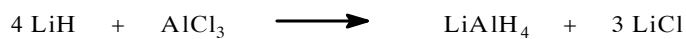


2) REDUKCIJE POMOĆU METALNIH HIDRIDA

Komercijalni proizvodi:



* Dobijanje



* Namena: redukcija polarnih funkcionalnih grupa: $\text{C}=\text{O}$, CO_2R , CO_2H , CONR_2 , CN , \triangle , $\text{CH}_2\text{-X}$, NO_2 itd.

BH_3 redukuje i alkene!

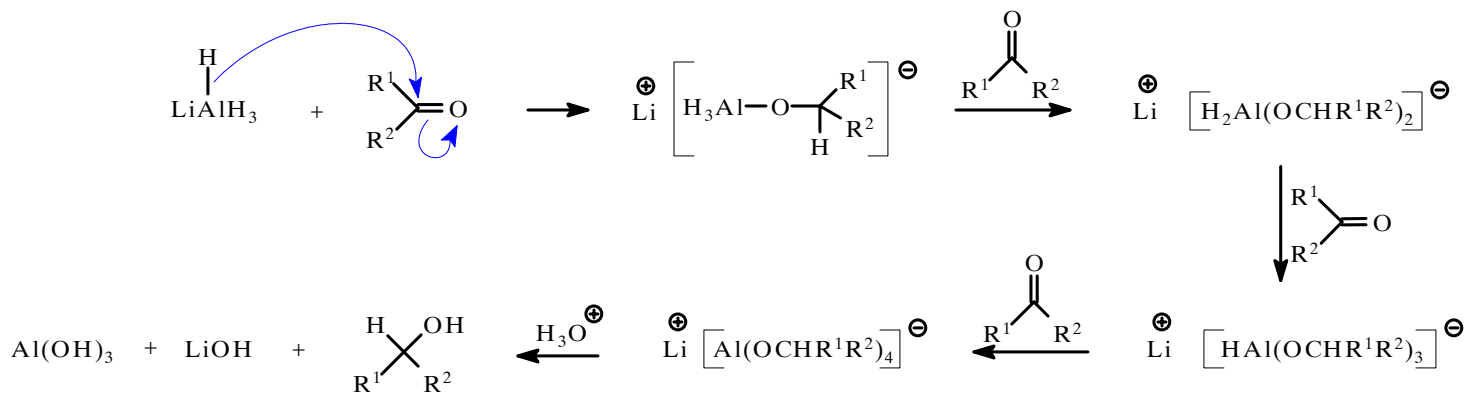
LiAlH₄

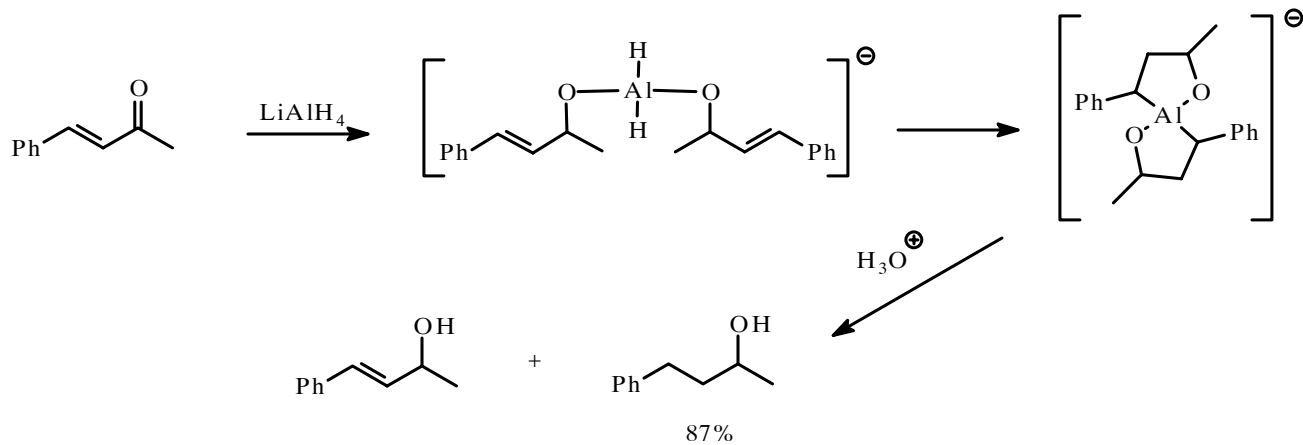
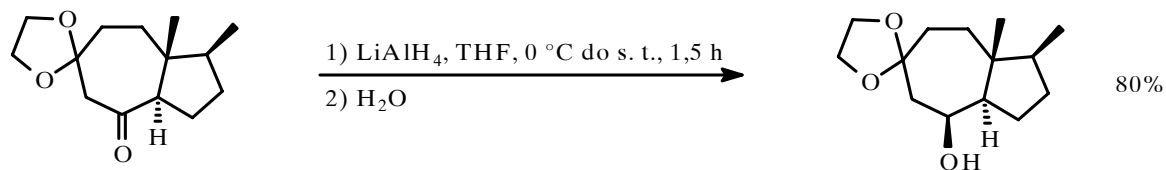
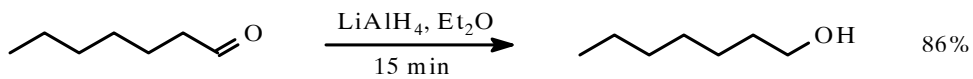
- * Jak redukциони agens
- * Koristi se u etarskim rastvaračima (Et_2O , THF)
- * Osetljiv na vlagu
- * Zapaljiv/eksploziv

Redukcije pomoću LiAlH₄

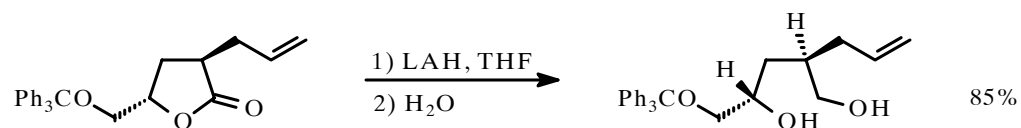
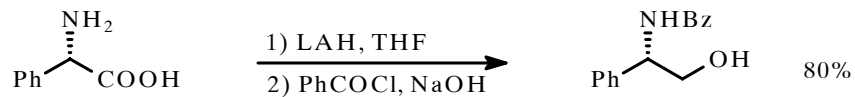
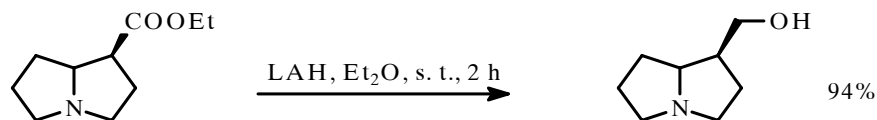
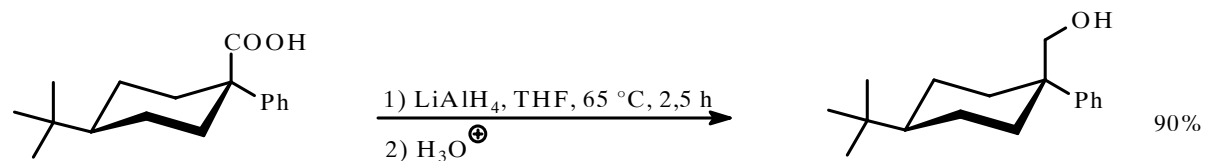
Reaktivnost opada ↓	Funkcionalna grupa	Proizvod
	—CHO	—CH ₂ OH
	—COCl	—CH ₂ OH
	—CO ₂ R	—CH ₂ OH + ROH
	—CO ₂ H ili —CO ₂ [⊖] Na [⊕]	—CH ₂ OH
	—CONR ₂	—CH ₂ NR ₂ ili $\left[\begin{array}{c} -\text{CH}-\text{NR}_2 \\ \\ \text{OH} \end{array} \right] \xrightarrow{\text{H}_2\text{O}} -\text{CHO}$
	—CONHR	—CH ₂ NHR
	—CN	—CH ₂ NH ₂ ili $\left[-\text{CH}:\text{NH} \right] \xrightarrow{\text{H}_2\text{O}} -\text{CHO}$
		i drugi proizvodi
	—CH ₂ ·O—SO ₂ ·C ₆ H ₅ ili —CH ₂ Br	—CH ₃
	ili	

Redukcija C=O grupe

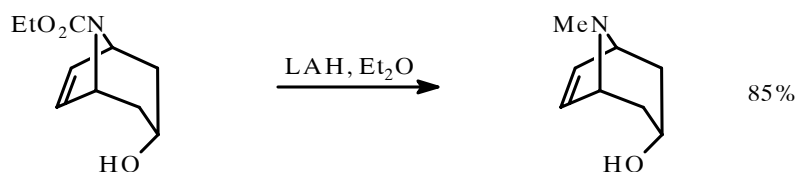
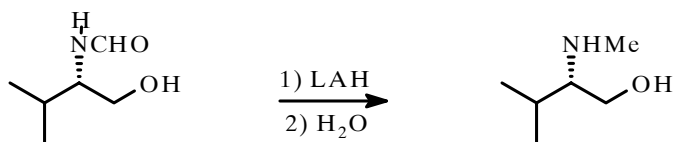
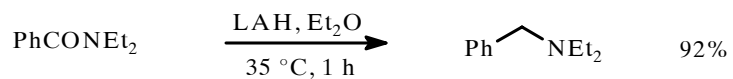
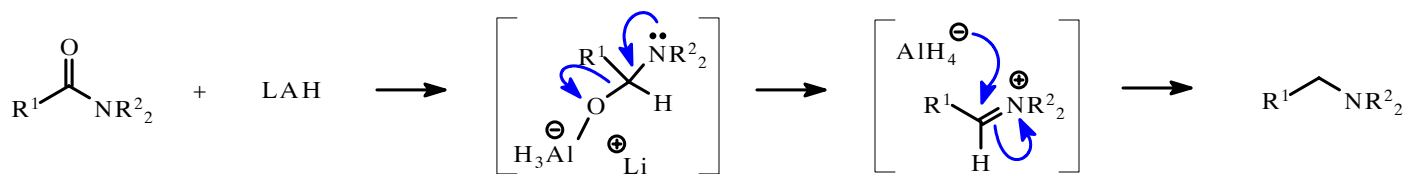




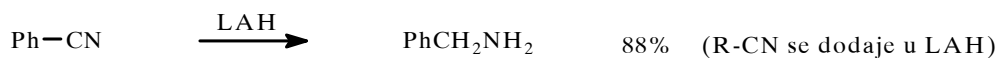
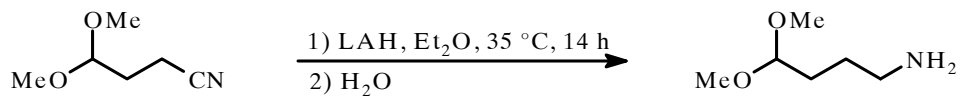
COOR, COOH



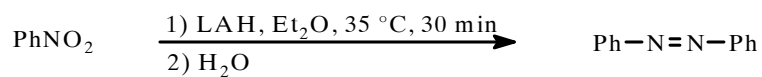
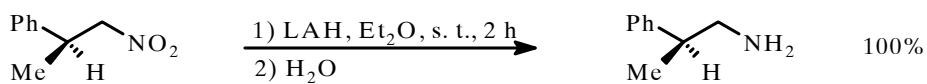
CONHR, CONR₂



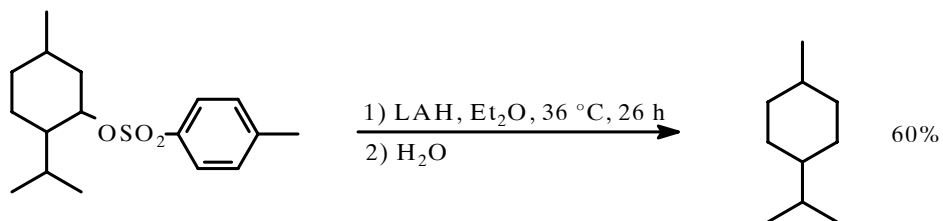
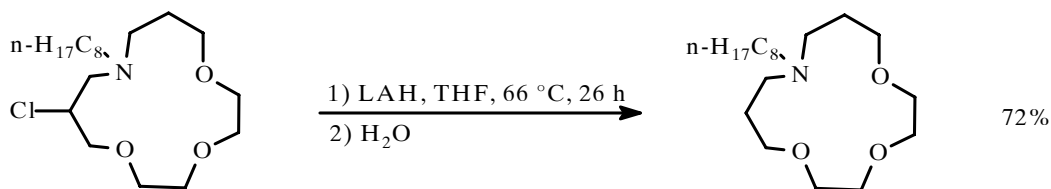
CN

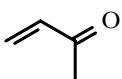


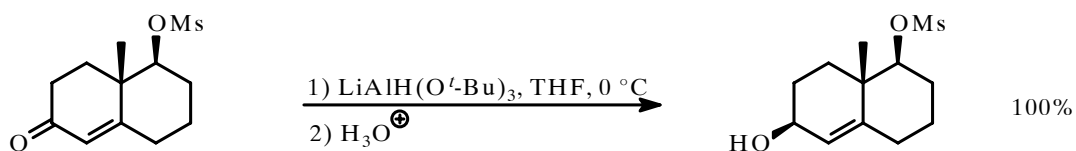
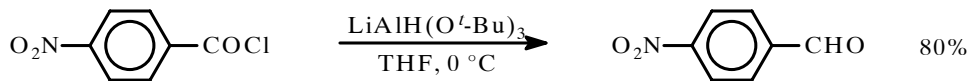
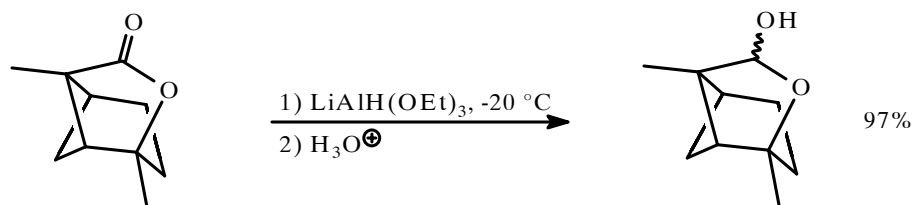
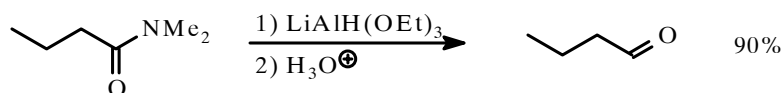
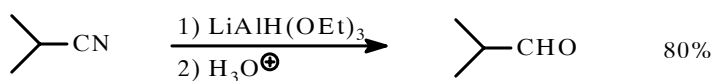
NO₂



