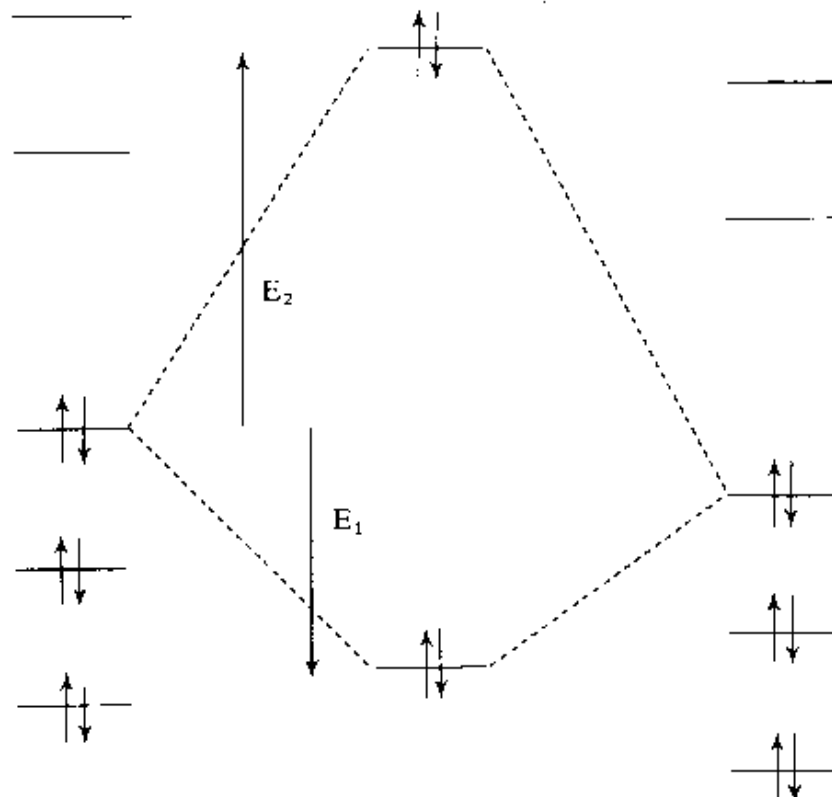


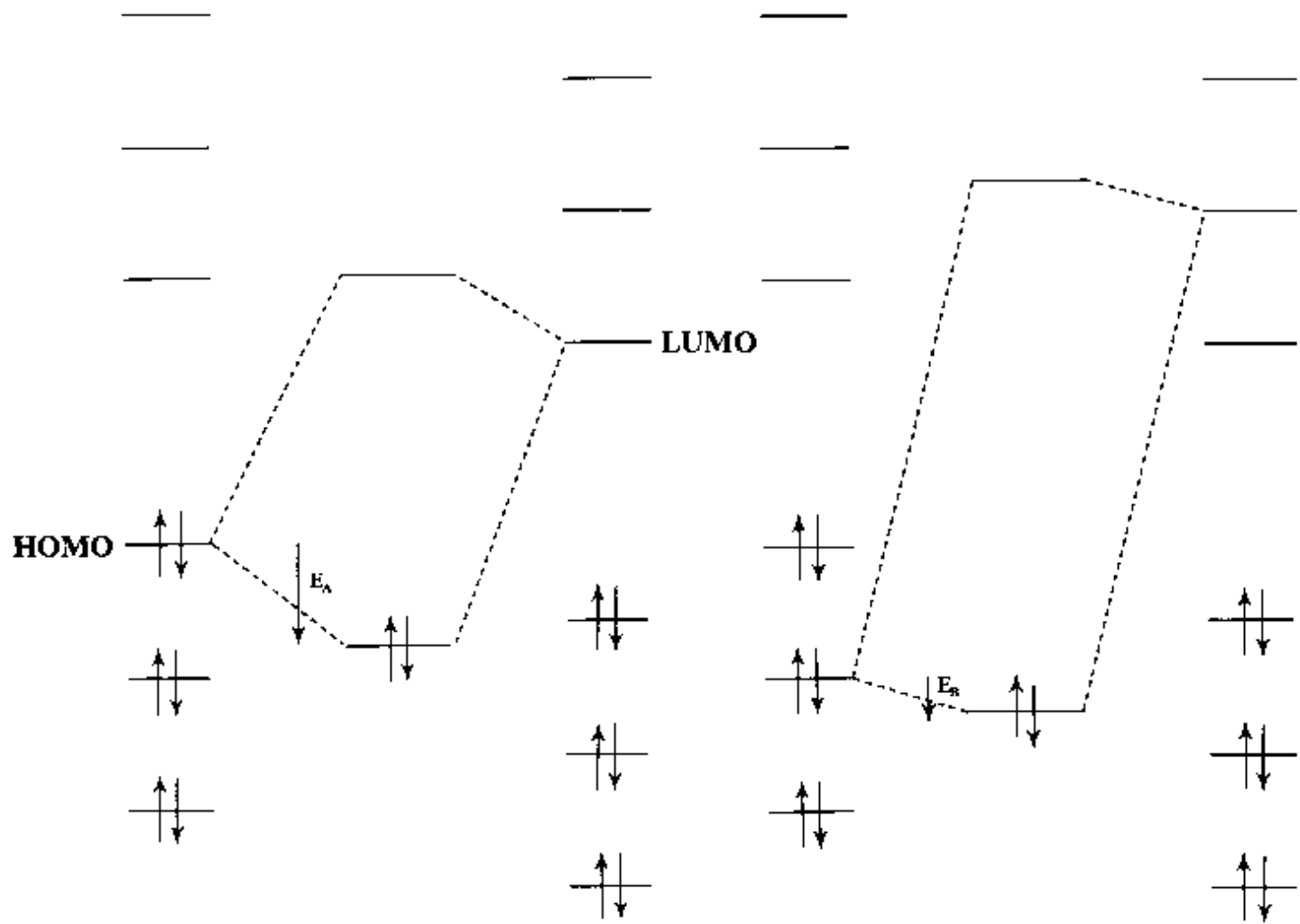
REAZIONI PERICICLICHE

Quando due molecole collidono vi sono tre forze in azione:

1. Gli orbitali occupati di una repellono gli occupati dell'altra;
2. Ogni carica positiva su di una attrae ogni carica negativa sull'altra;
3. Gli orbitali occupati (HOMO) di una interagiscono con quelli non occupati dell'altra (LUMO) causando un'attrazione tra le molecole.

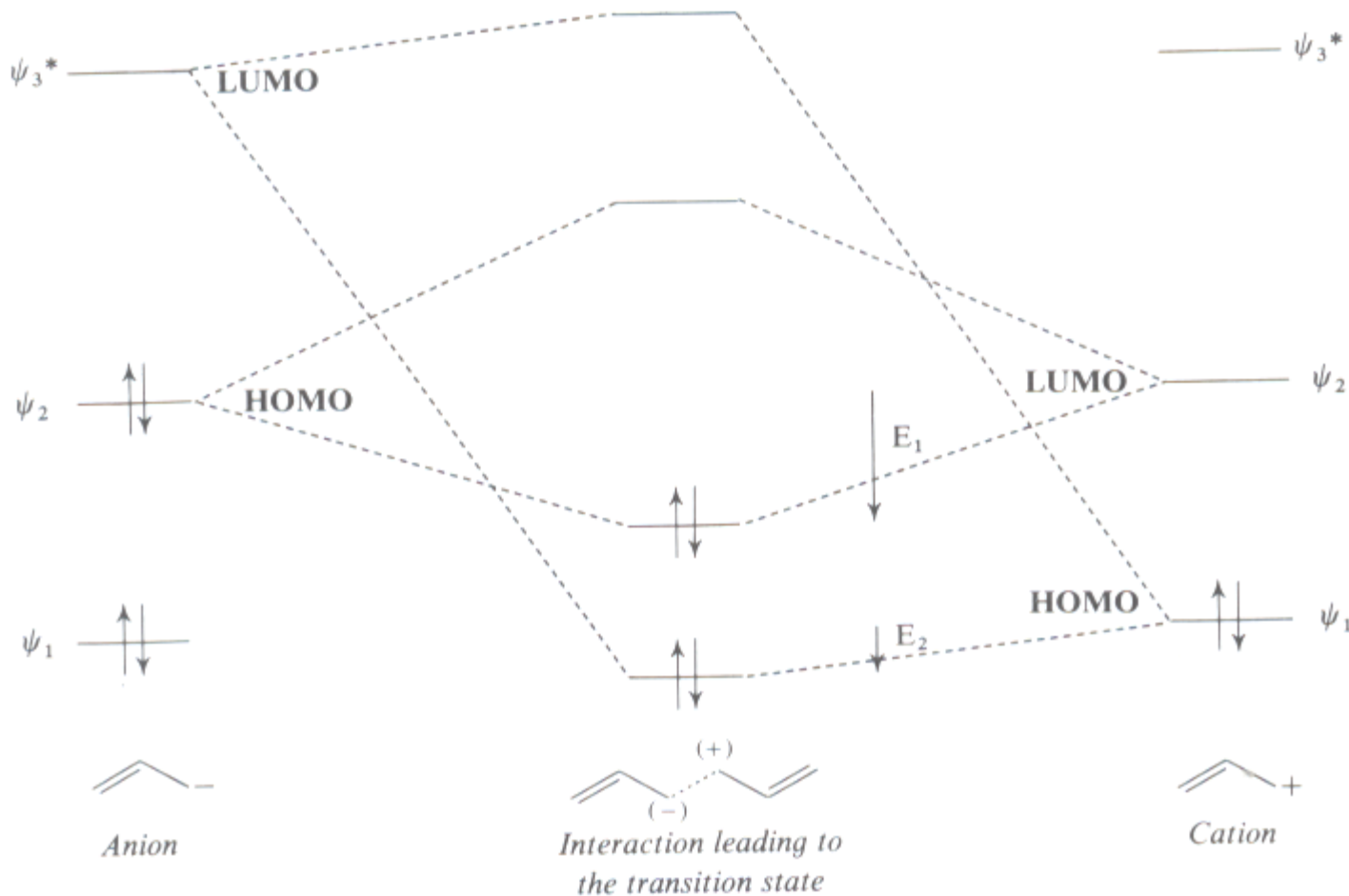


Interazione tra due orbitali HOMO di due molecole: l'interazione è energeticamente sfavorevole



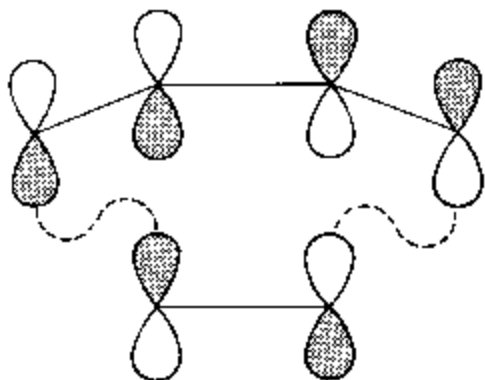
**Sinistra: interazione tra un orbitale HOMO ed un LUMO;
l'interazione è energeticamente favorevole**
**Destra: interazione tra un MO più basso e più alto in energia rispetto
ad HOMO e LUMO; l'interazione è energeticamente poco favorevole**

Gli orbitali di frontiera rilevanti per un nucleofilo che reagisce con un elettrofilo sono l'HOMO del nucleofilo e il LUMO dell'elettrofilo



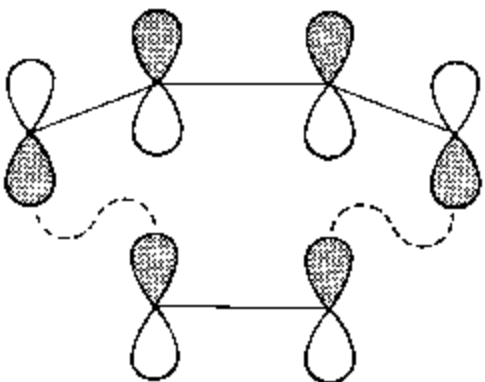
Interazioni tra gli orbitali HOMO e LUMO di un catione ed un anione allilico

CICLOADDIZIONI



HOMO of butadiene (ψ_2 , see p. 17)

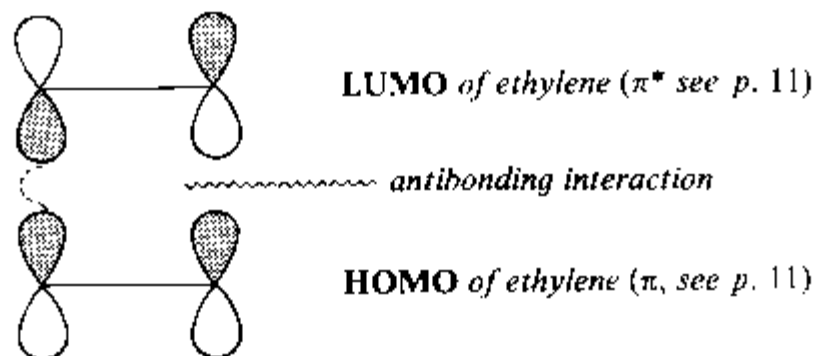
LUMO of ethylene (π^* , see p. 11)



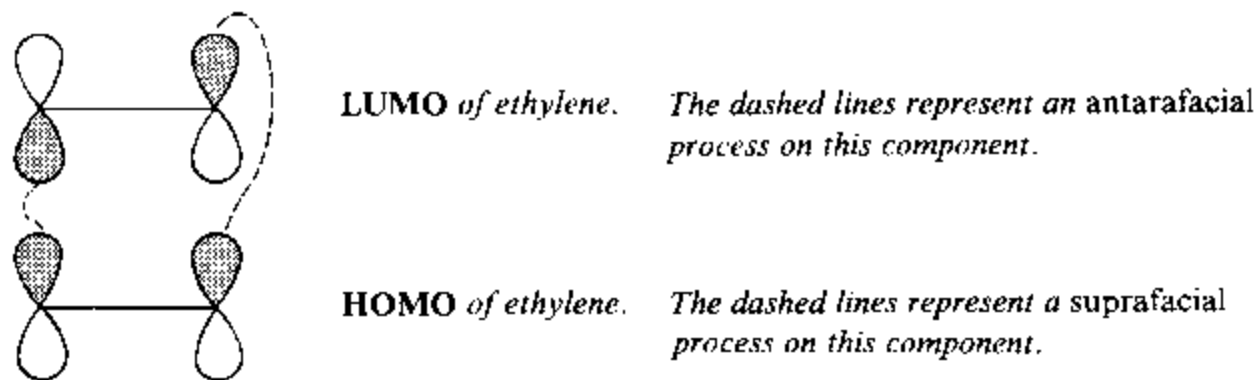
LUMO of butadiene (ψ_3^* , see p. 17)

HOMO of ethylene (π , see p. 11)

Sovrapposizione tra gli orbitali frontiera HOMO e LUMO in una reazione di Diels Alder

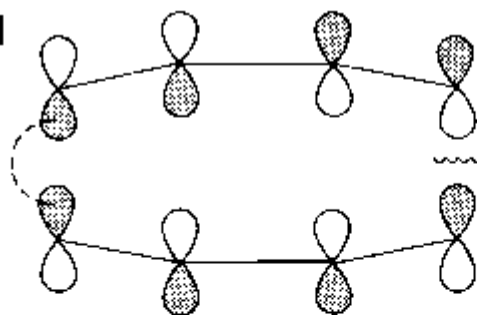


La sovrapposizione tra gli orbitali di frontiera in una cicloaddizione [2+2] tra due dieni



La sovrapposizione tra gli orbitali HOMO e LUMO in una reazione di cicloaddizione [$\pi 2s + \pi 2a$]

$[\pi 4s + \pi 4s]$

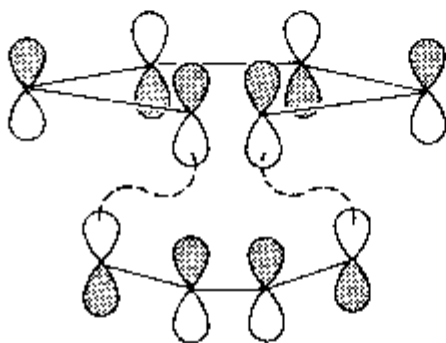


HOMO of butadiene

antibonding

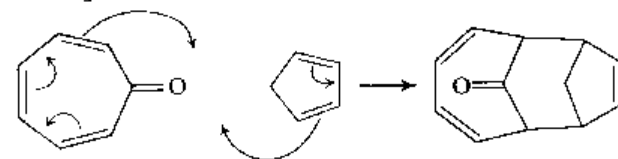
LUMO of butadiene

$[\pi 6s + \pi 4s]$

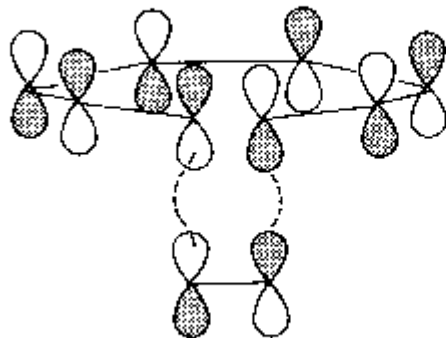


HOMO of hexatriene $[\pi 6s + \pi 4s]$

LUMO of butadiene

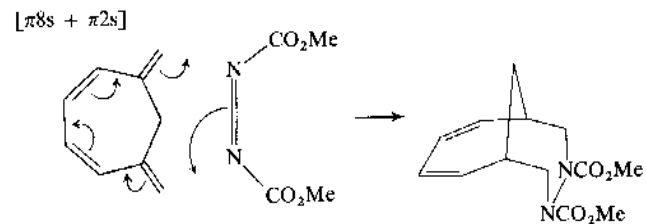


$[\pi 8s + \pi 2s]$



HOMO of octatetraene $[\pi 8s + \pi 2s]$

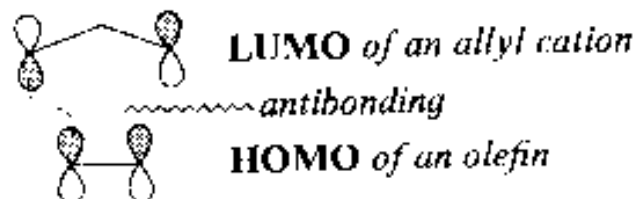
LUMO of ethylene



Interazione tra orbitali di frontiera in cicloaddizioni $[\pi 4s + \pi 4s]$, $[\pi 6s + \pi 4s]$ e $[\pi 8s + \pi 2s]$

(a) $[\pi 2s + \pi 2s]$

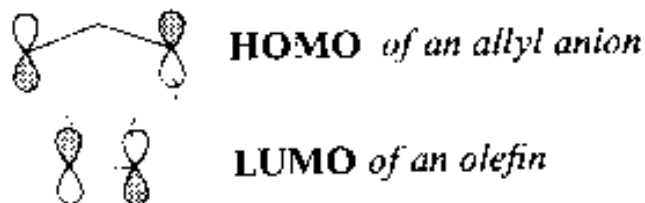
Frontier orbitals:



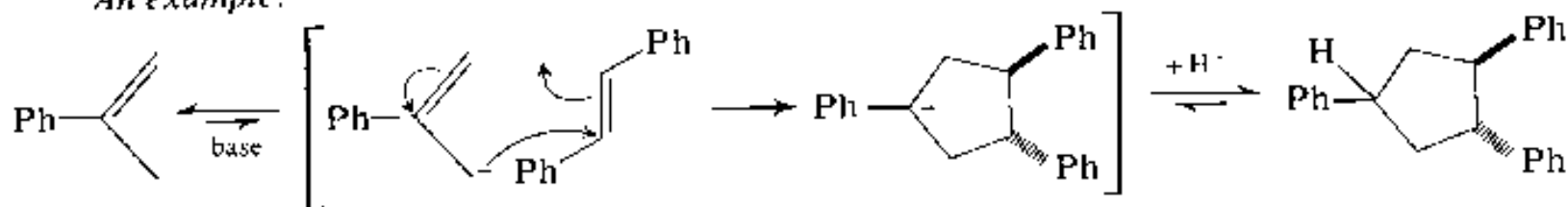
There are no known examples of a pericyclic reaction of an allyl cation with an olefin.

