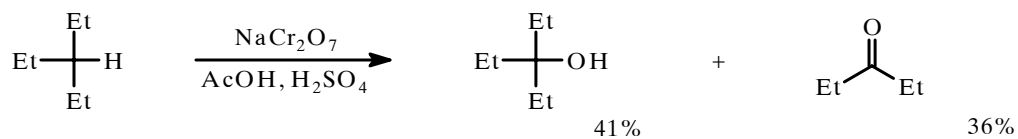


OKSIDACIJE

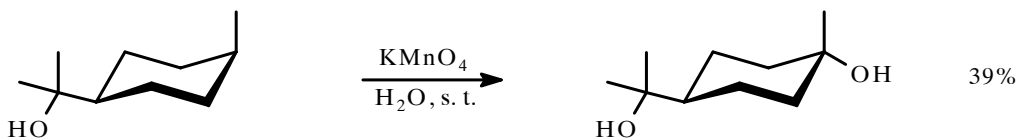
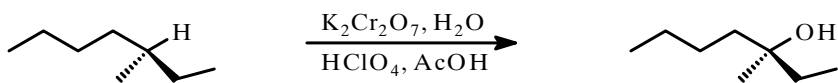
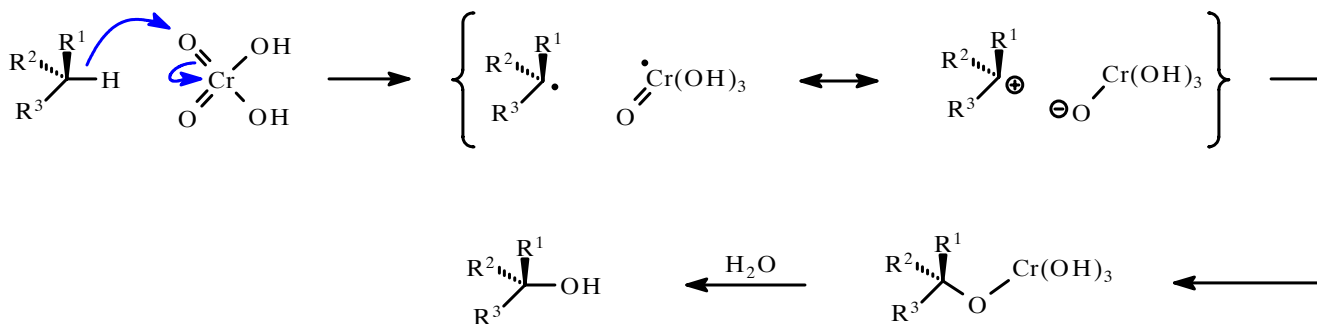
1) Zasićeni ugljovodonici

* Reaktivnost C-H veza: prim < sec < tert

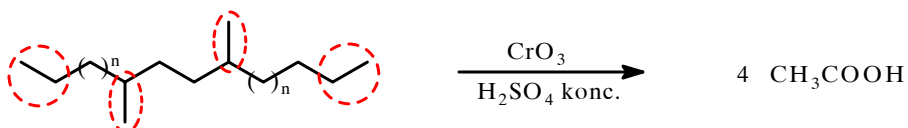
1 : 110 : 7000



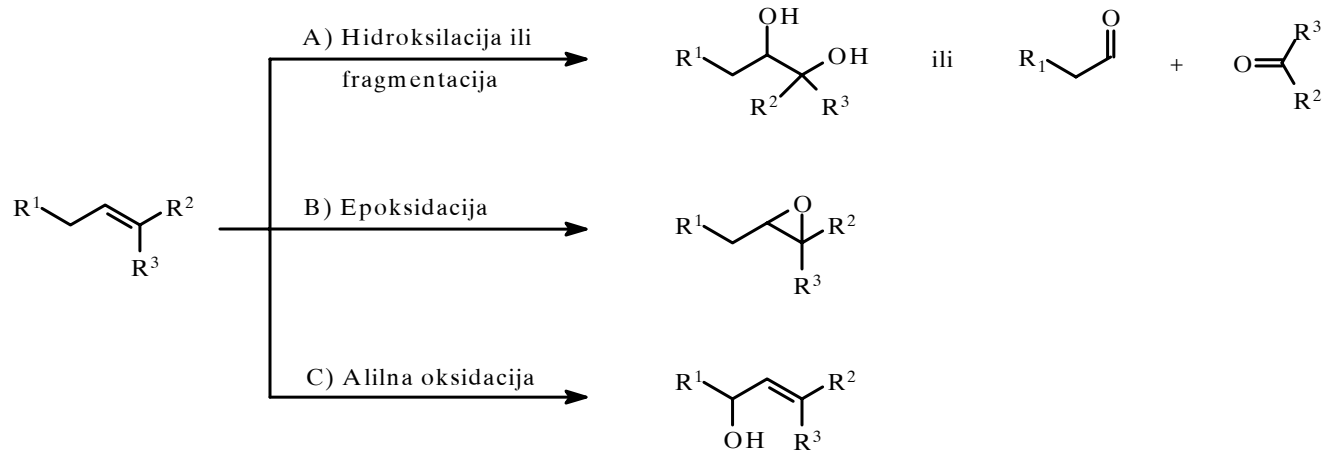
* Retencija konfiguracije



* Kuhn-Roth-ova oksidacija

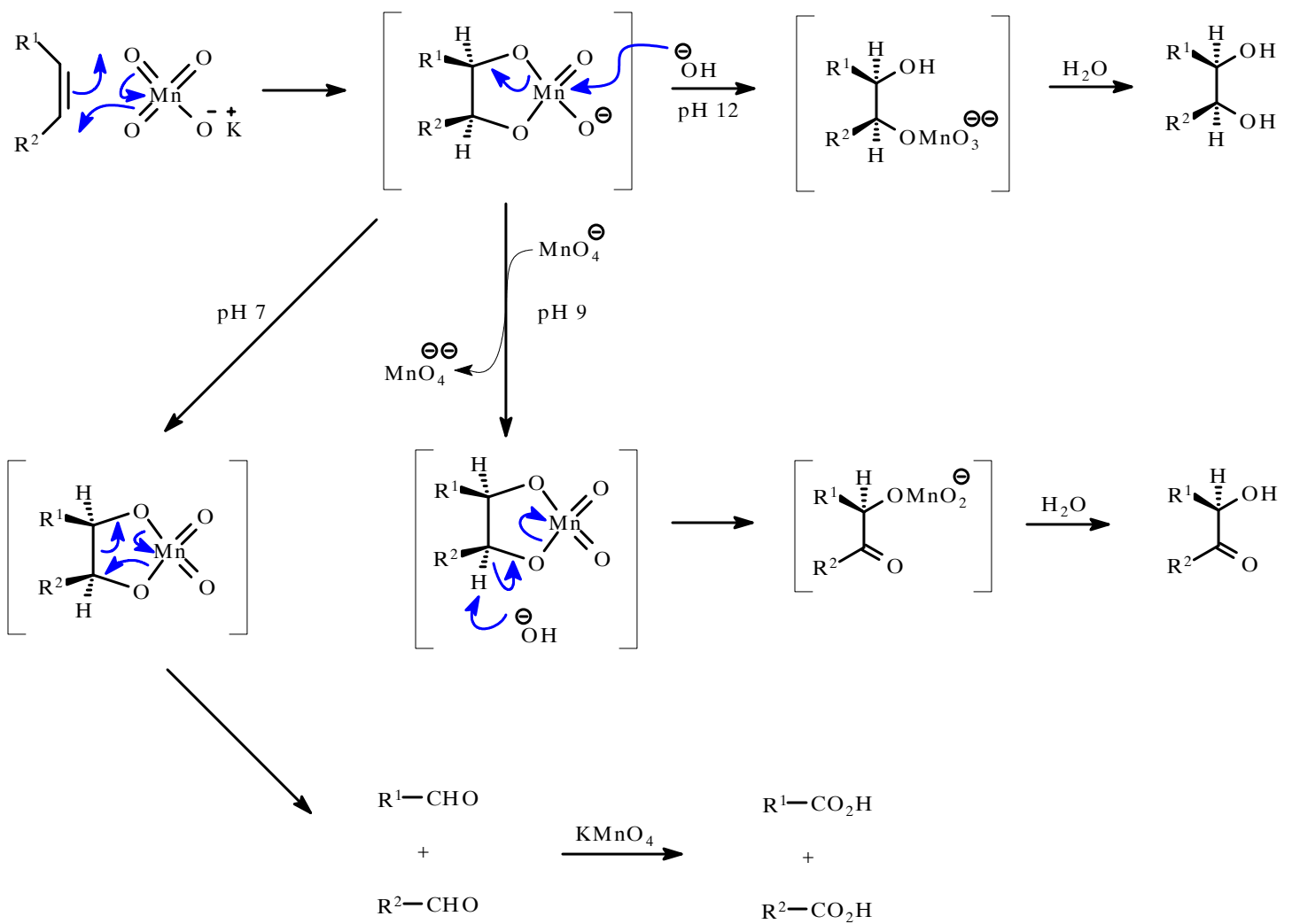


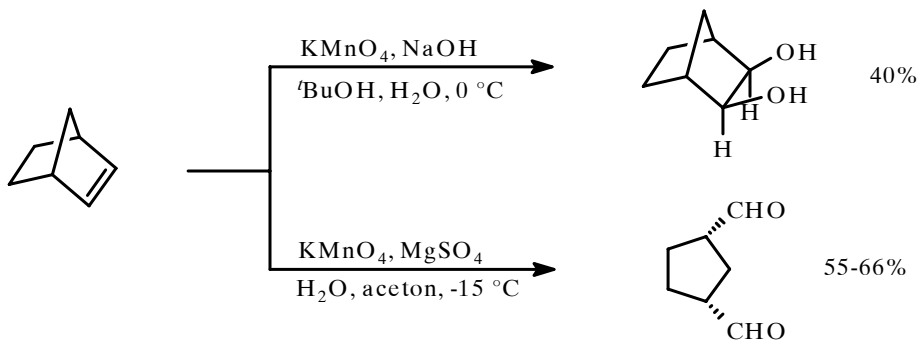
2) OKSIDACIJE ALKENA



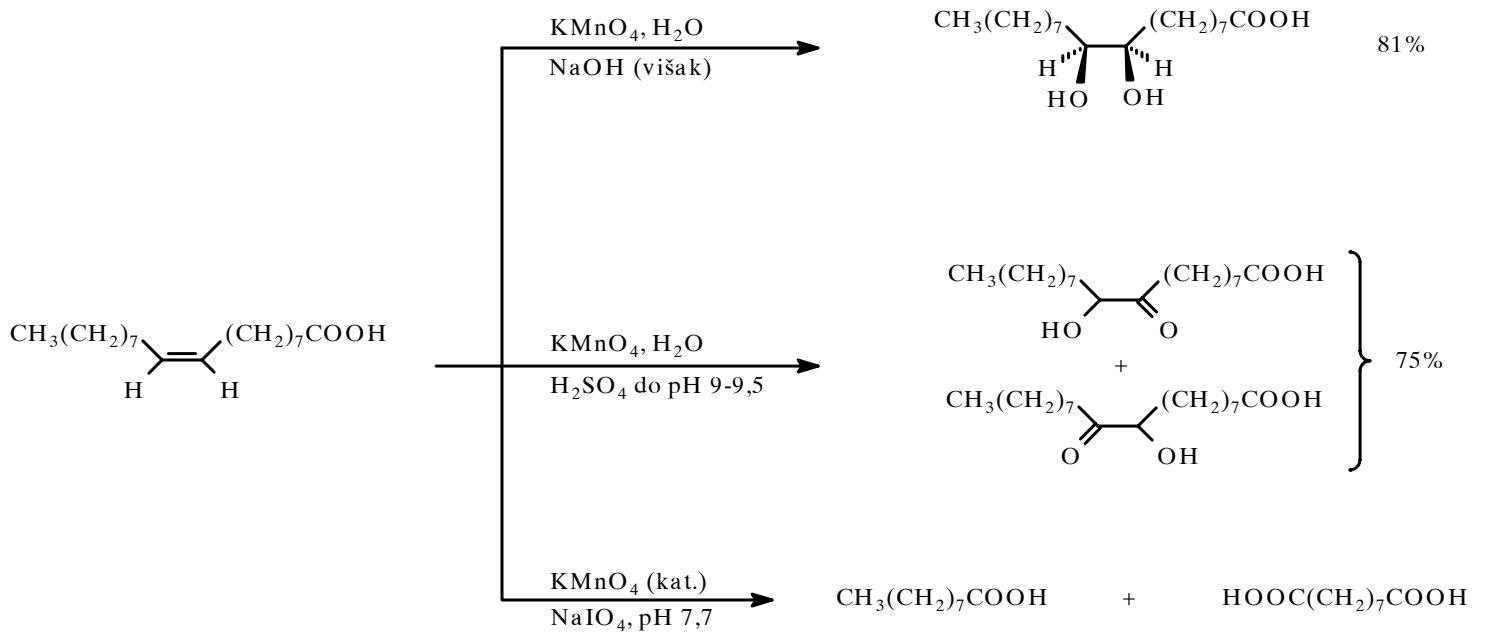
A) HIDROKSILACIJA I FRAGMENTACIJA C=C VEZE

KMnO₄ pH-zavisno

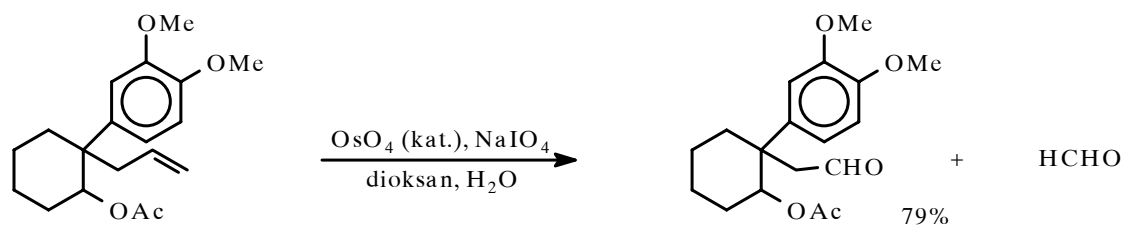




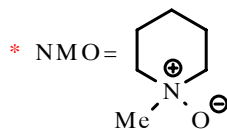
Stereospecifičnost dihidroksilacije



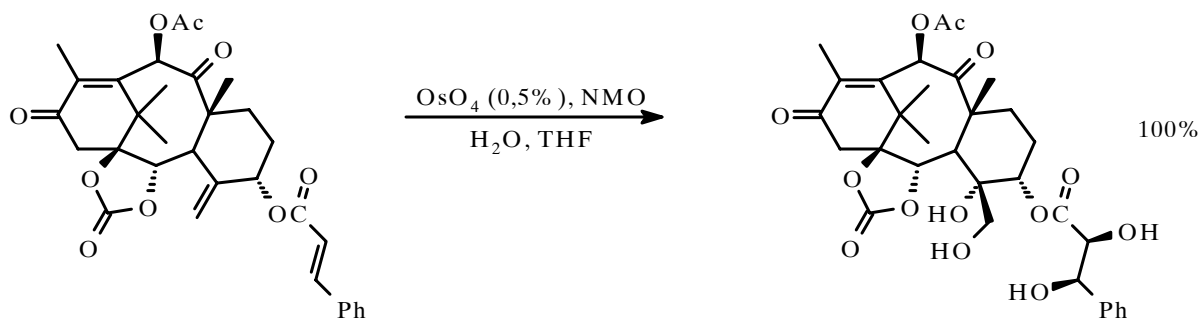
OsO₄ Superioran reagens u odnosu na KMnO₄;
 pogodan za asimetrične dihidroksilacije;
 ekstremno toksičan!



* Ko-oksidansi: K₃Fe(CN)₆, NMO*, H₂O₂, O₂,.....

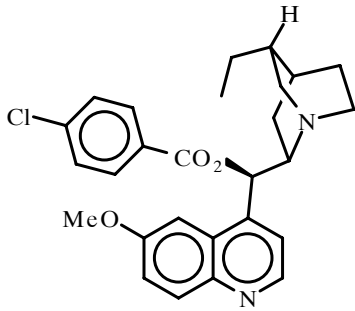


K₂OsO₄: bezbednija varijanta OsO₄

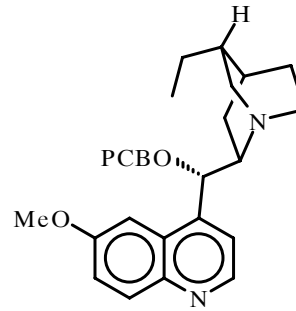


* Asimetrična dihidroksilacija (Sharpless-ov AD-proces)

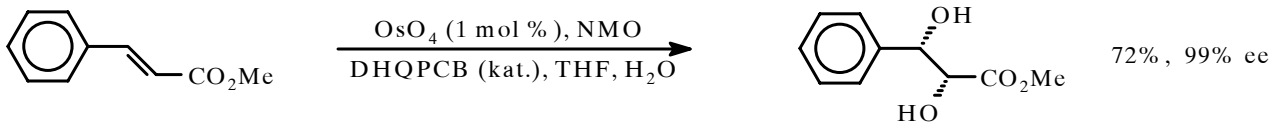
Hiralni ligandi na bazi Cinhona-alkaloida (kinin i kinidin - "pseudoenantiomeri")



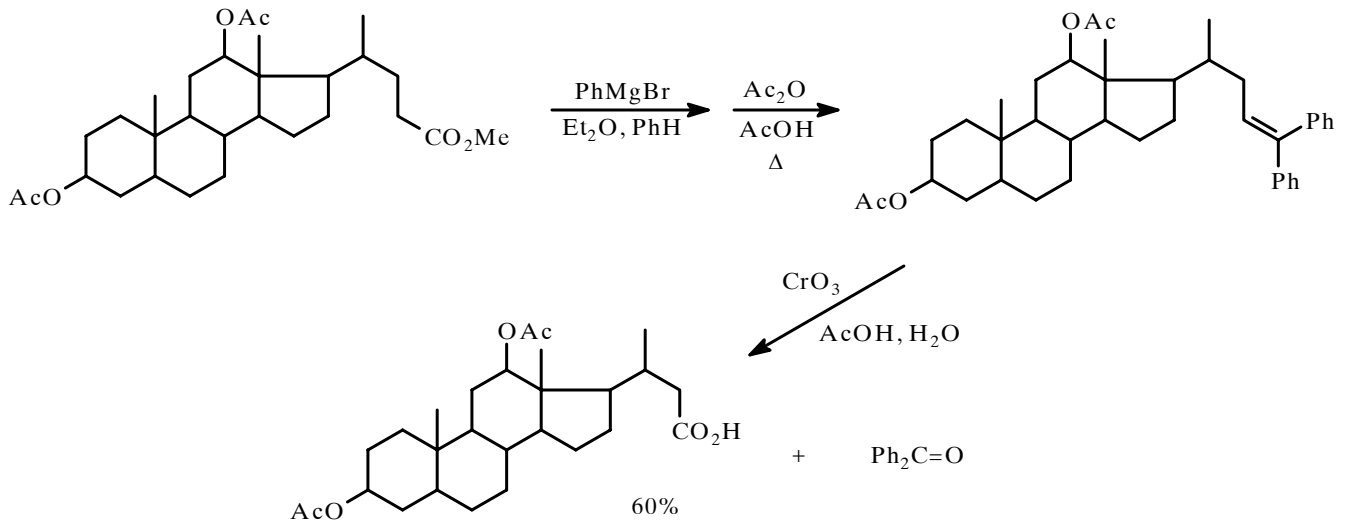
Dihidrokinin-p-hlorbenzoat (DHQPCB)