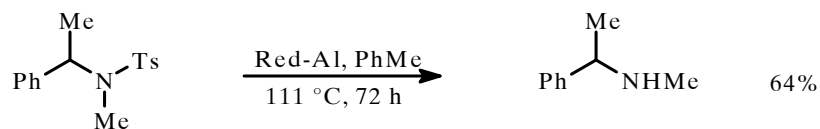
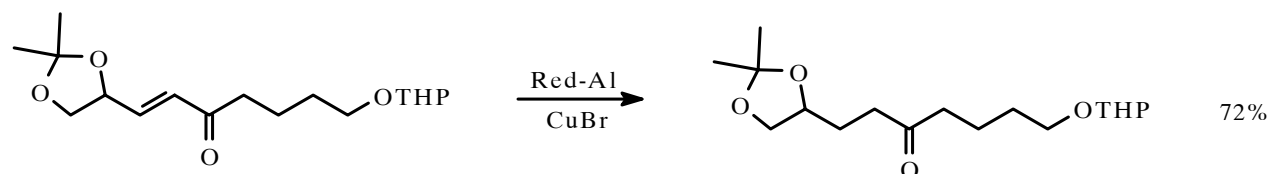
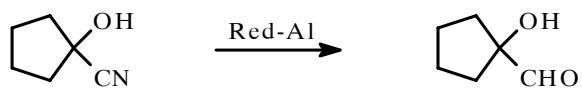
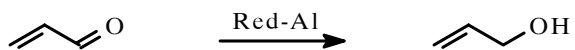
Hydrogenolize Cl, Br, I, OTs, OMs



LiAlH(OEt)₃ LiAlH(O^tBu)₃; ne redukuje COOR, C-X, 

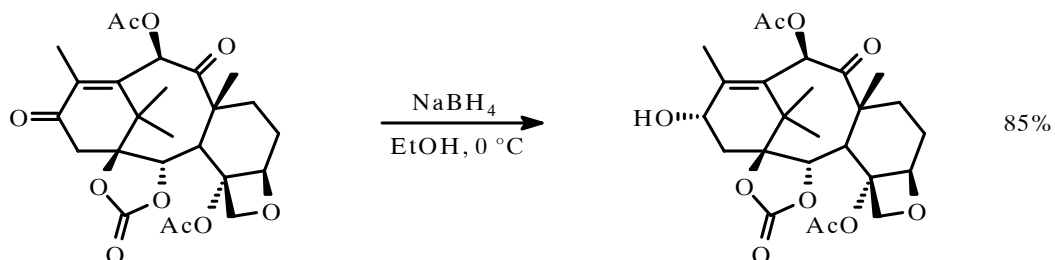
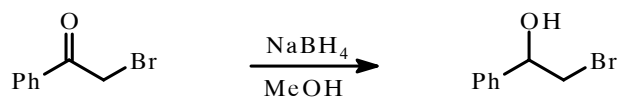
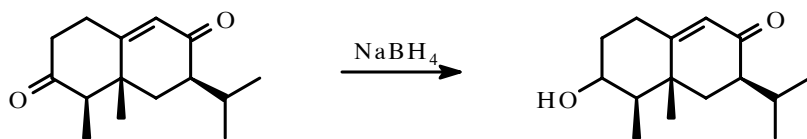
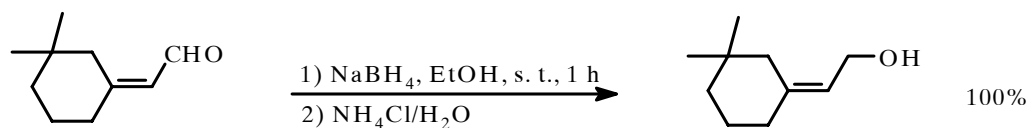


Red-Al sličan LiAlH_4 (u etarskim i ugljovodoničnim rastvaračima)

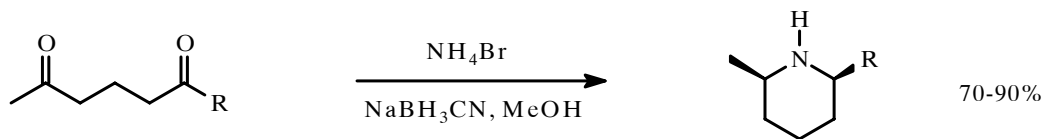
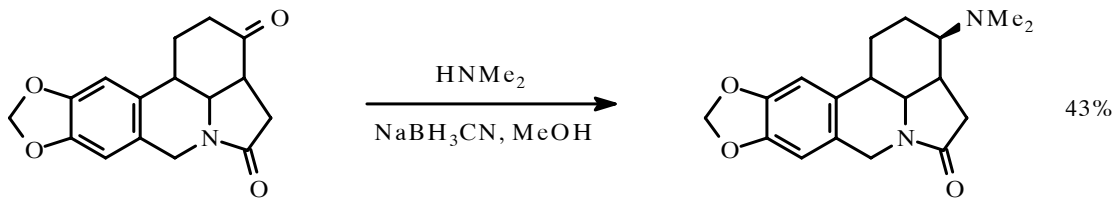


NaBH_4 Blaži od LiAlH_4 , redukuje samo $\text{C}=\text{O}$ i COCl (u prisustvu \triangle , CO_2R , CO_2H , CN , NO_2)

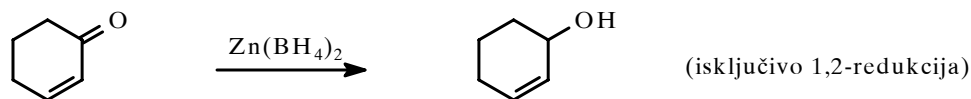
Rastvarači: EtOH, i PrOH, MeOH



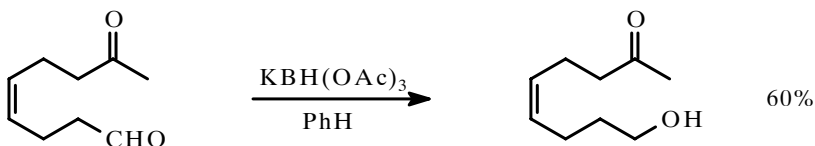
NaBH₃CN Stabilan na pH ≥ 3 Primenjuje se u reakcijama reduktivnog aminovanja



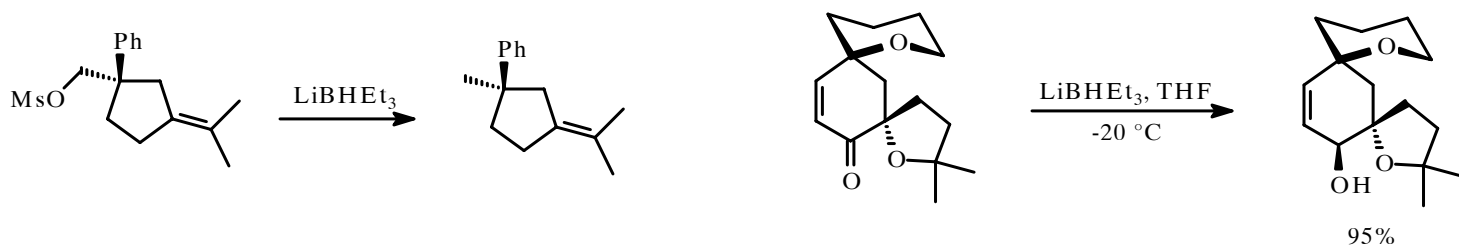
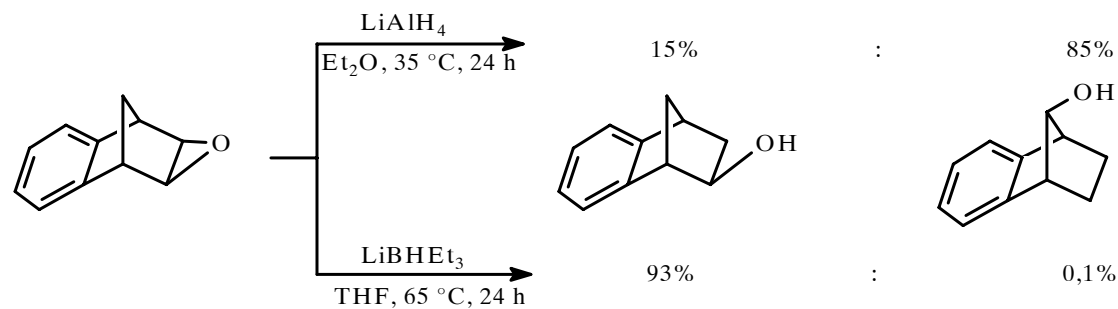
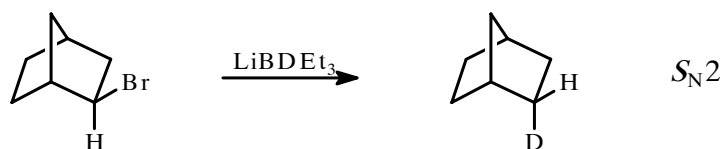
Zn(BH₄)₂ 2 NaBH₄ + ZnCl₂ $\xrightarrow{\text{Et}_2\text{O}}$ Zn(BH₄)₂ + 2 NaCl



KBH(OAc)₃ $\xleftarrow{\text{AcOH}}$ KBH₄



LiBHEt₃ Super-hidrid; najreaktivniji metalni hidrid: LiH + BEt₃ $\xrightarrow{\text{THF, 65 }^\circ\text{C, 15 min}}$ LiBHEt₃

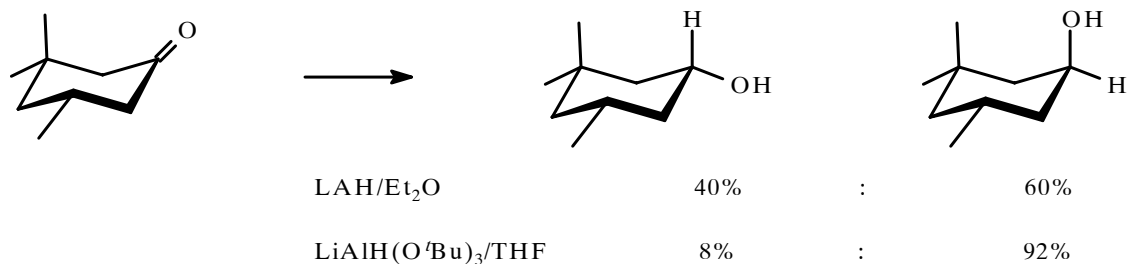
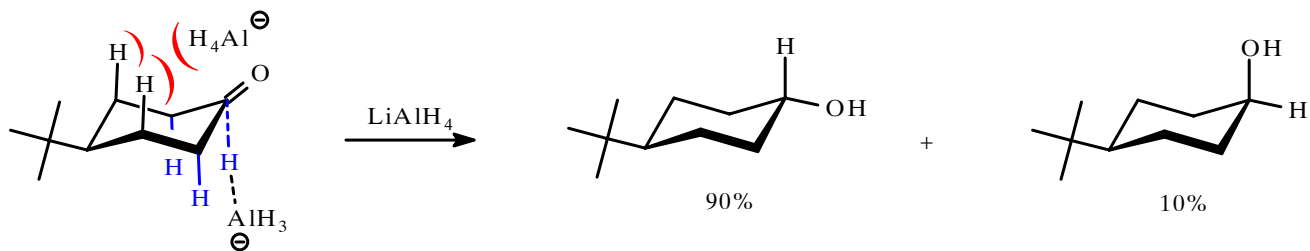
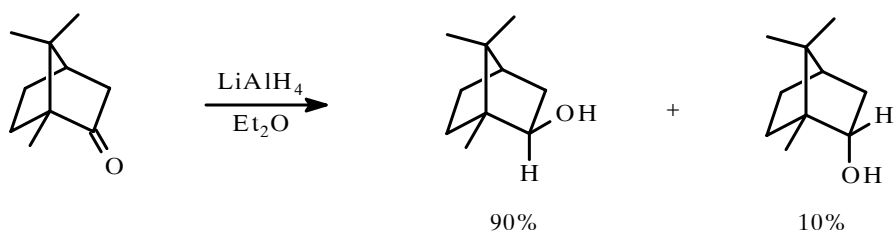
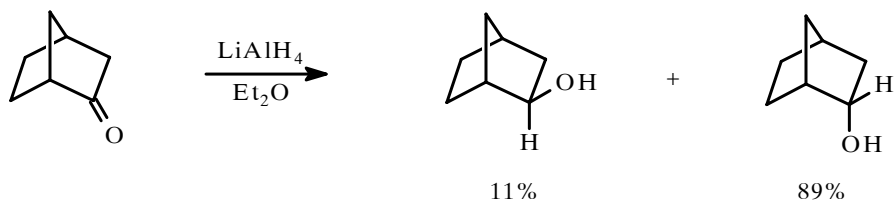