(b) $[\pi 4s + \pi 2s]$

Frontier orbitals:

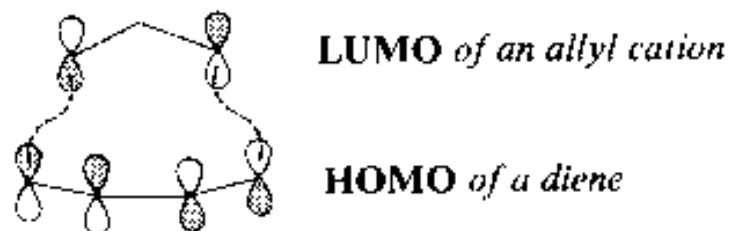


An example:^{1,2,2}

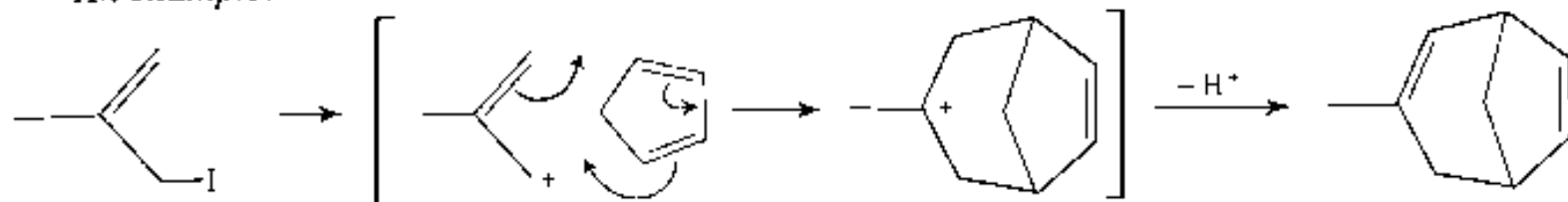


(c) $[\pi 4s + \pi 2s]$

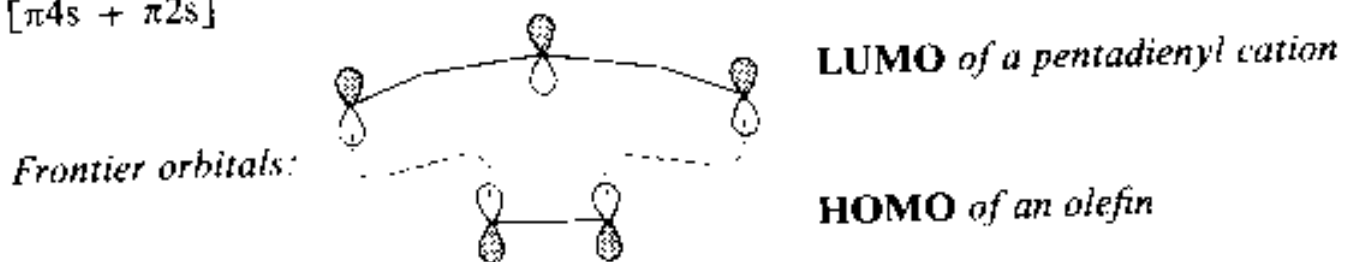
Frontier orbitals:



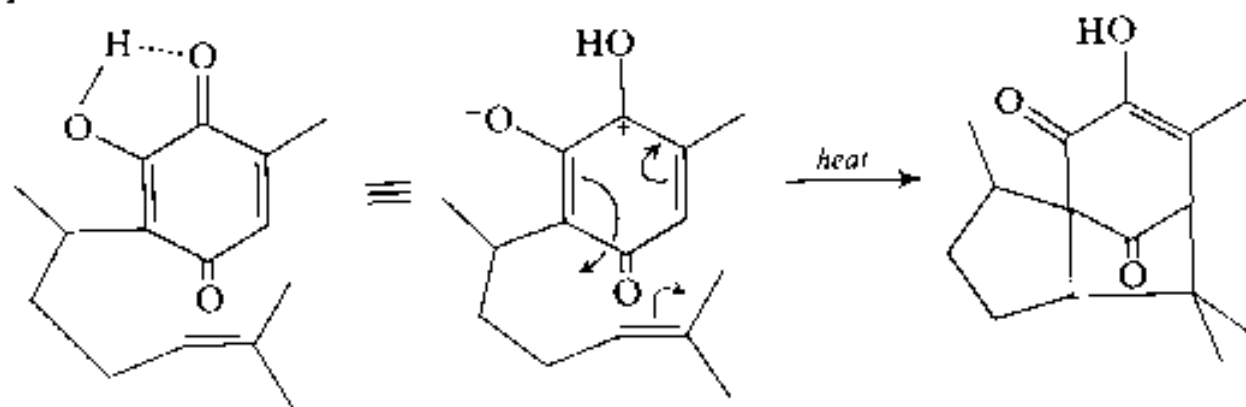
An example:^{1,2,3}



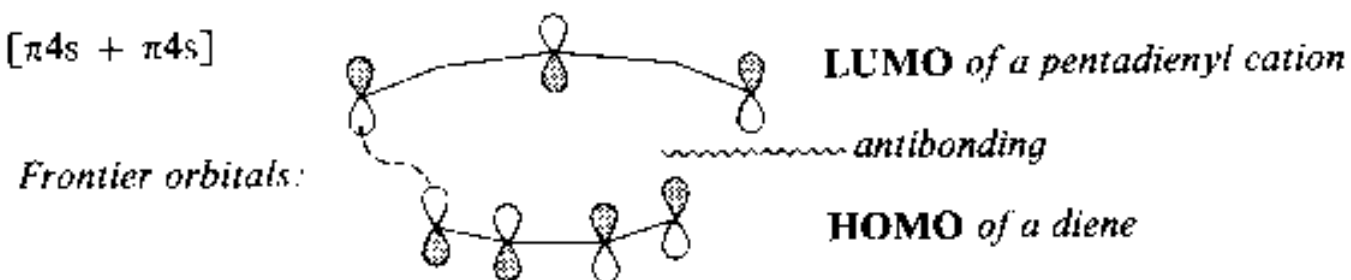
(d) $[\pi 4s + \pi 2s]$



An example:¹²⁴

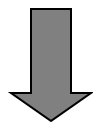
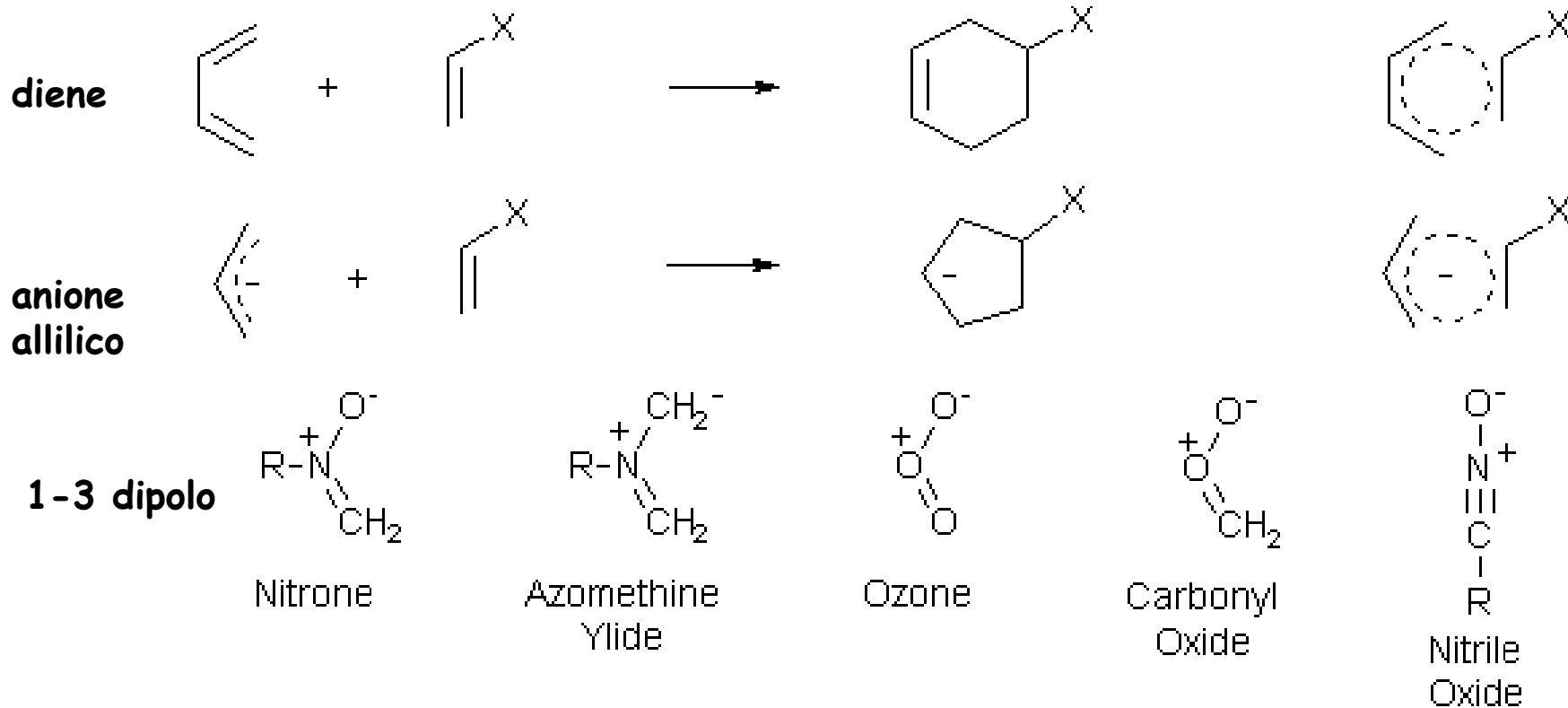


(c) $[\pi 4s + \pi 4s]$

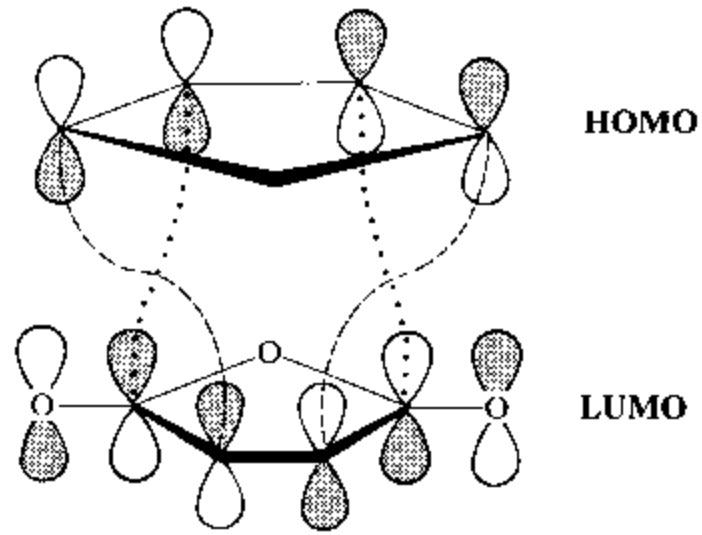
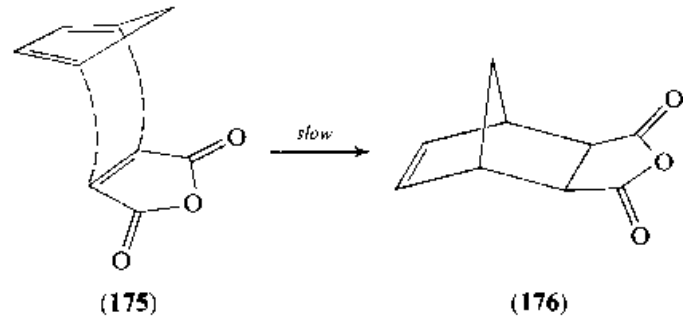
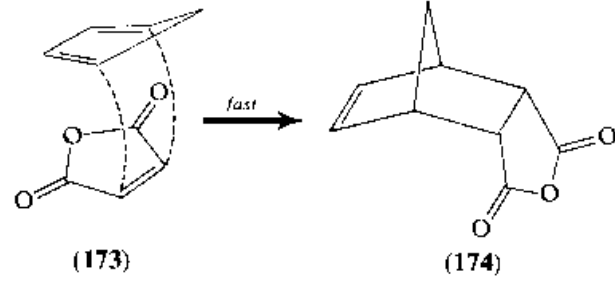


There are no known examples of a pericyclic reaction of a pentadienyl cation with a diene.

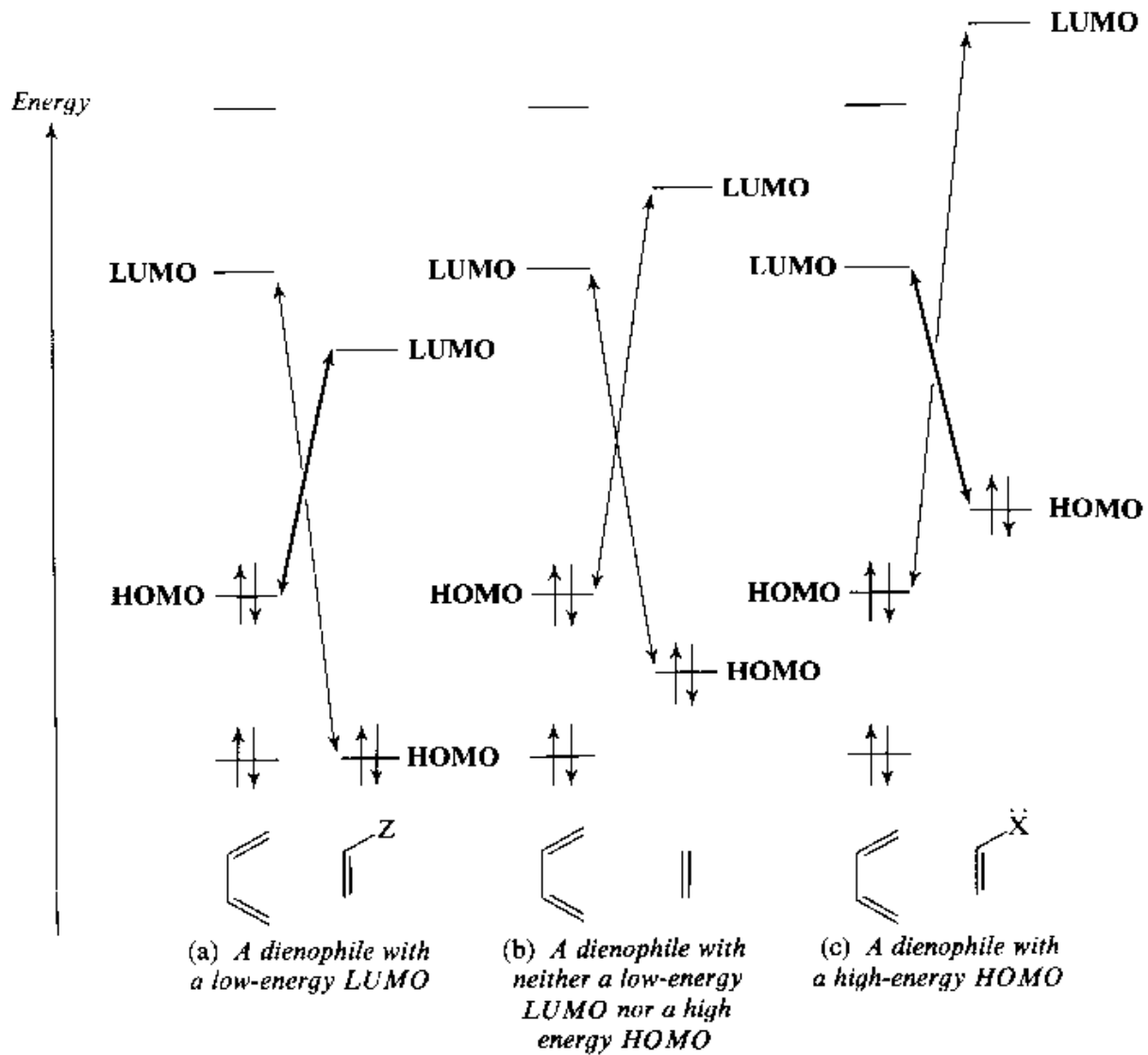
Vari esempi di cicloaddizioni [$\pi 4s + \pi 2s$]



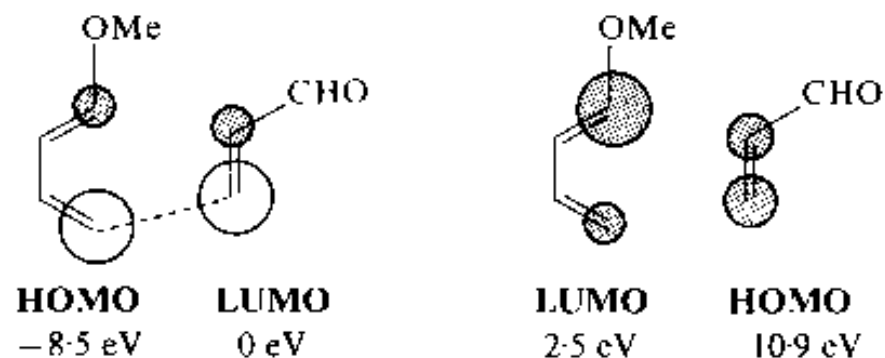
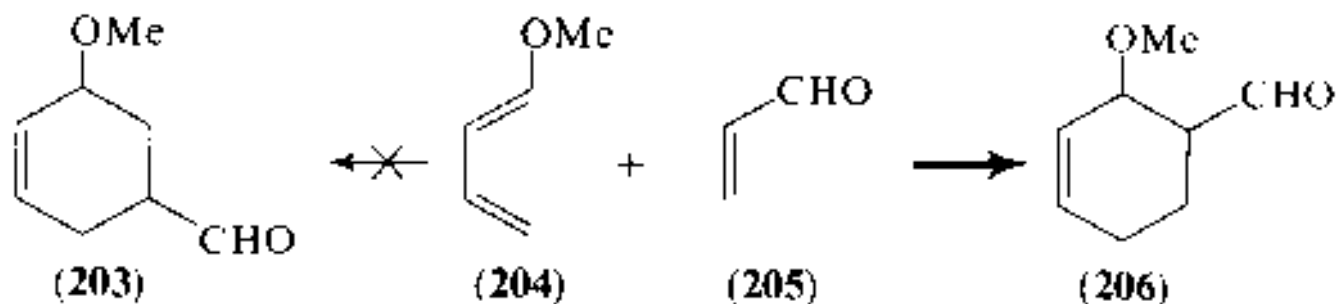
tutti sistemi
a 4 e- π



Interazioni secondarie tra gli orbitali frontiera nella reazione di cicloadizione che porta in maniera preferenziale all'addotto endo



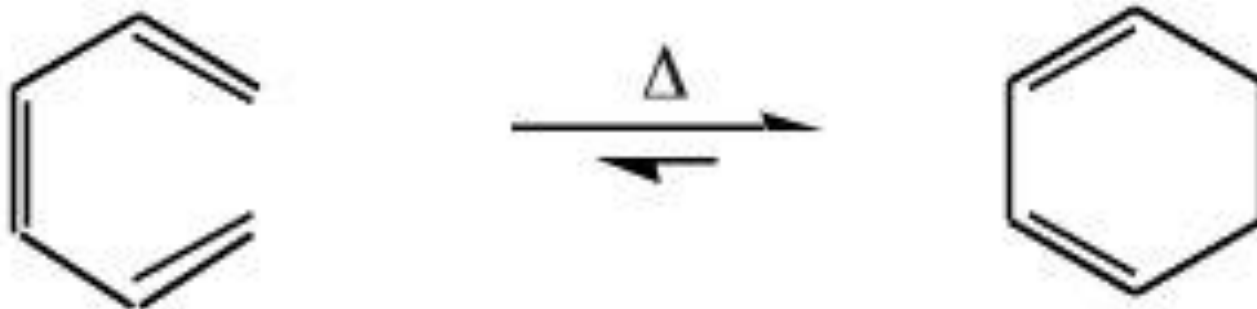
Interazioni tra orbitali di frontiera in reazioni di Diels Alder



I coefficienti degli orbitali di frontiera che interagiscono in una reazione di Diels Alder controllano la regiochimica della reazione

Reazioni elettrocicliche

Le reazioni elettrocicliche sono reazioni unimolecolari che coinvolgono lo scambio di elettroni π per chiudere un anello mediante un legame σ come nell'esempio qui sotto: l'1,3,5-esatriene da chiusura di anello elettrociclica per dare l'1,3-cicloesadiene.

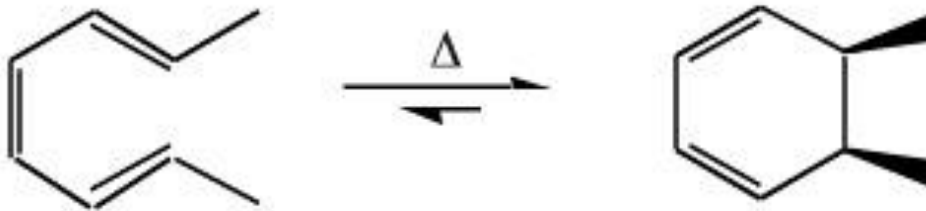


Perchè la reazione avvenga l'alchene in 3 deve essere cis!

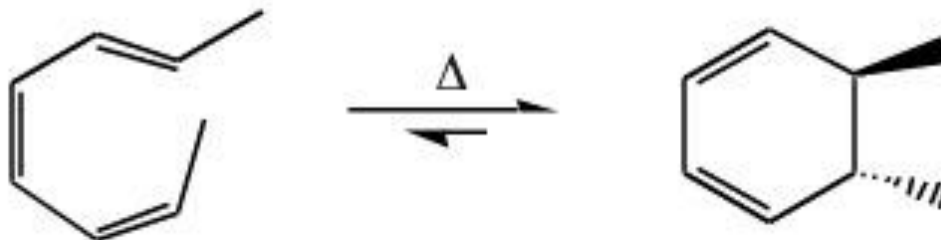
E' ovviamente possibile la cicloversione, cioè l'apertura dell'anello come nel caso del ciclobutene:



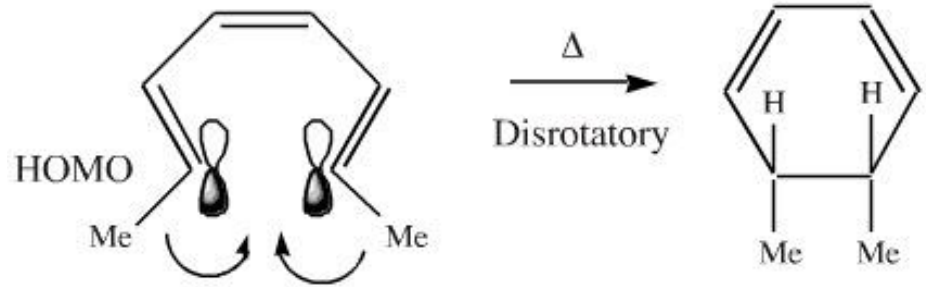
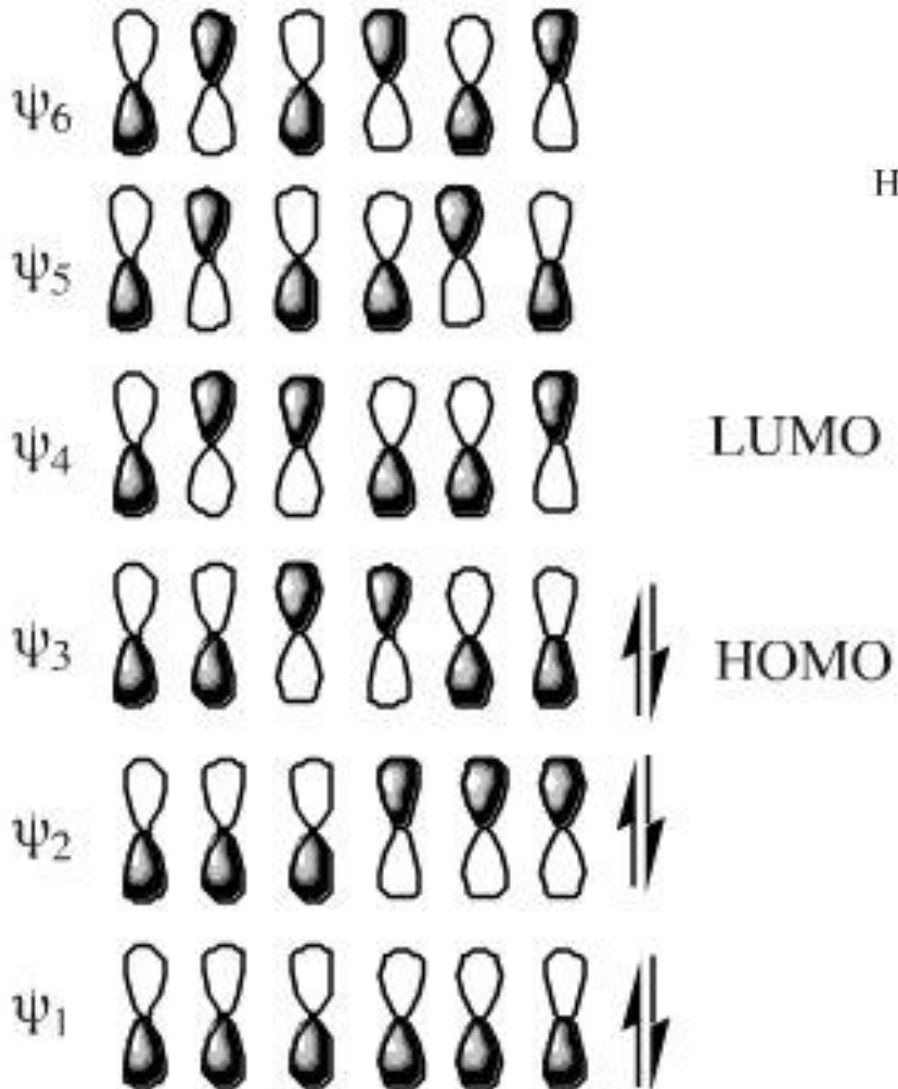
Come tutte le reazioni pericicliche anche le reazioni elettrocicliche presentano una elevata stereoselettività. Nel caso del sistema esatrienico sostituito ai due alcheni terminali (trans-cis-trans-2,4,6-octatriene) il prodotto è un ciclo con i due sostituenti in cis:



Al contrario il trans-cis-trans-2,4,6-ottatriene si chiuderà ad anello per dare un legame con i due sostituenti in trans:



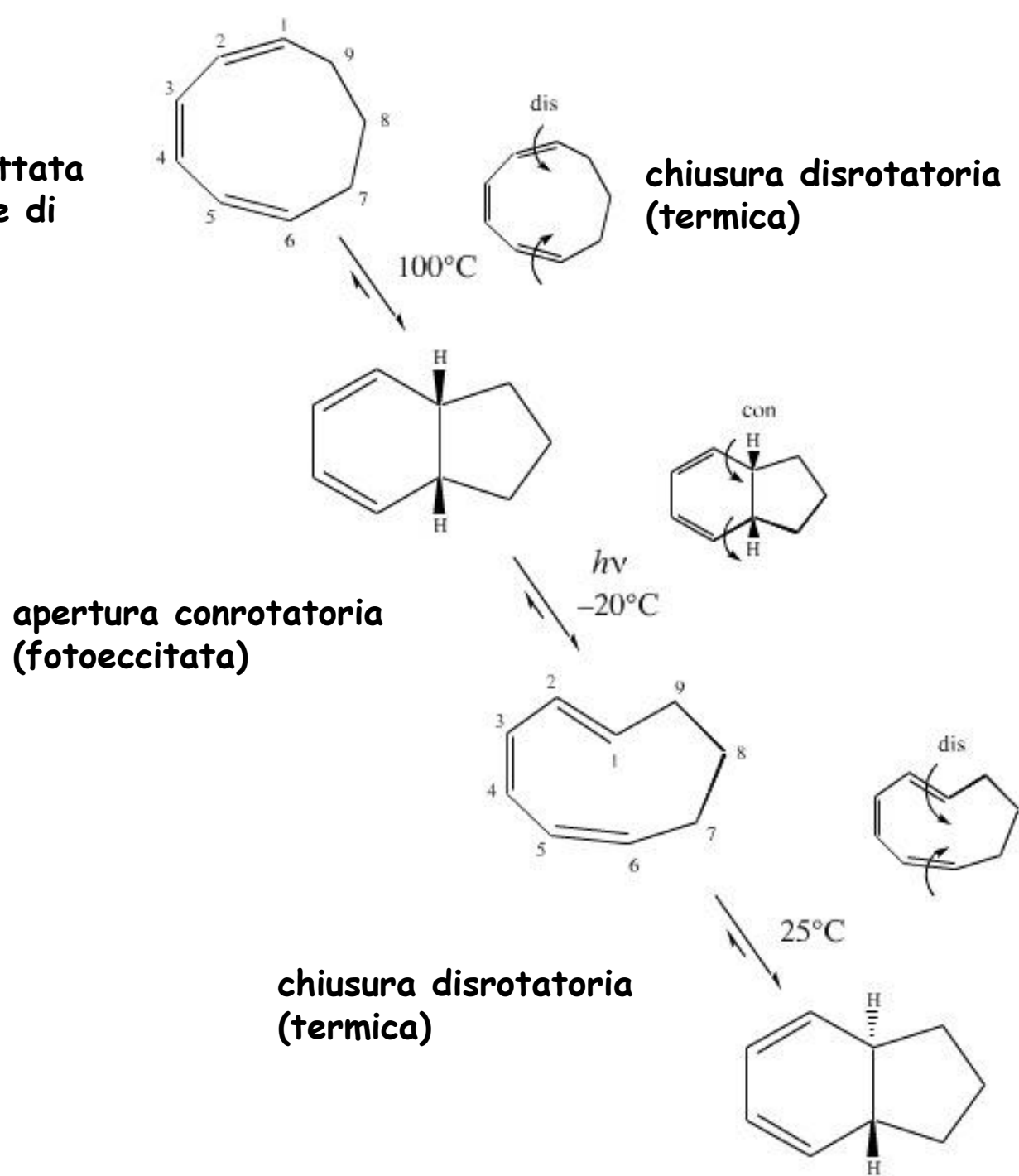
Un esame degli orbitali di frontiera spiega la ragione (in questo caso devo vedere l'orbitale HOMO):



e se volessimo ciclizzare il butadiene?

e se irradiassimo il sistema?

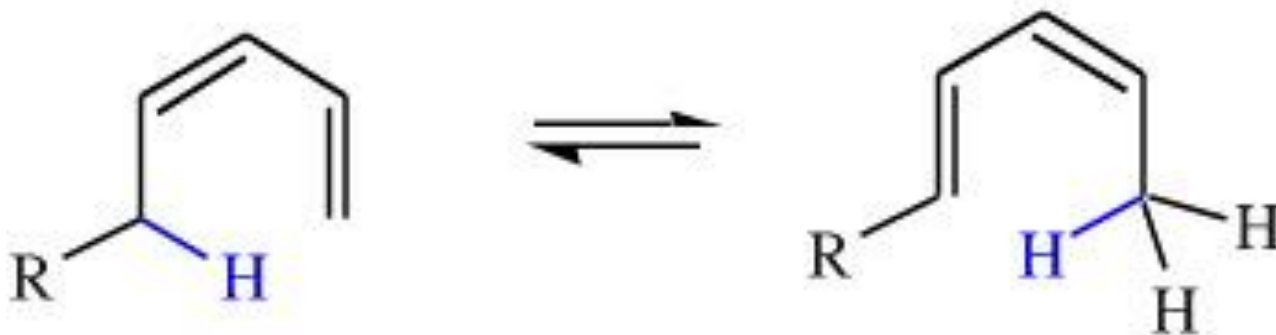
La selettività delle reazioni elettrocicliche termiche o fotochimiche può essere sfruttata a proprio vantaggio in cascate di reazioni consecutive come nel caso del 1,3,5-ciclononatriene....



RIARRANGIAMENTI SIGMATROPICI

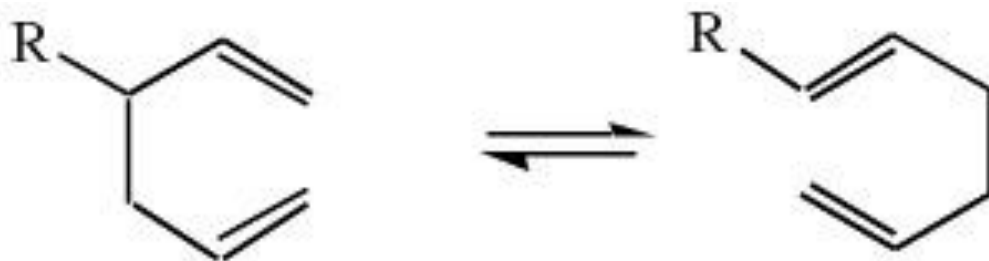
I riarrangiamenti sigmatropici, al pari delle reazioni elettrocicliche, sono processi unimolecolari. I riarrangiamenti sigmatropici coinvolgono il movimento di un legame sigma con il riarrangiamento simultaneo dei legami π .

Ad esempio lo shift [1,5] dell'idrogeno in un sistema 1,3-pentadienico:



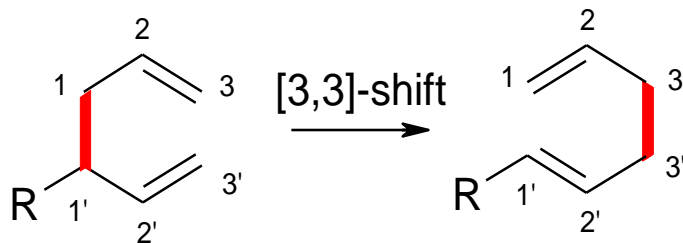
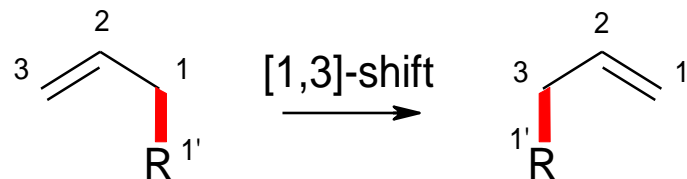
Lo shift può avvenire in maniera antarafacciale o suprafacciale a seconda del numero di doppi legami coinvolti (e quindi della fase dell'orbitale atomico p dell'atomo di C dell'alchene di arrivo)

Il riarrangiamento [3,3] di Cope:



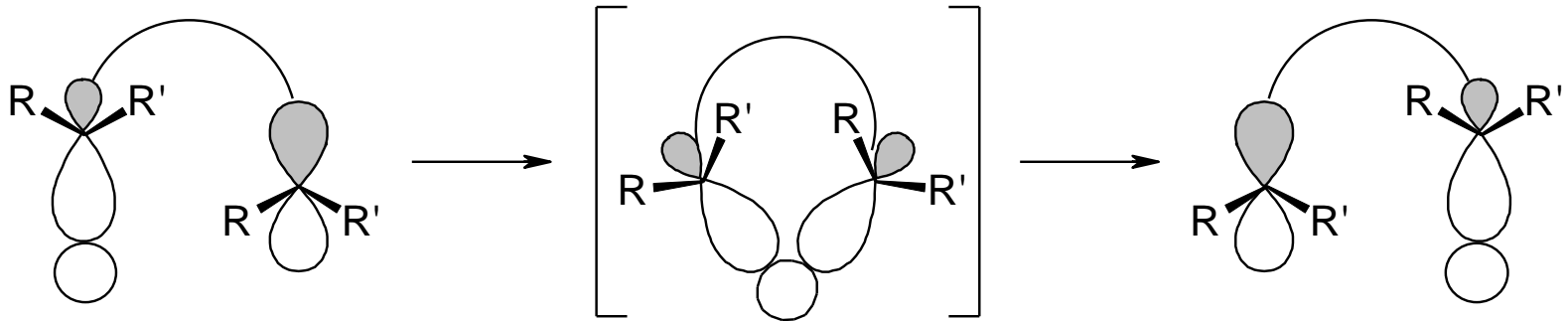
Riarrangiamenti Sigmatropici

- Migrazione (shift) di un legame σ attraverso un sistema π coniugato
- Migrazione (shift) [**m,n**] quando il legame σ migra attraverso **m** atomi di un sistema e **n** dell'altro

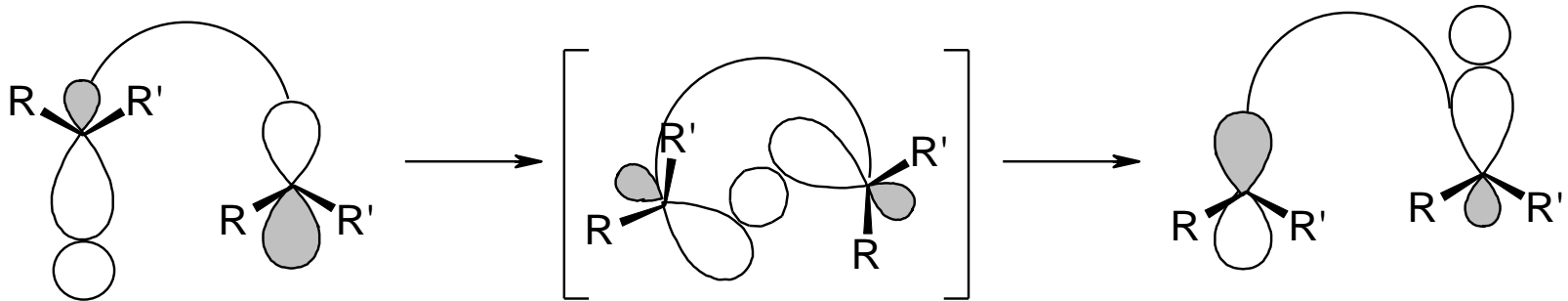


Suprafacciale/Antarafacciale

- migrazione suprafacciale: Il gruppo si muove sulla stessa faccia

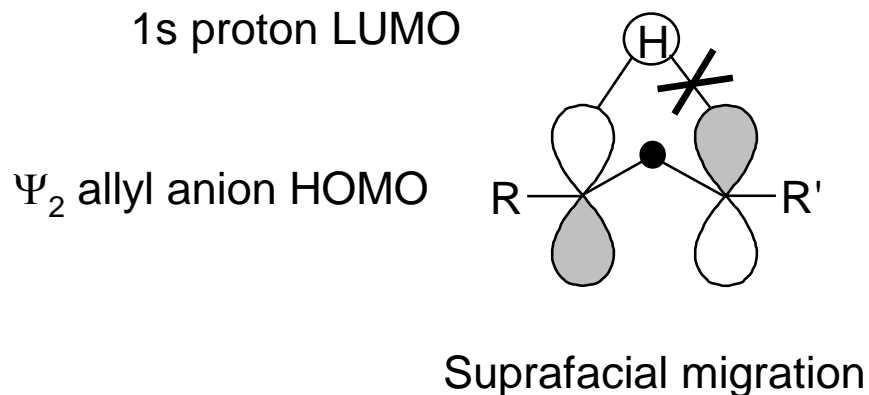
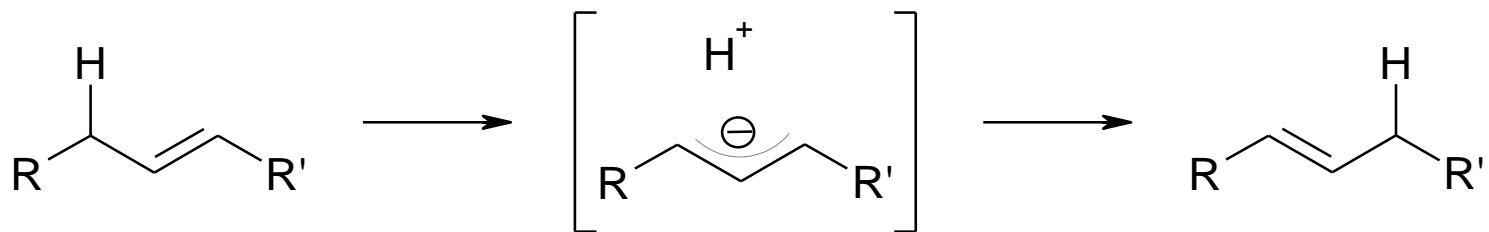


- Migrazione antarafacciale: il gruppo si muove da una faccia all'altra

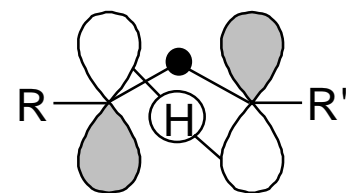


Analisi FMO

- [1,3] Riarrangiamento sigmatropico: migrazione di H



FORBIDDEN

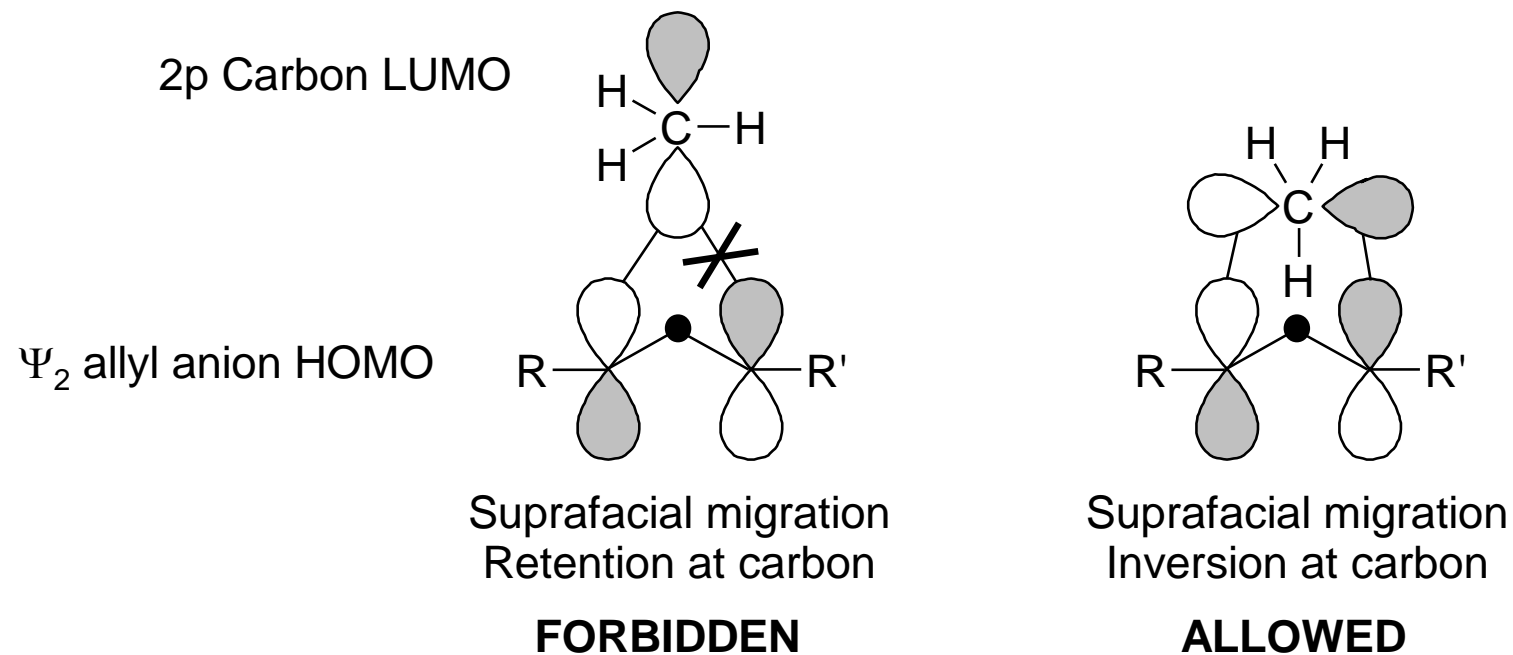
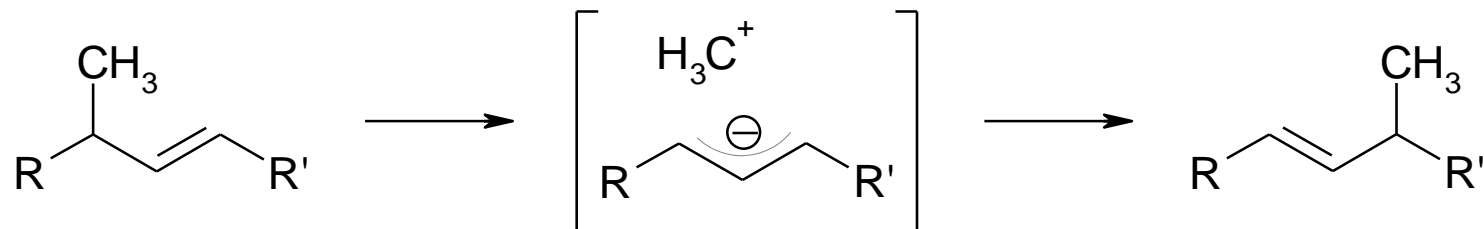


Antarafacial migration

**ORBITALLY ALLOWED BUT
H CANNOT BRIDGE DISTANCE**

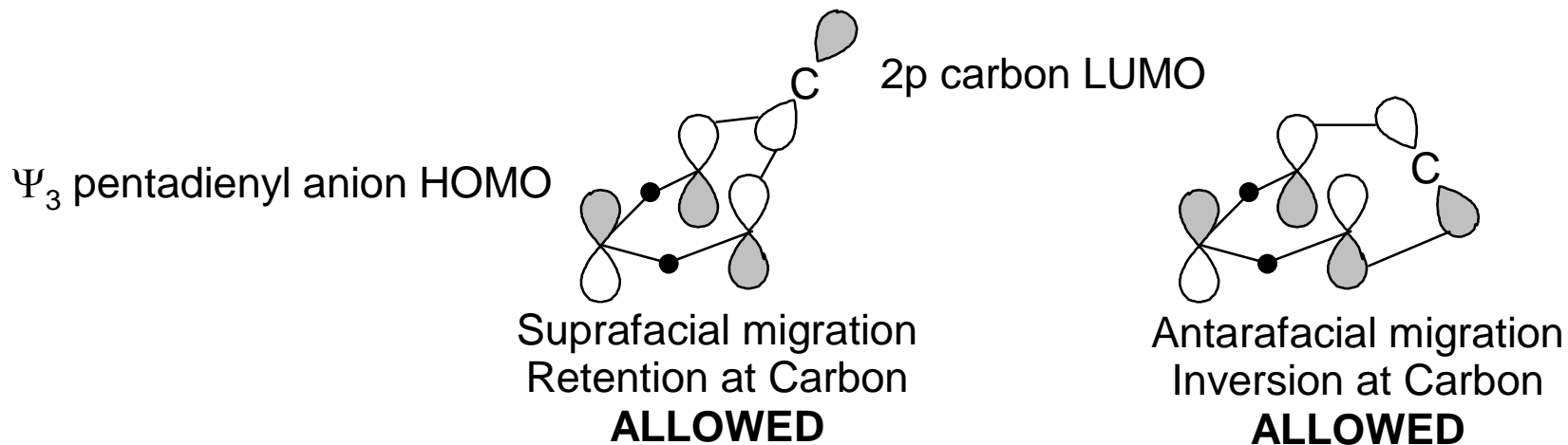
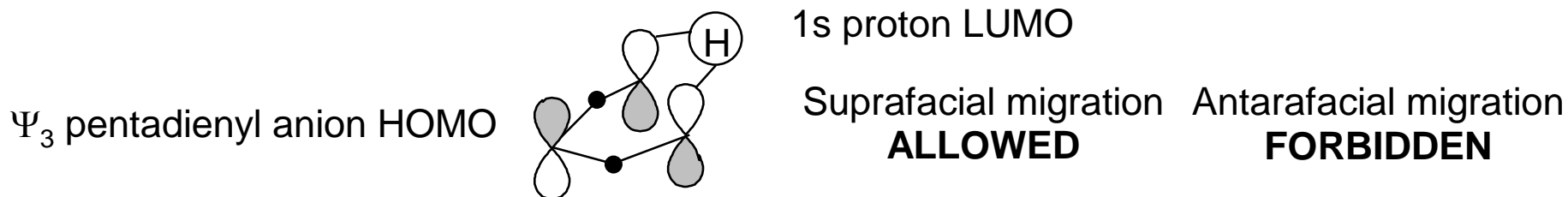
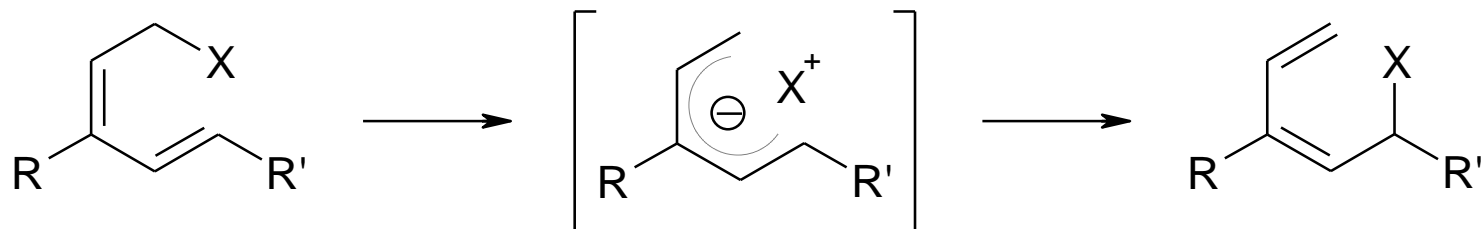
Analisi FMO