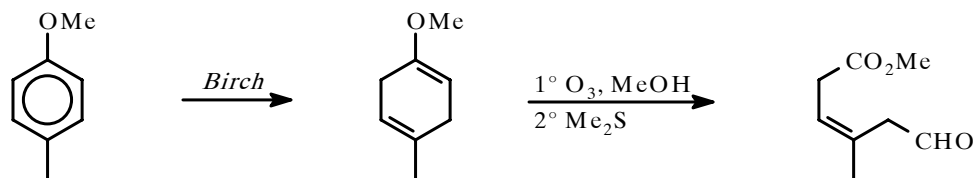
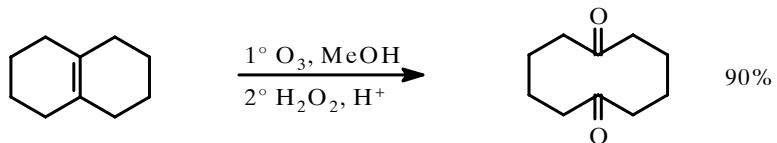
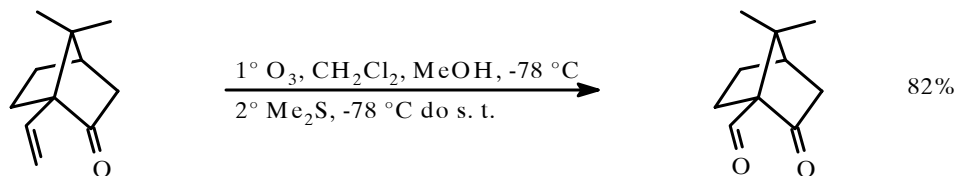
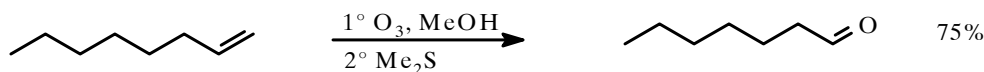
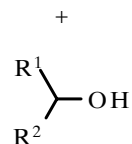
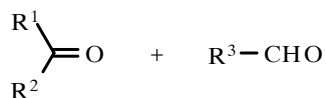
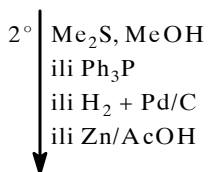
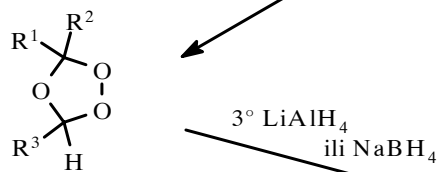
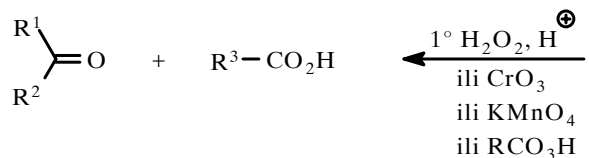
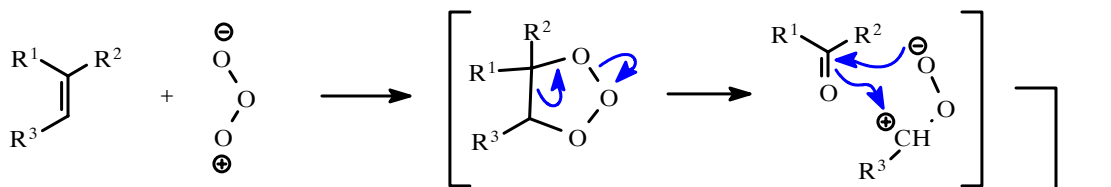
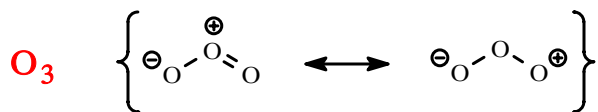


Dihidrokinidin-p-hlorbenzoat (DHQDPCB)

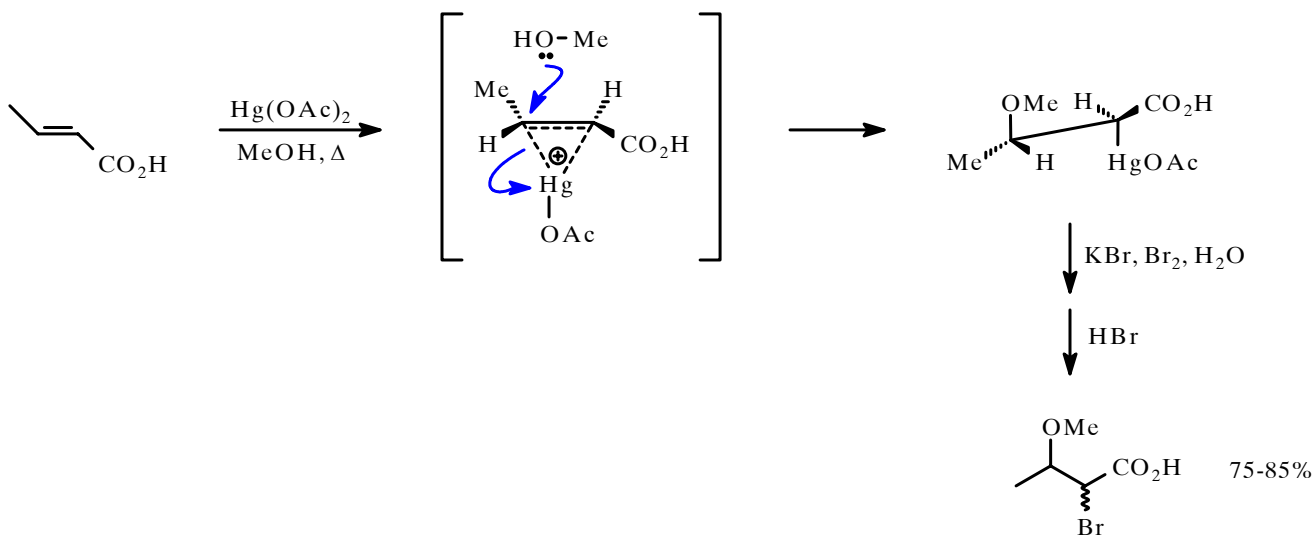
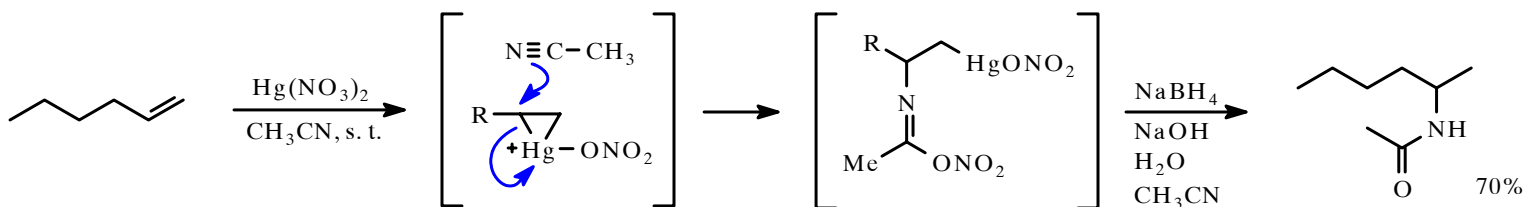
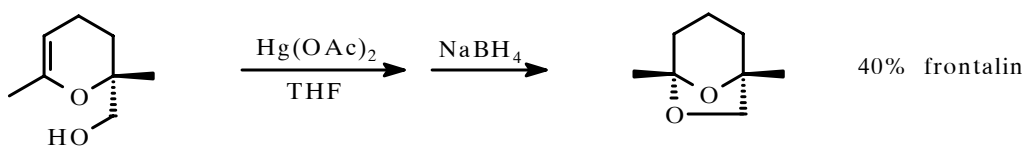
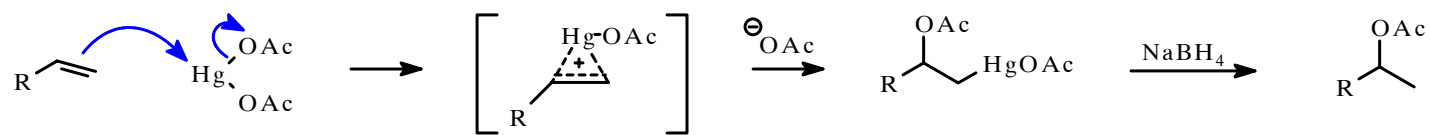


CrO₃ za oksidaciju 1,1-difenil-alkena u karboksilne kiseline

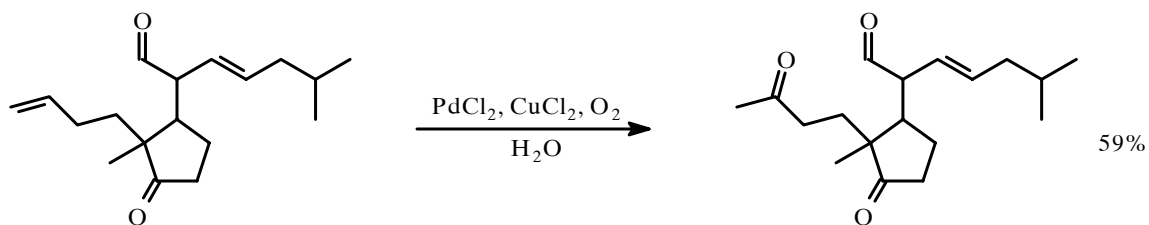
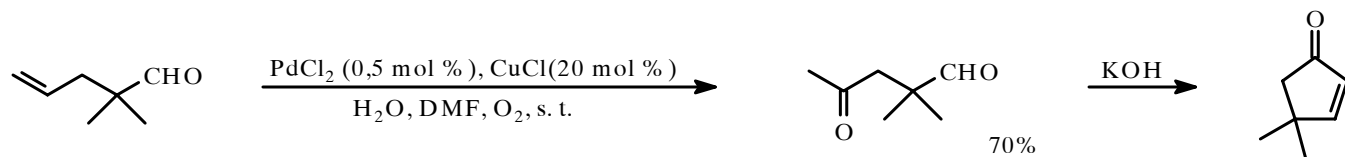
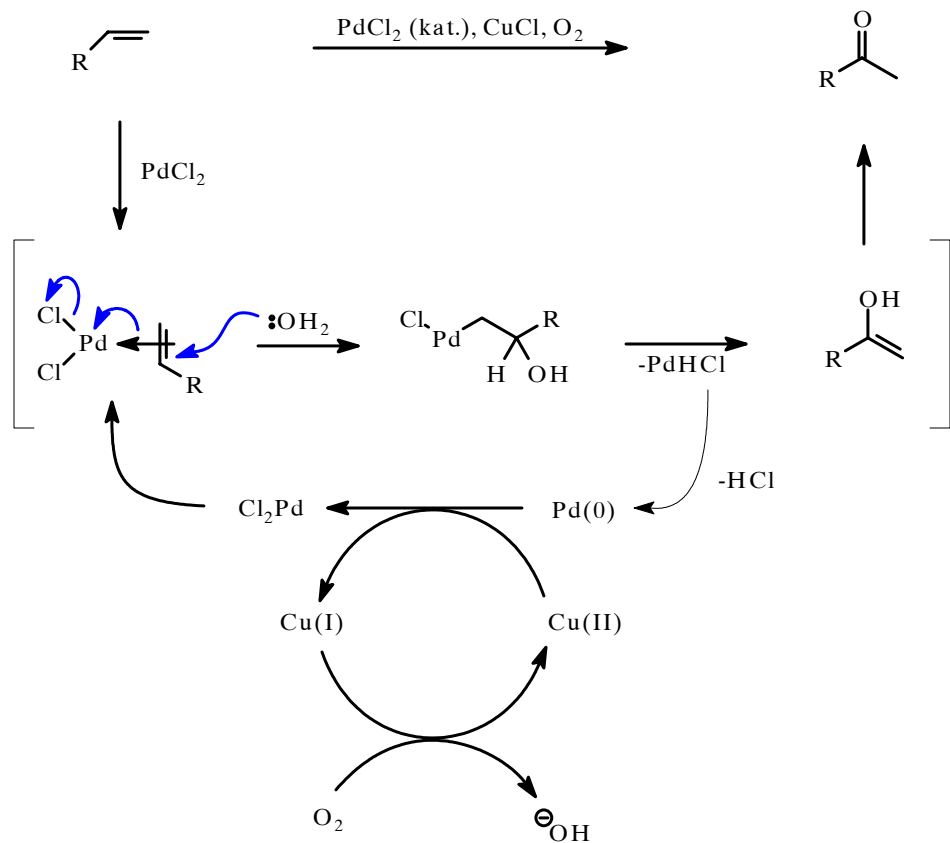




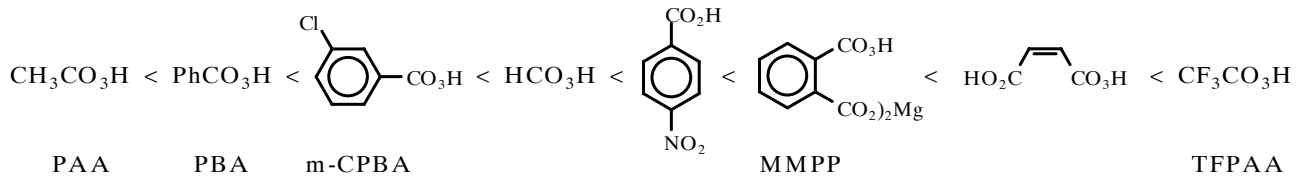
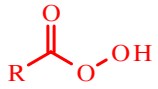
Hg(OAc)₂ Hg(O₂CCF₃)₂, Hg(ONO₂)₂



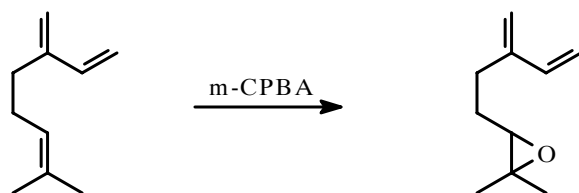
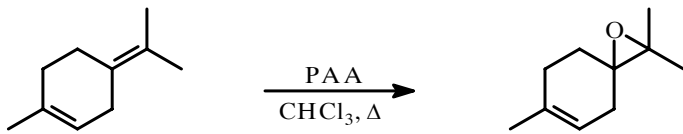
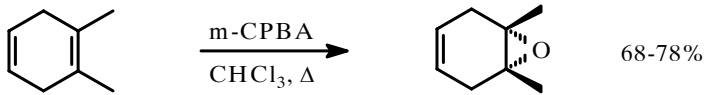
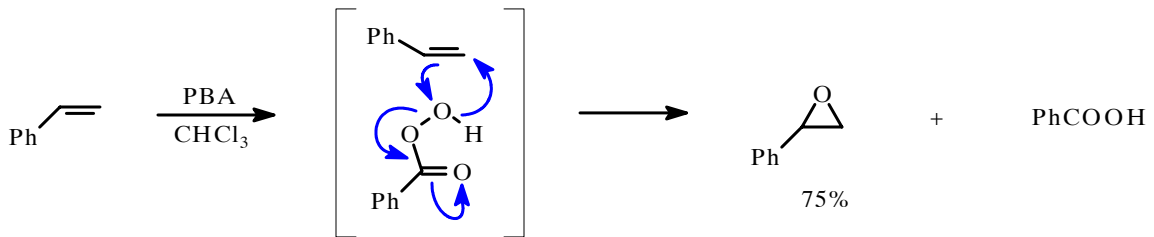
Wacker-ova oksidacija: PdCl₂ / CuCl / O₂



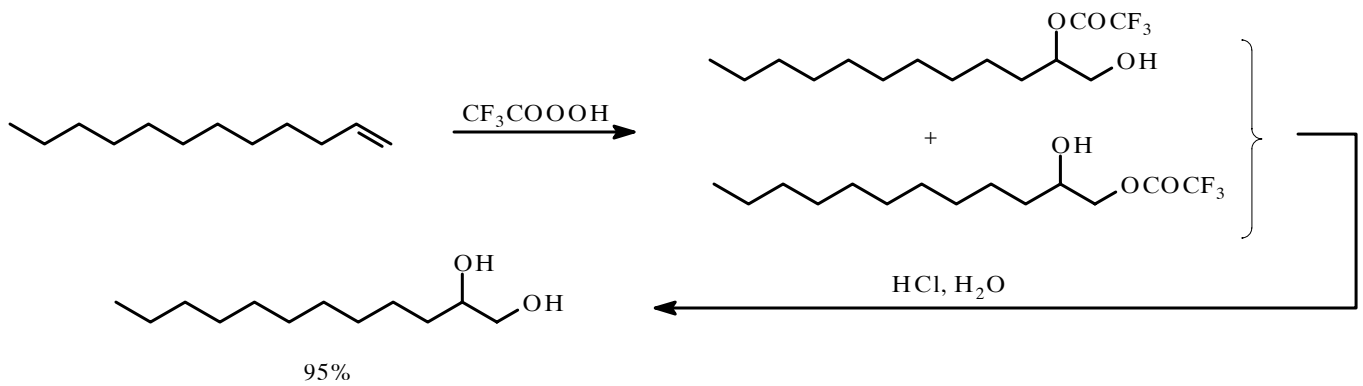
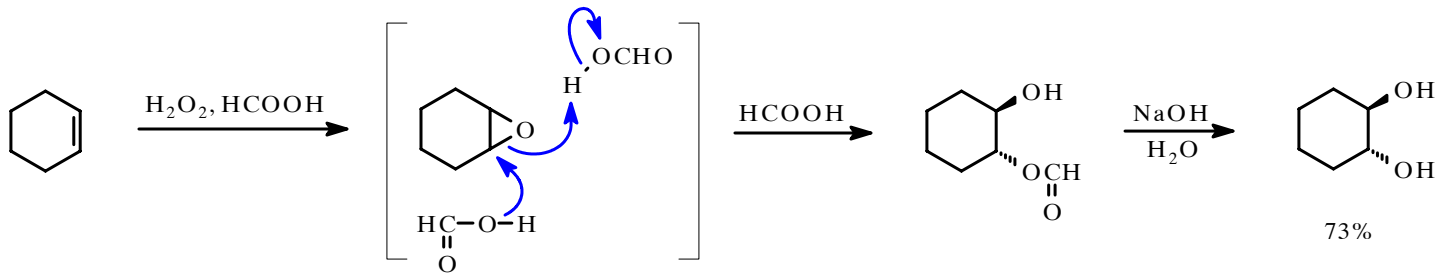
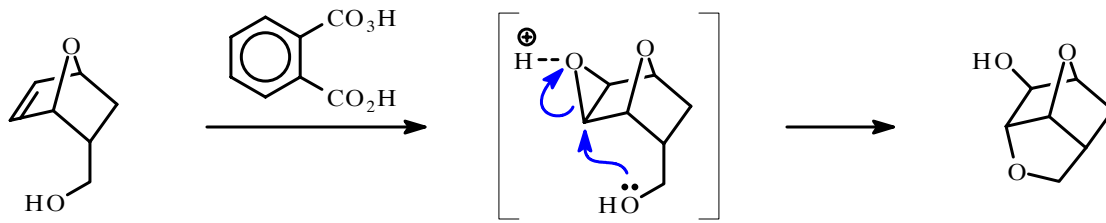
B) EPOKSIDACIJA