STEREOSELEKTIVNOST REDUKCIJA POMOĆU METALNIH HIDRIDA

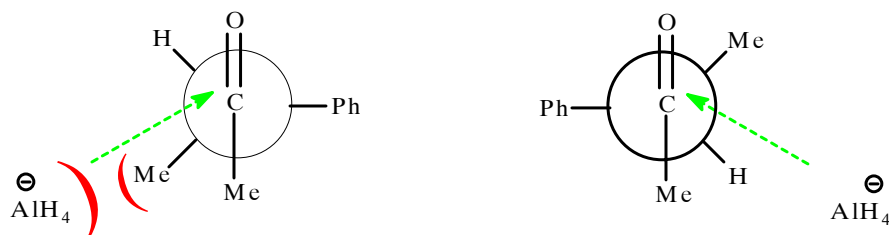
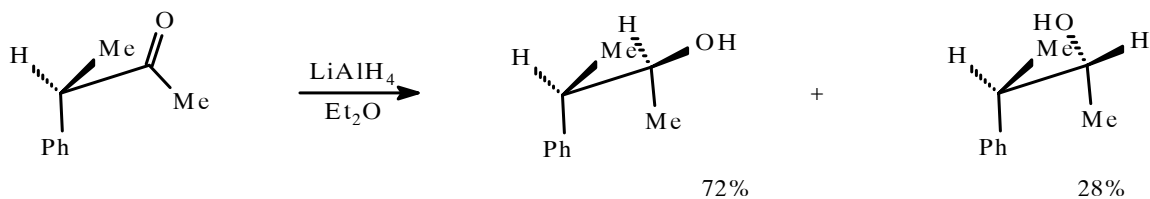
* Napad sa sterno manje zaštićene strane;

* *Cram-ovo* i *Felkin-Anh-ovo* pravilo;

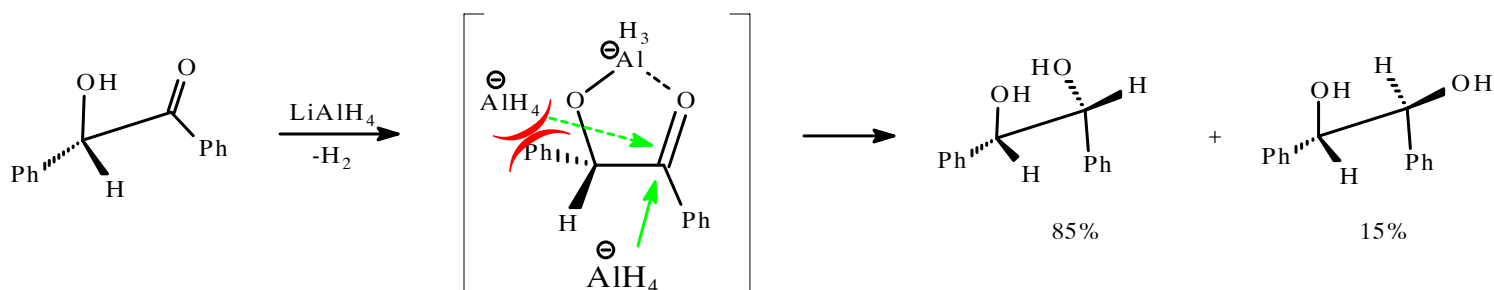
* kod cikloalkanona: torzioni i sterni efekti



Stereoselektivnost na acikličnim sistemima; asimetrična indukcija

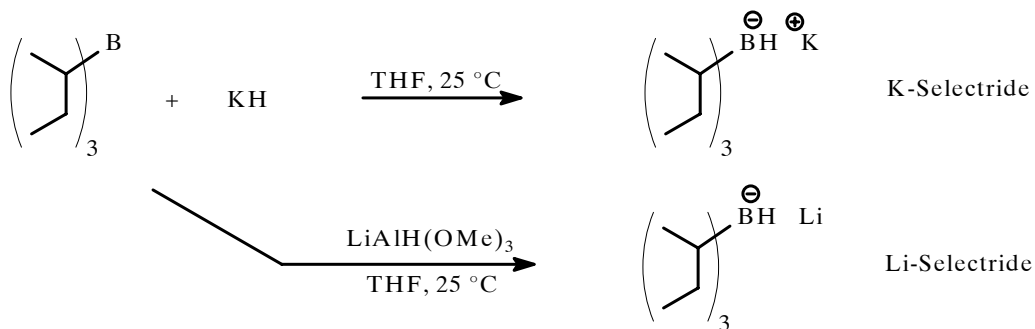


* α -OH-karbonilna jedinjenja: helatacija

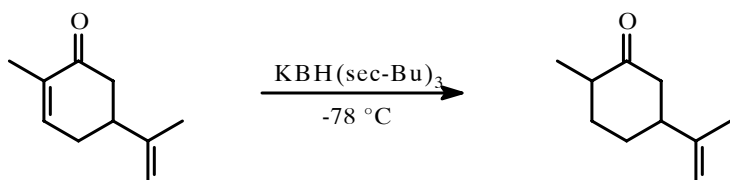


Selektridi **$\text{KBH}^{\text{sec-Bu}}_3$** **$\text{LiBH}^{\text{sec-Bu}}_3$**

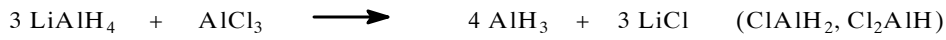
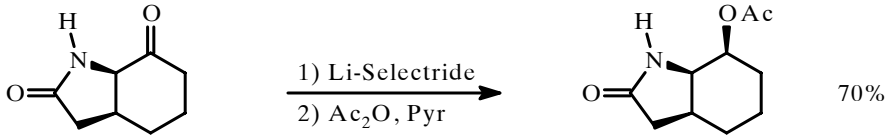
* Stereoselektivniji od LiAlH_4 ili NaBH_4



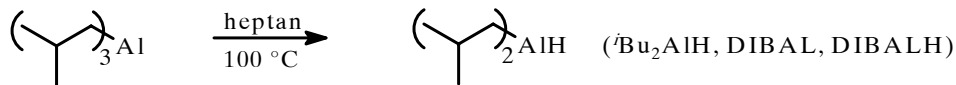
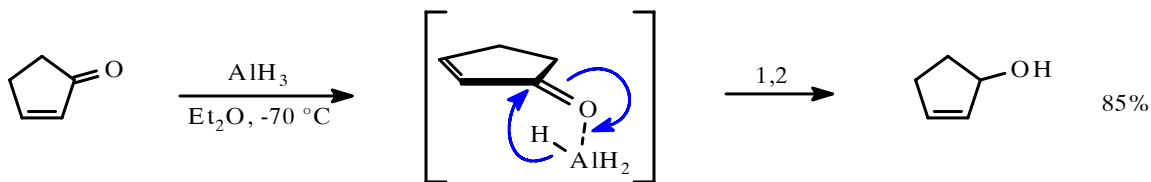
* Sa enonima: 1,4



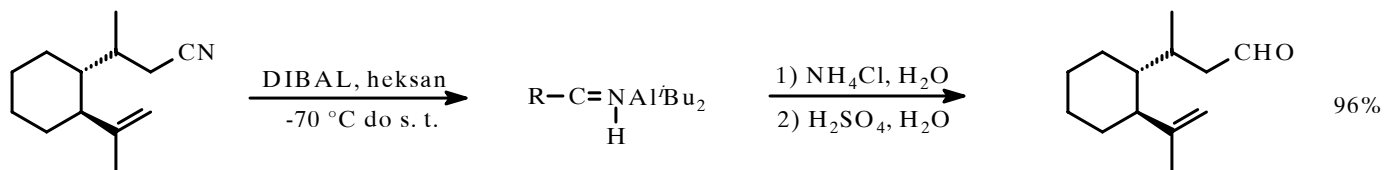
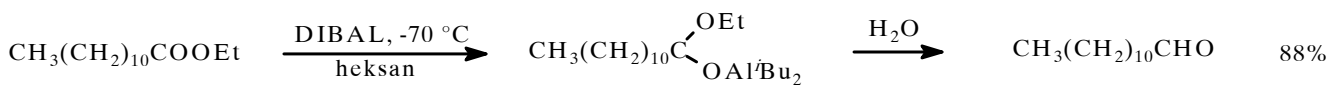
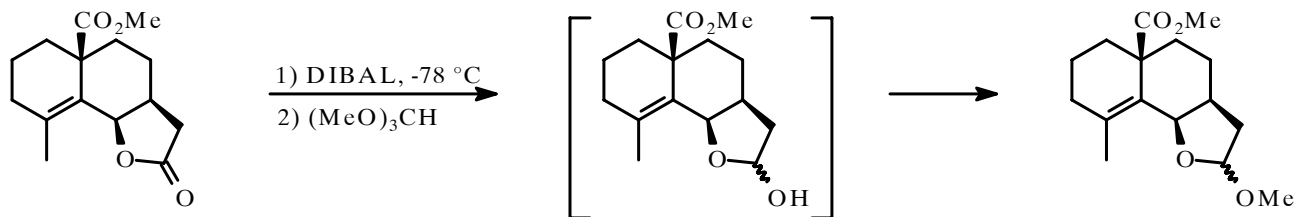
* Ketone redukuje stereoselektivno



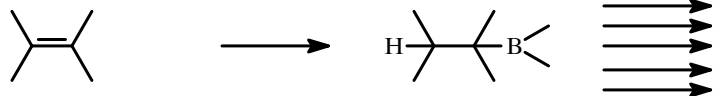
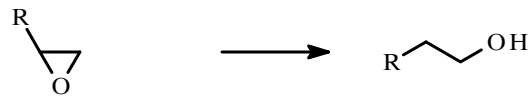
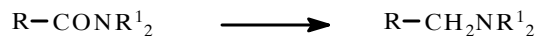
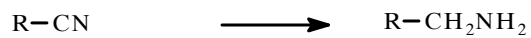
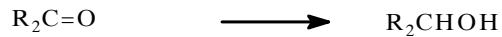
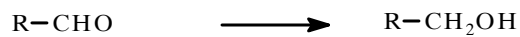
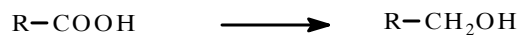
Lako redukuje: R-CHO, RC(O)R', R-COOH, R-COCl, R-CN, R-CONR₂



* Rastvarači: heptan, toluol, Et₂O

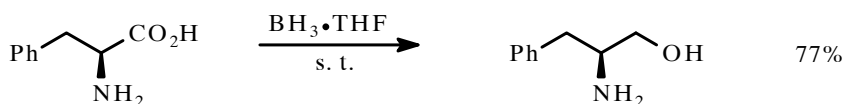
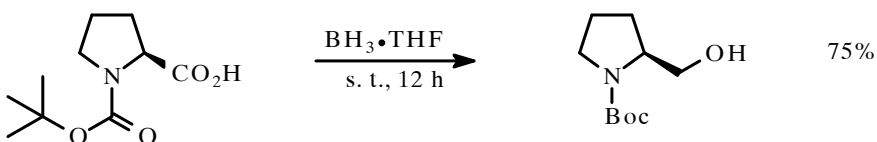
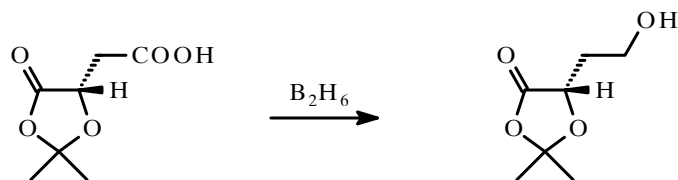
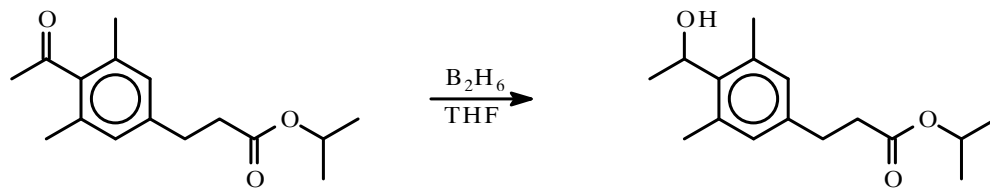
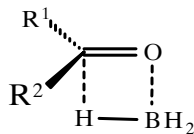
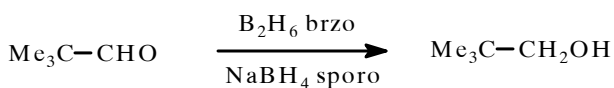
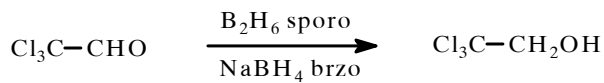


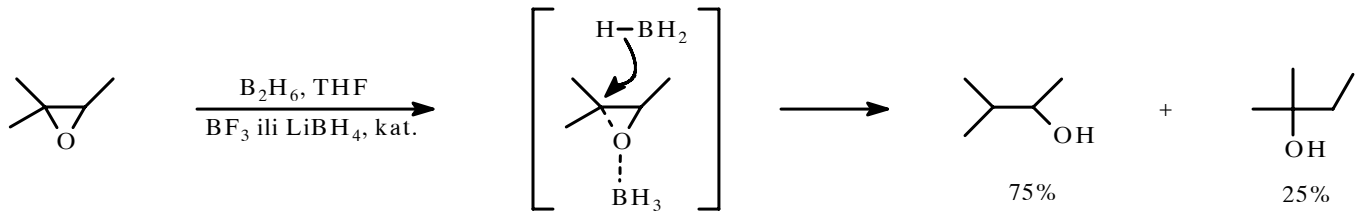
B₂H₆ Diboran



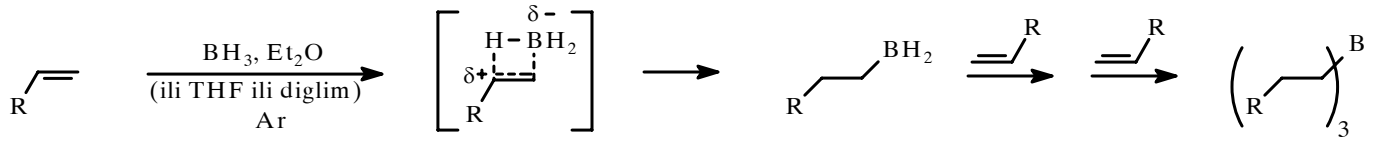
1° Koordinacija BH₃ sa C=O

2° Prenos hidrida

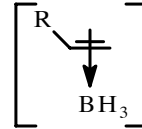




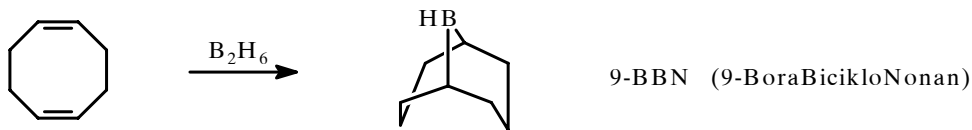
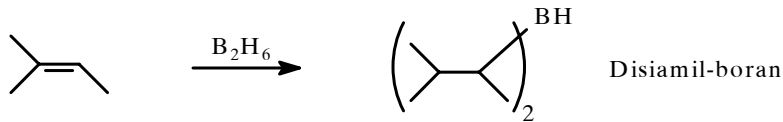
* Hidroborovanje alkena i reakcije alkil-borana