- [1,3] Riarrangiamenti: migra C



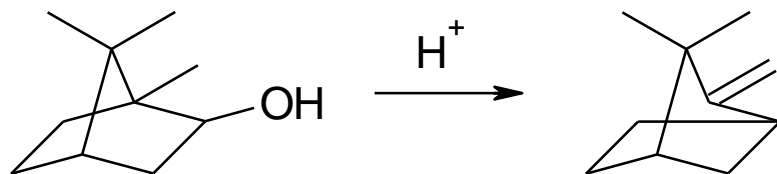
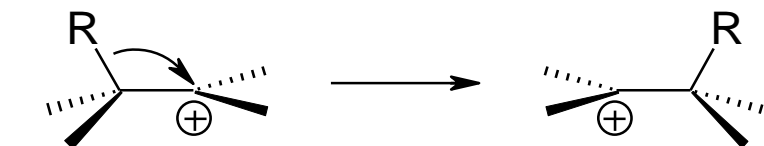
Analisi FMO

- [1,5] Riarrangiamenti sigmatropici



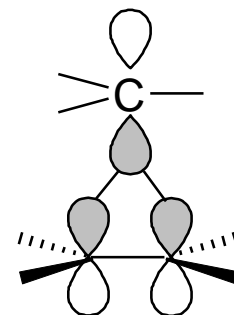
[1,2] Sigmatropic Rearrangements

- [1,2]-C shift su carbocatione : Wagner-Meerwein Rearrangement



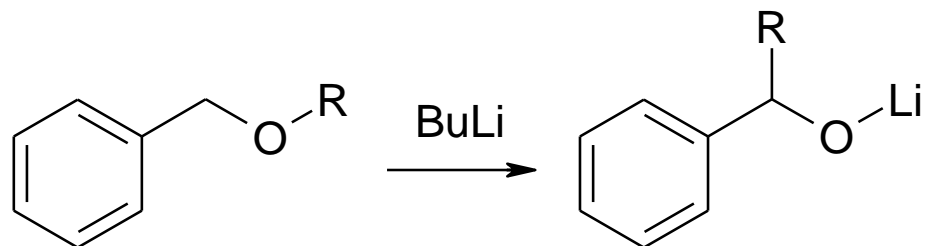
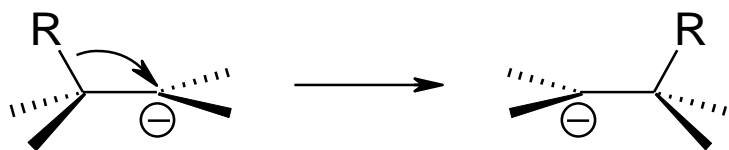
2p Carbon radical

Ψ_1 olefin
radical cation



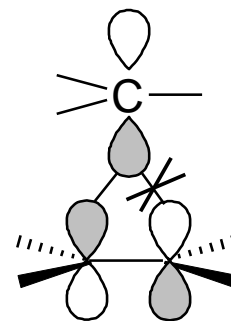
Suprafacial migration: **ALLOWED**

- [1,2]-C shift su anione: Wittig Rearrangement



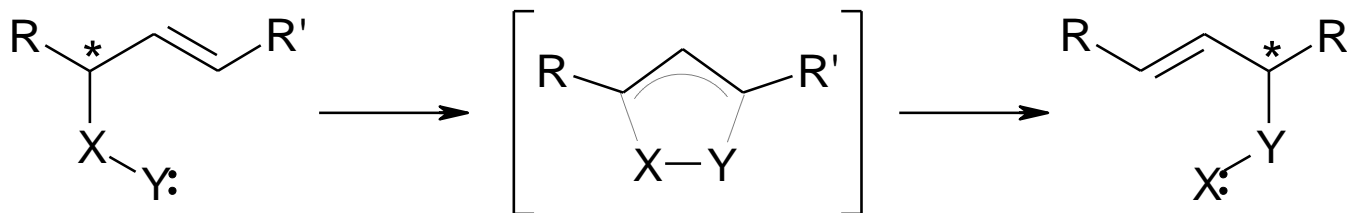
2p Carbon radical

Ψ_2 olefin
radical anion



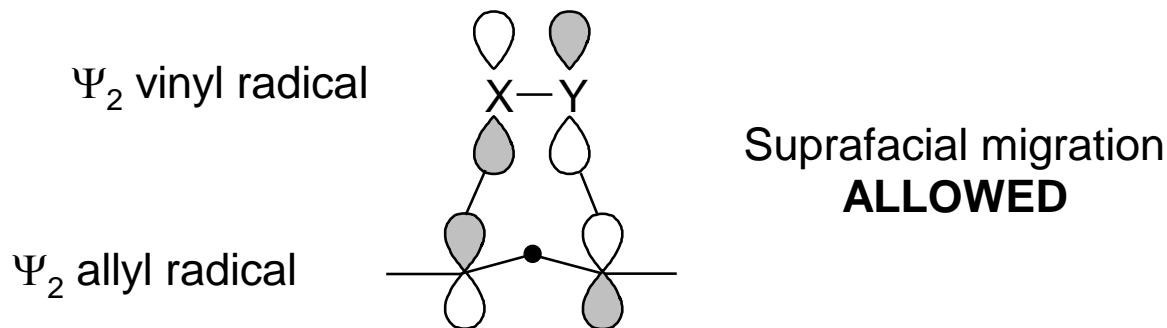
Suprafacial migration: **FORBIDDEN**
∴ Must be stepwise

[2,3] Sigmatropic Rearrangements



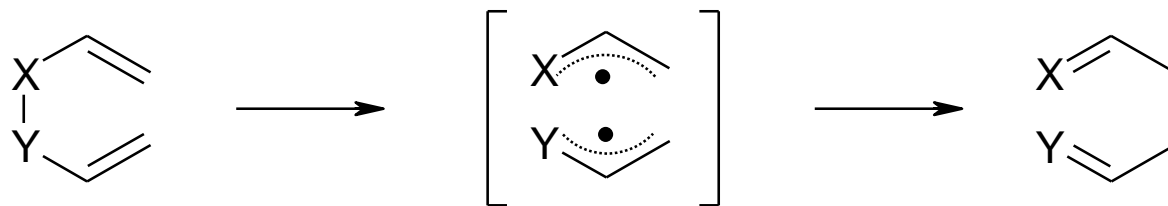
X, Y = C, N, O, S, Se, P

- **FMO Analysis**

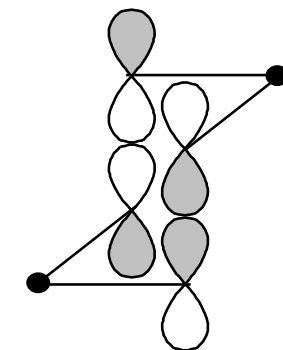
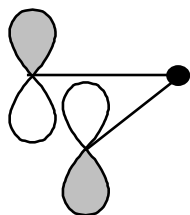


[3,3] Sigmatropic Rearrangements

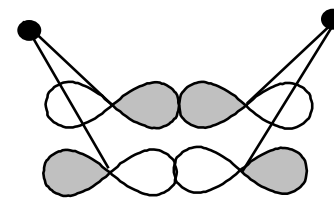
- FMO Analysis



Ψ_2 allyl radical

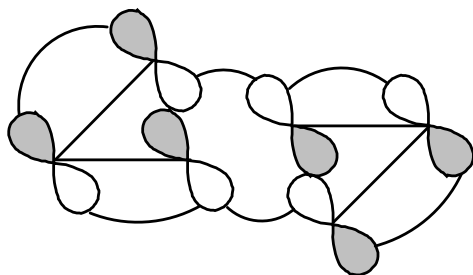
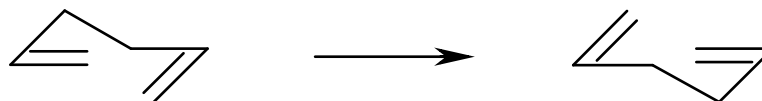


Chair geometry
ALLOWED



Boat geometry
ALLOWED

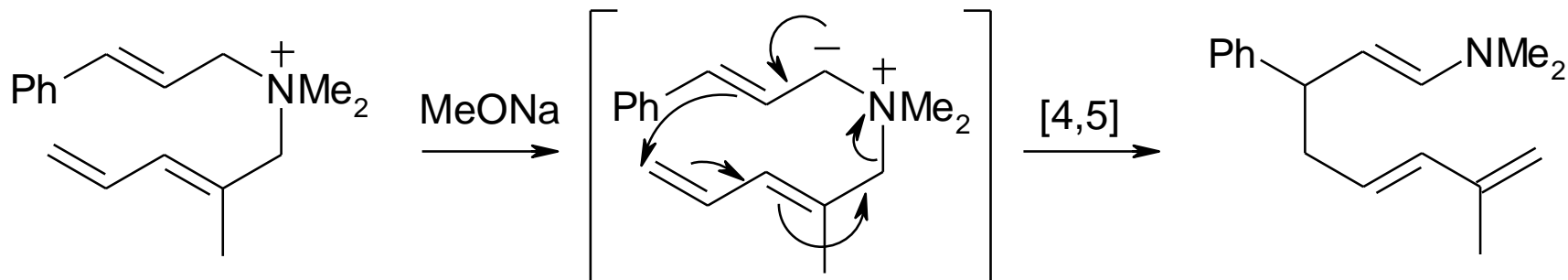
- Dewar-Zimmerman



Zero Phase Inversions
Hückel Topology
Six electrons
THERMALLY ALLOWED

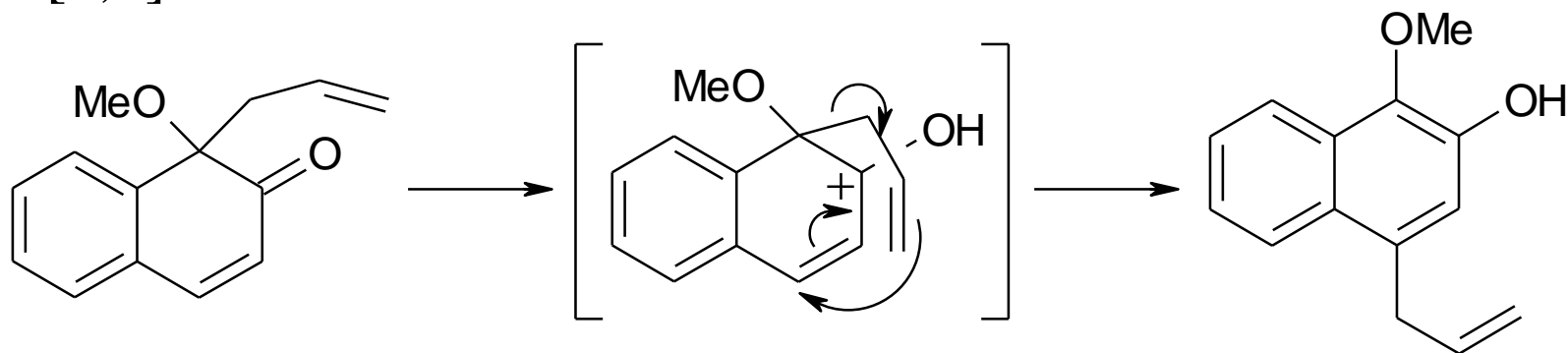
[m,n] Sigmatropic Rearrangements

- [4,5] shift



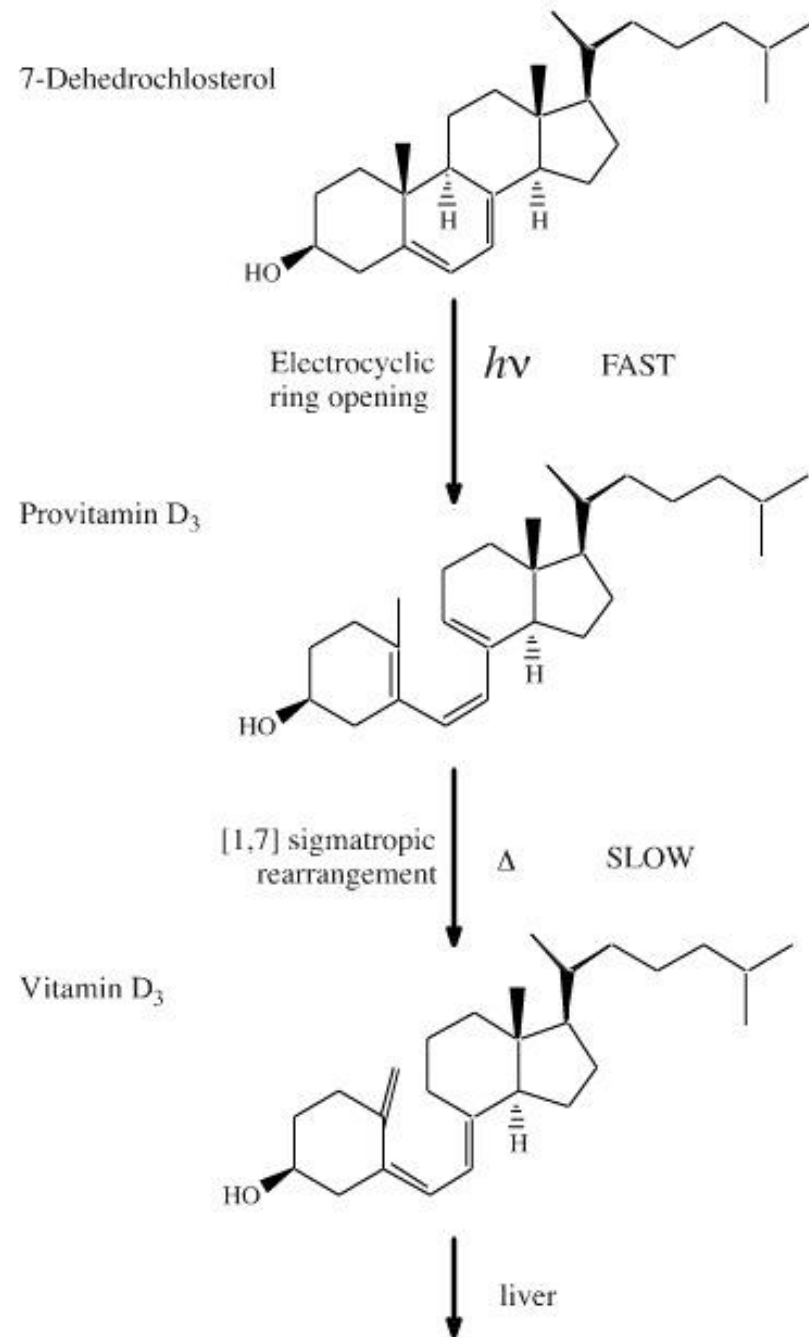
– [2,3] possible but [4,5] favoured. [2,5] and [3,4] forbidden

- [3,4] shift



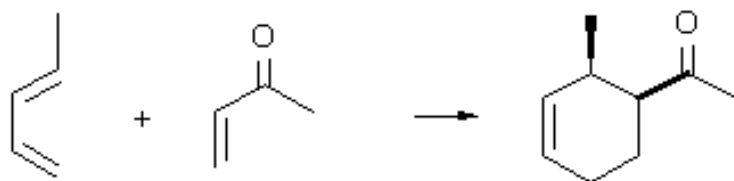
Vitamin D Biosynthesis

Un esempio di riarrangiamento sigmatropico è la biosintesi della vitamina D che avviene allo stato fotoeccitato. Tutto parte da un sistema 1,3-cicloesadienico dell'anello b di uno steroide che si apre attraverso un processo retroelettrrociclico fotoeccitato. Successivamente si ha un processo [1,7] sigmatropico termico che porta al prodotto finale. Perché nel primo passaggio la reazione non va per via termica?

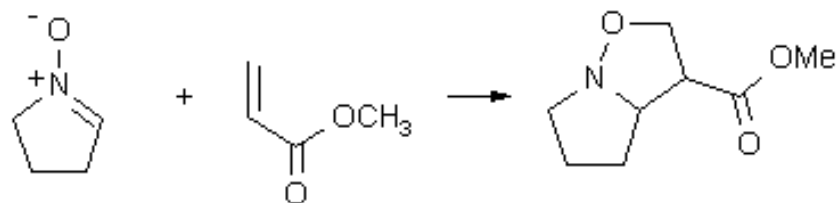


Cycloadditions

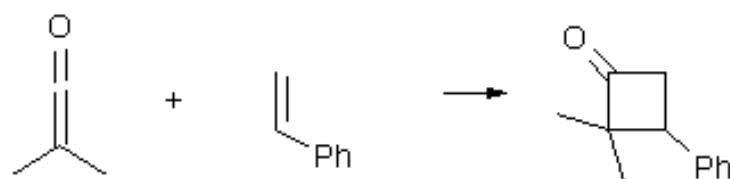
$2\pi + 4\pi$ Cycloadditions - Diels-Alder Reaction



1,3-Dipolar Cycloaddition



$2\pi + 2\pi$ Cycloadditions

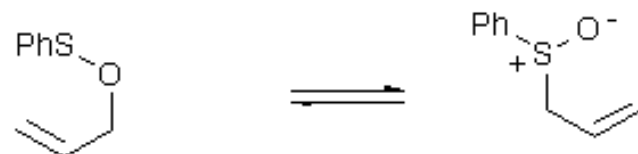


Sigmatropic Rearrangements

Claisen [3,3] Sigmatropic

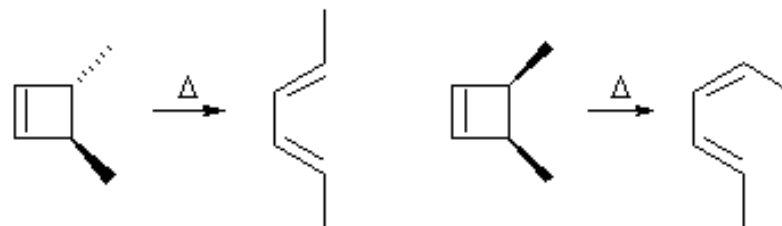


[2,3] Sigmatropic



Electrocyclic Reactions

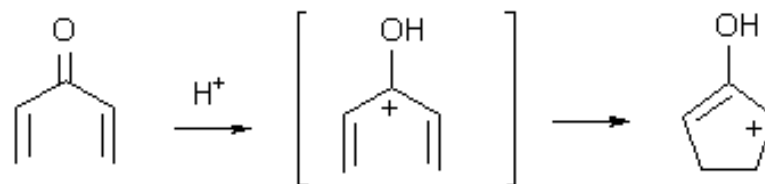
Cyclobutene - butadiene



Hexatriene - cyclohexadiene

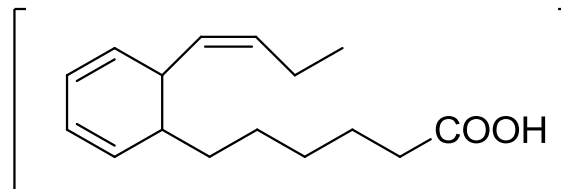
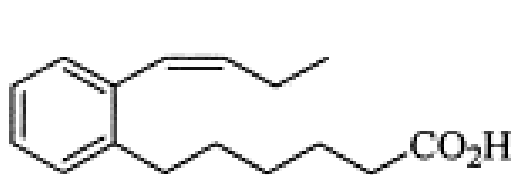
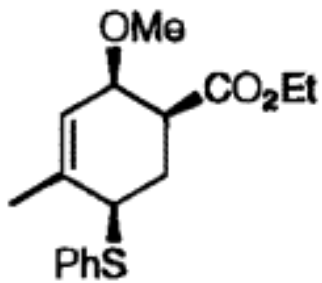
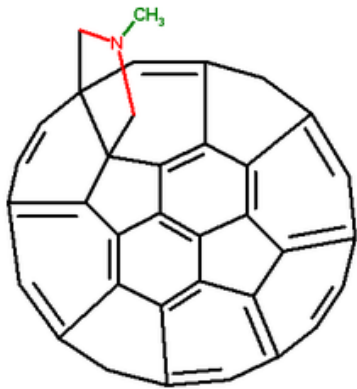


Nazarov cyclization



**Riassunto delle reazioni pericicliche
prese in considerazione**

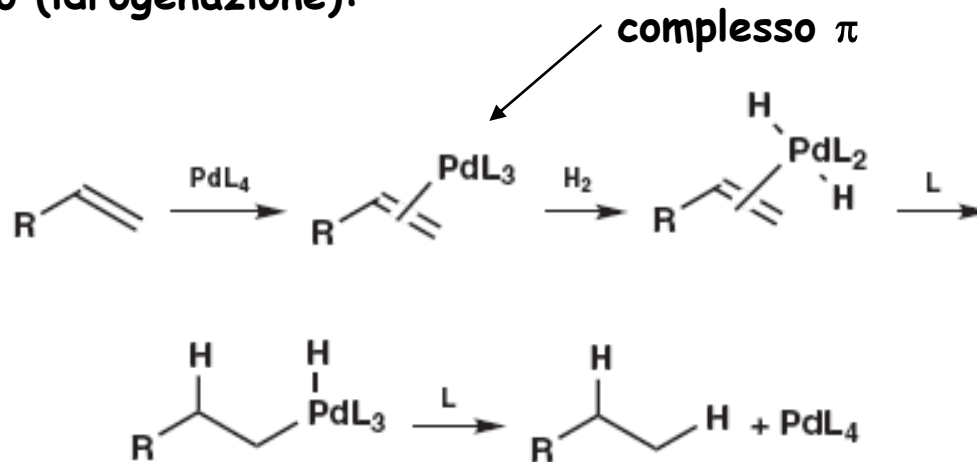
Proporre disconnessioni per i seguenti composti:



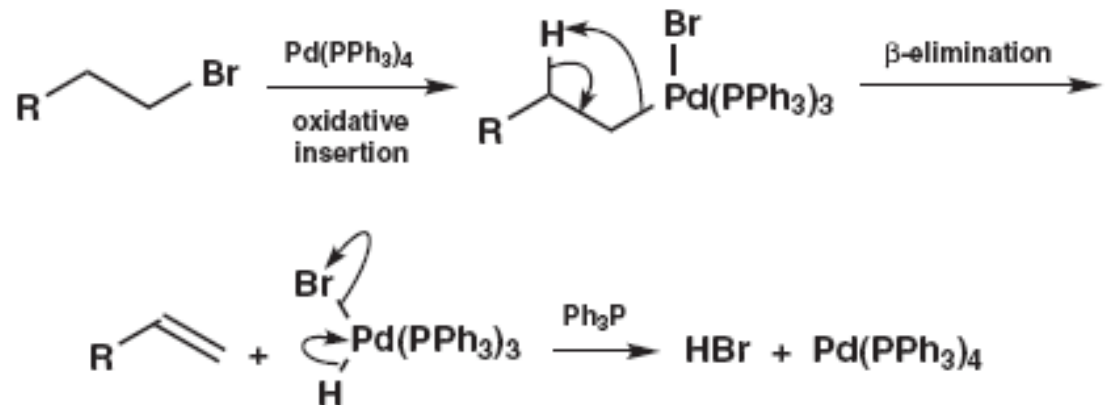
ALTRI MODI DI FORMAZIONE DEL LEGAME C-C

COMPLESSI σ e π DEL PALLADIO

esempio noto (idrogenazione):

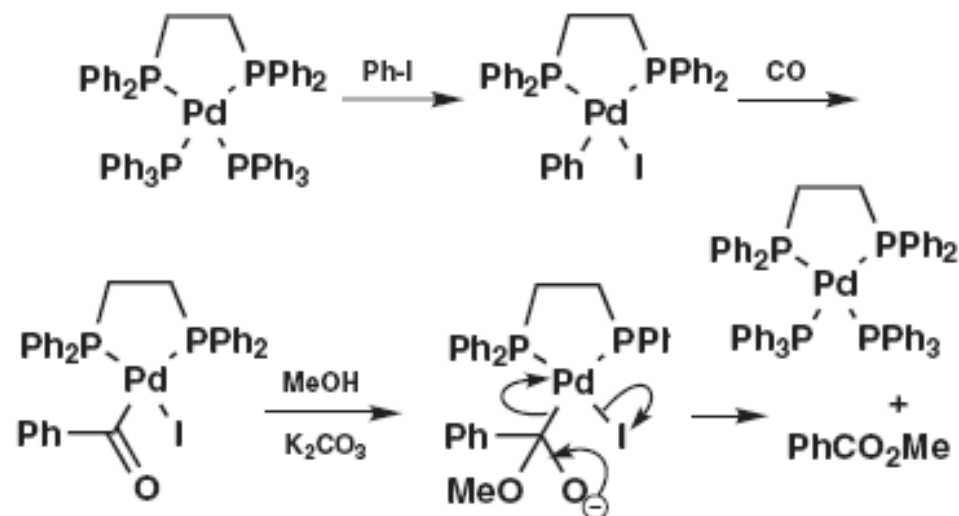


la ragione è che vi può essere β eliminazione!