* Prilježajevljeva reakcija

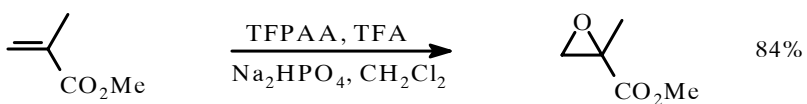
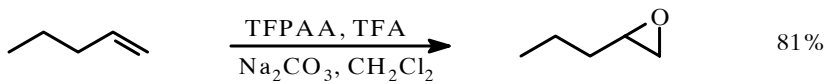
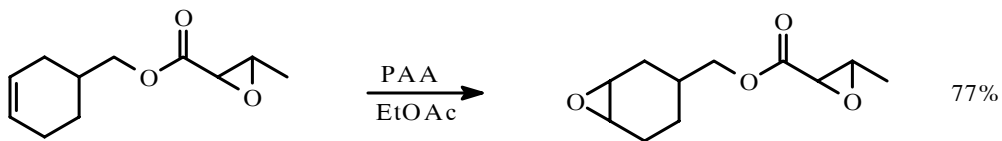


* Efekat susjednih grupa, pH, puferi

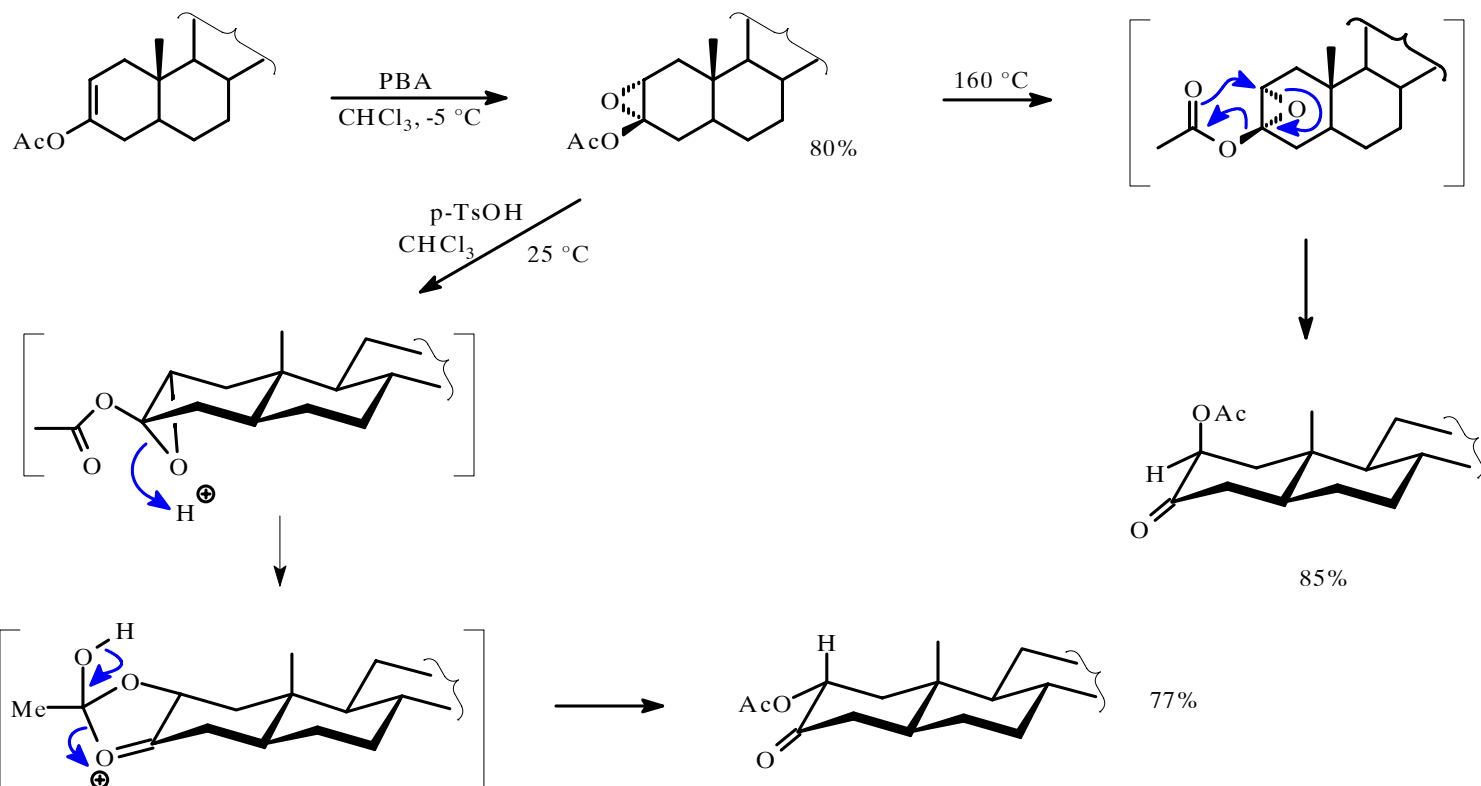
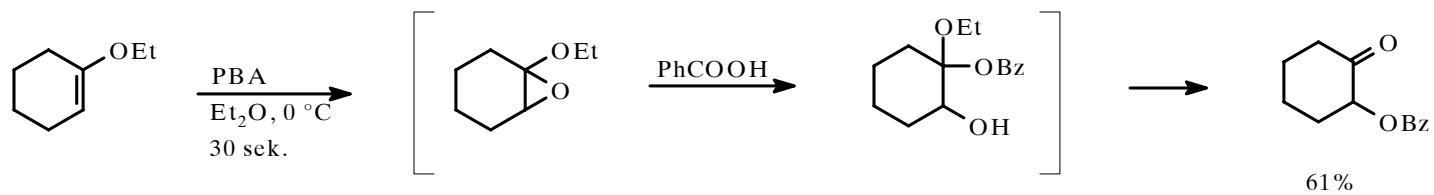


* Kombinacije koje ne otvaraju epoksidni prsten: PBA / CH₂Cl₂ ili CHCl₃; MMPP / Et₂O; PAA / EtOAc

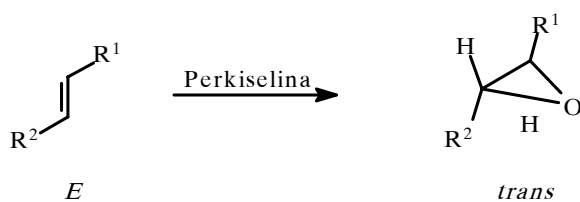
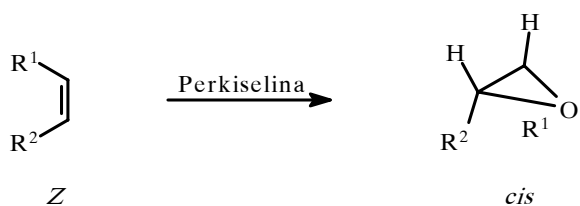
* Bolje rešenje: puferi



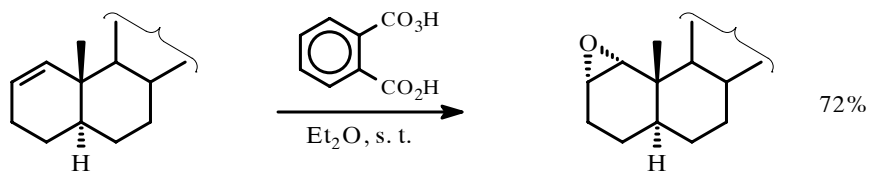
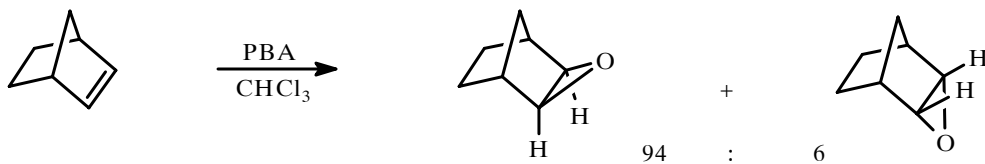
* Enol-etri, enol-estri



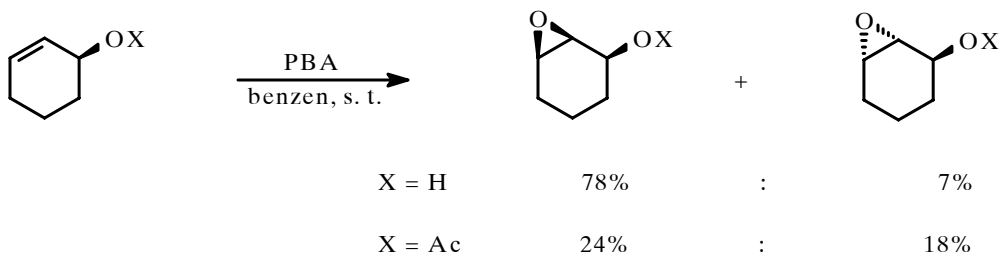
* *cis*-Stereospecificnost



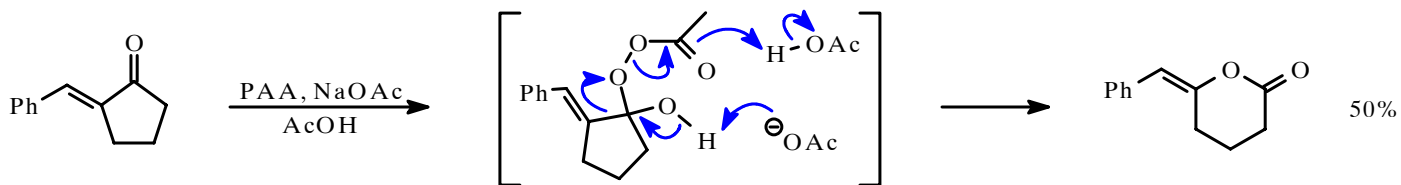
* Napad sa sterno manje zaštićene strane



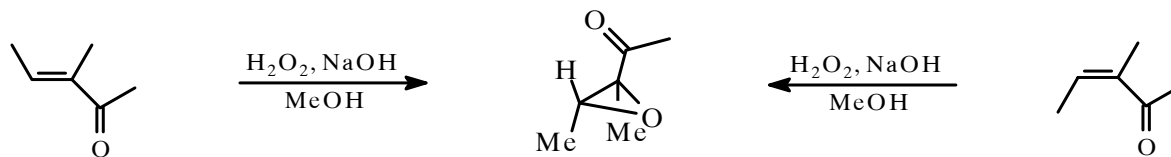
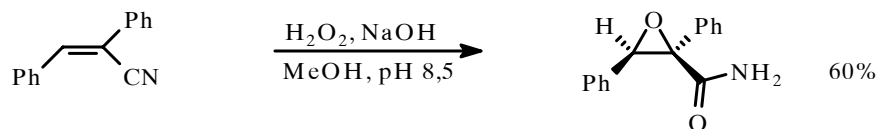
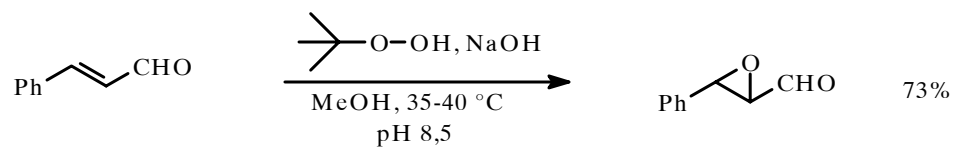
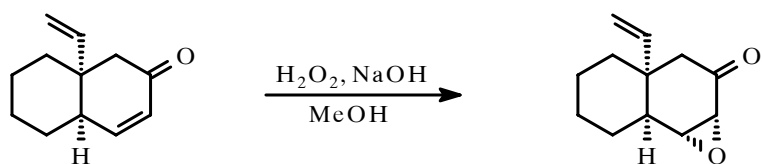
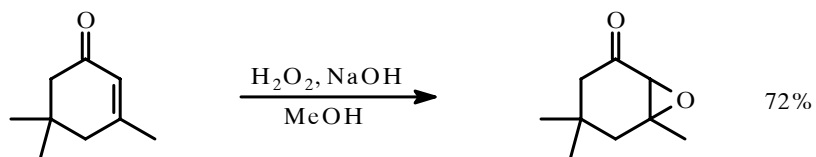
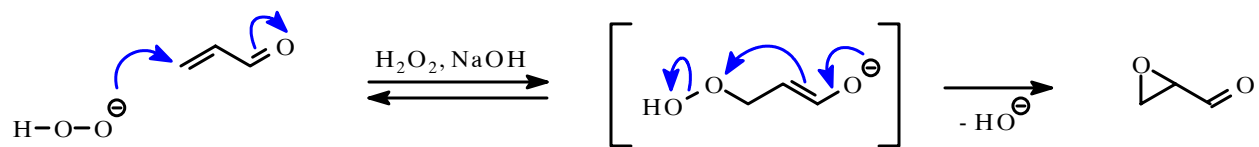
* Direkcionni efekat OH-grupe



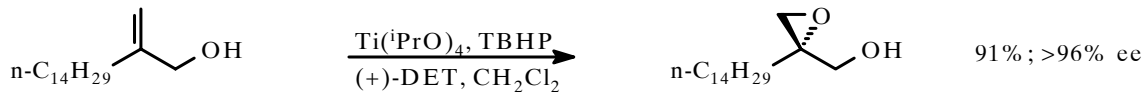
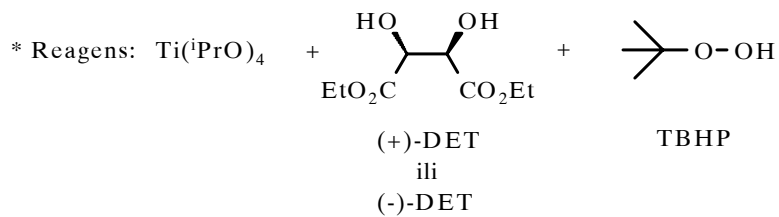
* Sporedna reakcija: *Baeyer-Villiger*-ovo premeštanje



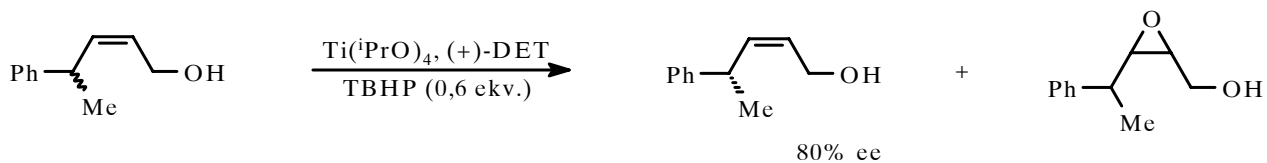
$\text{H}_2\text{O}_2 / \text{NaOH}$; $t\text{BuOOH} / \text{NaOH}$



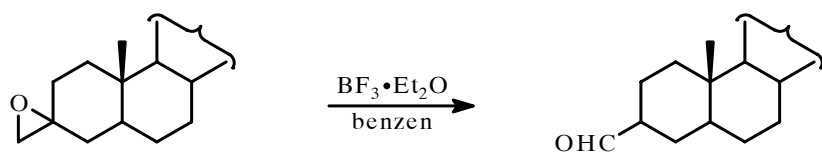
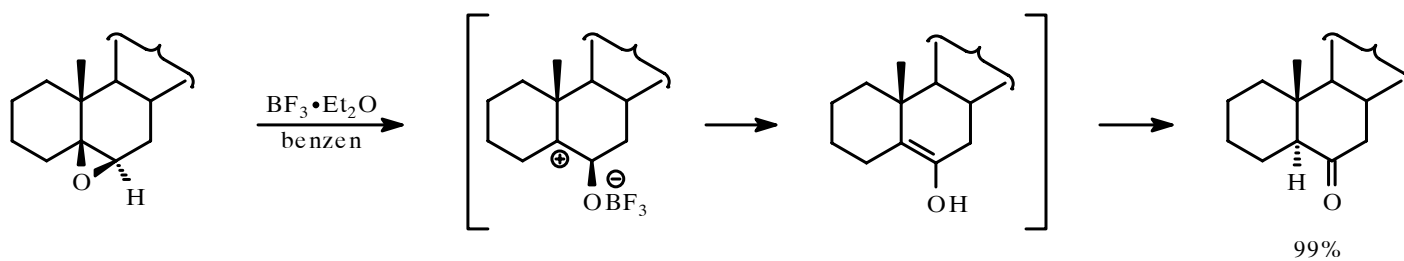
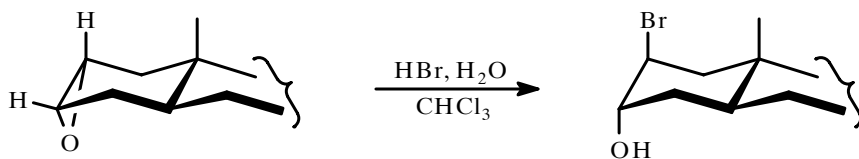
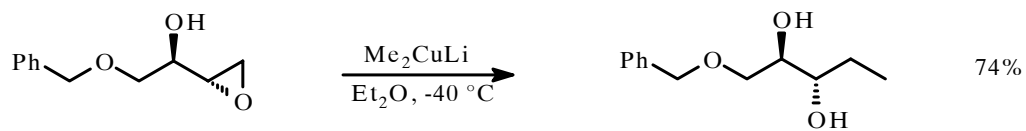
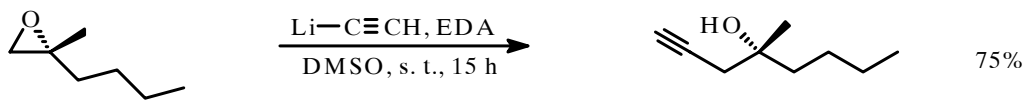
Sharpless-Katsuki-jeva asimetrična epoksidacija alilnih alkohola