* *cis*-adicija "suprotno" Markovnikov-ljevom pravilu

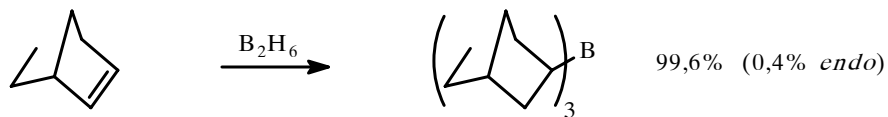
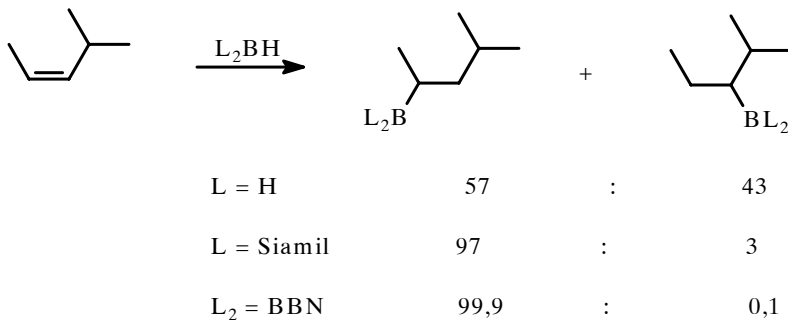


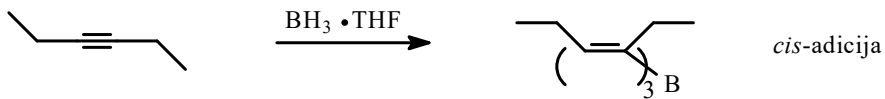
* moguće prisustvo grupa: OR, OH, COOR, Cl, NH₂, SR



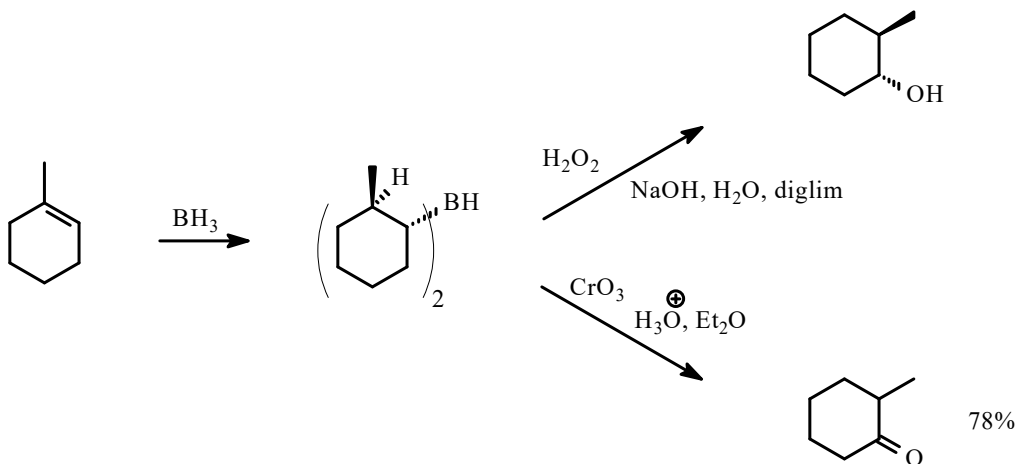
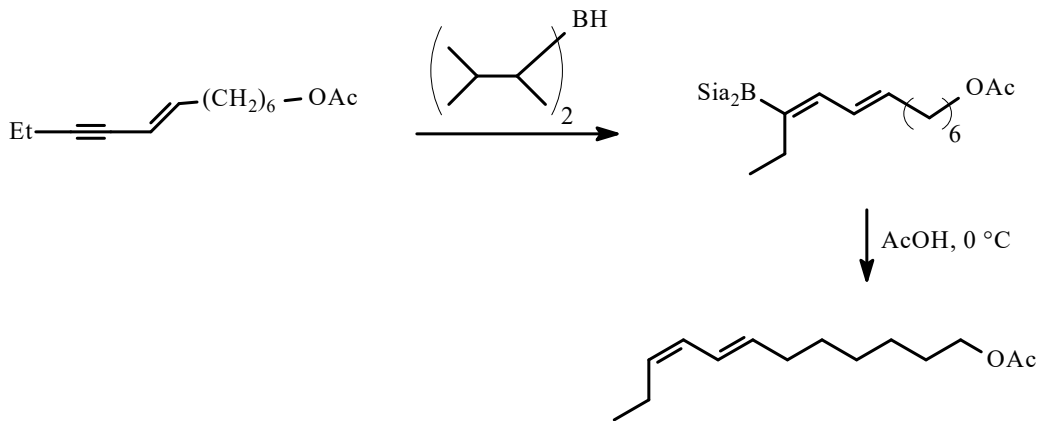
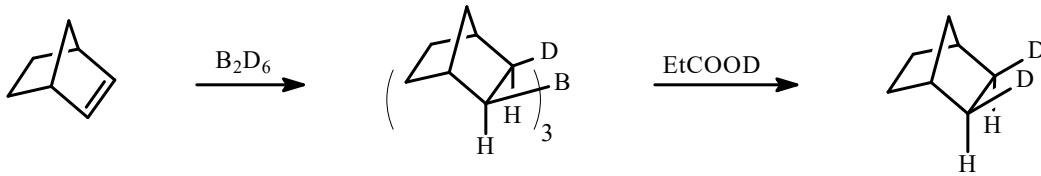
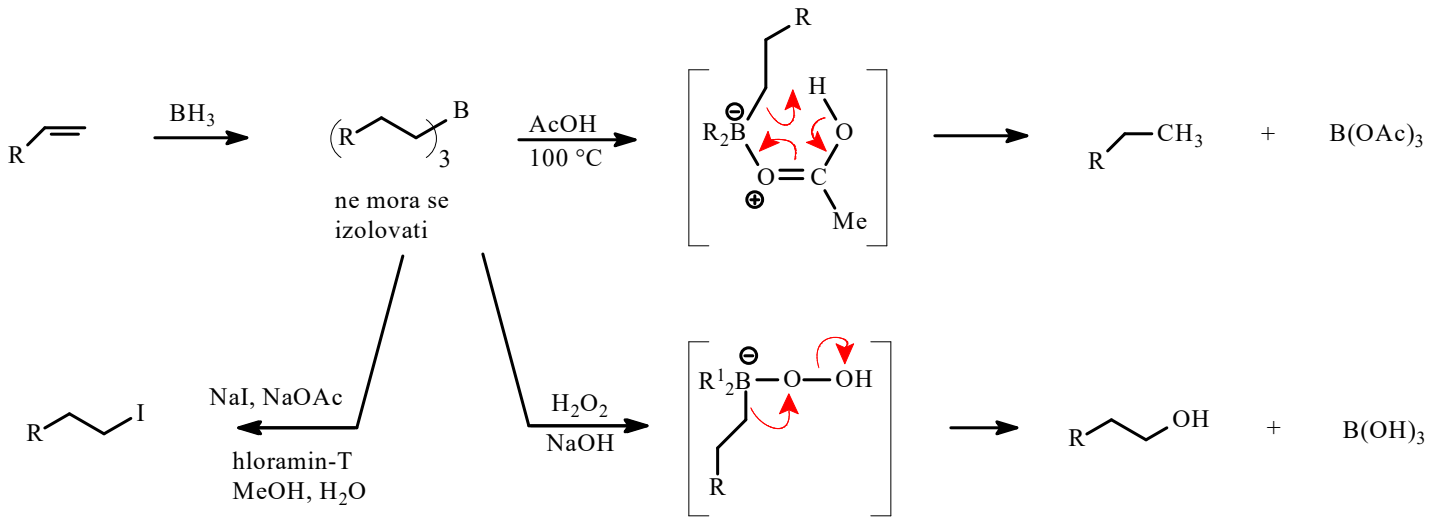
* Napad borana sa sterno manje zaštićene strane

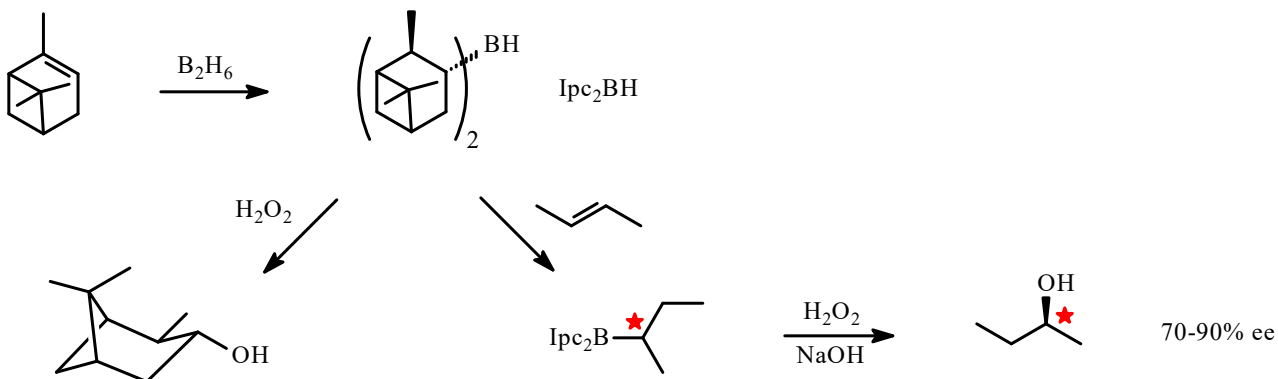
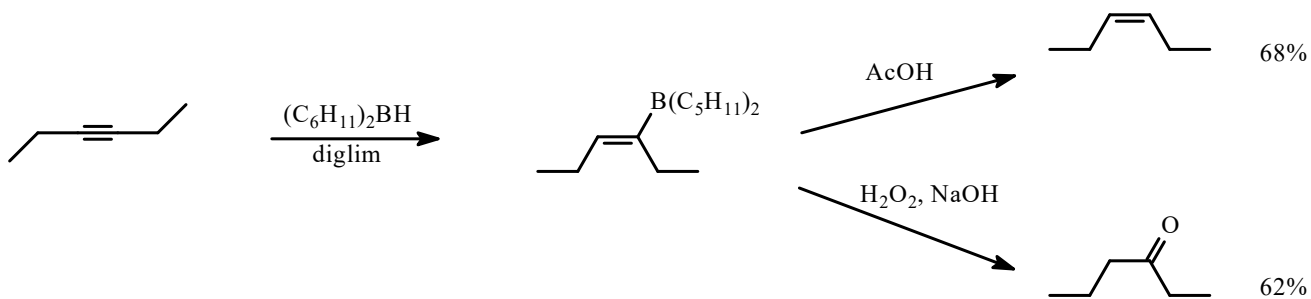
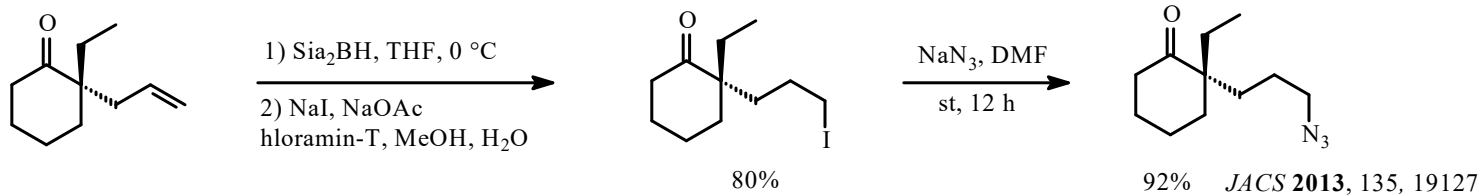
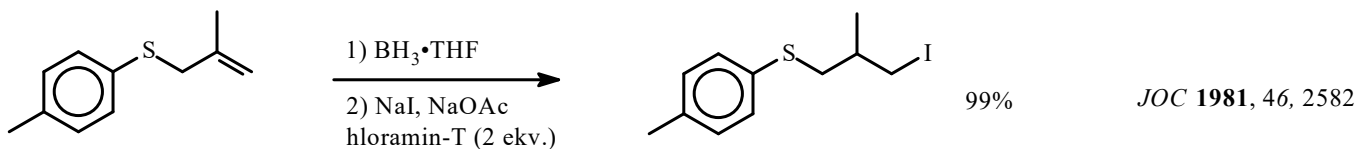
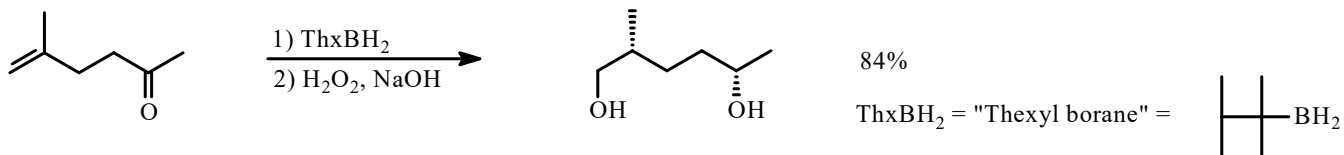
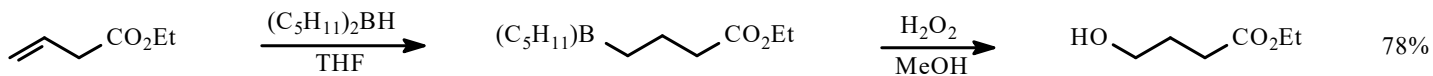
* Voluminozniji borani su stereoselektivniji