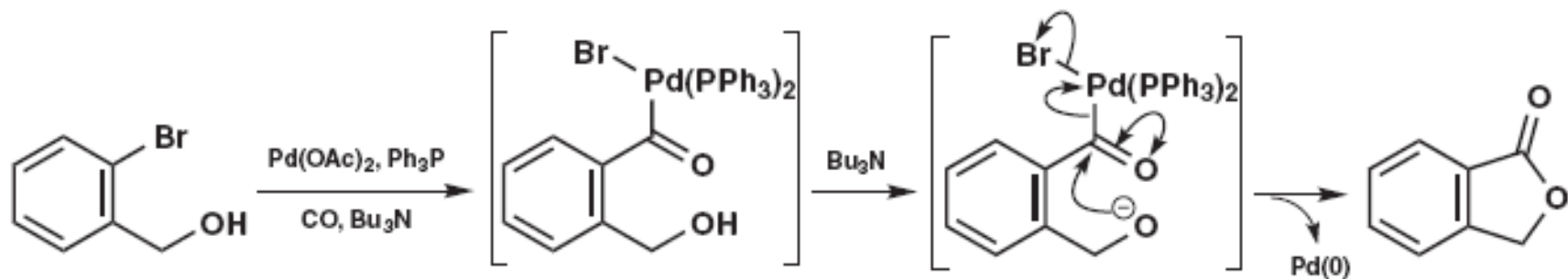


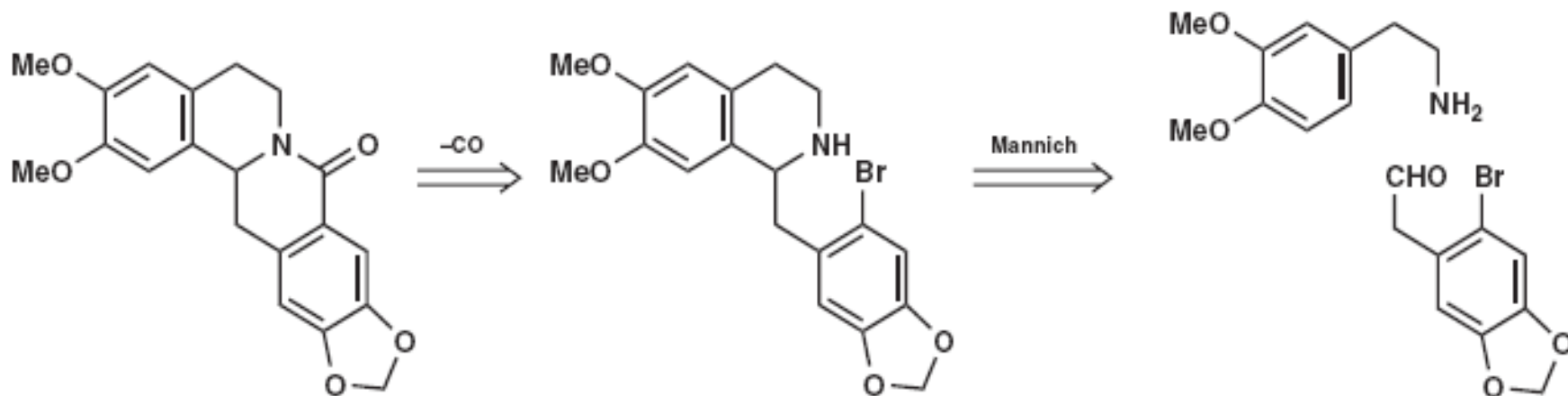
COMPLESSI σ DEL PALLADIO SI POSSONO OTTENERE CON ArX , CH_3X E CON DERIVATI ALCHILICI PRIVI DI H IN POSIZIONE β

POSSONO REAGIRE CON C_{sp^2} - ESEMPI:

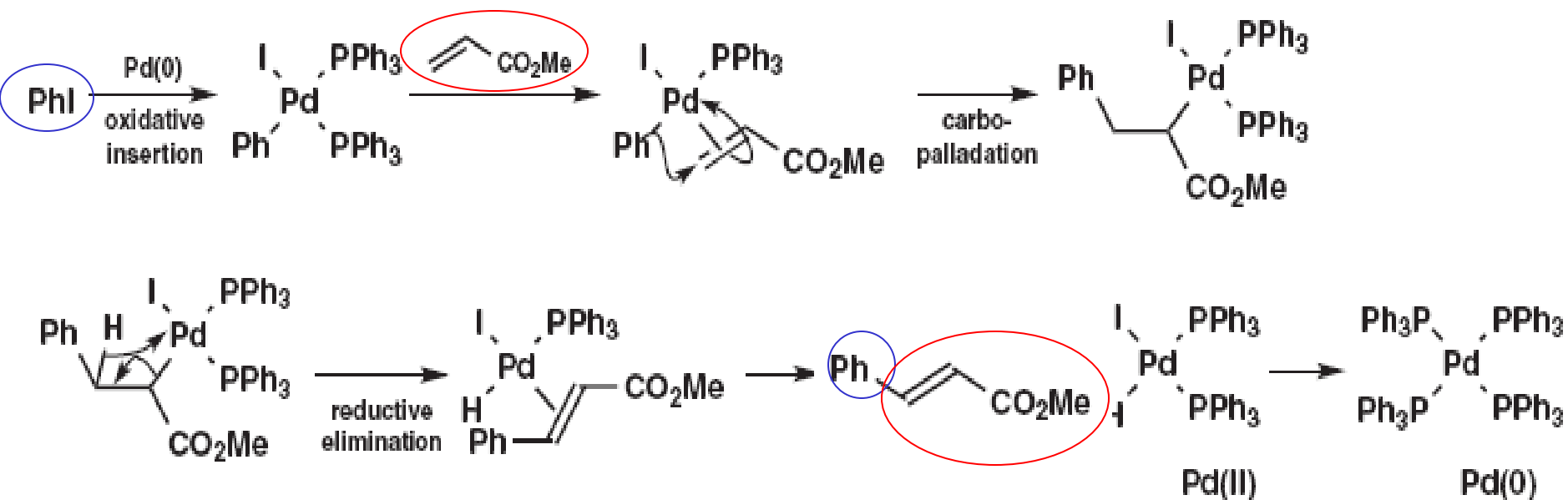


Carbonilazione seguita da formazione dell'estere





Possono reagire con alcheni:

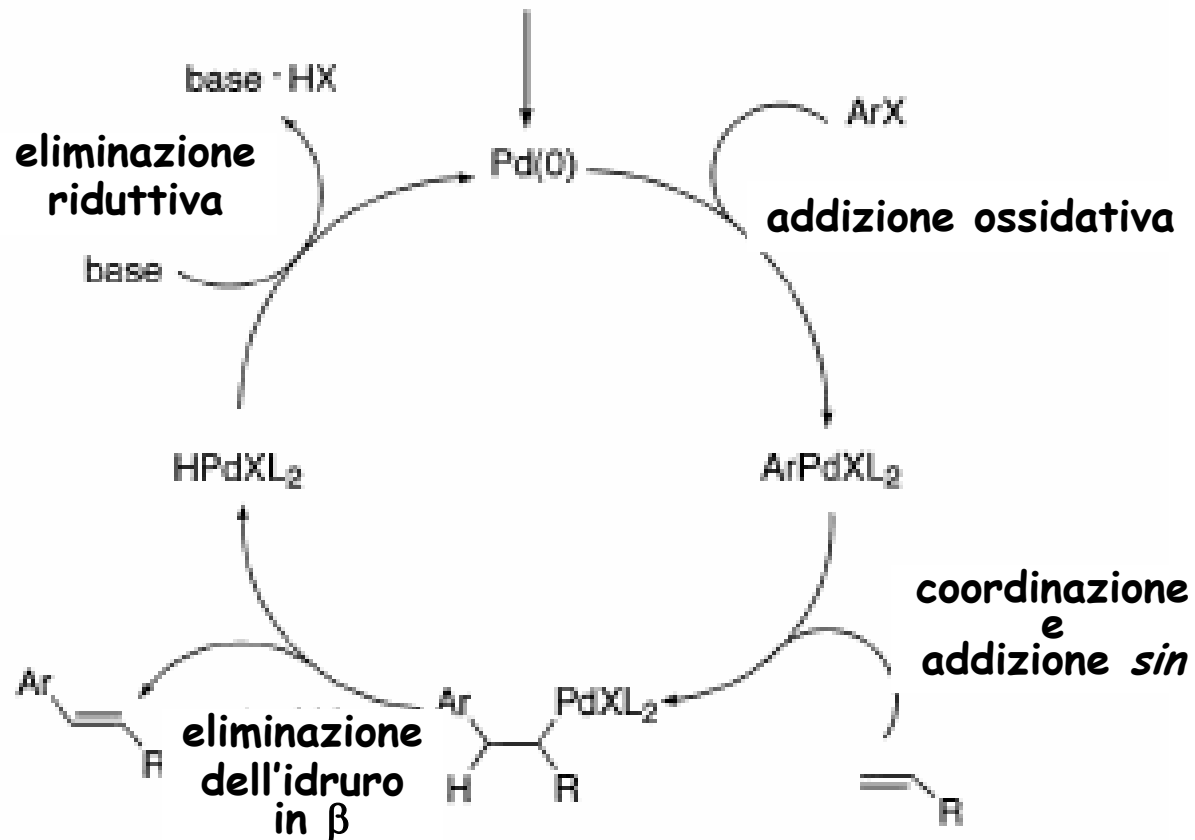


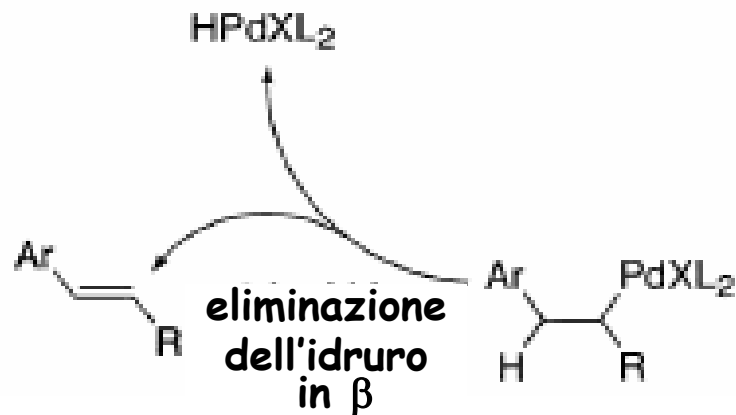
QUESTA REAZIONE E' NOTA COME REAZIONE DI HECK

Heck Reaction

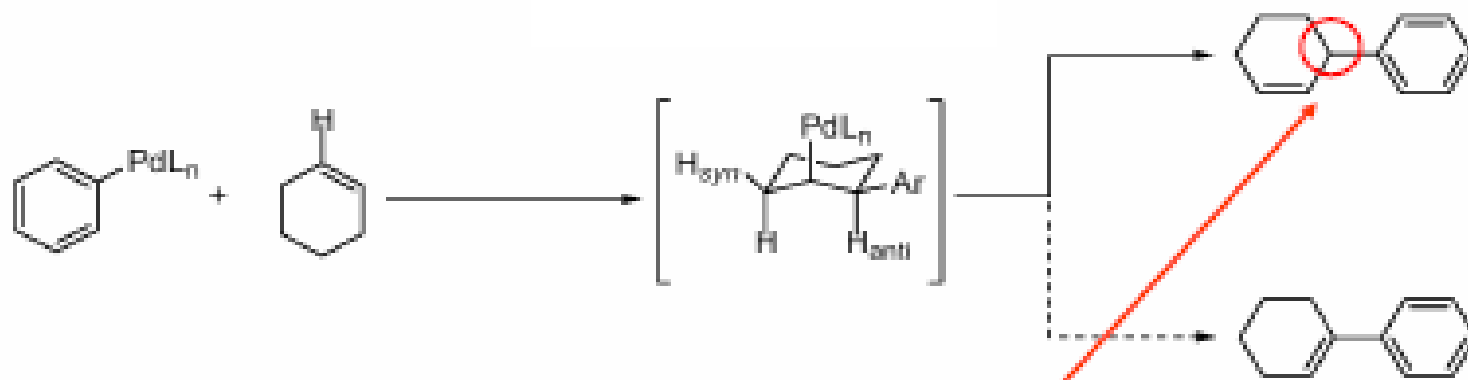


Precatalizzatore
Pd(0) o Pd(II)



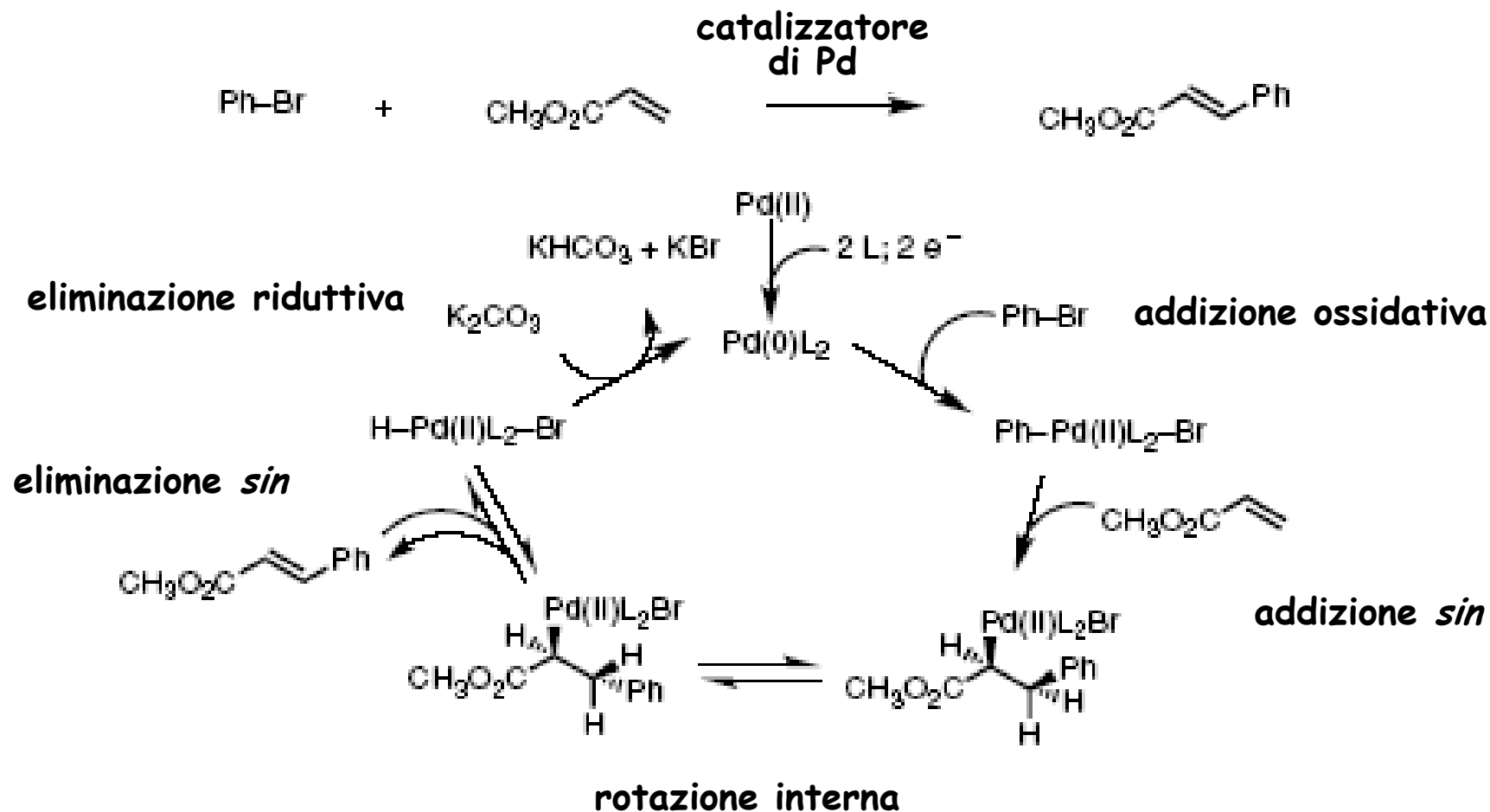


l'eliminazione dell'idruro in β avviene in sin rispetto al Pd

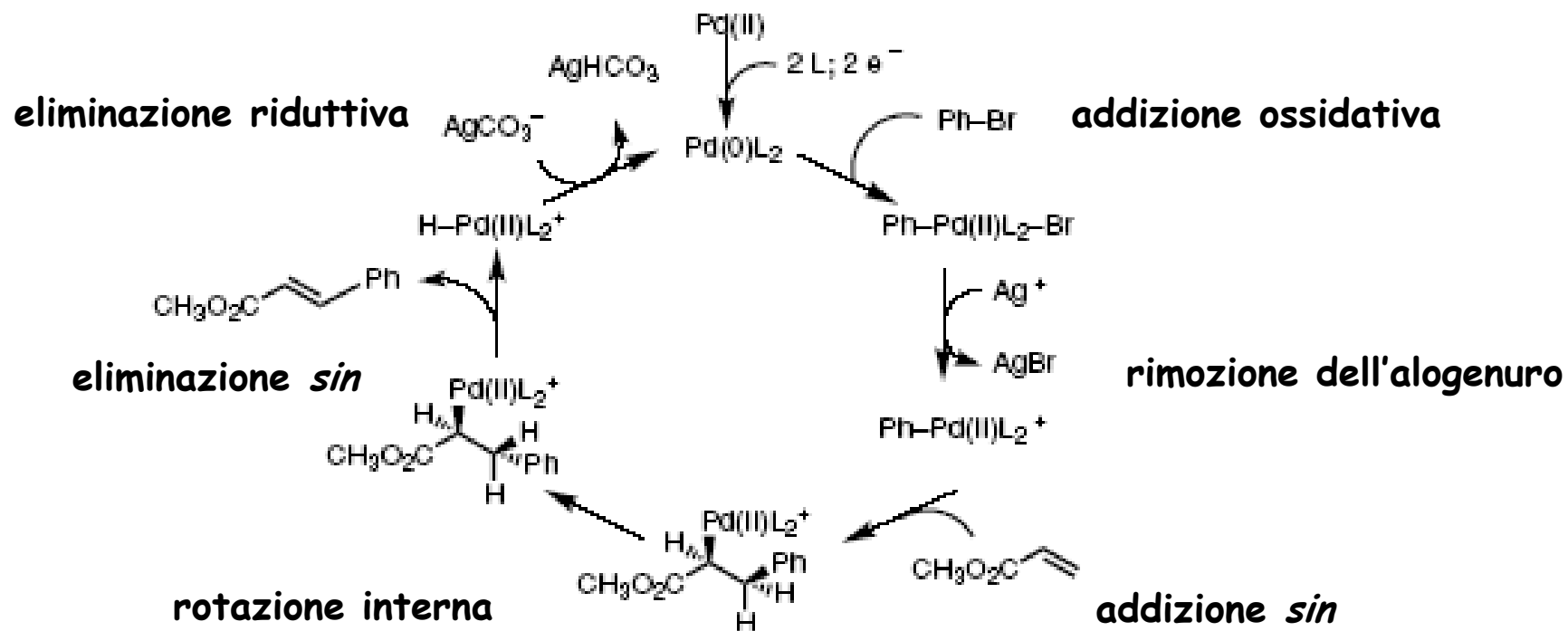


la cosa è rilevante in quanto si forma uno stereocentro

Pd neutro...