* Kinetičko odvajanje



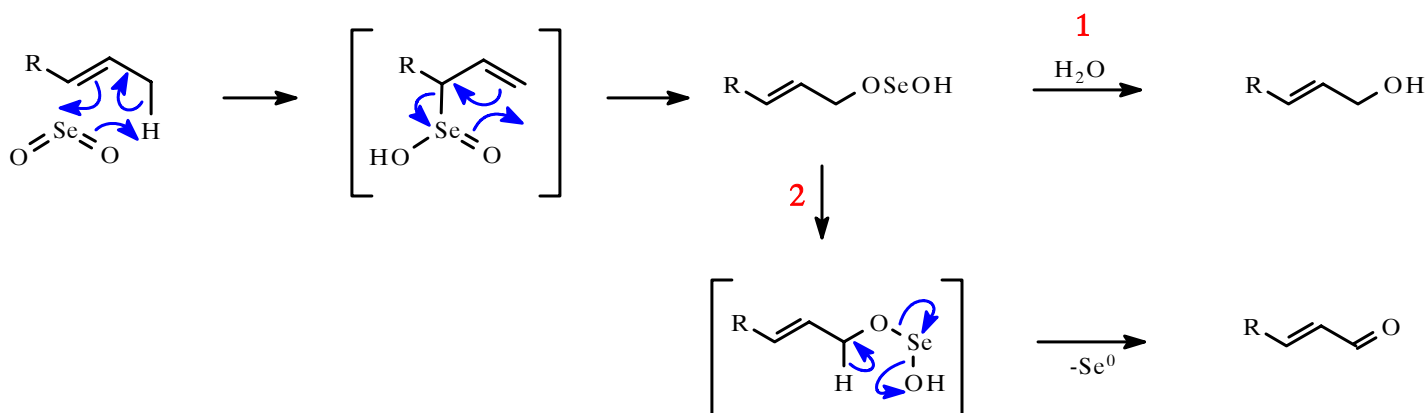
* Reakcije epoksida



C) ALILNE I BENZILNE OKSIDACIJE

Alilne oksidacije

SeO_2



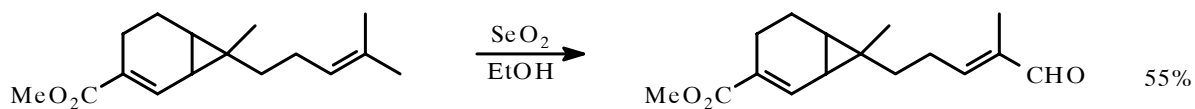
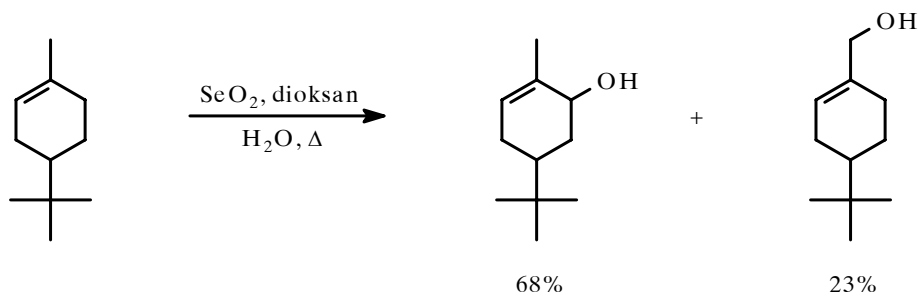
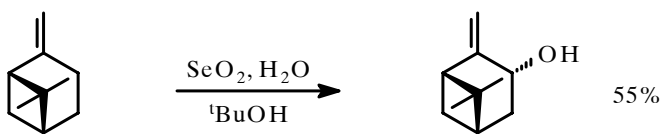
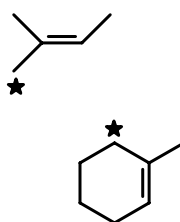
Redosled reaktivnosti alkena:

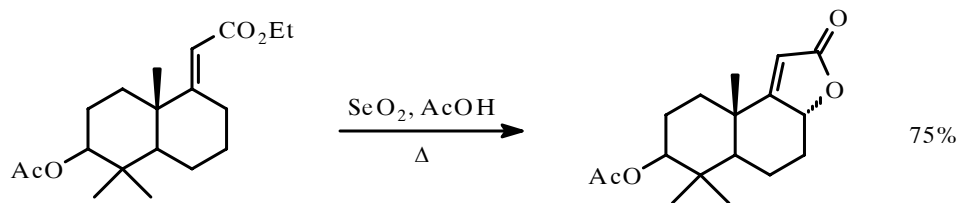
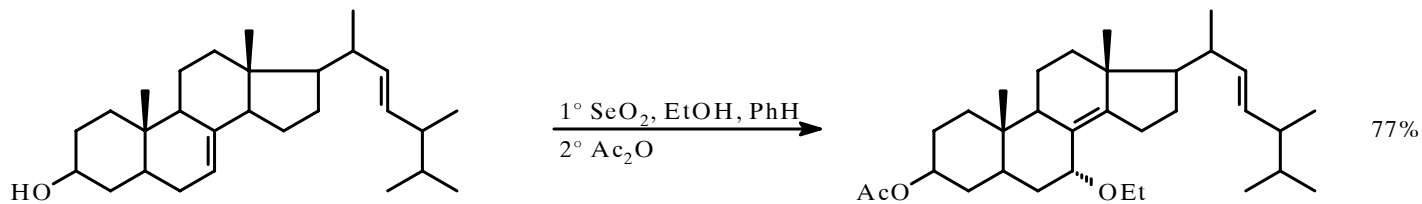
* disupstituisani > monosupstituisani

* $\text{CH}_2 > \text{CH}_3 > \text{CH}$

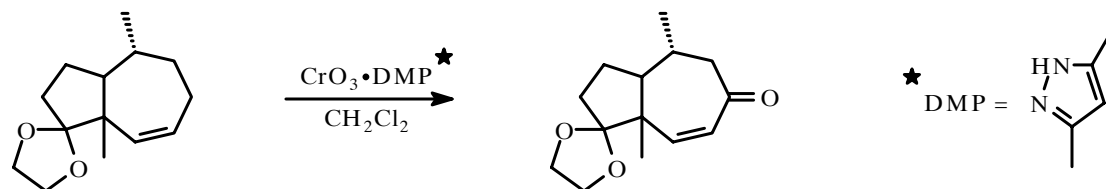
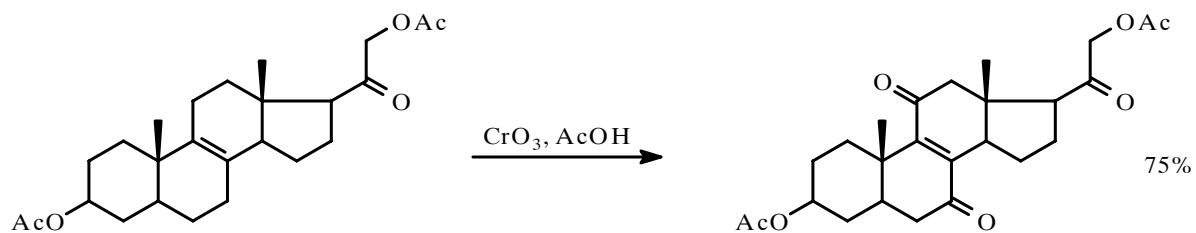
* *endo* > *exo*

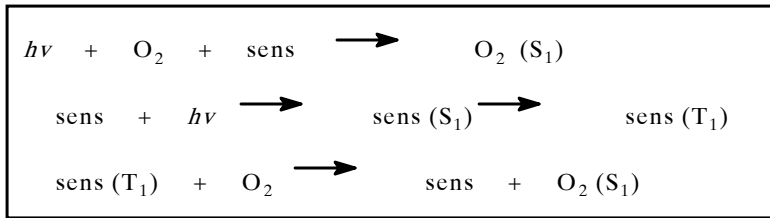
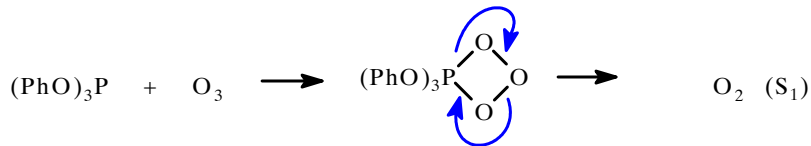
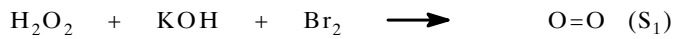
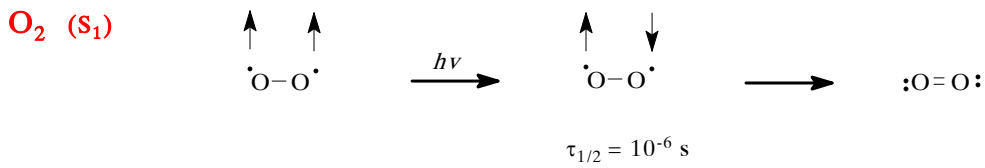
* moguće je alilno premeštanje



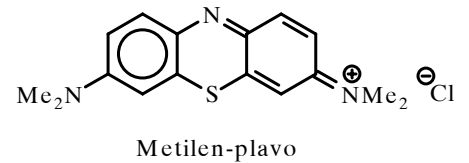
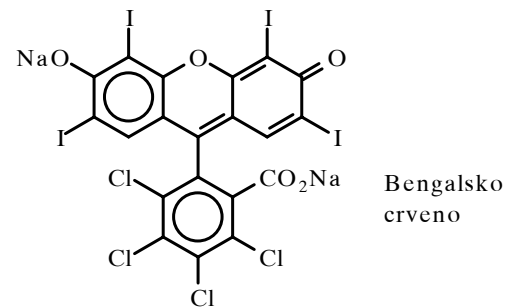
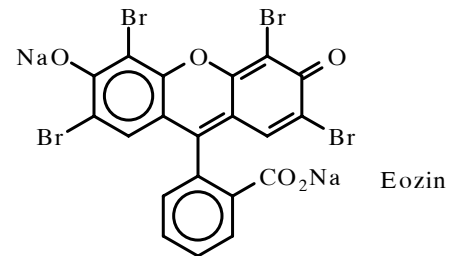


CrO₃

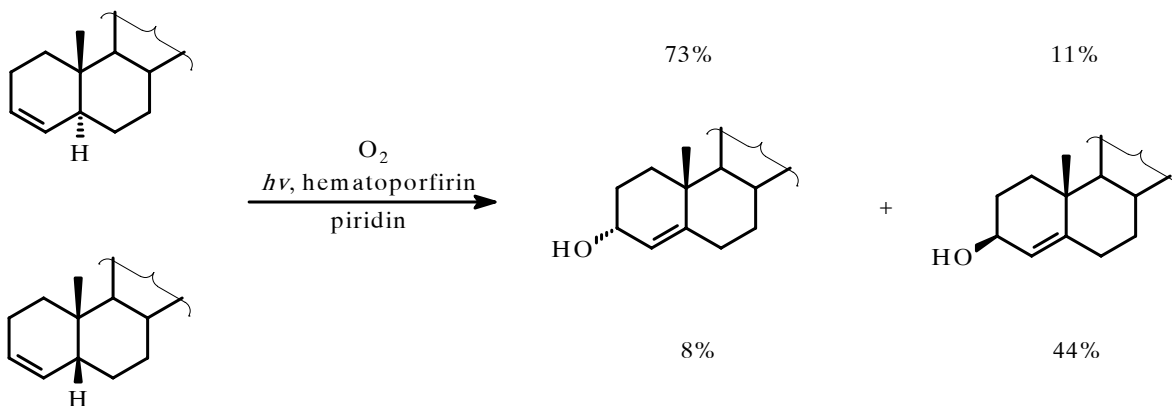
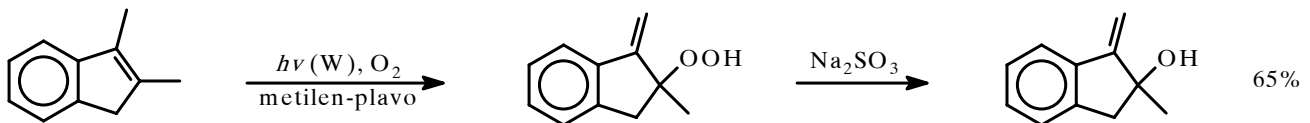
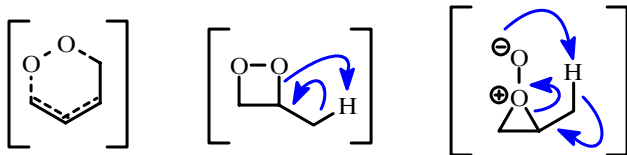




sens:

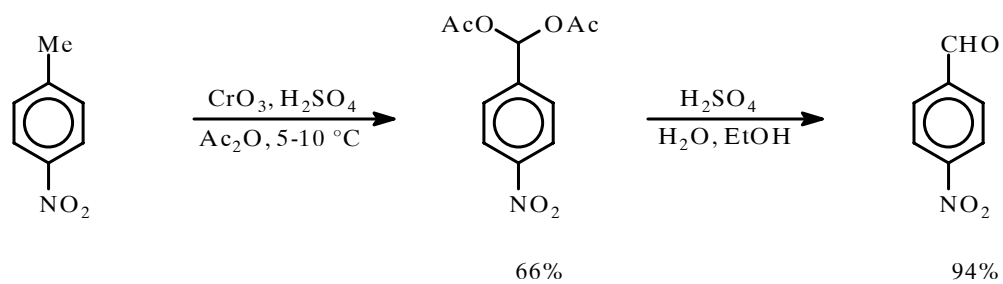
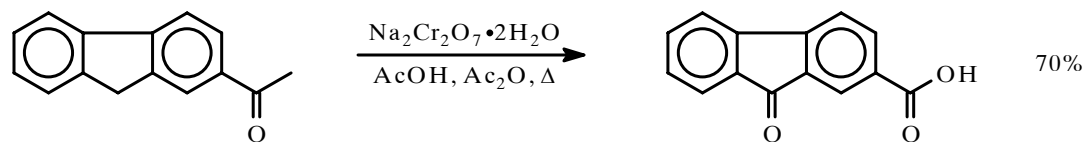
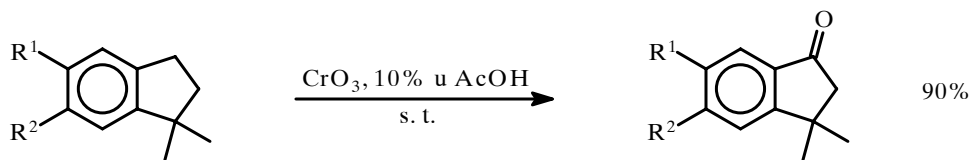
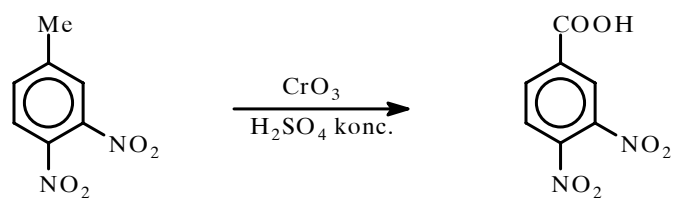
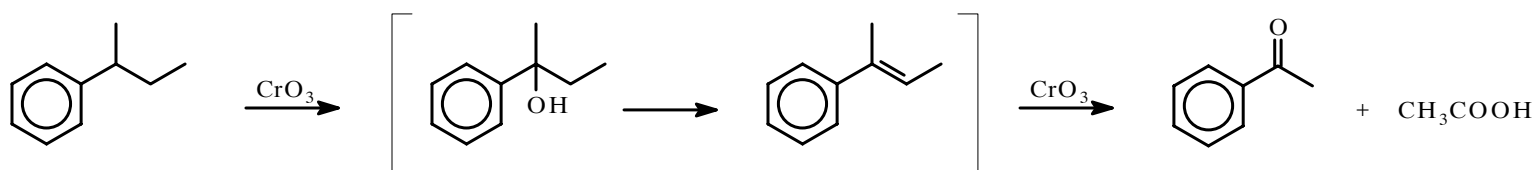
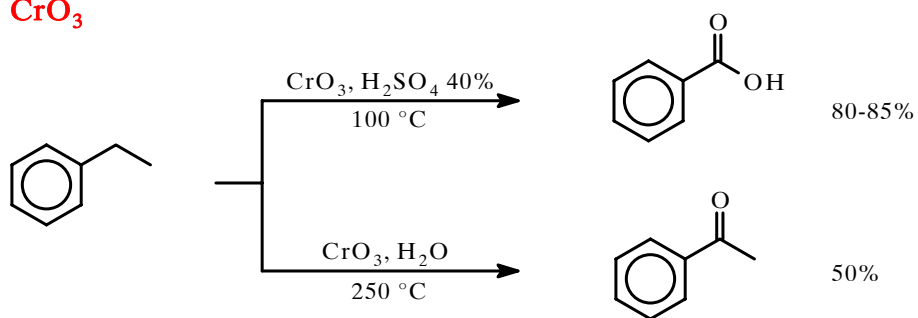


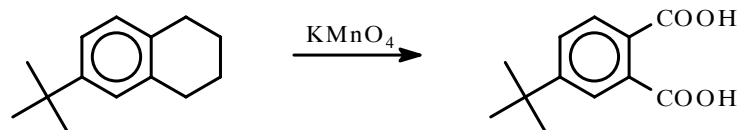
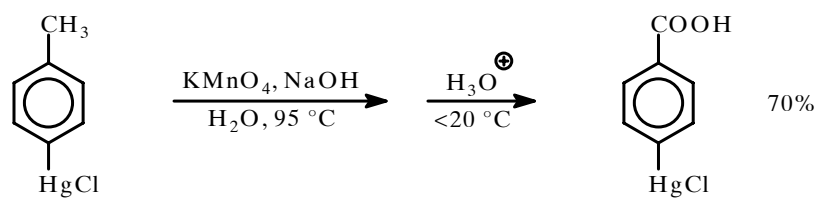
Moguća prelazna stanja



BENZILNE OKSIDACIJE

CrO₃

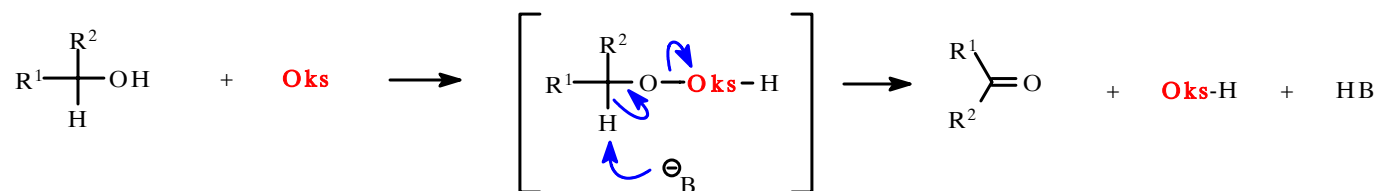




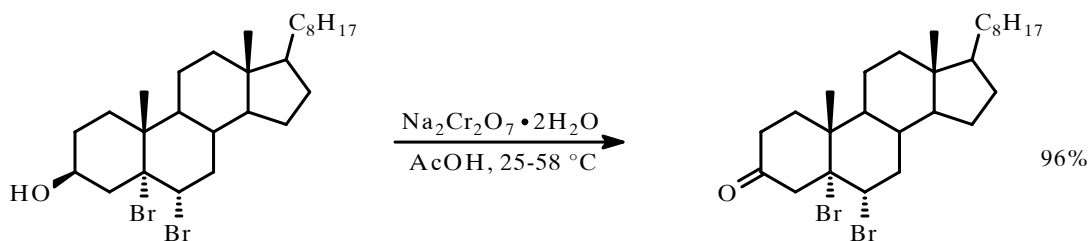
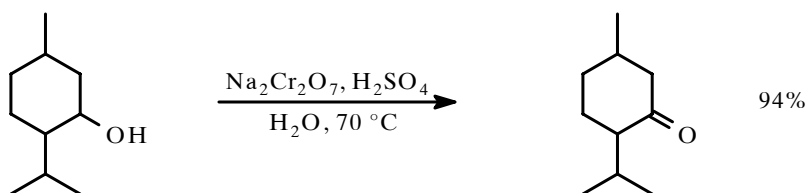
HNO₃