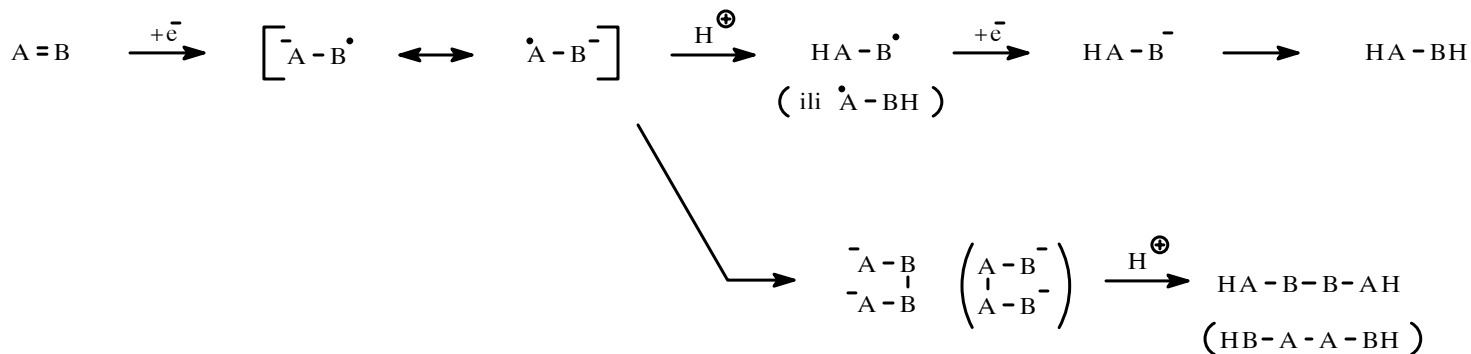


*Reakcije organoborana





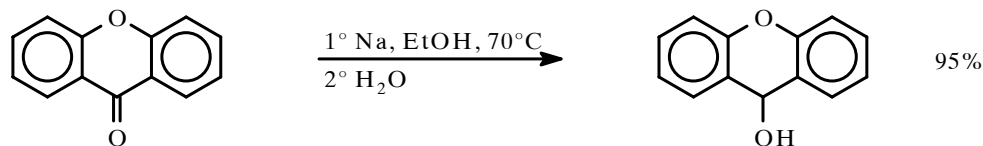
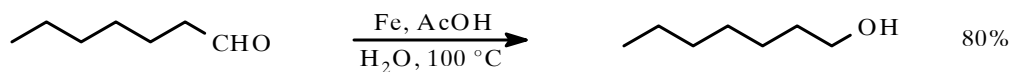
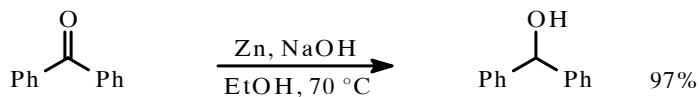
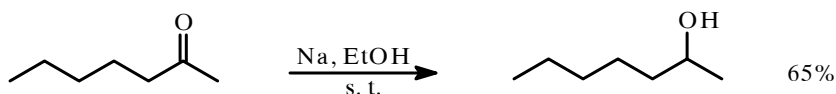
3) REDUKCIJE POMOĆU RASTVORNIH METALA



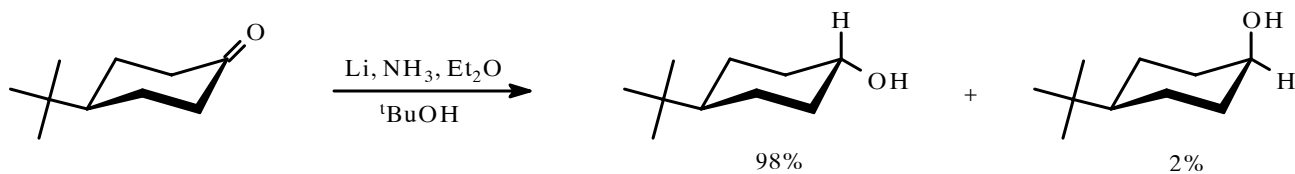
* Metali: Li, Na, K, Ca, Mg, Zn, Fe, Sn, Ti, Al, Sm,

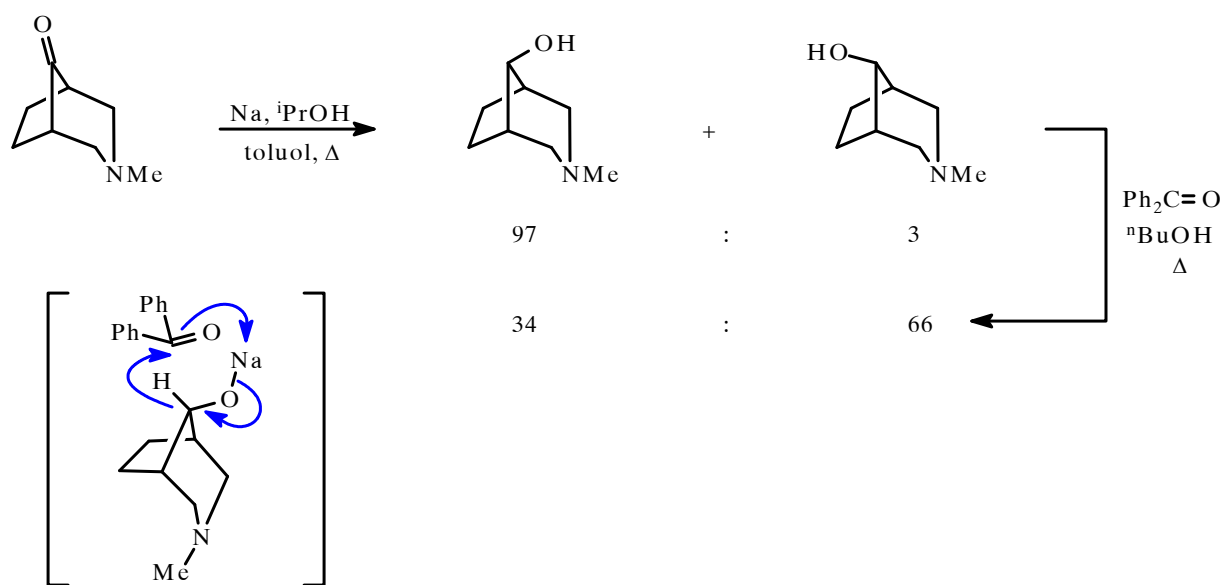
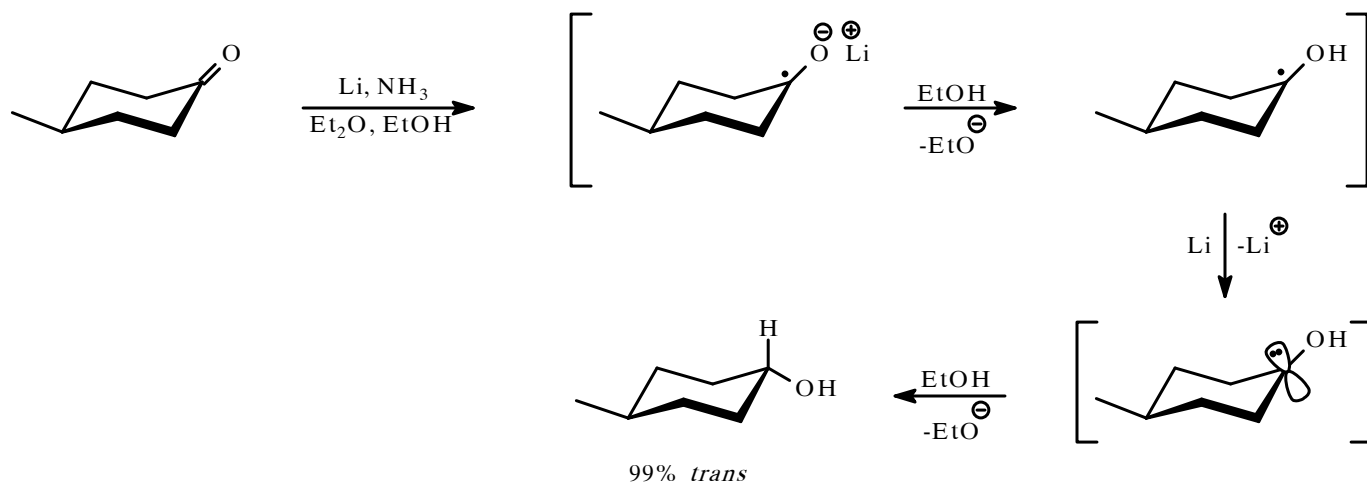
* Rastvarači: ROH, NH₃ liq/ROH, etarski i ugljovodonični rastvarači, ... Izbor rastvarača zavisi od tipa transformacije

Redukcija **C=O** i **COOR** u prisustvu H[⊕]-donora

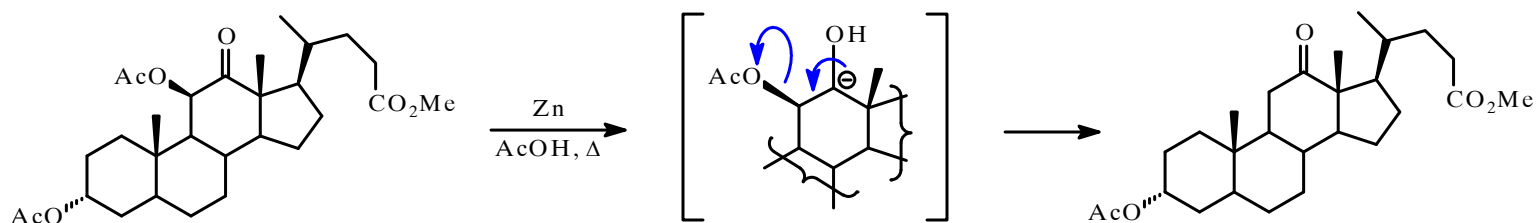
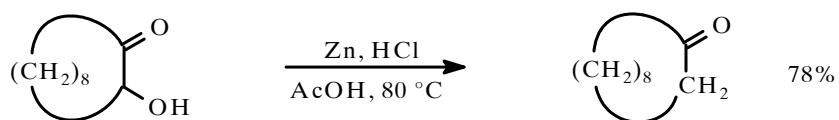


* Redukcijom cikloalkanona **obično** nastaje termodinamički stabilniji proizvod

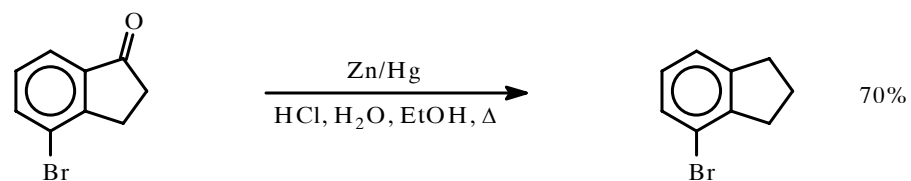
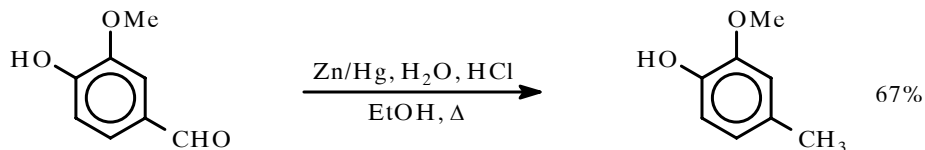
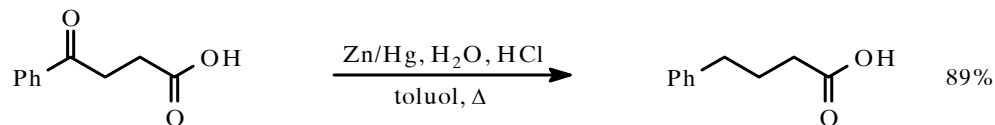
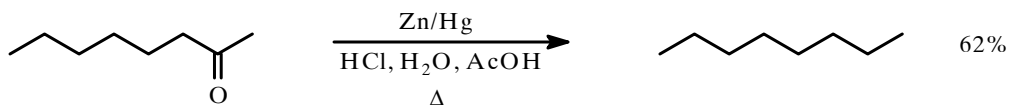