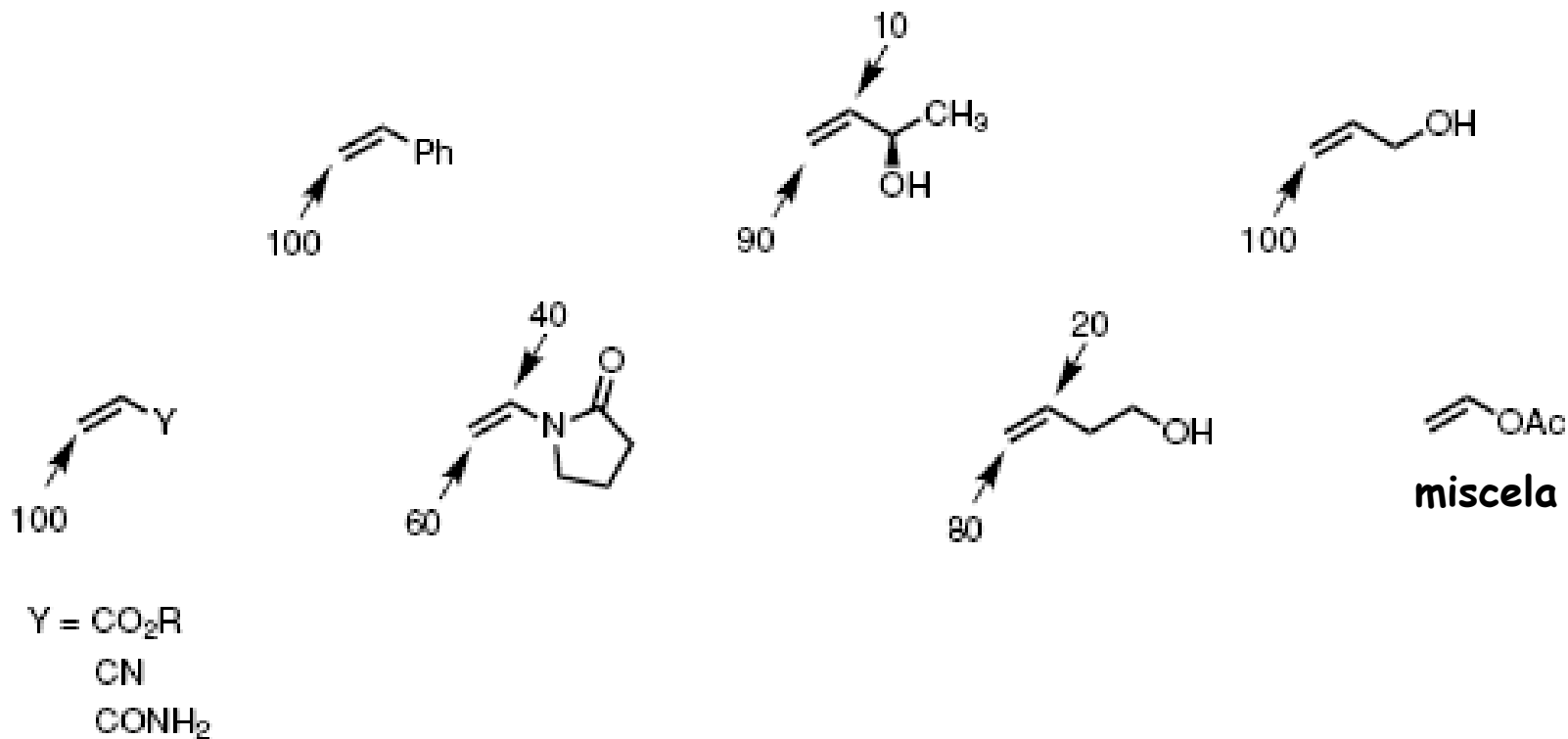


Pd cationico...



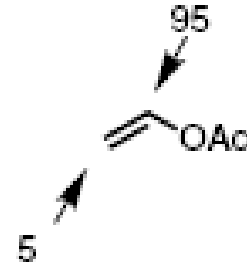
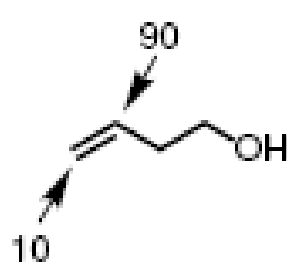
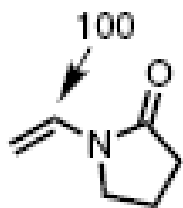
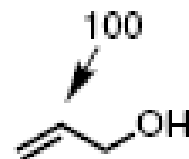
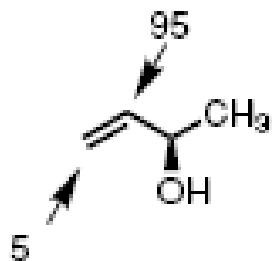
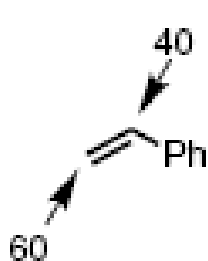
Regiochimica dell'addizione:

Con catalizzatori di Pd "neutri" la regiochimica è controllata da ragioni steriche



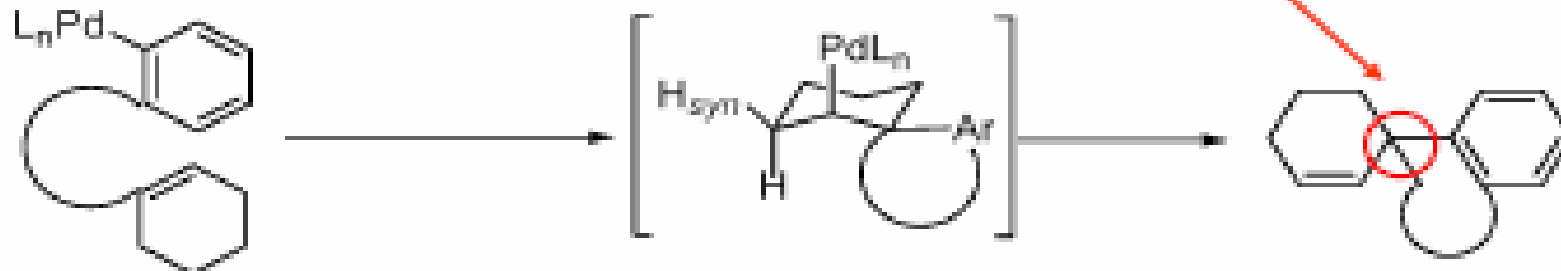
La freccia indica dove si lega Ar(%)

Con Pd "cationico" la regiochimica è influenzata da ragioni elettroniche, Il complesso cationico aumenta la polarizzazione dell'alchene favorendo il trasferimento del gruppo Ar (o vinile) al sito di minor densità elettronica.



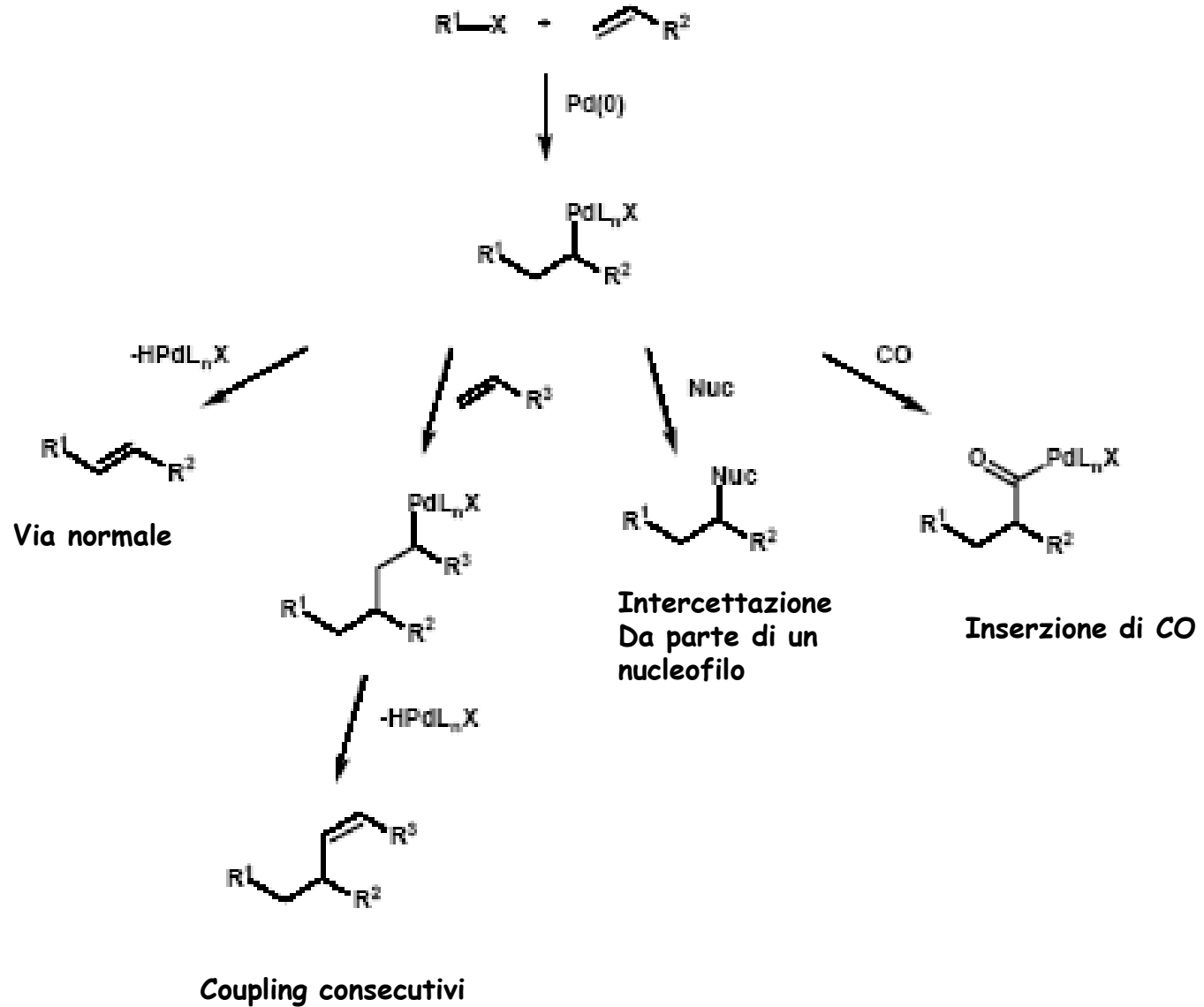
Y = CO_2R
CN
 CONH_2

Se i due reagenti appartengono alla stessa molecola la reazione diviene **INTRAMOLECOLARE** dando luogo ad un **C quaternario**.

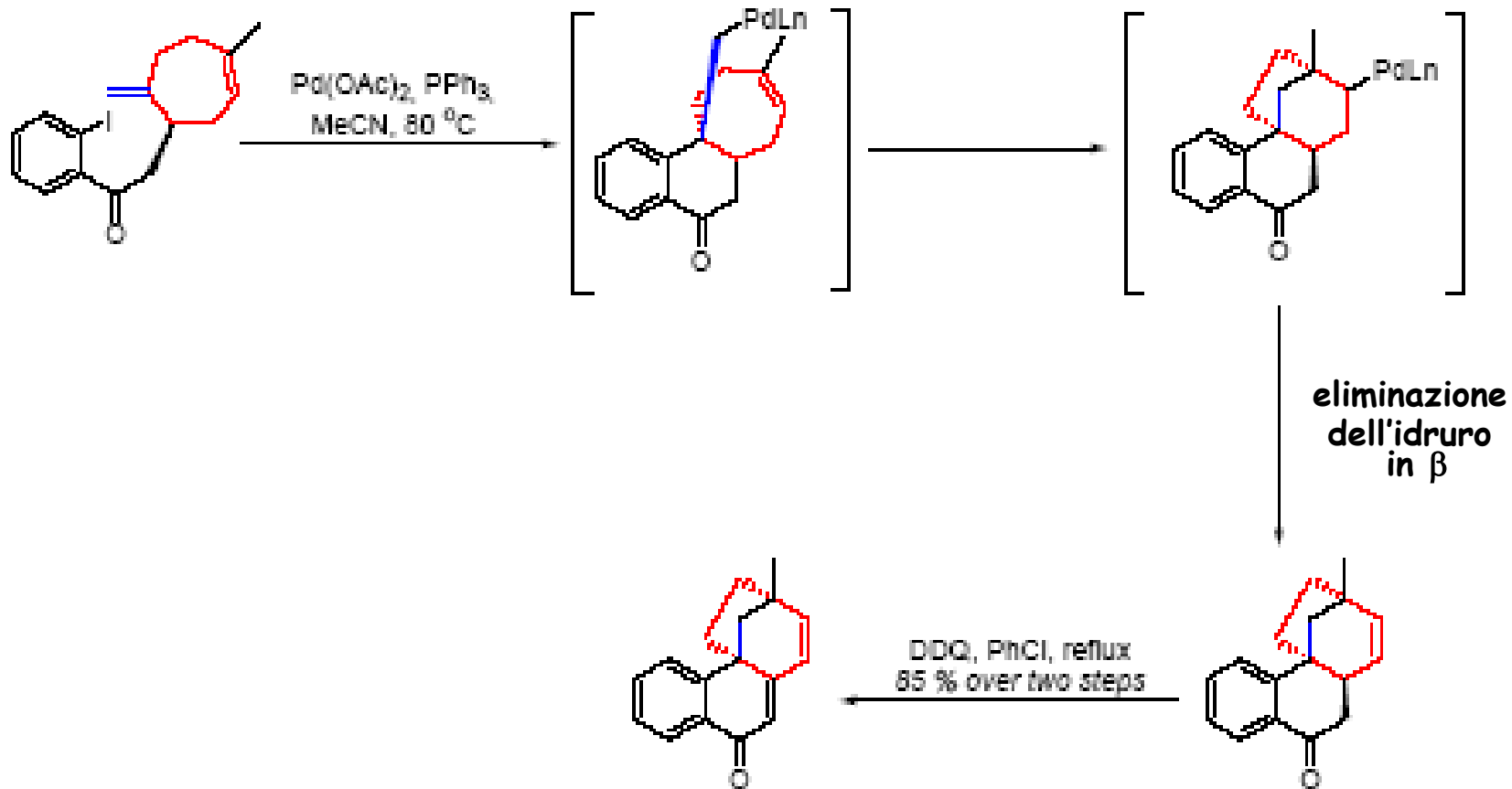


Si noti: sempre eliminazione sin!

REAZIONI DI HECK: ALTERNATIVE ALL'ELIMINAZIONE



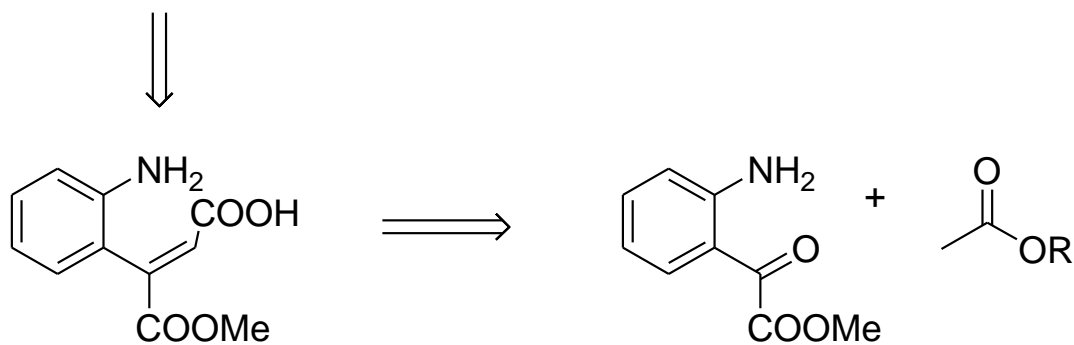
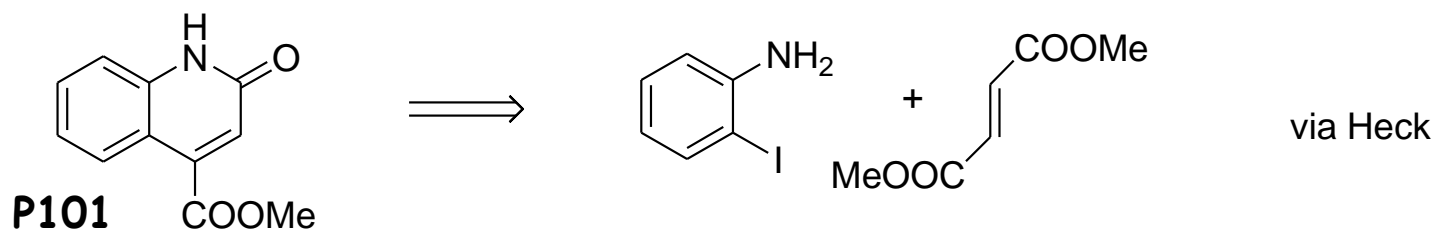
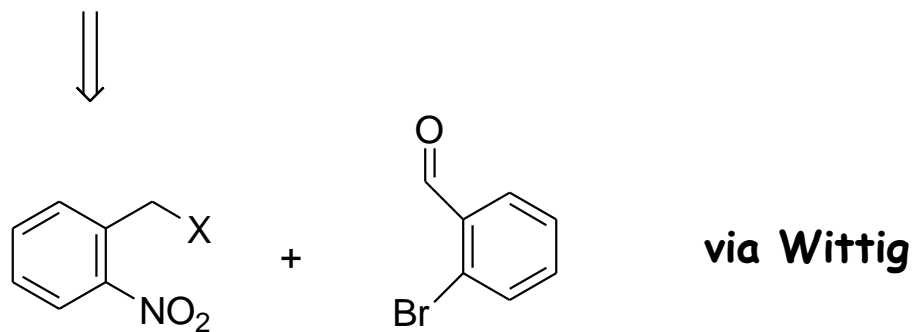
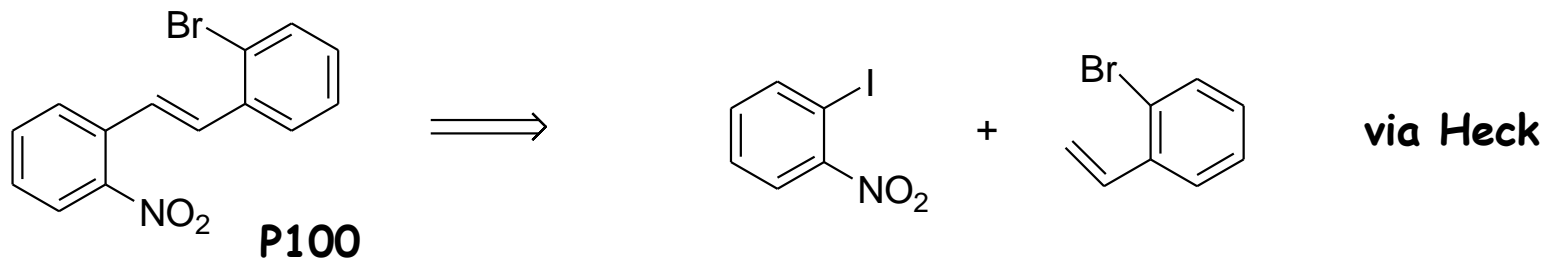
ESEMPIO DI REAZIONI DI HECK CONSECUTIVE



eliminazione
dell'idruro
in β

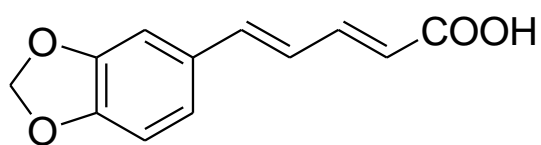
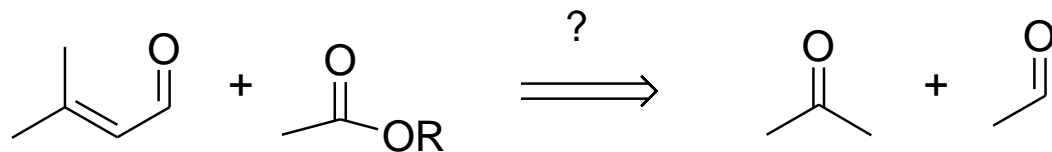
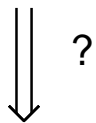
DDQ, PhCl, reflux
85 % over two steps

DDQ=2,3-dicloro-5,6-dicianobenzochinone

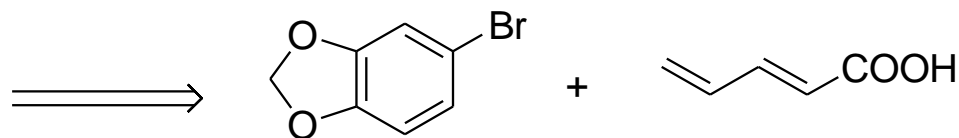




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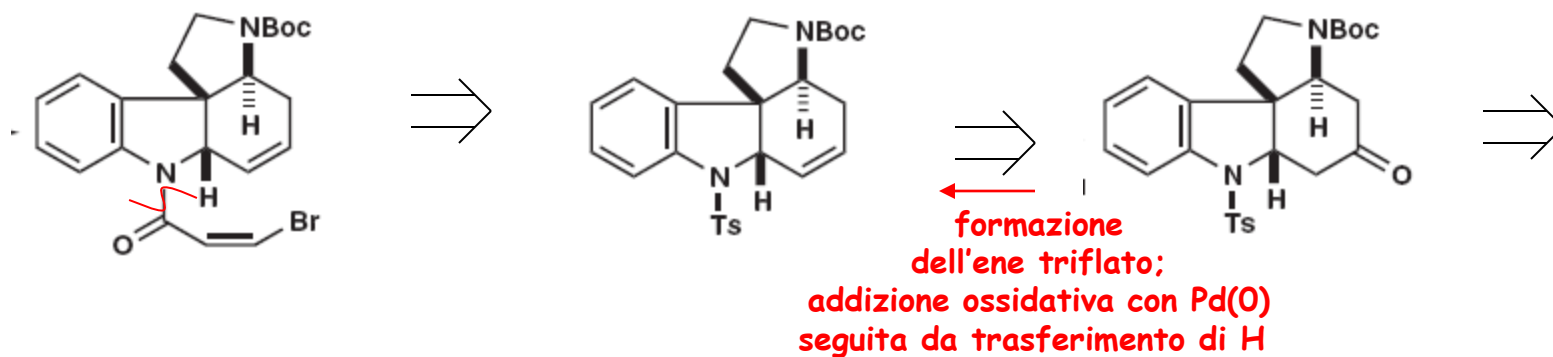
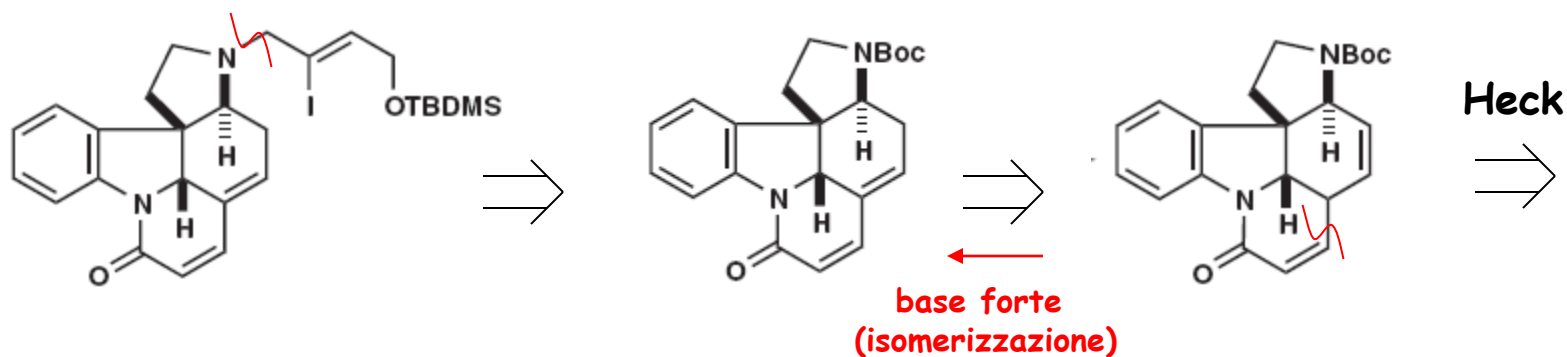
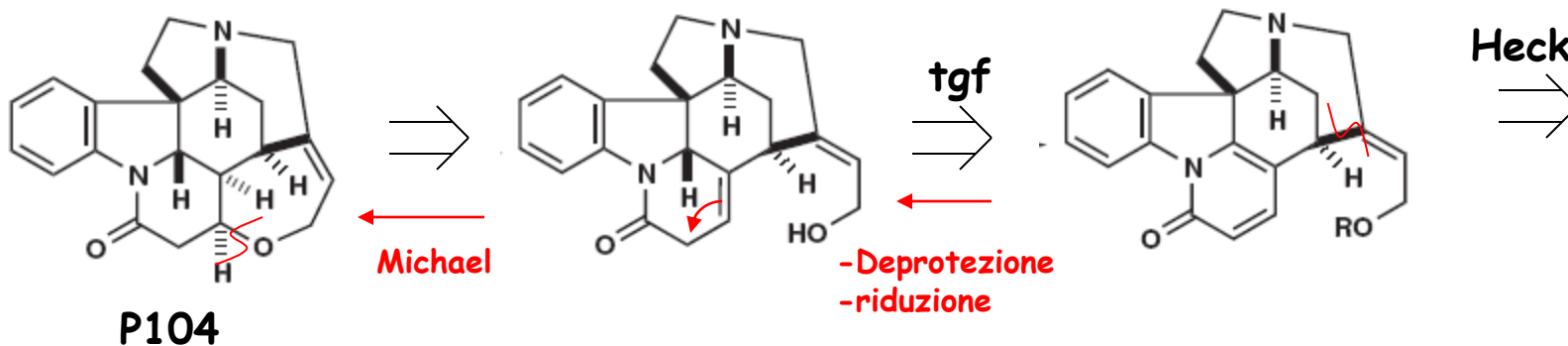