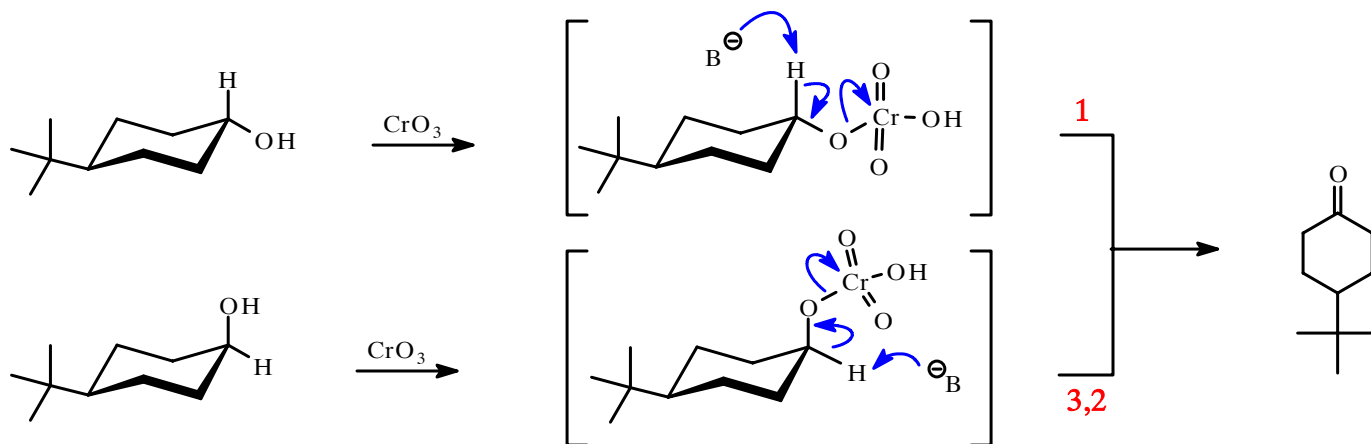
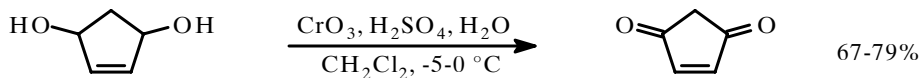
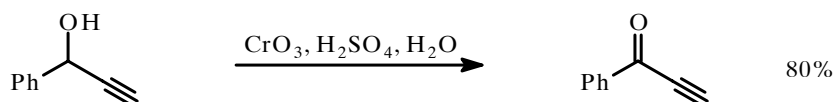
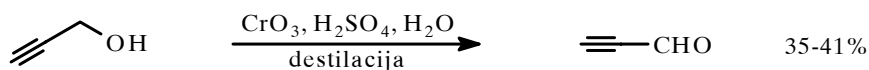
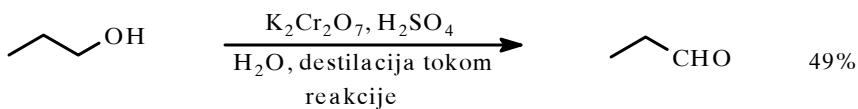
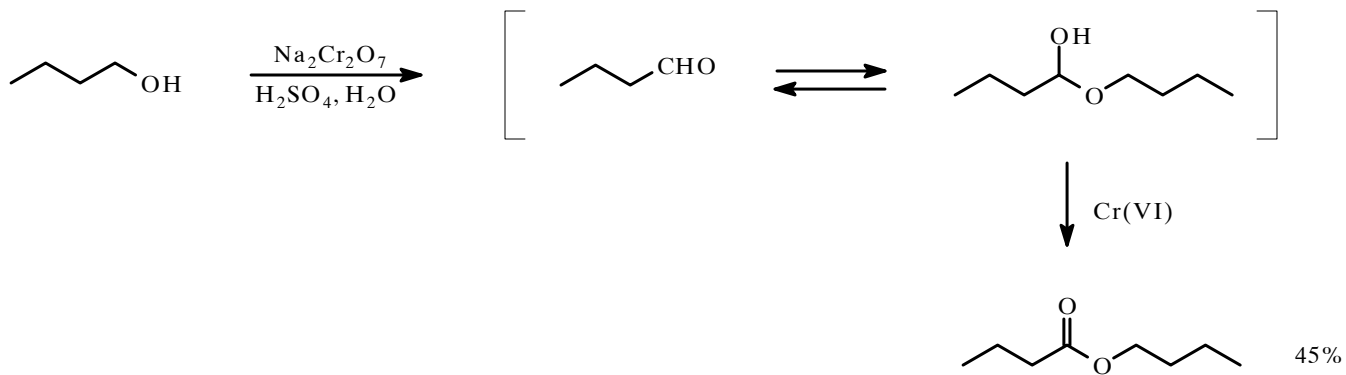


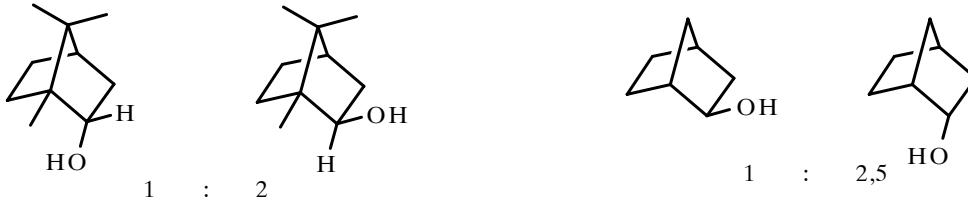
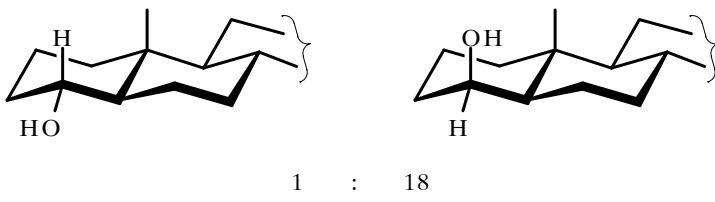
3) OKSIDACIJE ALKOHOLA



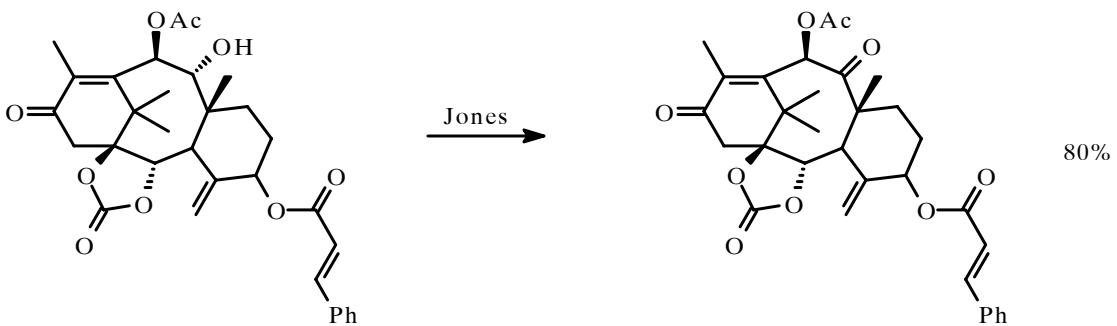
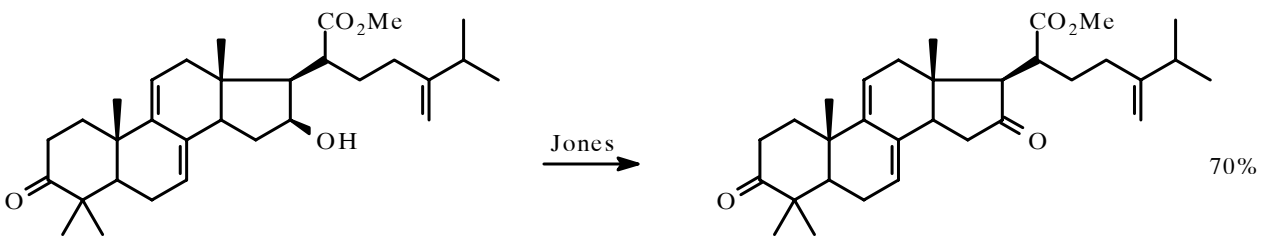
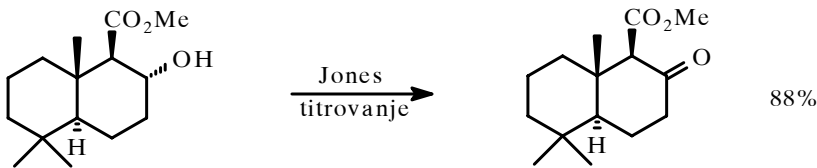
H₂CrO₄ (H₂Cr₂O₇)



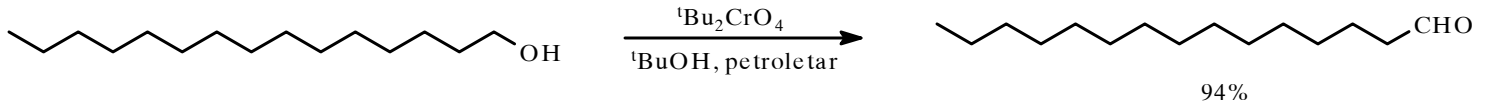
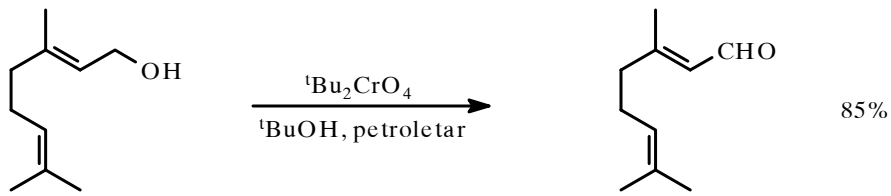




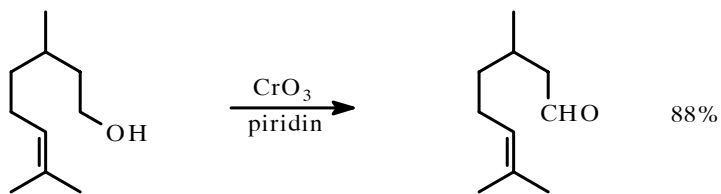
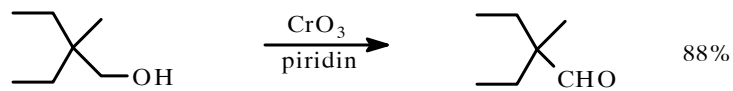
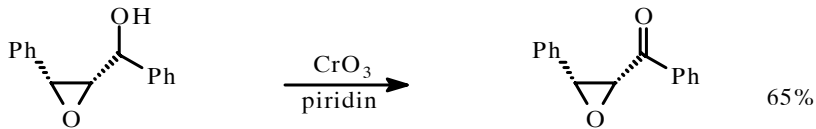
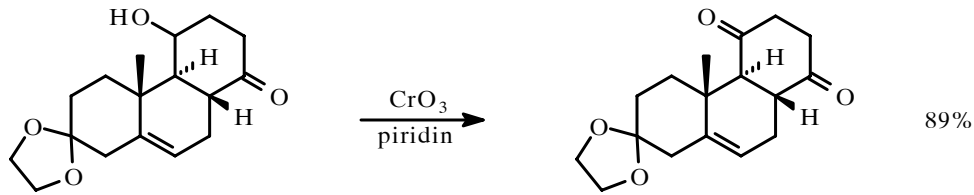
Jones-ov reagens : $\text{CrO}_3 + \text{aceton} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$



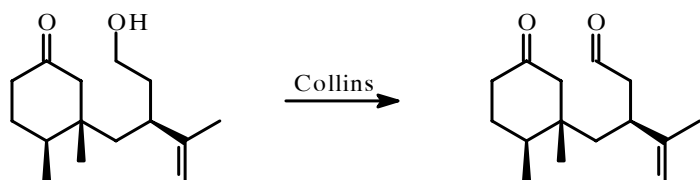
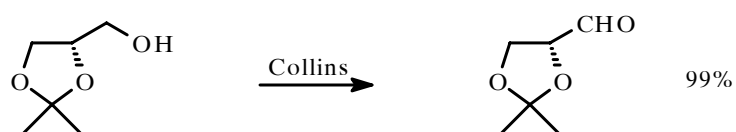
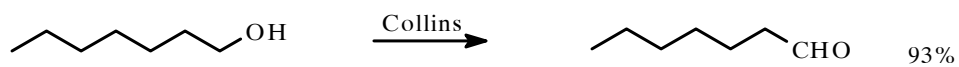
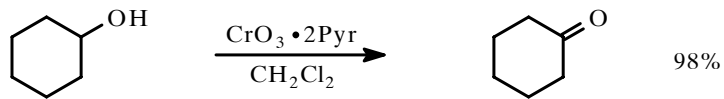
(^tBuO)₂CrO₂ (eksplozivan)



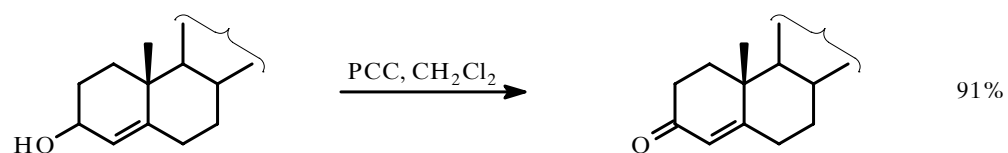
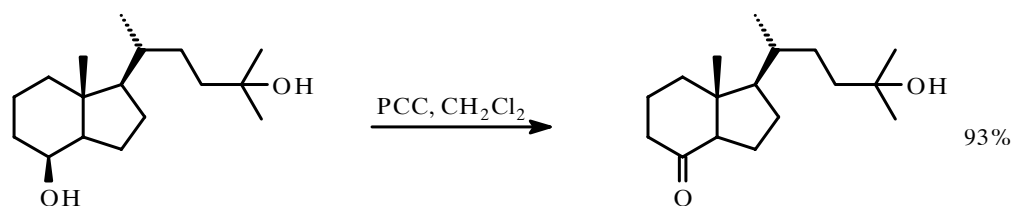
Sarett-ov reagens: CrO₃ 2Pyr u piridinu

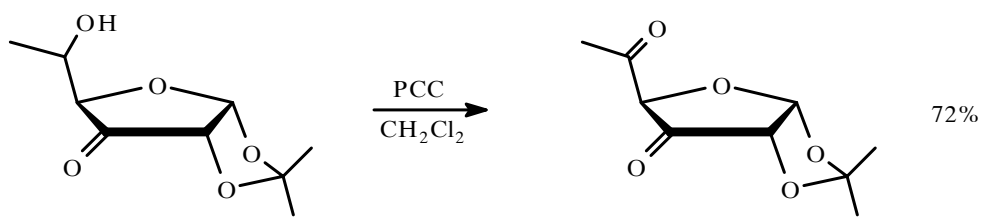
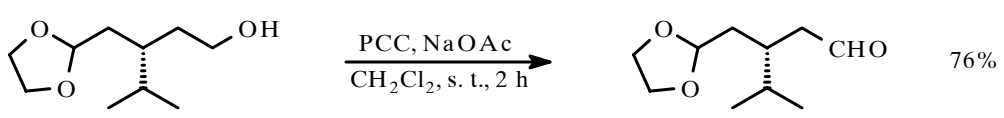
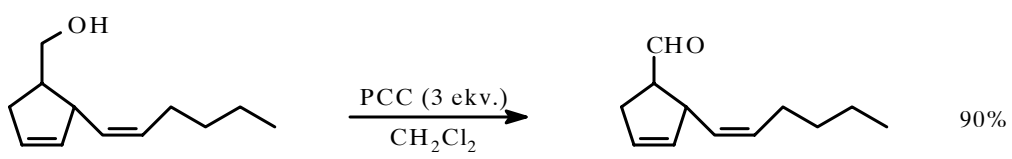
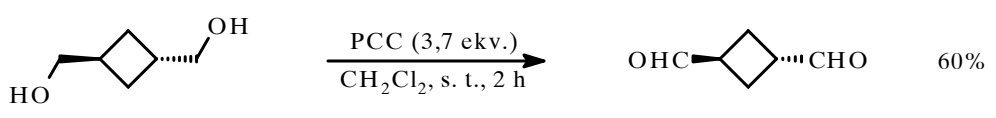
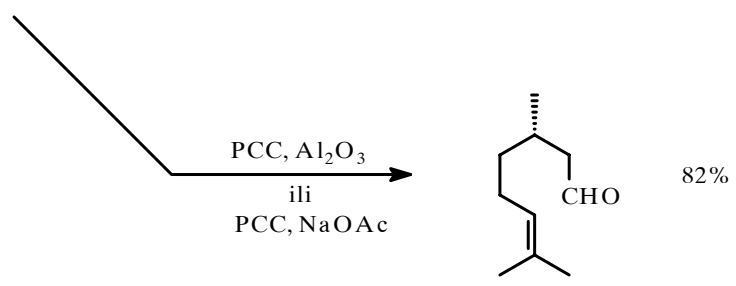
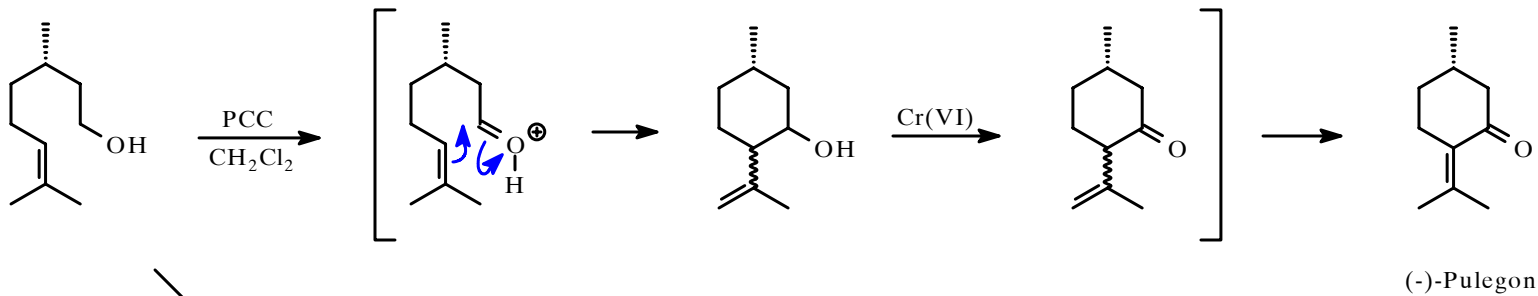
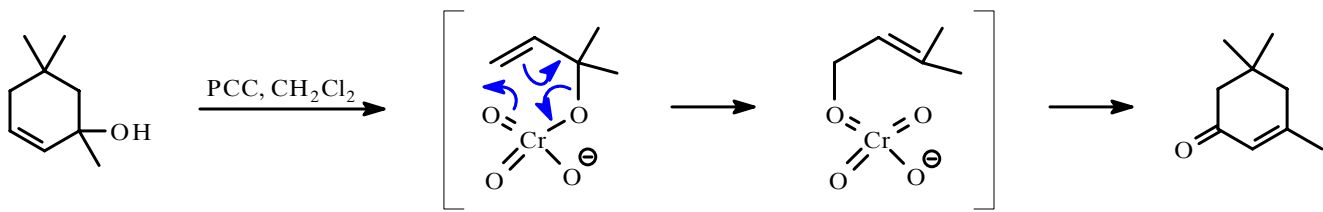