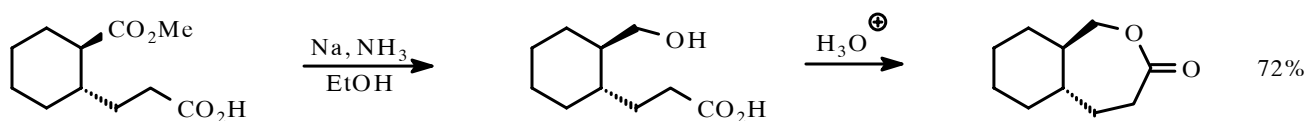
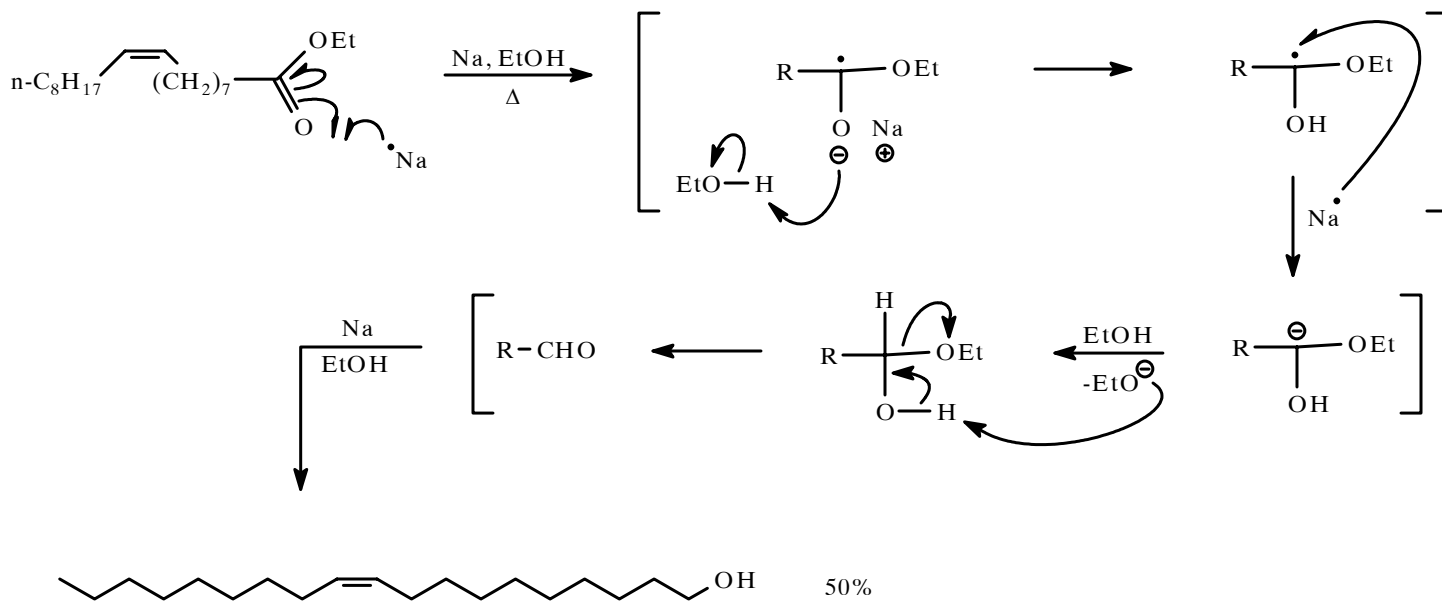
* Eliminacija -OAc, -OH, -Cl, -Br, -NHR u α -položaju



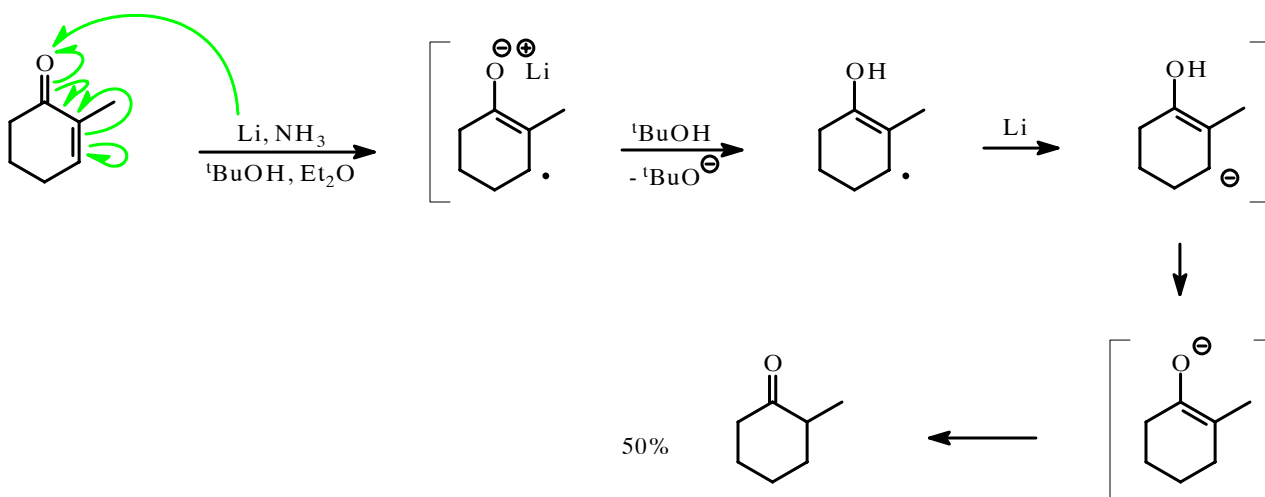
* *Clemmensen-ova redukcija*



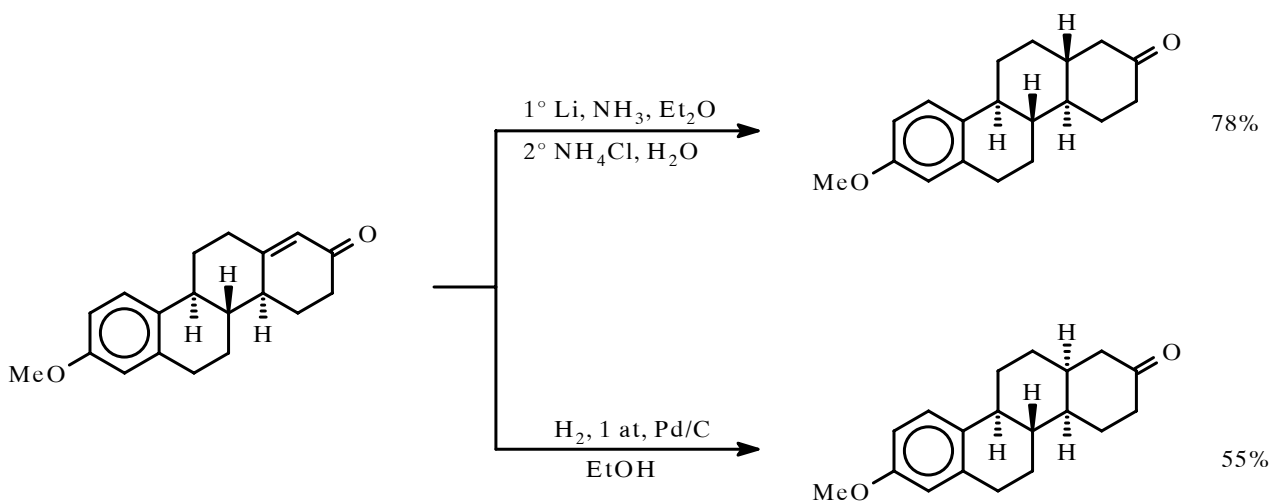
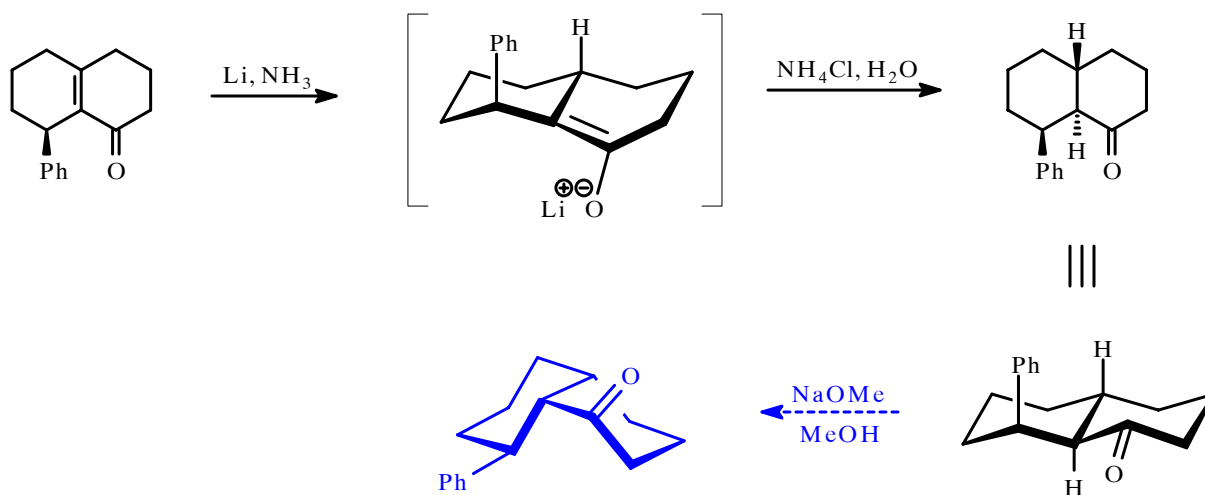
* *Bouveault-Blanc-ova redukcija*



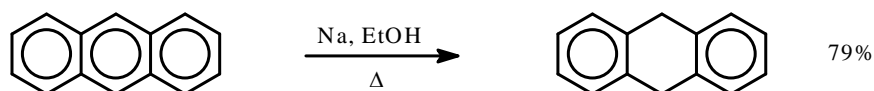
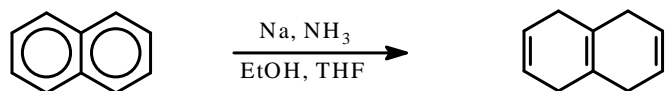
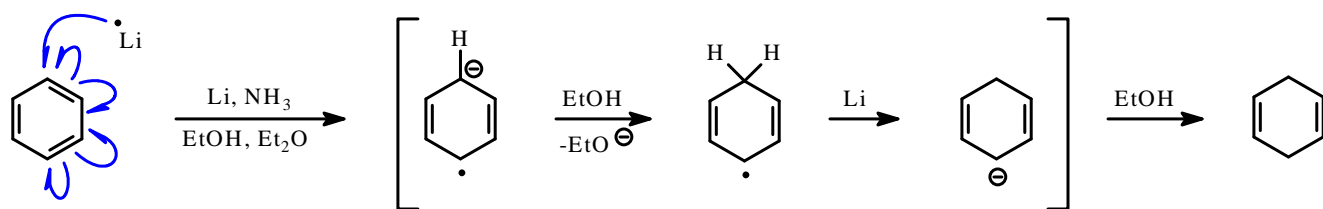
* Redukcije 



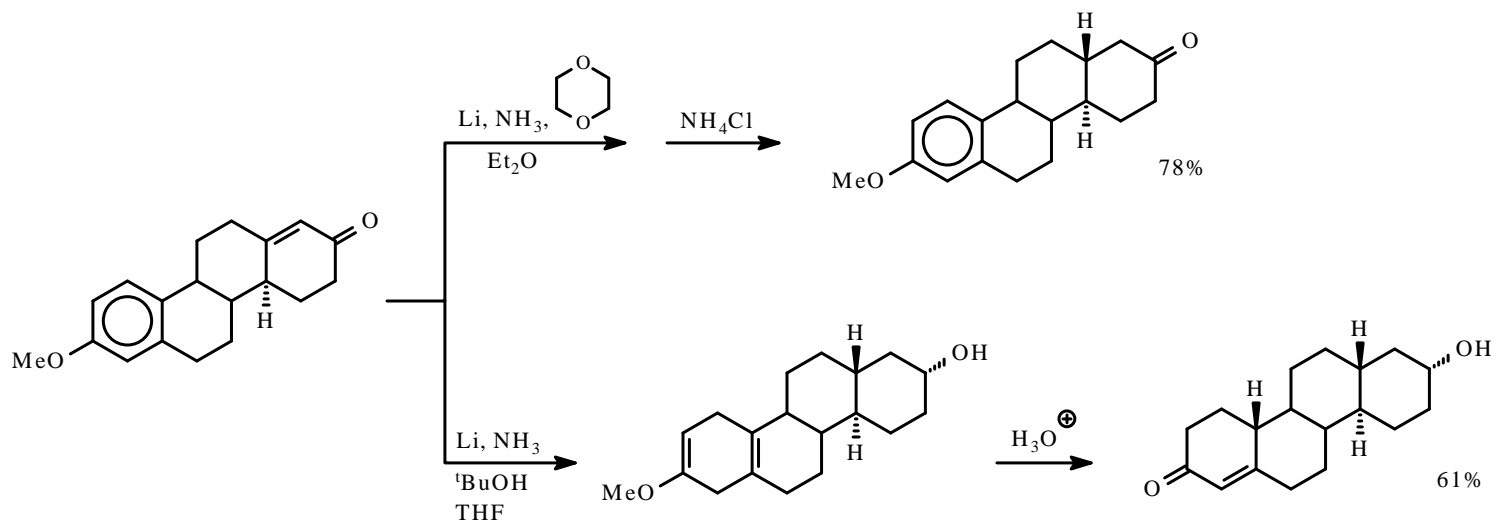
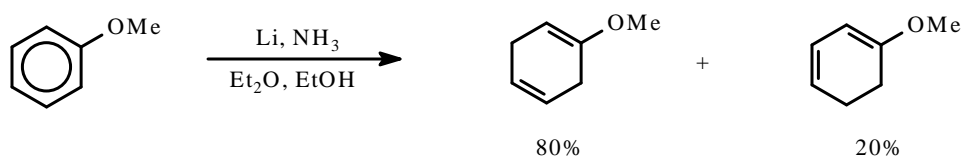
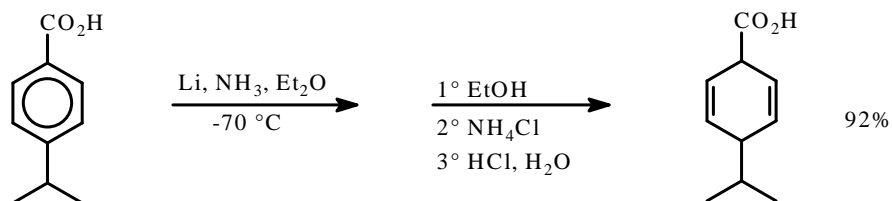
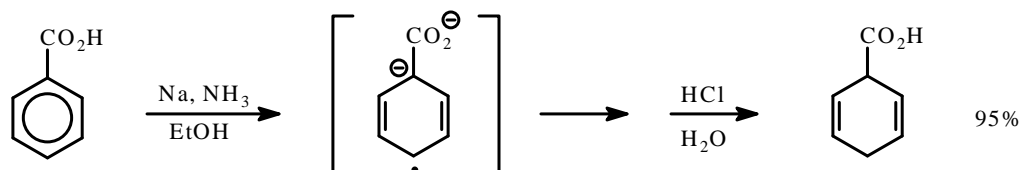
Kondenzovani sistemi: *trans*