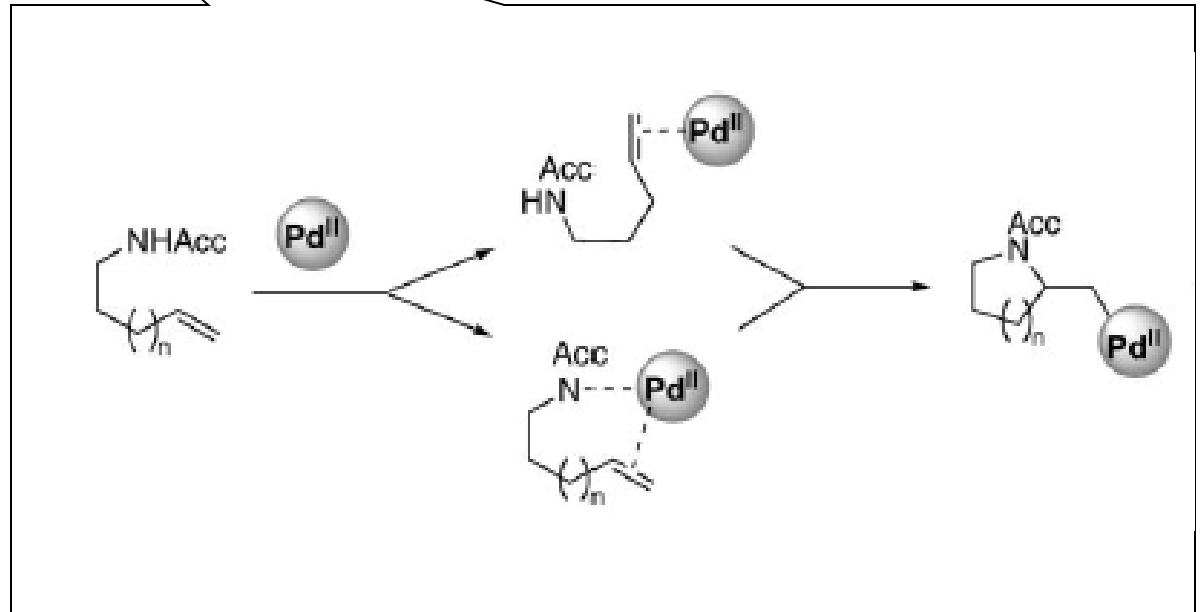
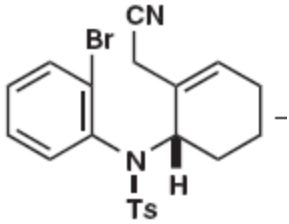
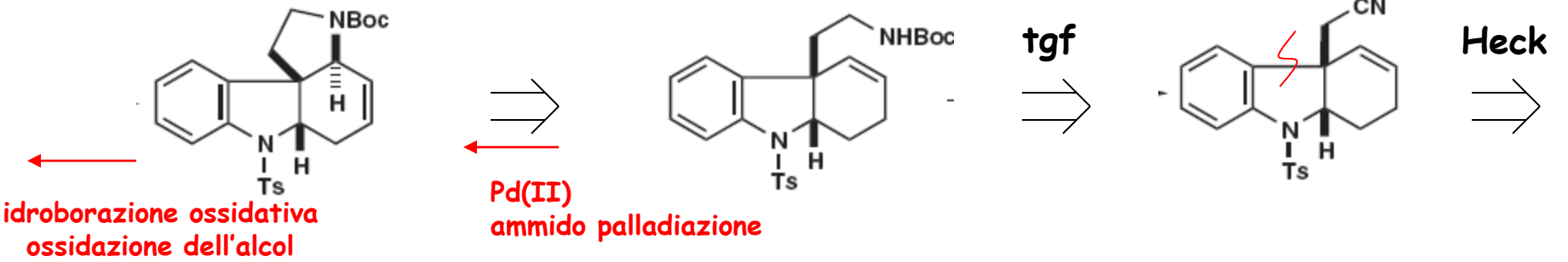
P103



v. P102

Retrosintesi della STRICNINA (Vedi: Nakanishi, Mori Angew. Chem. 2002, 41, 1934)





ALTRE REAZIONI DI CROSS-COUPLING



- ➔ R1 e R2 sono normalmente atomi di carbonio sp² o sp (anche se sono recentemente state introdotte varianti che impiegano C sp³)
- ➔ X è un gruppo uscente elettronattrattore. Si possono usare gruppi diversi ma i più usati sono alogenuri o triflati
- ➔ Il tipo di M (metallo) determina il tipo di accoppiamento

Kumada
M = MgX
Catalyst = Ni(0) or Pd(0)

Suzuki
M = BR₃
Catalyst = Pd(0) + base

Negishi
M = ZnX
Catalyst = Pd(0)

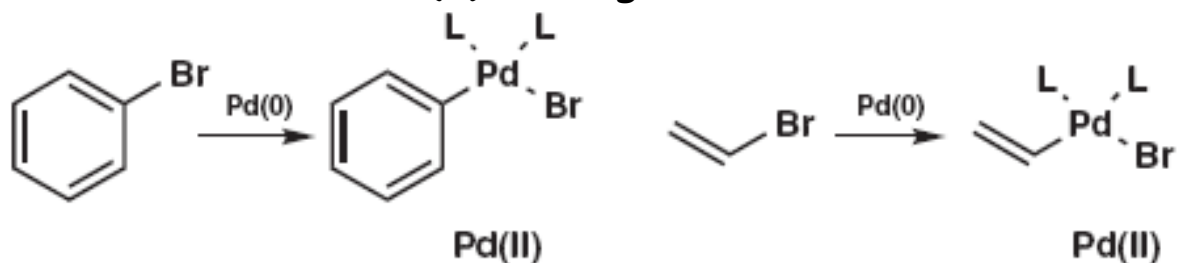
Stille
M = SnR₃
Catalyst = Ni(0) or Pd(0)

PASSAGGI CHE CARATTERIZZANO QUESTE REAZIONI

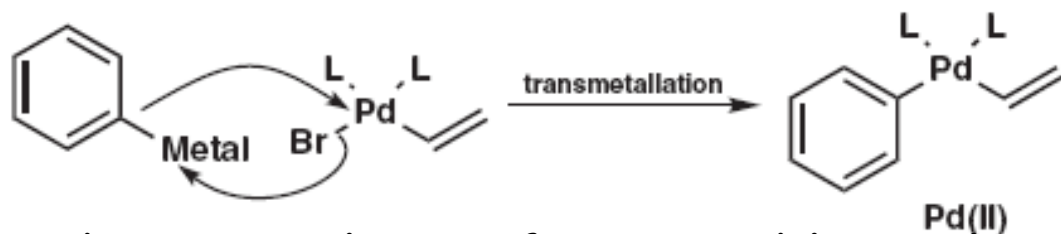
1. Preparazione del reagente organometallico



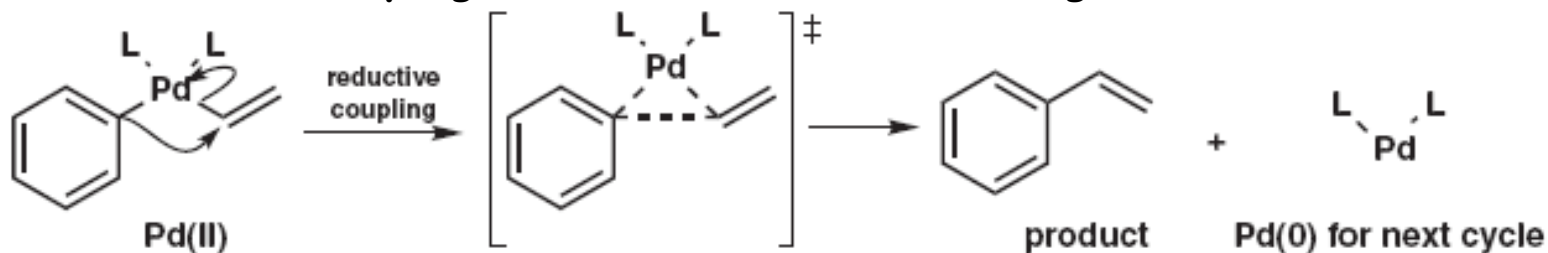
2. Addizione ossidativa di Pd(0) all'alogenuro vinilico o arilico



3. Reazione di transmetallazione



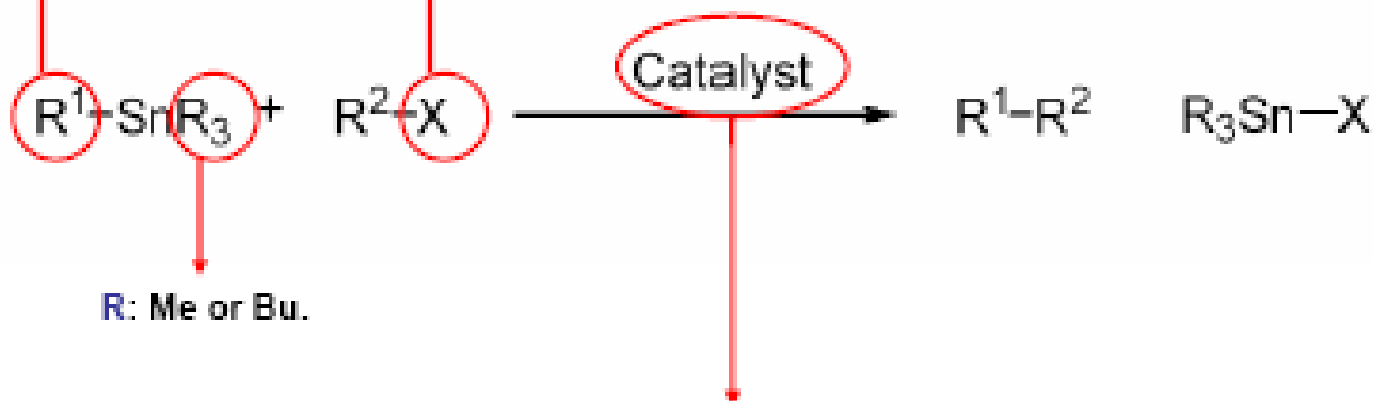
4. Reazione di cross-coupling con formazione del nuovo legame C-C e rilascio di Pd(0)



REAZIONE DI CROSS-COUPLING DI STILLE

R^1 or R^2 : Any
unsaturated functional
group

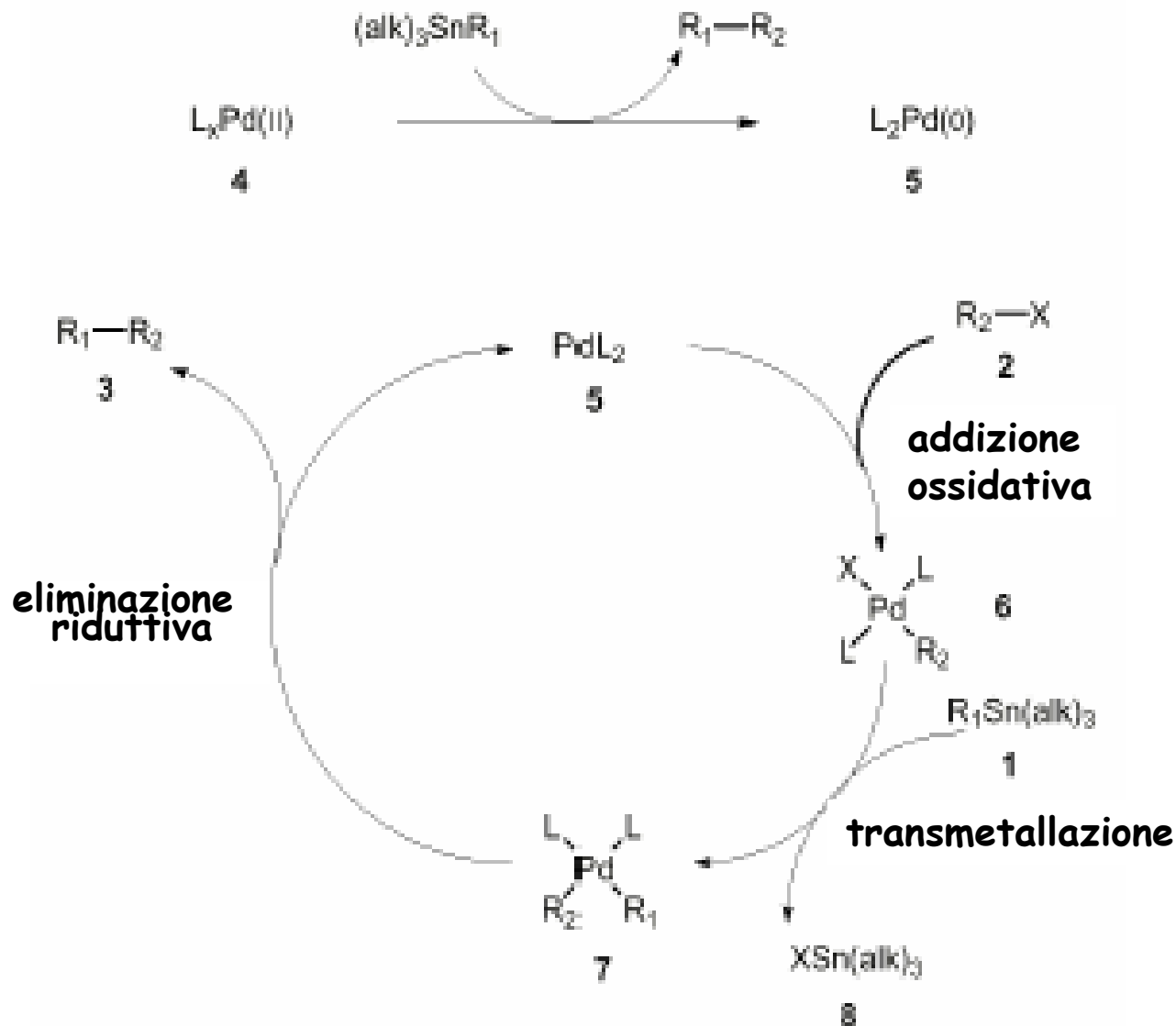
X : I, Br, OTf, ONf, OPO(OPh)₂, (Cl)
Reactivity: I > Br ~ Nf, Tf >>> Cl



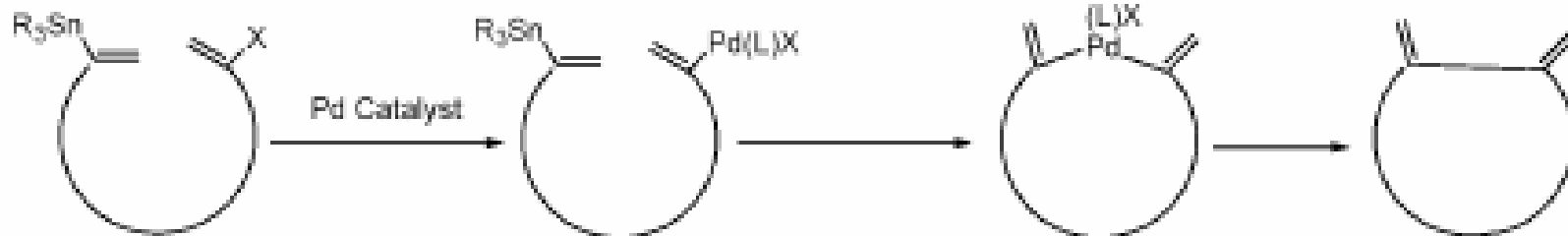
R: Me or Bu.

Catalyst: Palladium Source: Pd(PPh₃)₄, Pd₂(dba)₃, Pd(OAc)₂, PdCl₂(PPh₃)₂, PdCl₂(PhCN)₂, PdCl₂(MeCN)₂. Various other ligands can be added, including other additives that influence the reactivity of various partners.

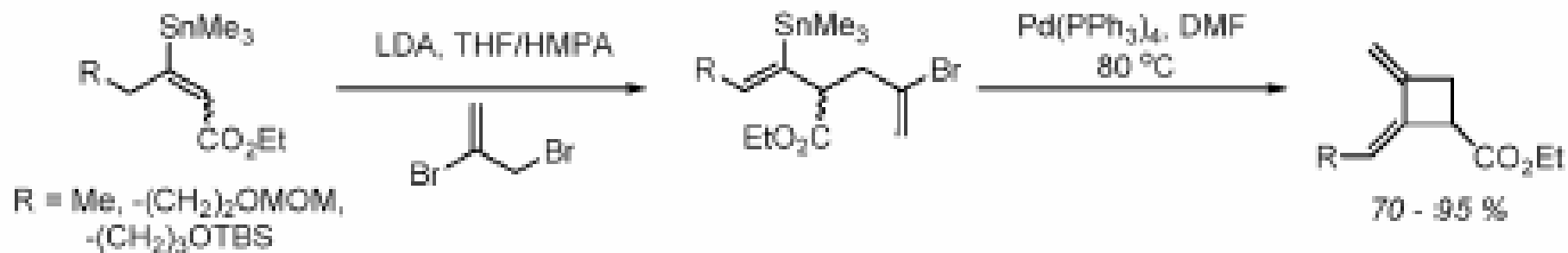
MECCANISMO GENERALE DELLA REAZIONE DI STILLE