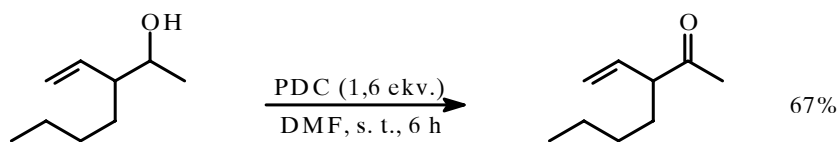
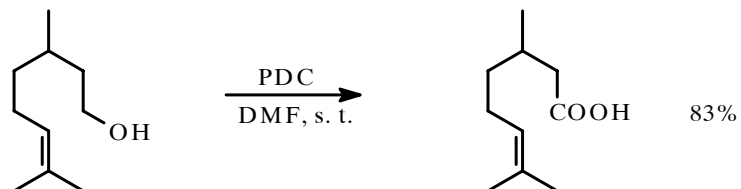
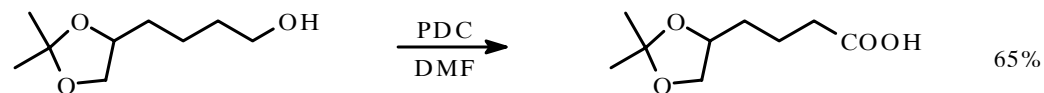
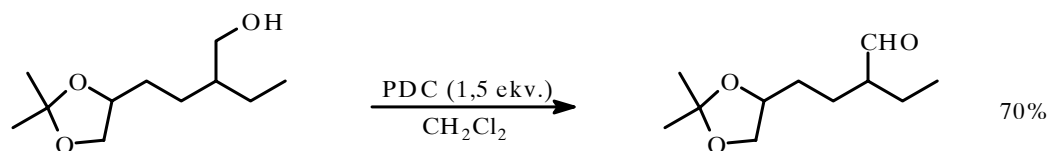
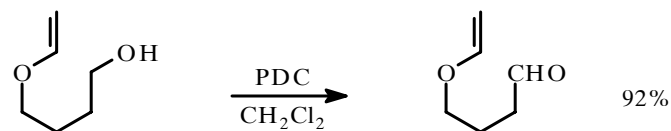
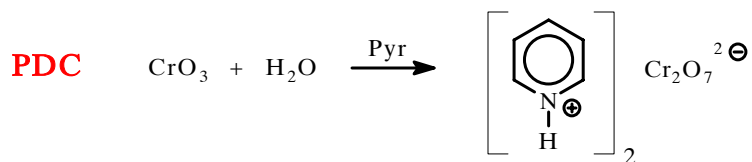
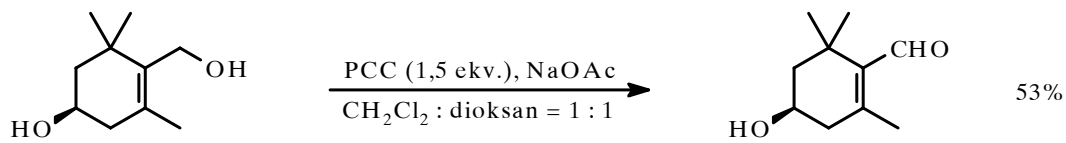
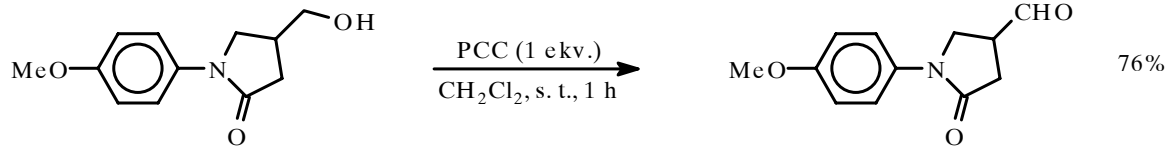
Collins-ov reagens: $\text{CrO}_3 \cdot 2\text{Pyr}$ u CH_2Cl_2 [ROH] : [Cr(VI)] = 1:5 - 1:6



PCC "piridin-hlor-hromat" $\text{CrO}_3 \cdot \text{Pyr} \cdot \text{HCl}$ \leftarrow $\underbrace{\text{CrO}_3 + \text{HCl}} + \text{Pyr}$



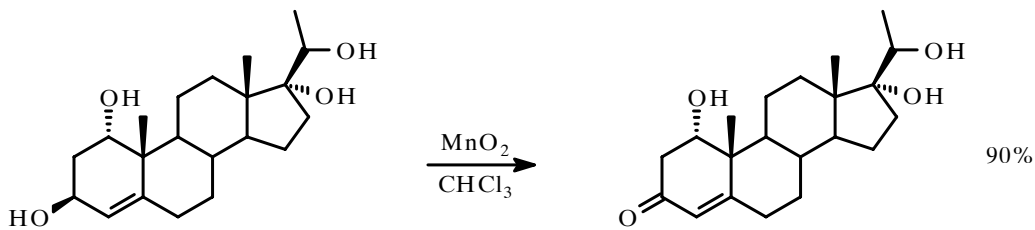
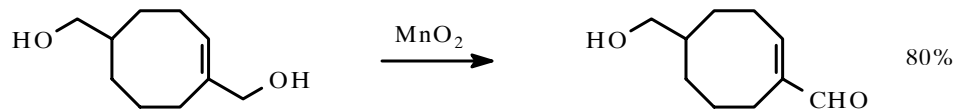
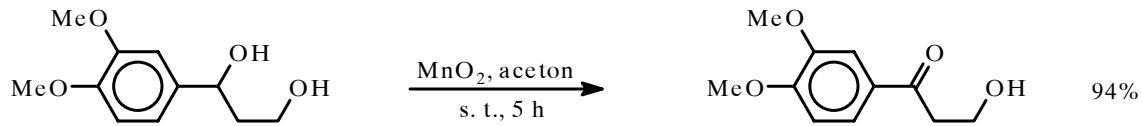
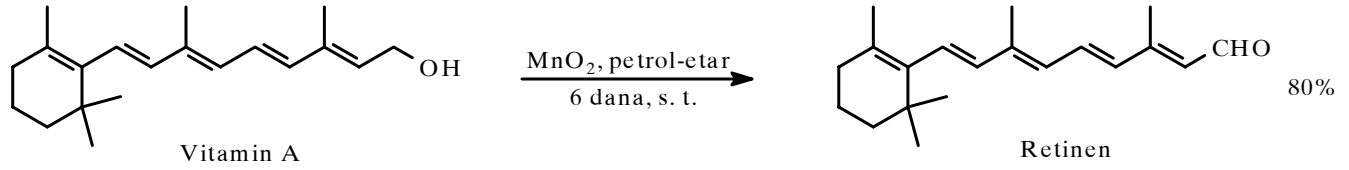


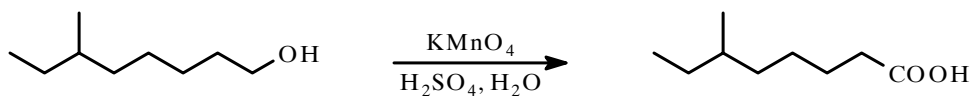
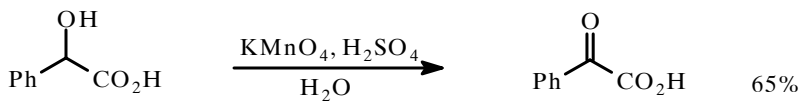
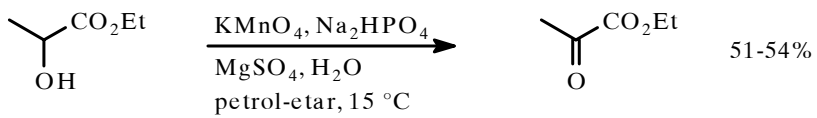
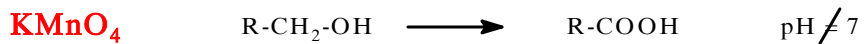


MnO₂ za oksidacije alilnih i benzilnih alkohola

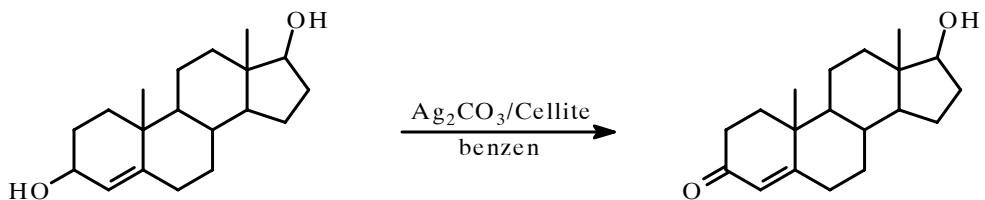
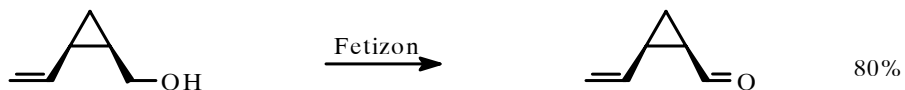
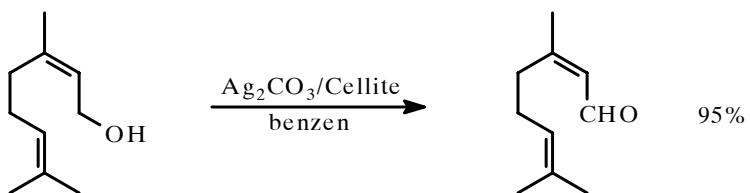


* Rastvarači: petrol-etar, Et₂O, CH₂Cl₂, THF, CH₃CN, aceton, DMSO, DMF, ...

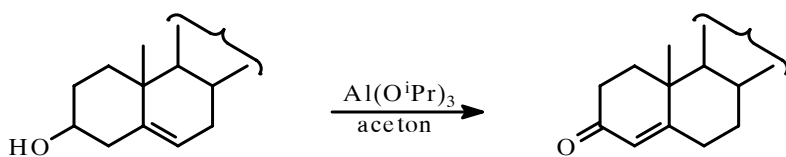
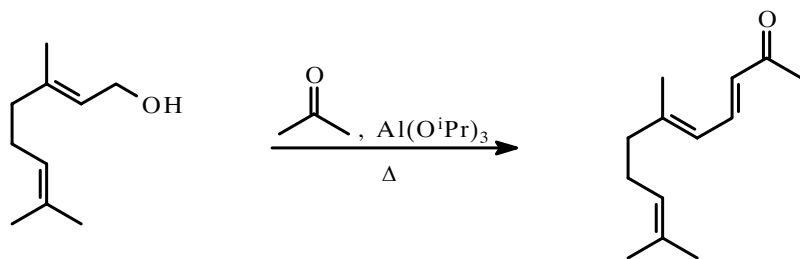
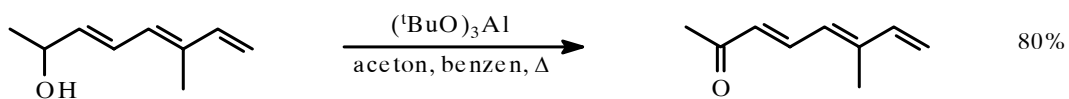
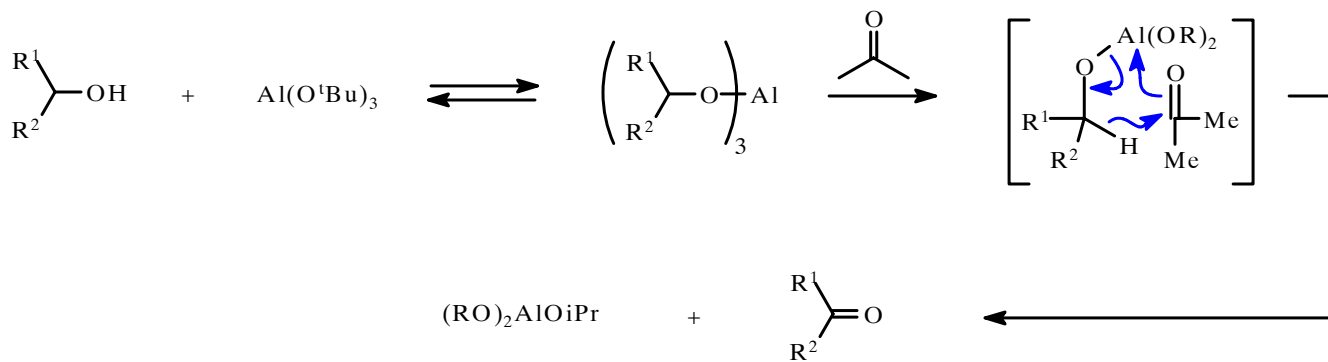


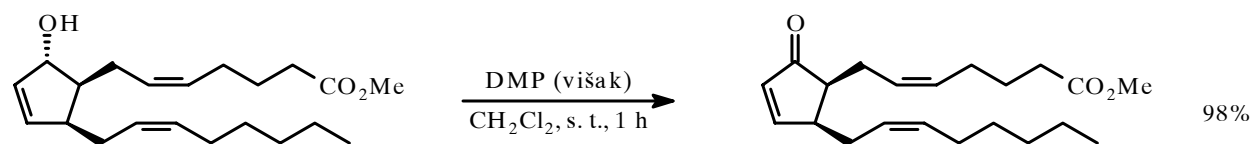
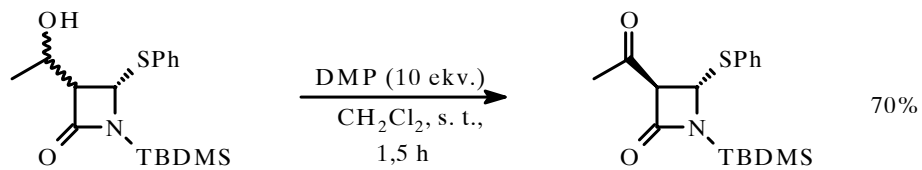
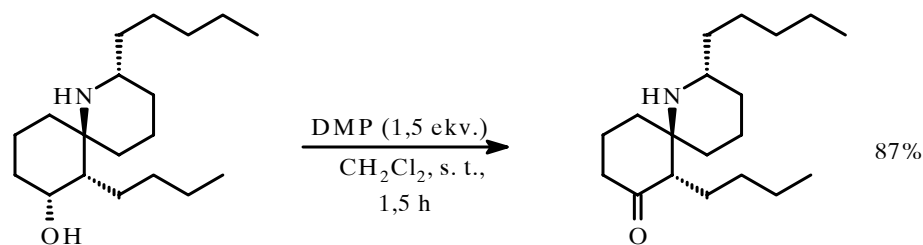
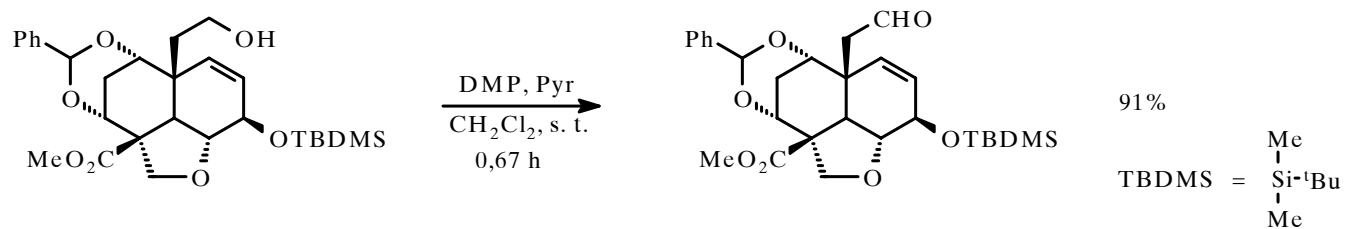
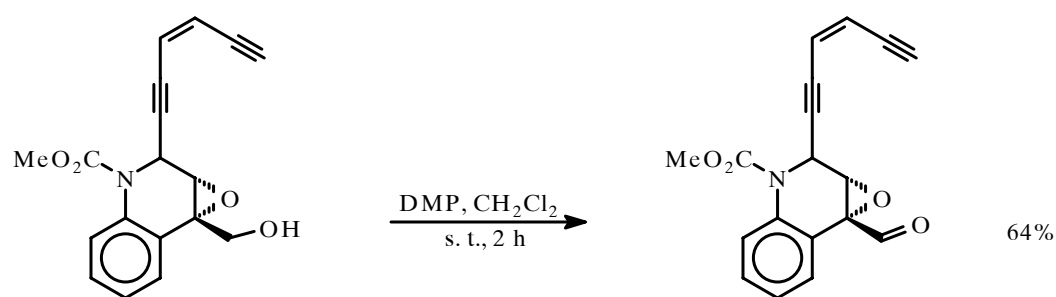
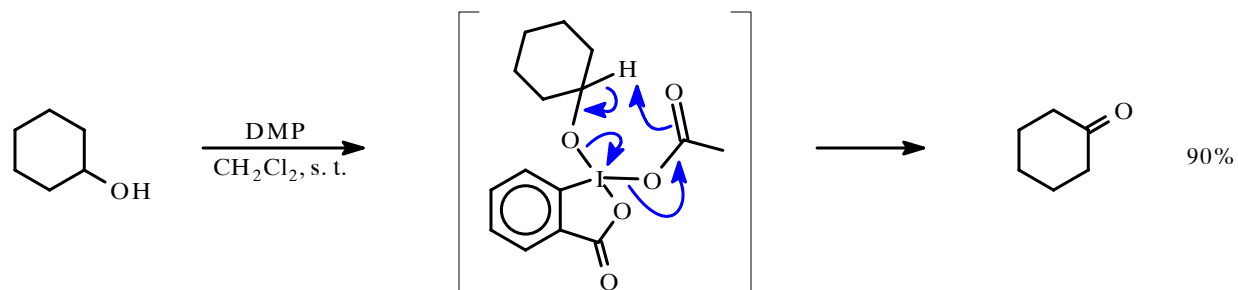
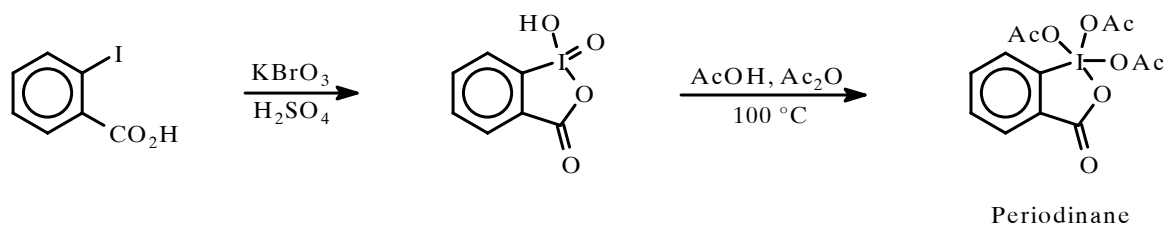