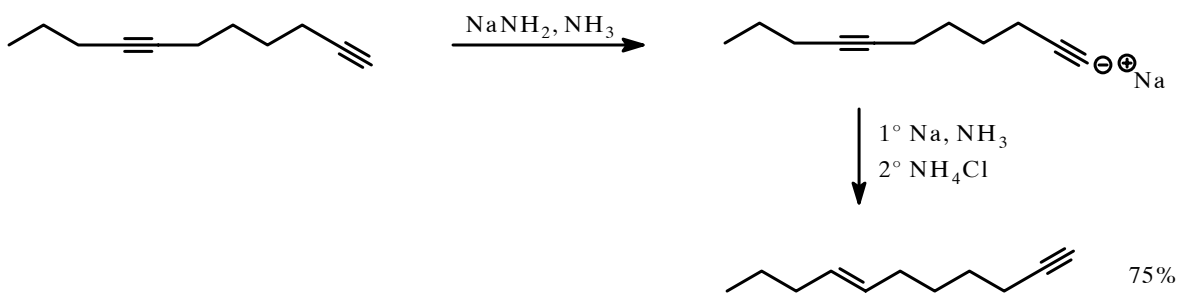
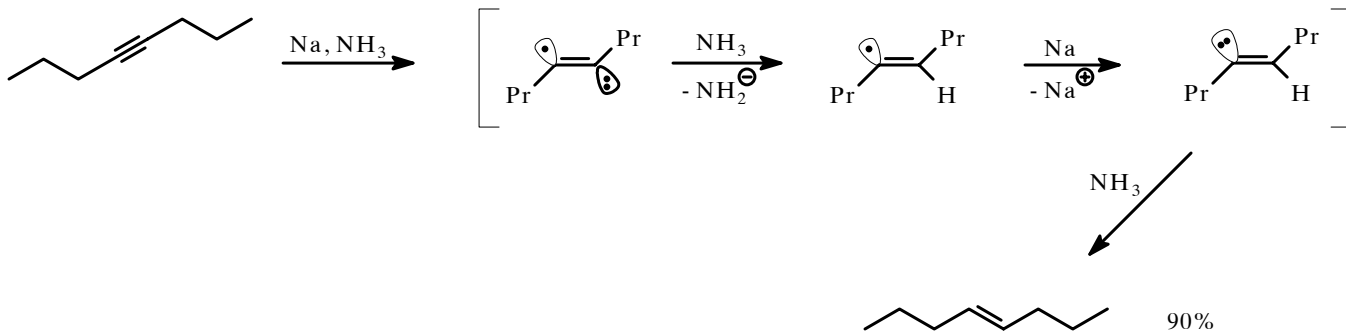
* Birch-ova redukcija



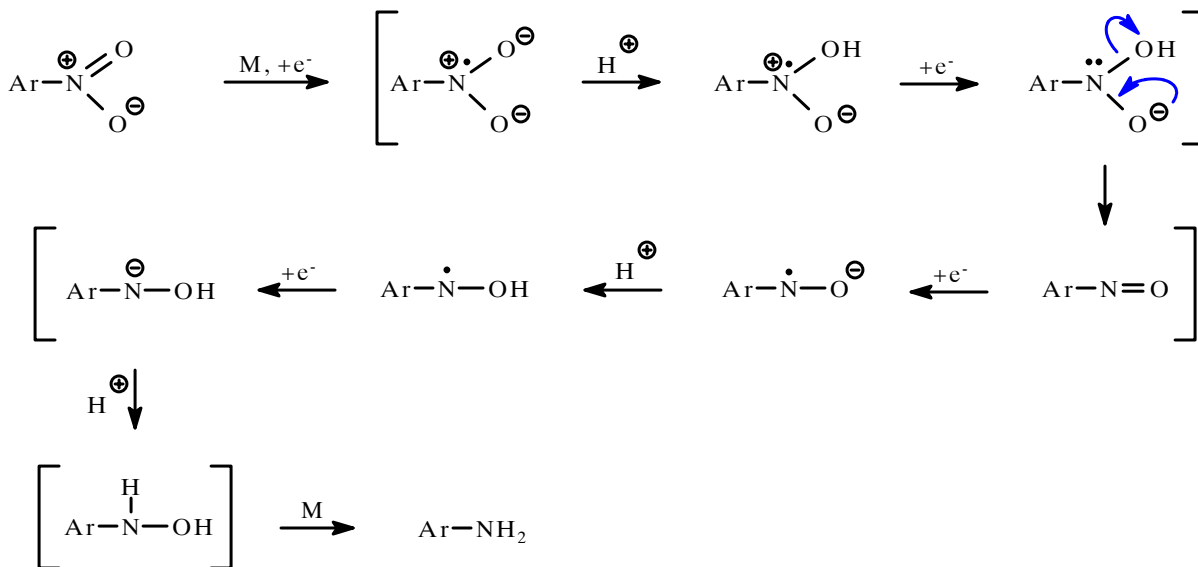
* Uticaj supstituenata, ROH, Fe



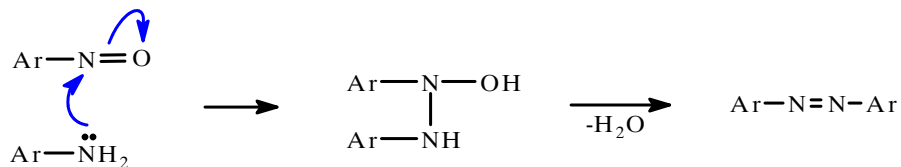
* Redukcija $C\equiv C$

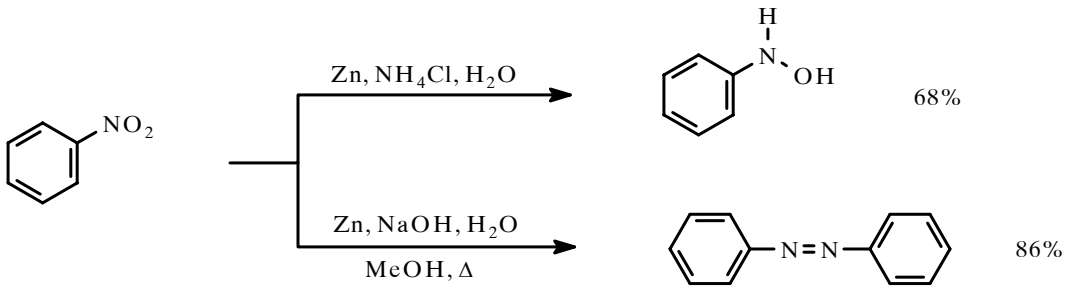
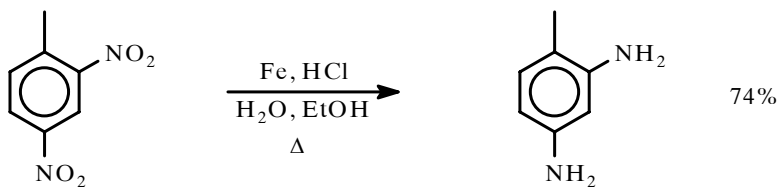


NO_2 $M = \text{Fe, Sn, Zn, \dots}$

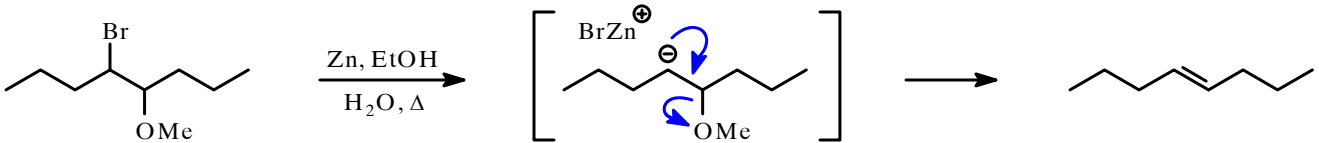
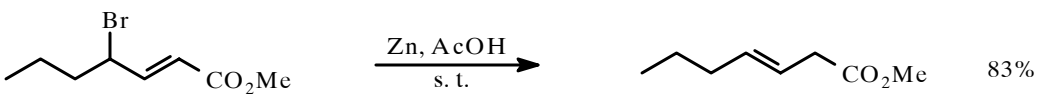
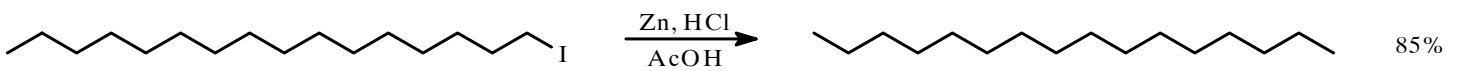
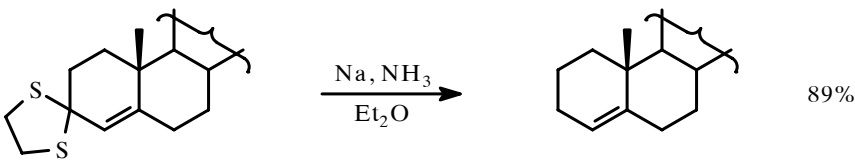


Sporedne reakcije:



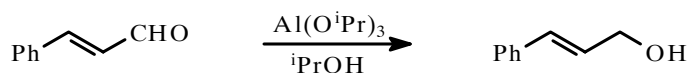
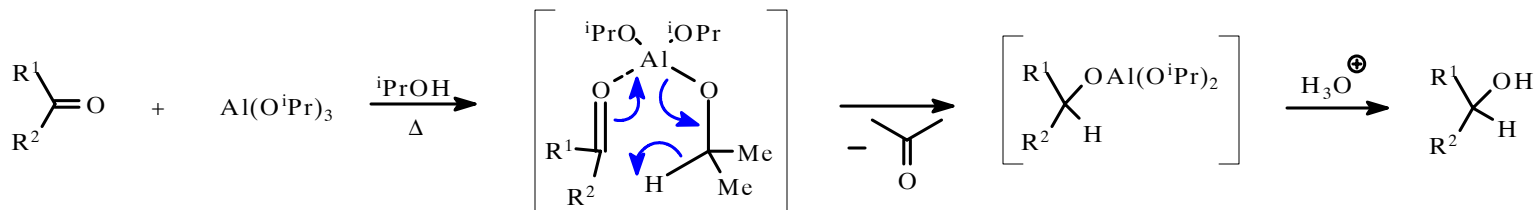