Ag₂CO₃ / Cellite Fetizon-ov reagens

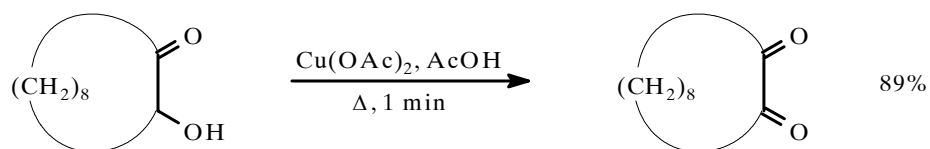
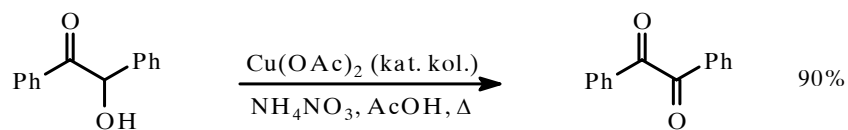
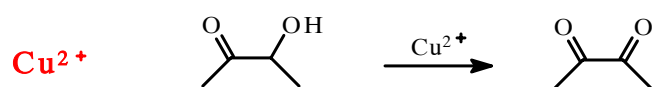
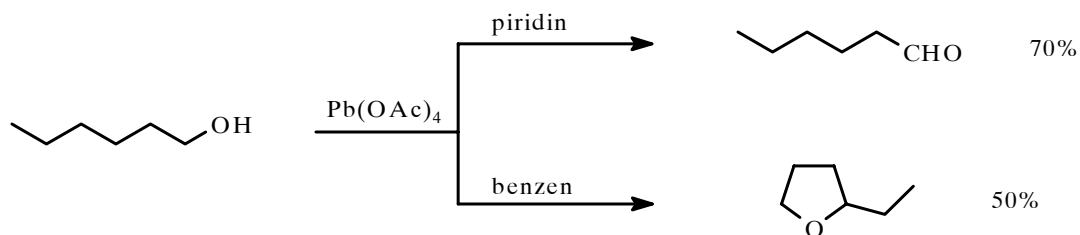
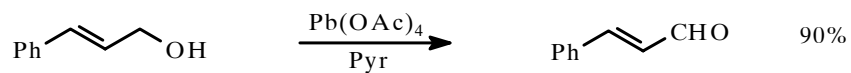


Oppenauer-ova oksidacija $\text{Al}(\text{O}^i\text{Pr})_3$, $\text{Al}(\text{O}^t\text{Bu})_3$, $\text{Al}(\text{OPh})_3$





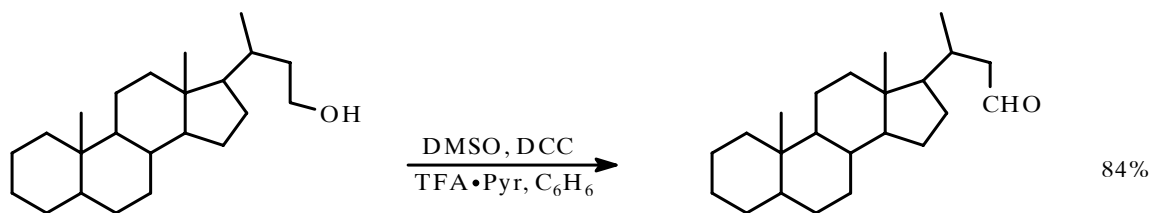
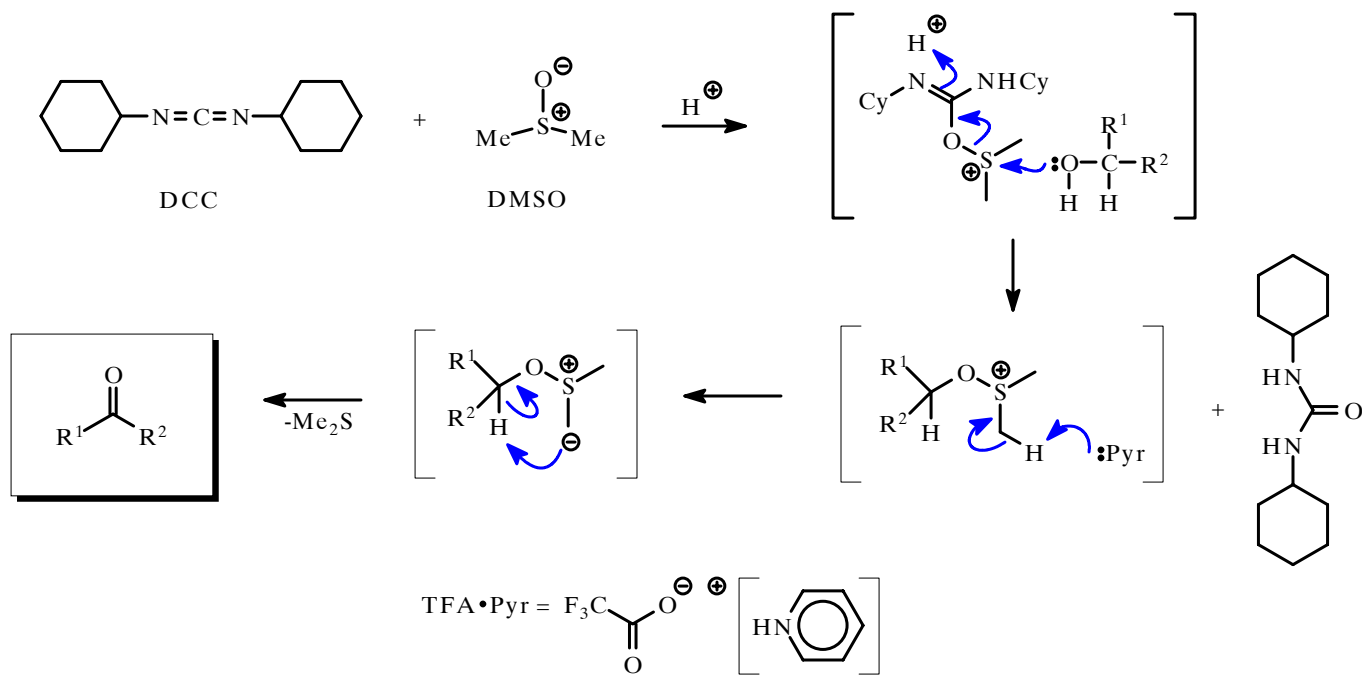
Pb(OAc)₄ 2Pyr



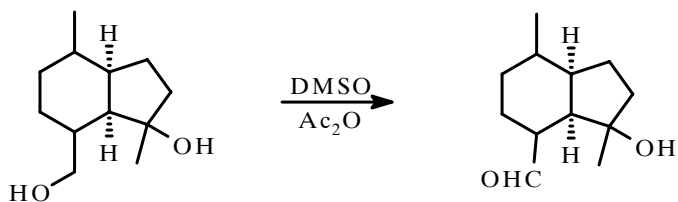
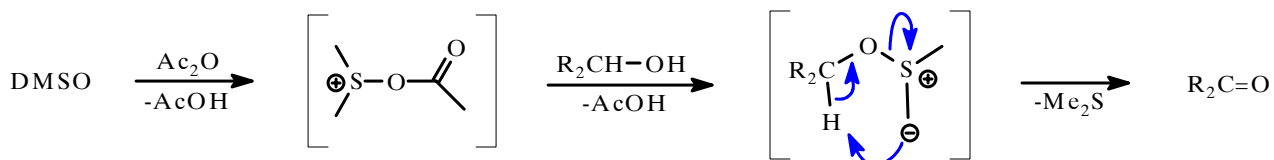
Oksidacije pomoću **DMSO**-a

* Pfizner-Moffat-ova oksidacija: DMSO + DCC + TFA Pyr

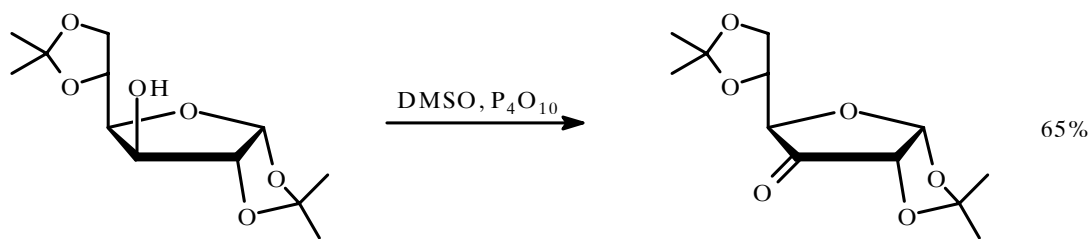
višak 3 ekv. kat. kol.



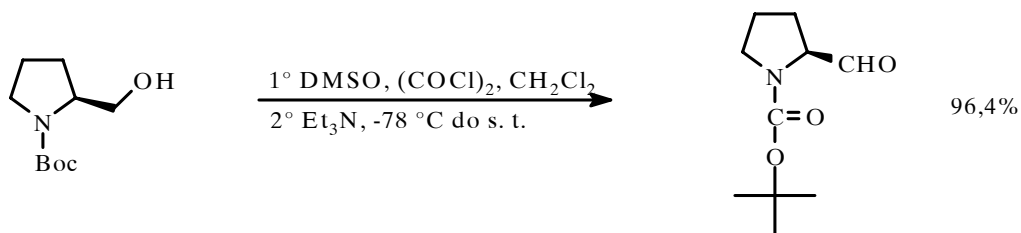
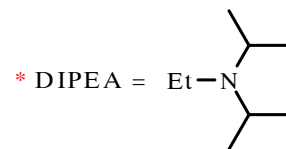
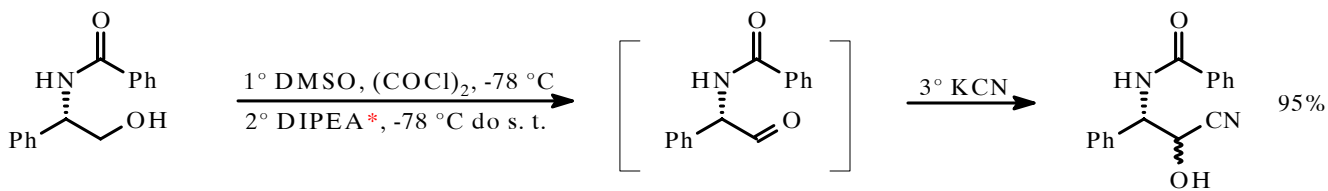
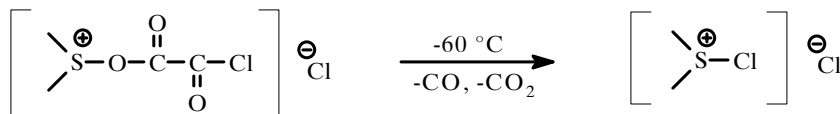
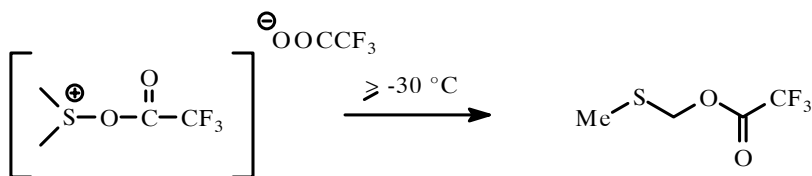
* **DMSO / Ac₂O**



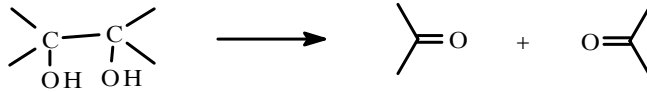
* DMSO/P₄O₁₀; DMSO/SO₃ Pyr•



Swern-ova oksidacija: DMSO + TFA + Et₃N ili DMSO + (COCl)₂ + Et₃N
 višak 2 ekv.
 CH₂Cl₂, -78 °C → 0 °C

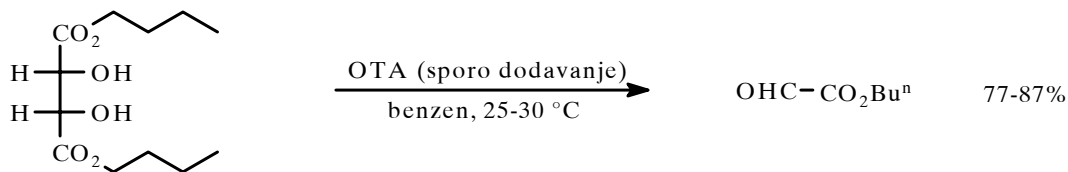
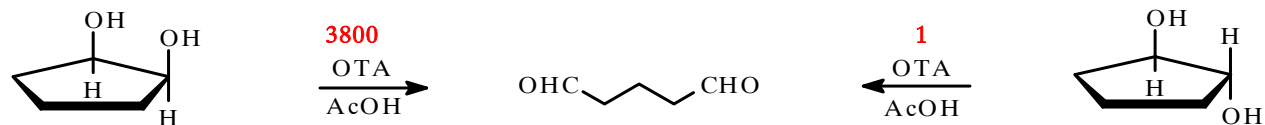
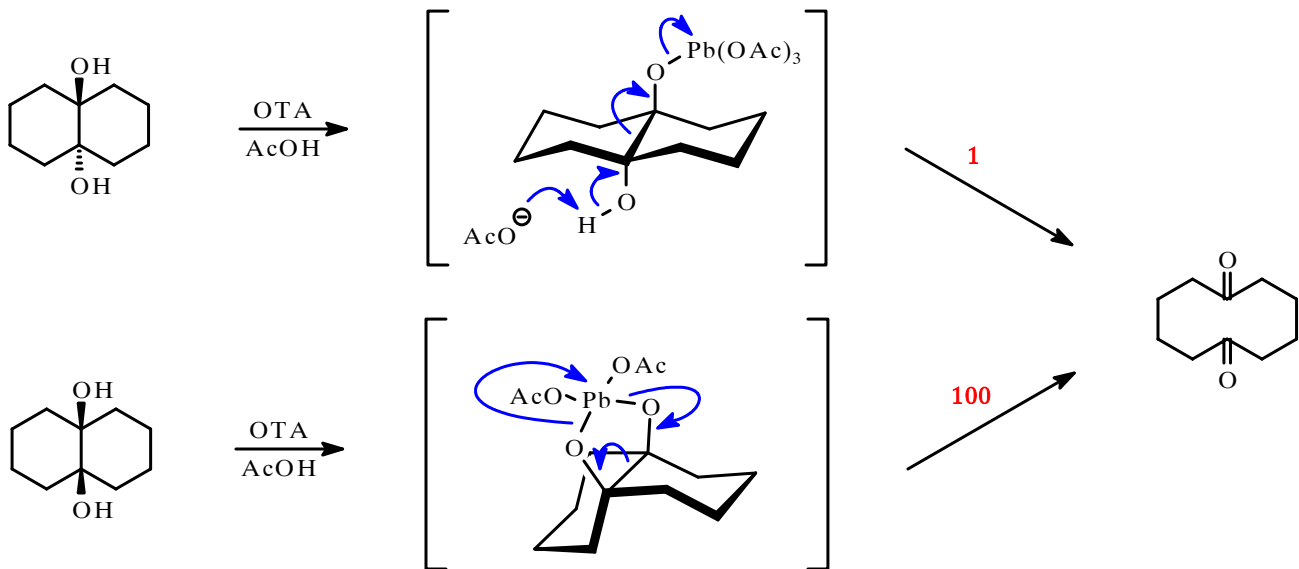
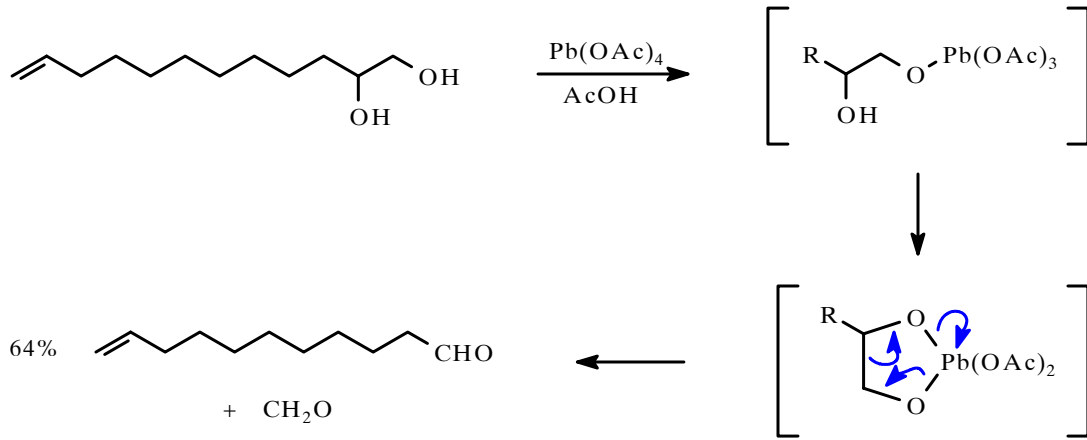


OKSIDACIJA GLIKOLA

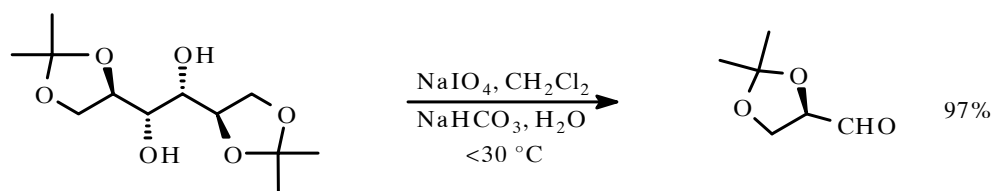
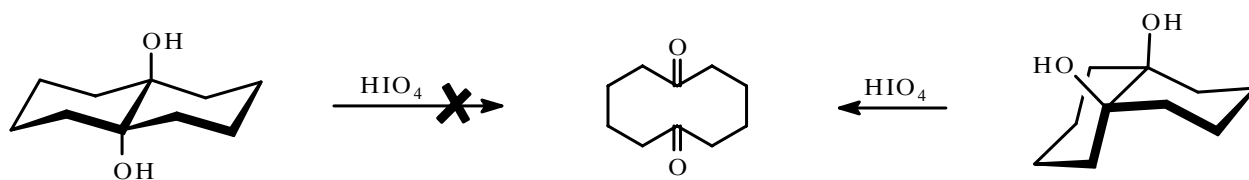
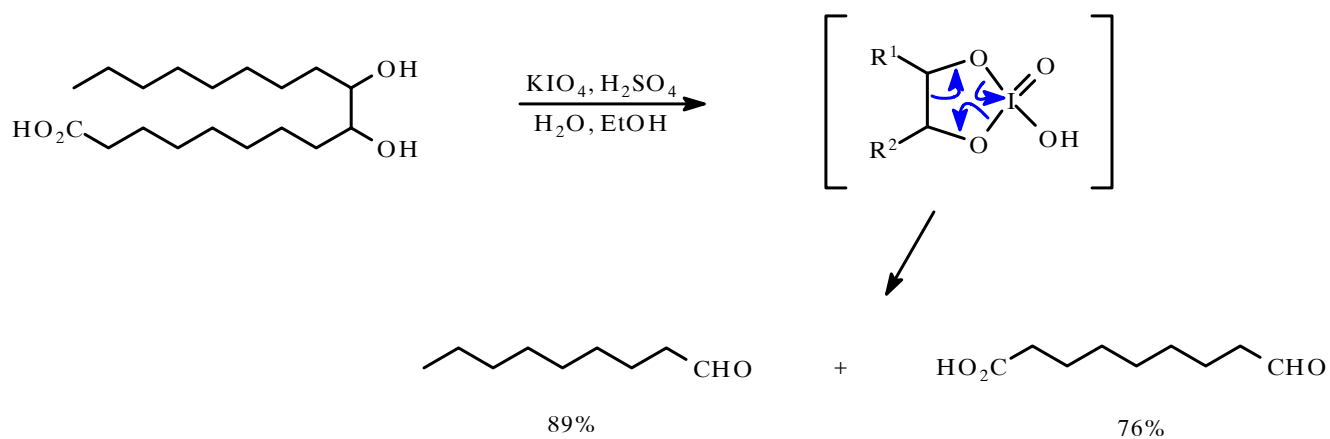


Glikolno raskidanje
Criegee-ova oksidacija

Pb(OAc)₄ (OTA)

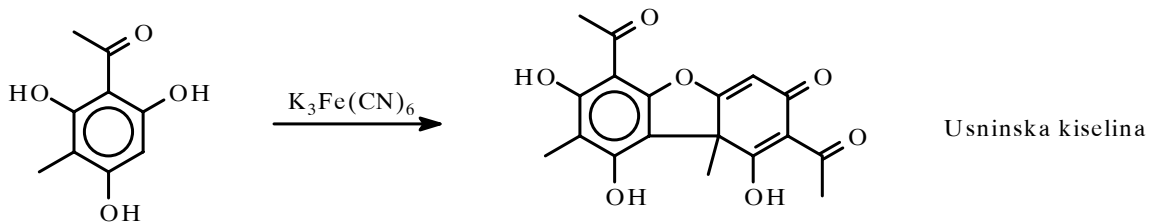
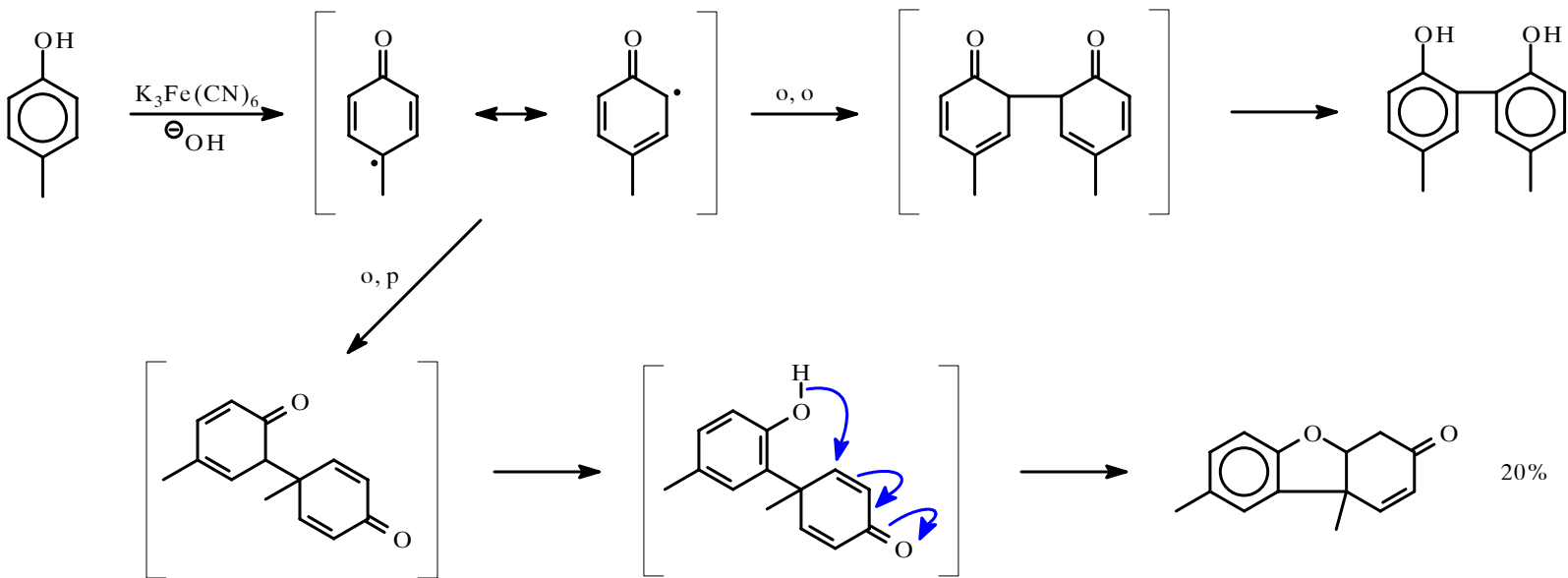
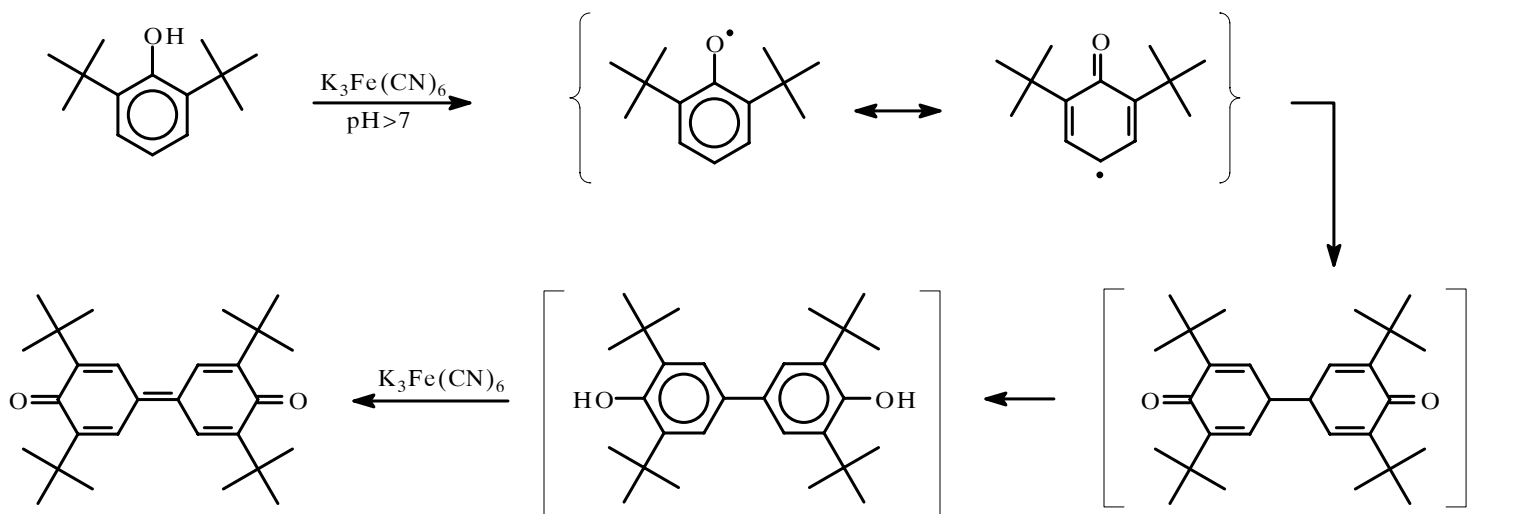


HIO_4 , NaIO_4 Malprad-eova reakcija

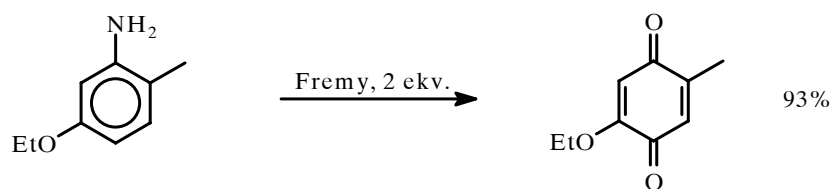
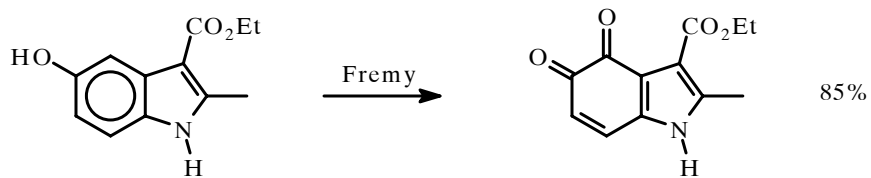
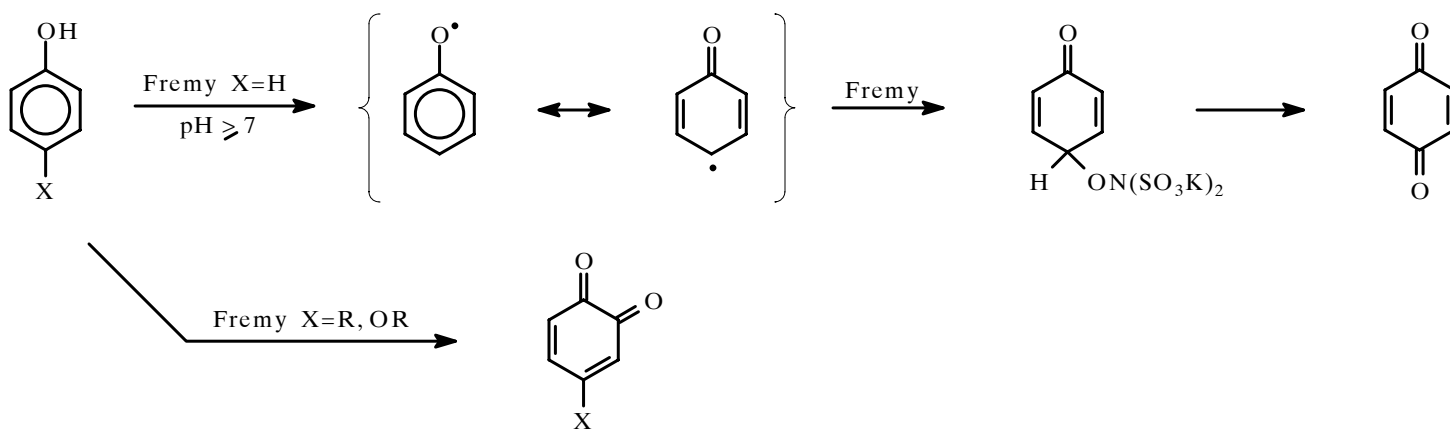


4) OKSIDACIJE FENOLA $K_3Fe(CN)_6$, H_2O_2/Fe^{2+} , $ON(SO_3K)_2$

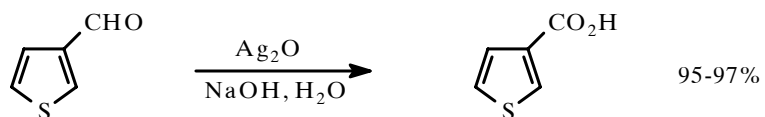
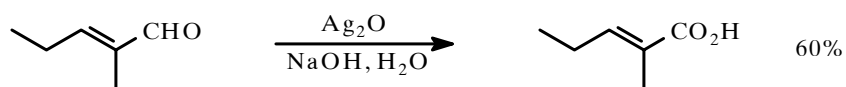
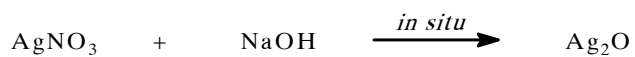
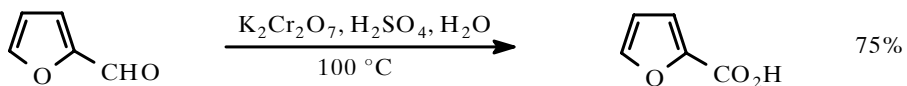
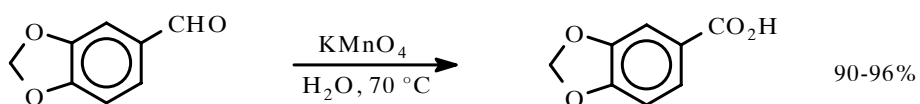
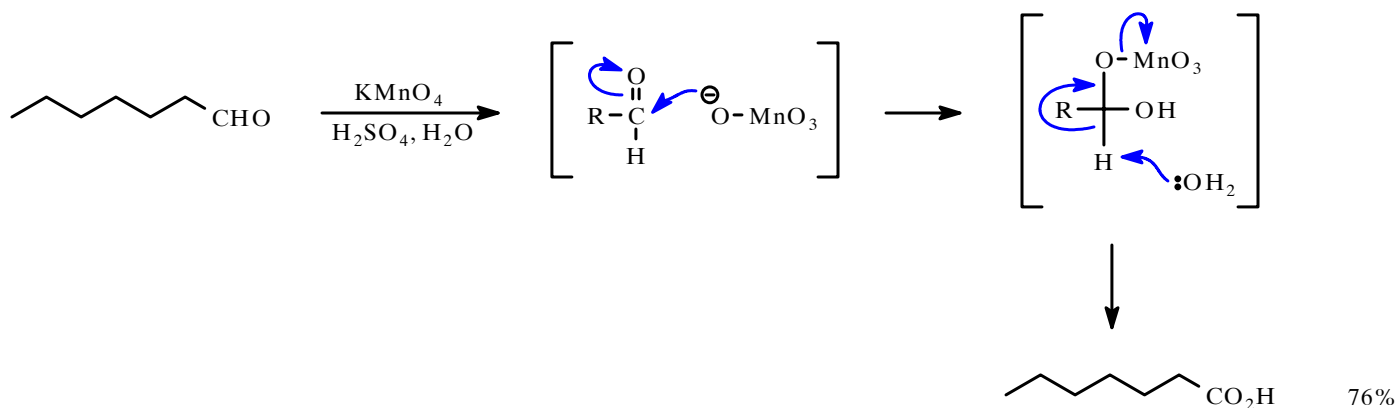
$K_3Fe(CN)_6$

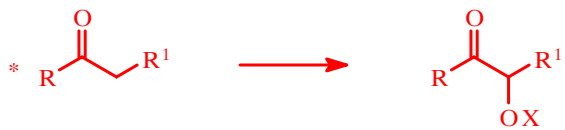


ON(SO₃K)₂ Fremy-jeva so

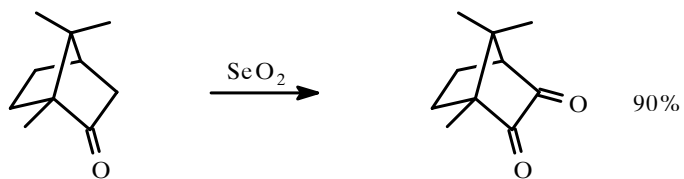
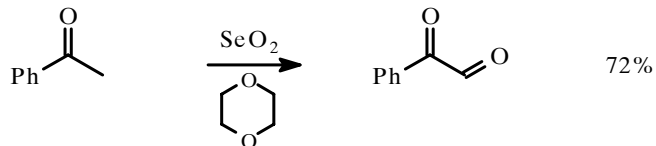
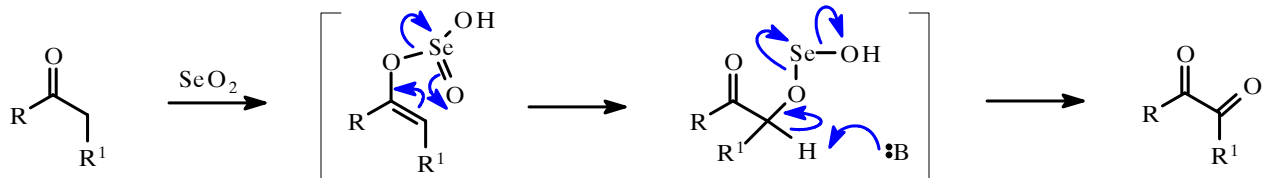


5) OKSIDACIJE KARBONILNIH JEDINJENJA

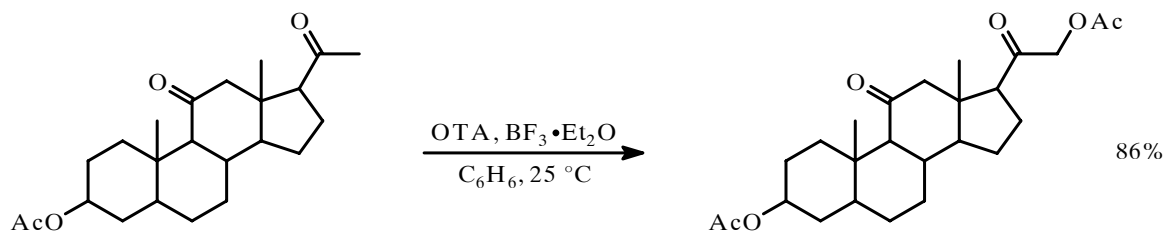
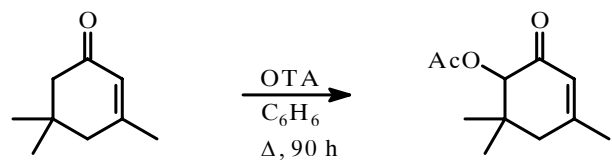
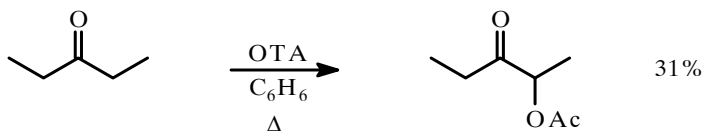


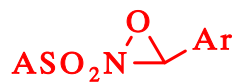


SeO₂



Pb(OAc)₄





Davies-ov reagens