* Desulfurizacija, dehalogenovanje



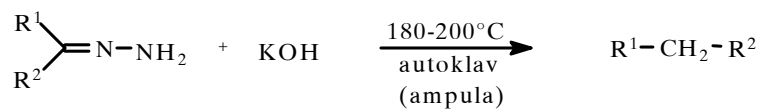
4) OSTALE REDUKCIJE

* *Meerwein-Ponndorf-Verley*-jeva redukcija

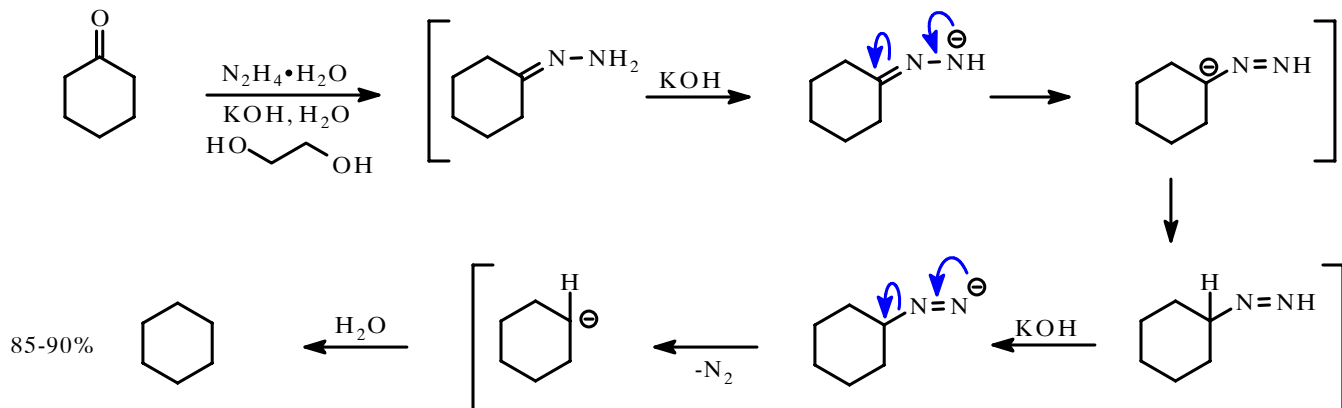


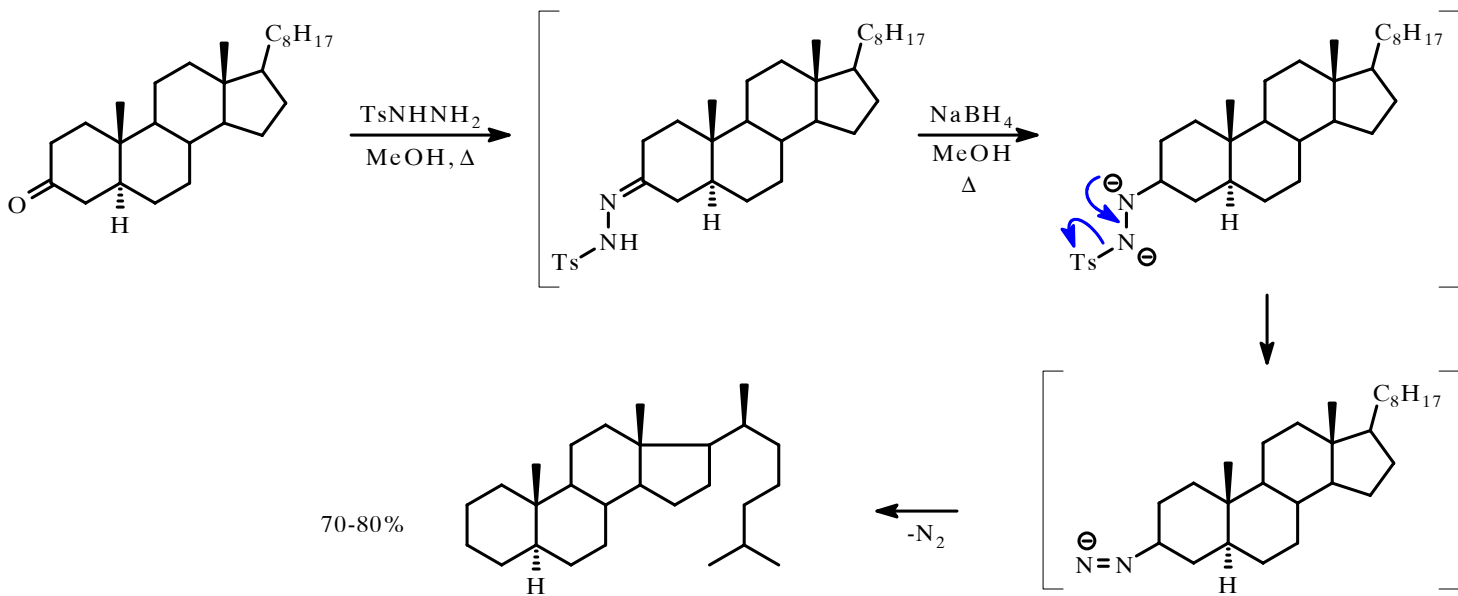
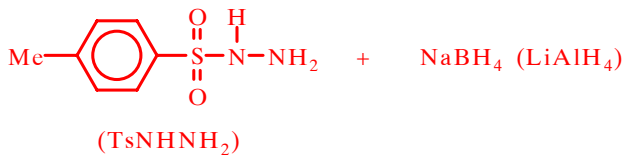
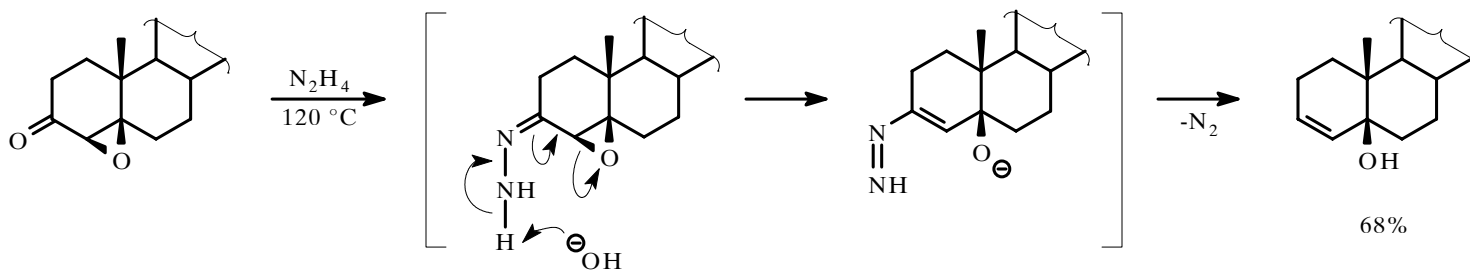
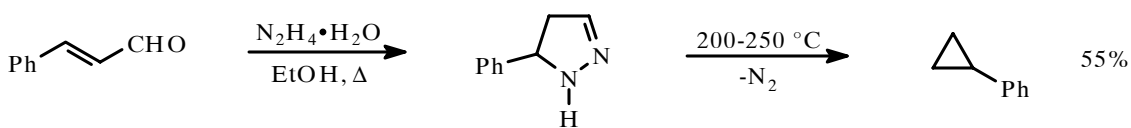
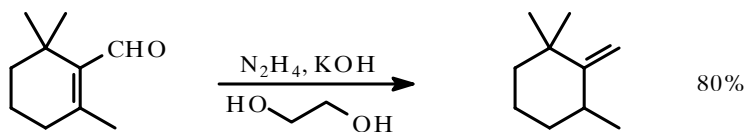
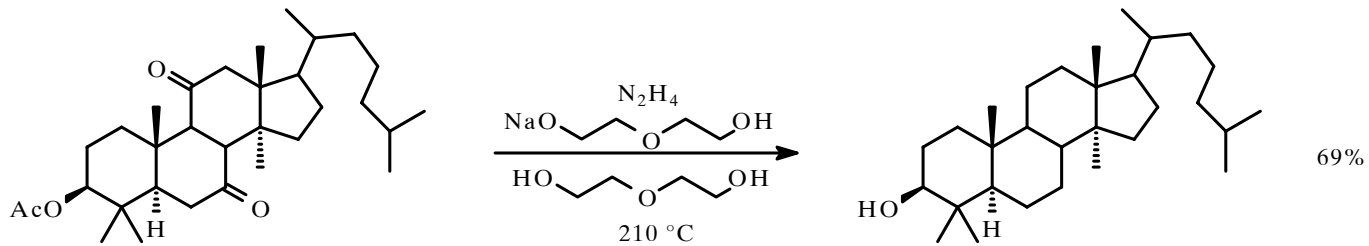
* Redukcije pomoću N_2H_4 i njegovih derivata

* *Wolff-Kishner*-ova redukcija

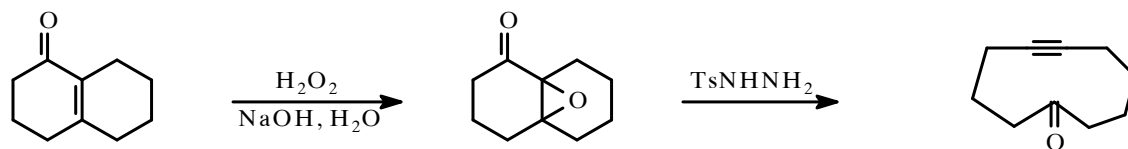
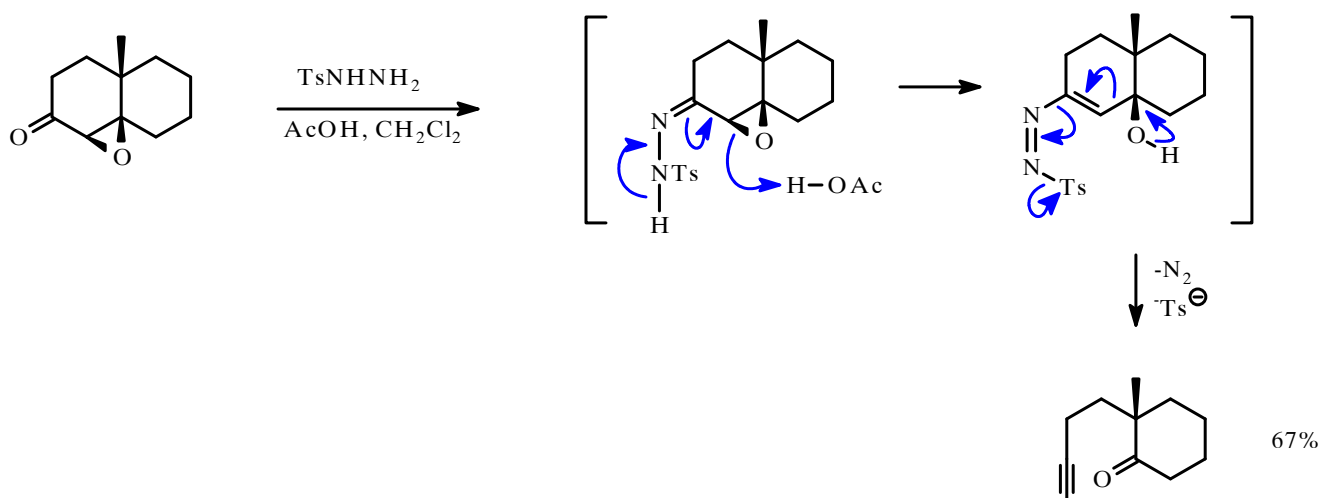
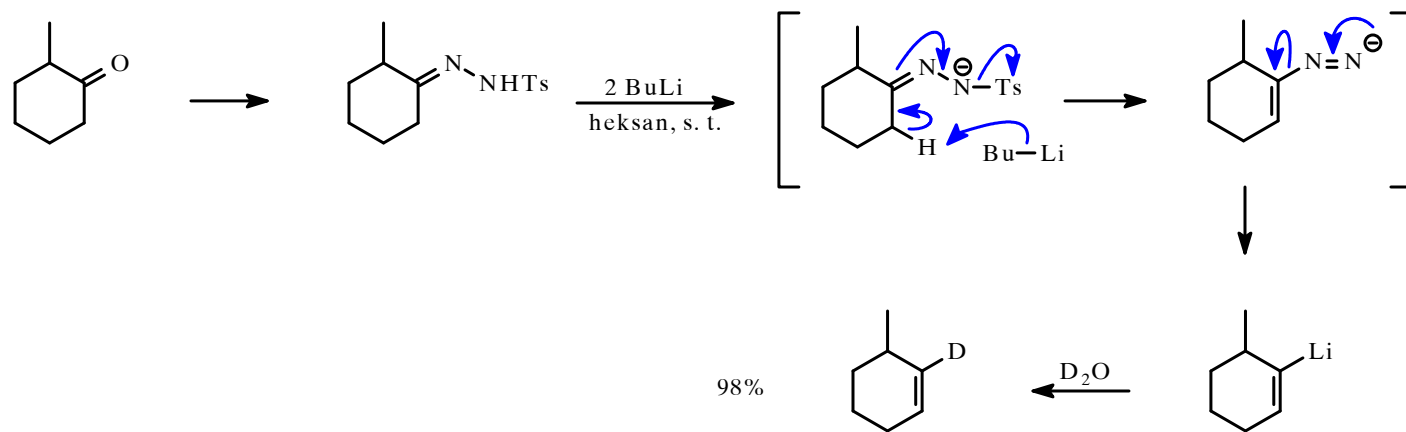


* *Huang-Minlon*-ova modifikacija

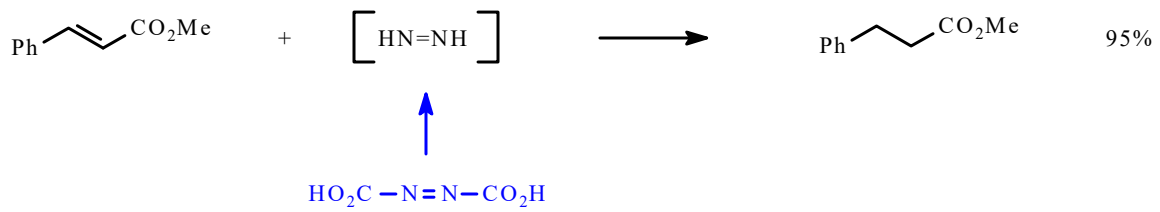
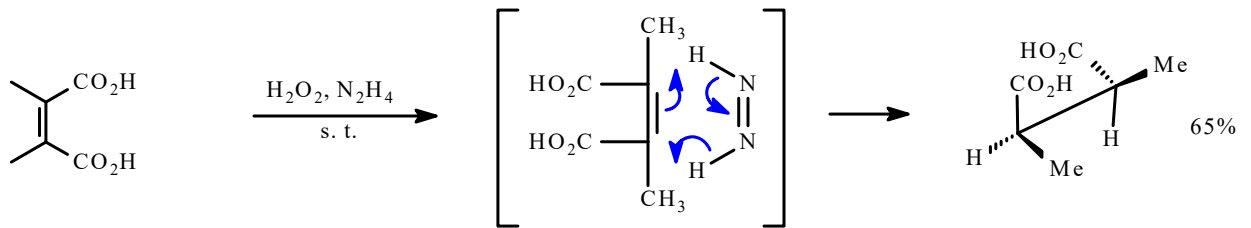
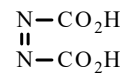




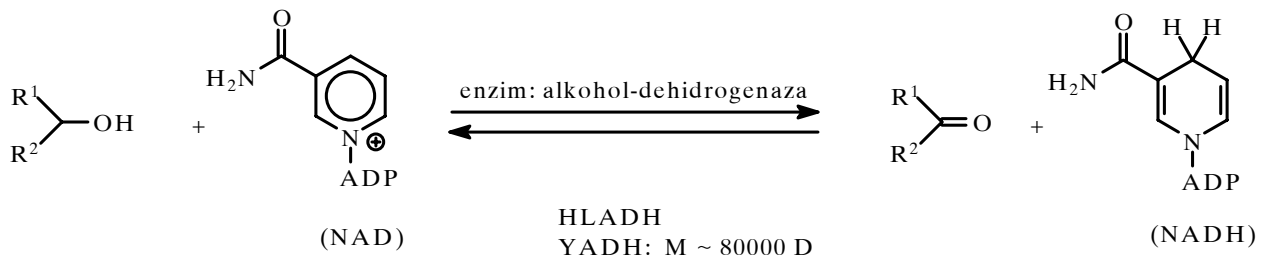
Bamford-Stevens-ova reakcija (Shapiro-va reakcija)



* **HN=NH** Diimid



* Enzimske redukcije



* Pekarski kvasac (PK), *Saccharomyces cerevisiae* (Baker's yeast, BK)