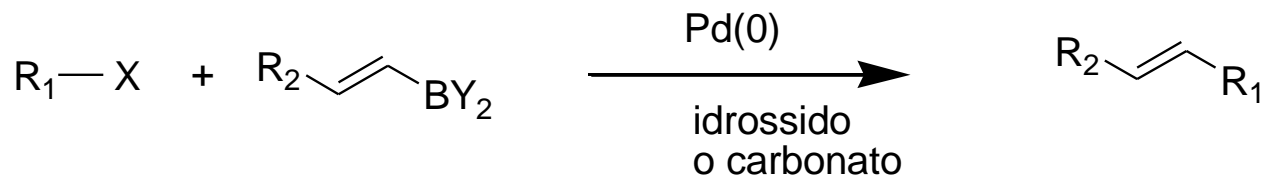
COUPLING DI STILLE INTRAMOLECOLARE



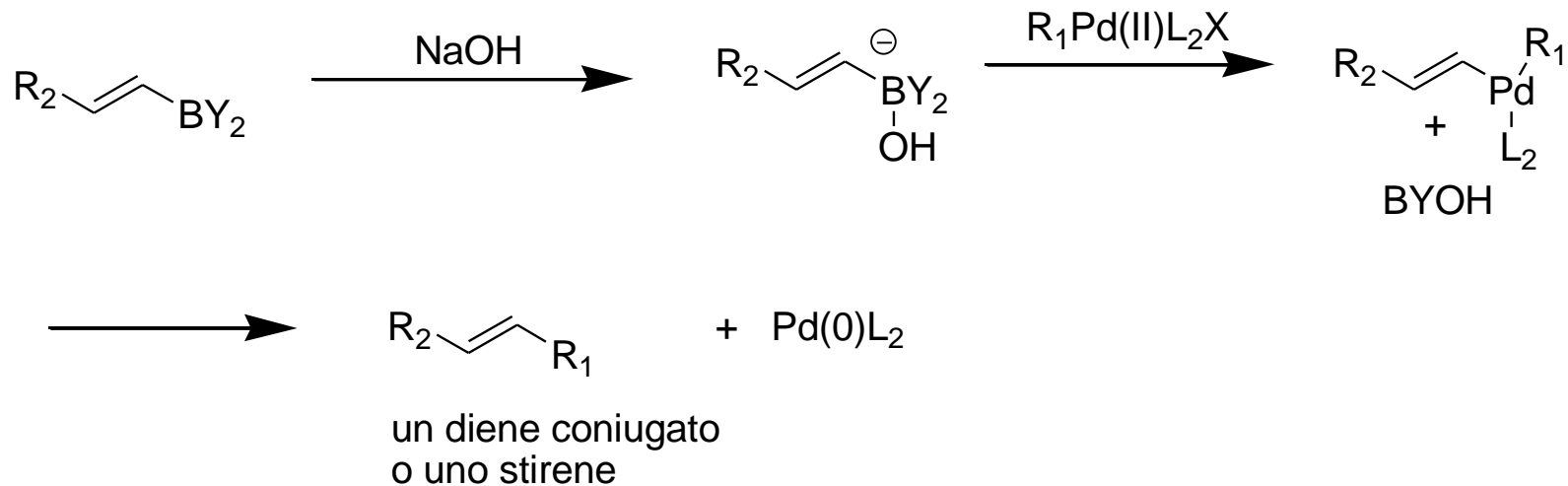
...PERMETTE ANCHE LA FORMAZIONE DI ANELLI A 4 MEMBRI



REAZIONE DI COUPLING DI SUZUKI

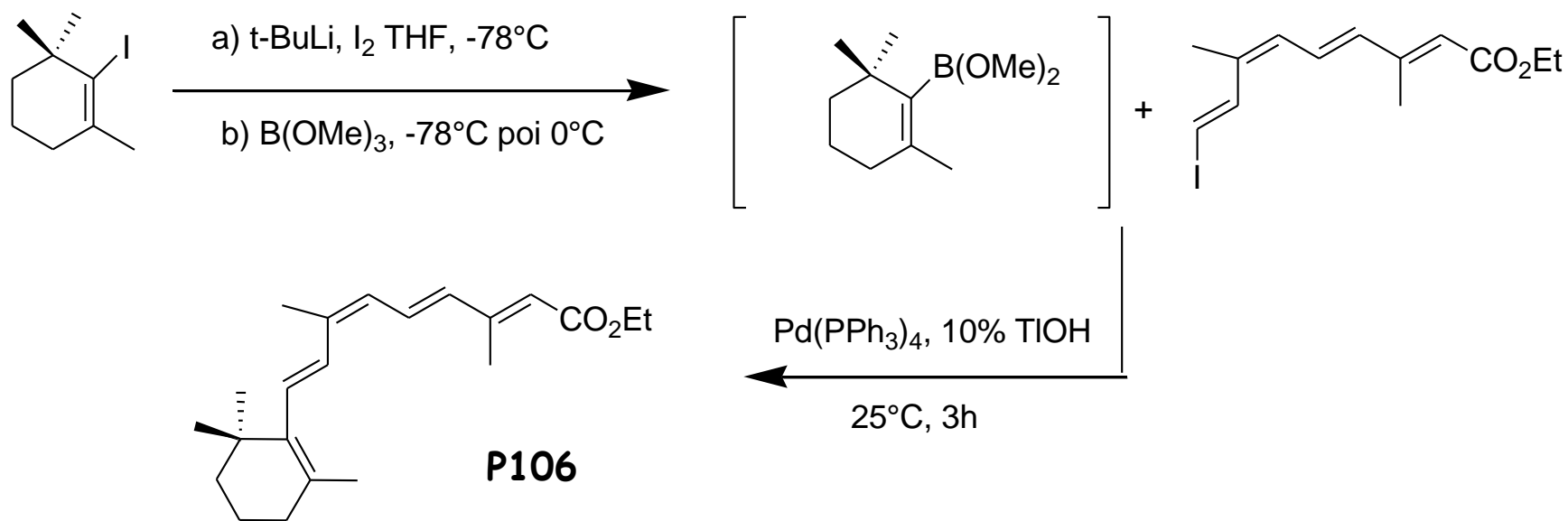
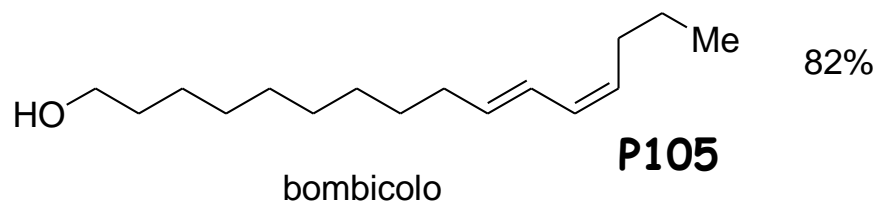
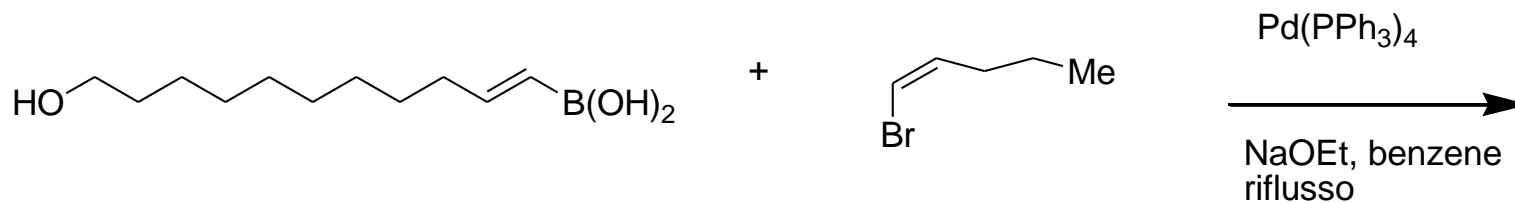


R₁: alchenile, arile o allile; X: alogeno

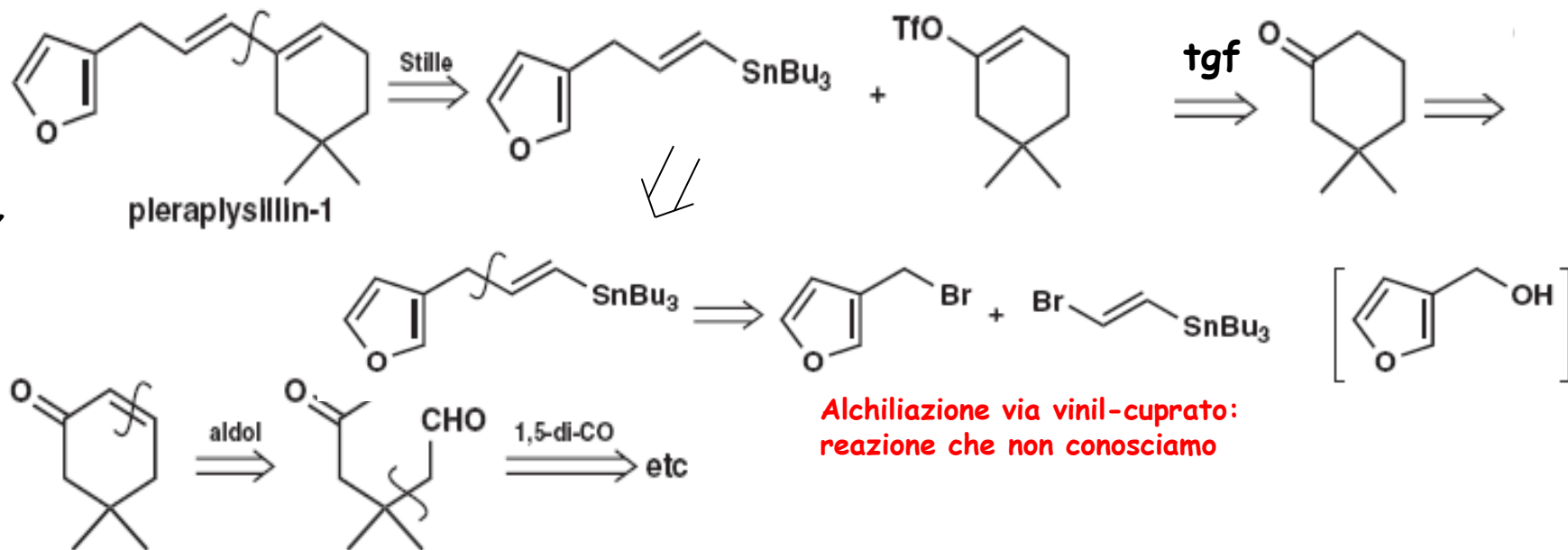


Il legame C-B è particolarmente forte: 100 kcal mol⁻¹

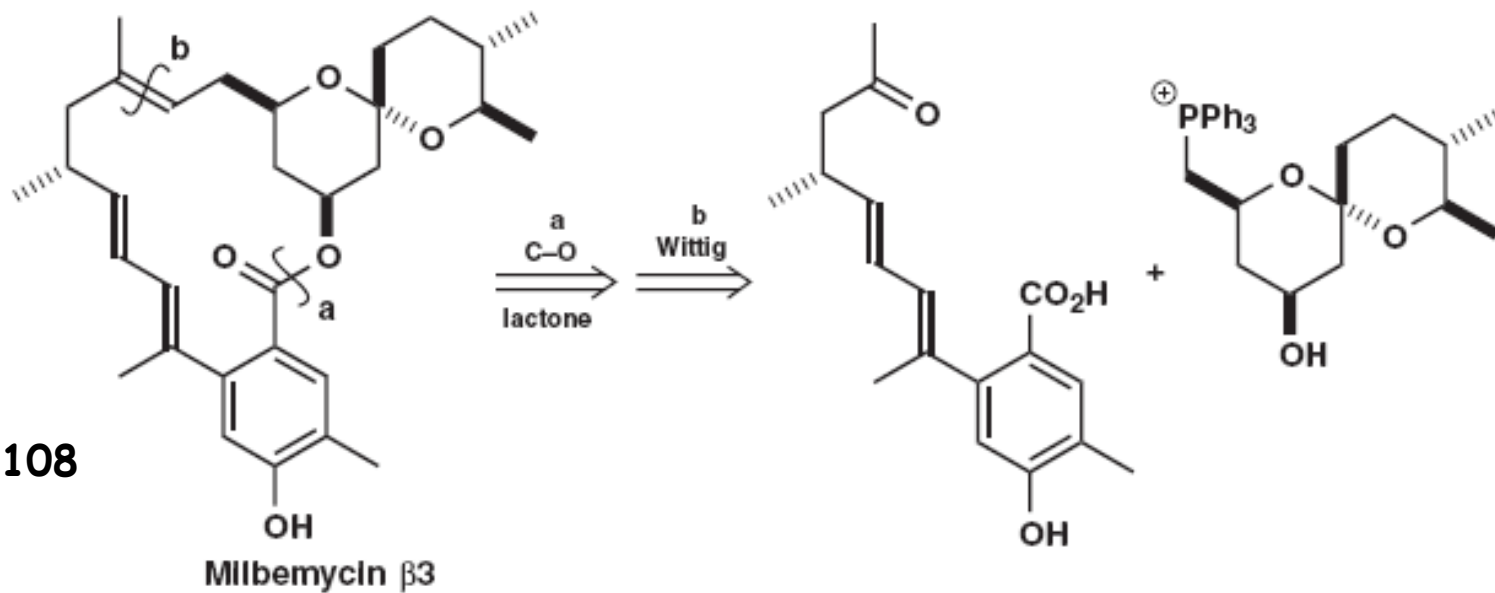
ESEMPI DI COUPLING DI SUZUKI

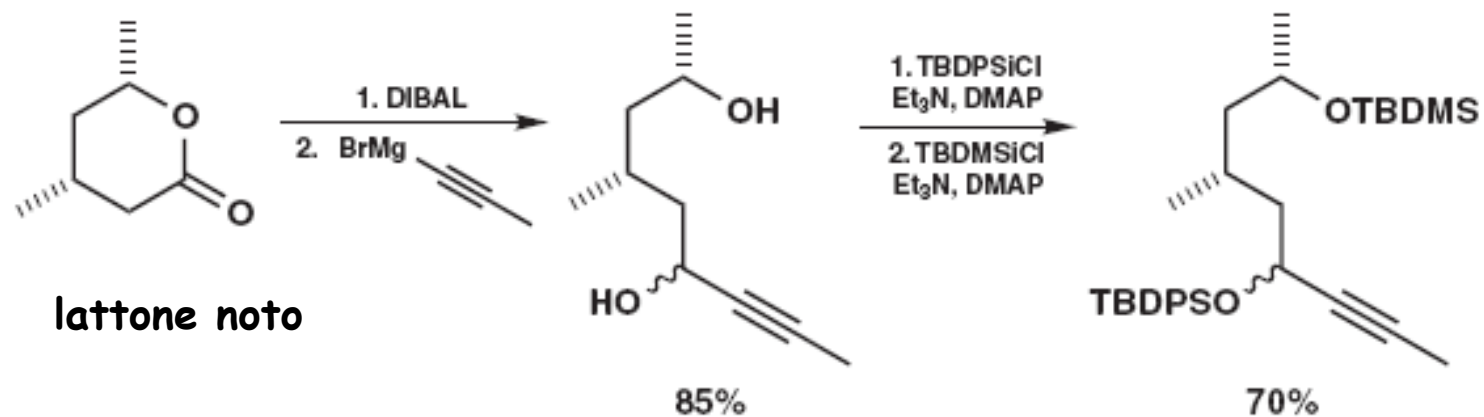
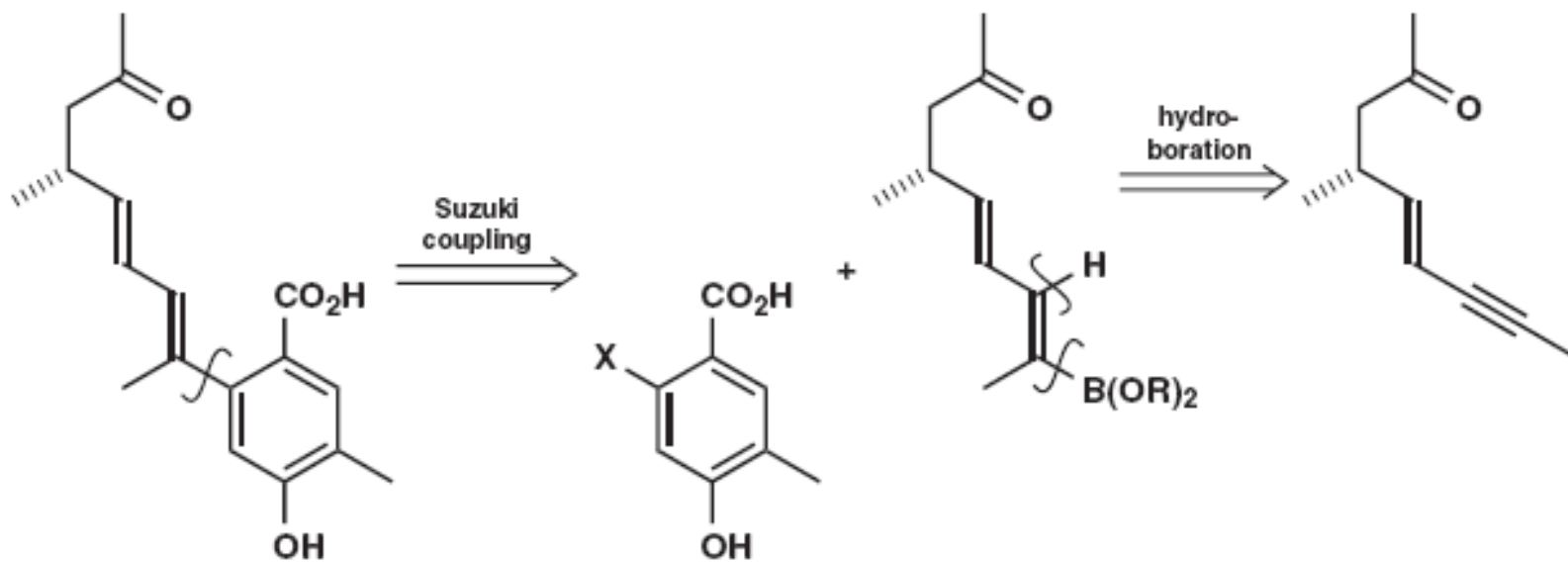


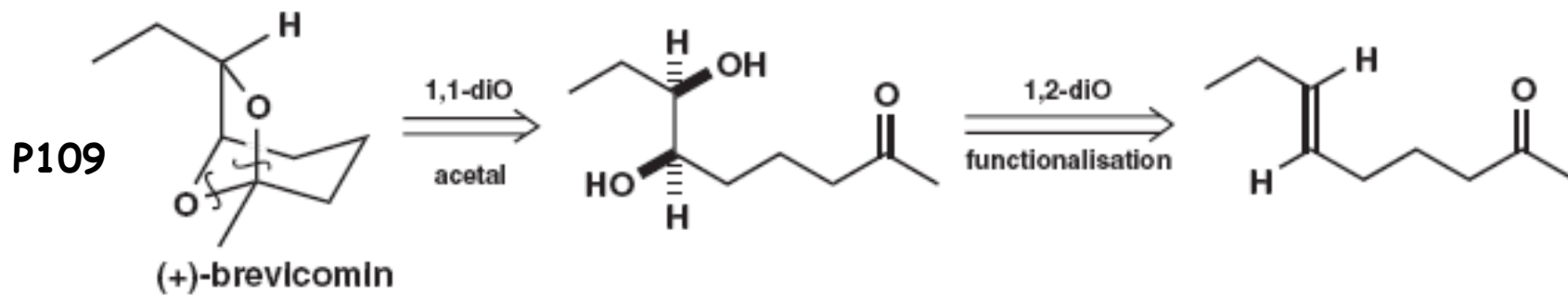
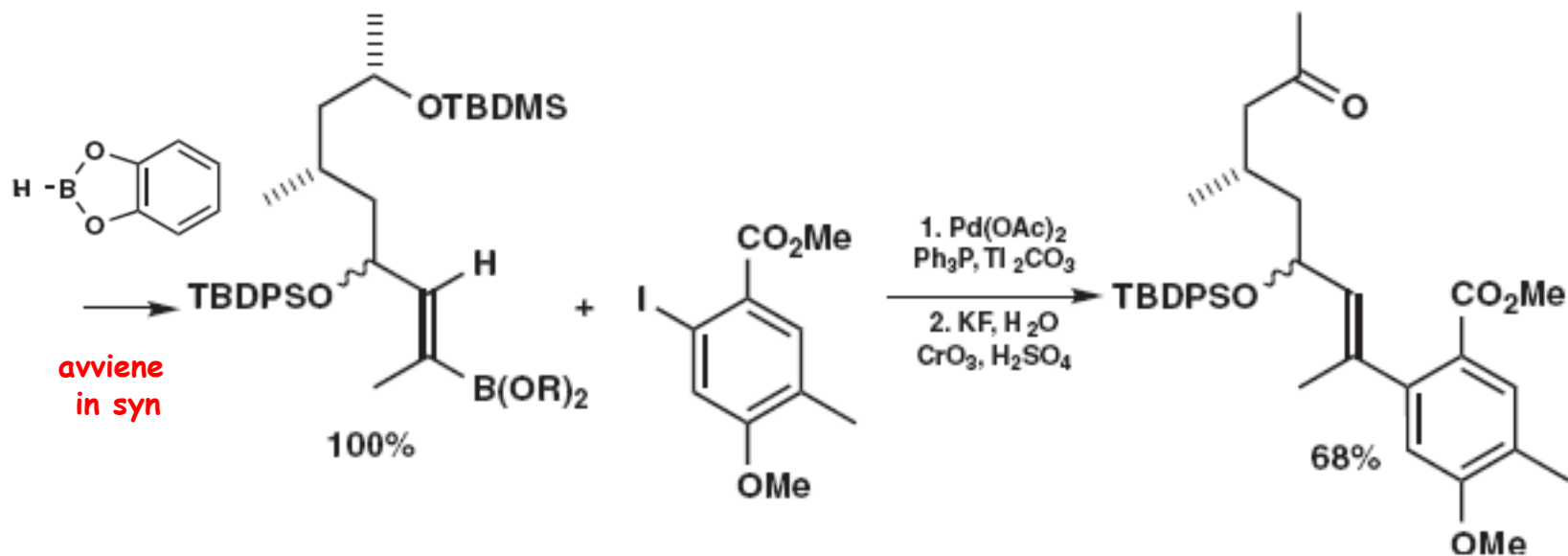
P107

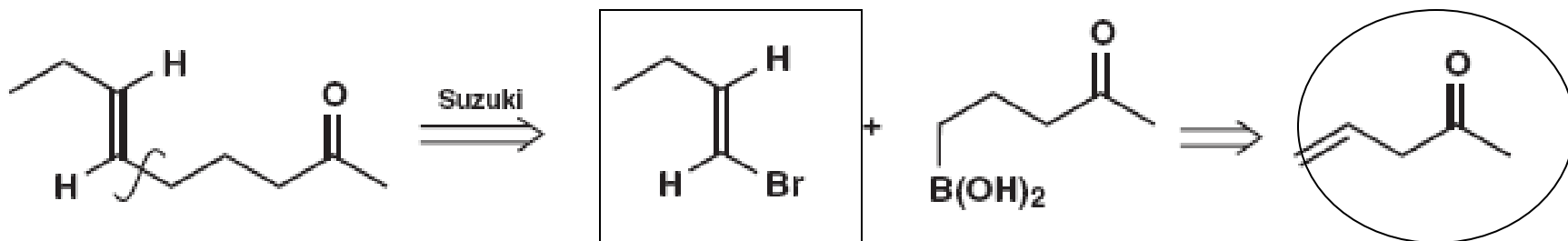


P108

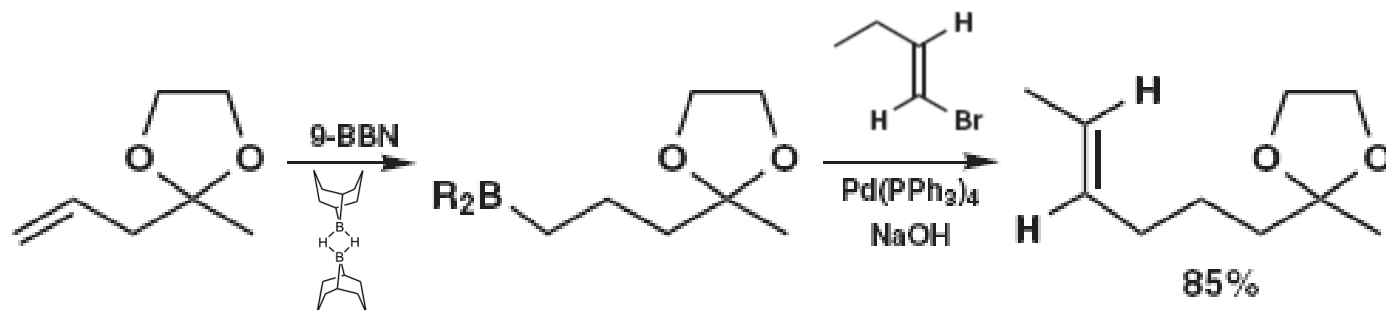
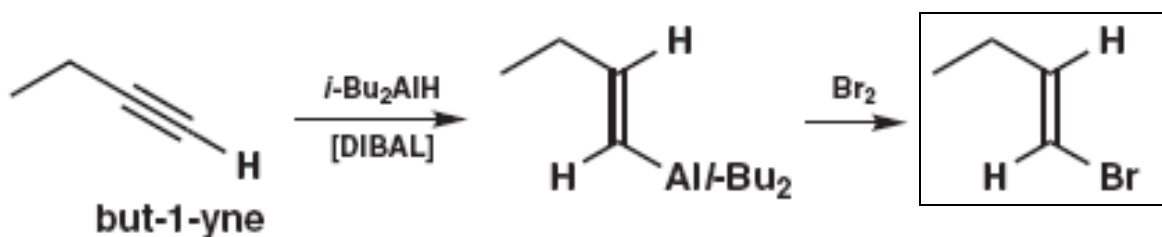
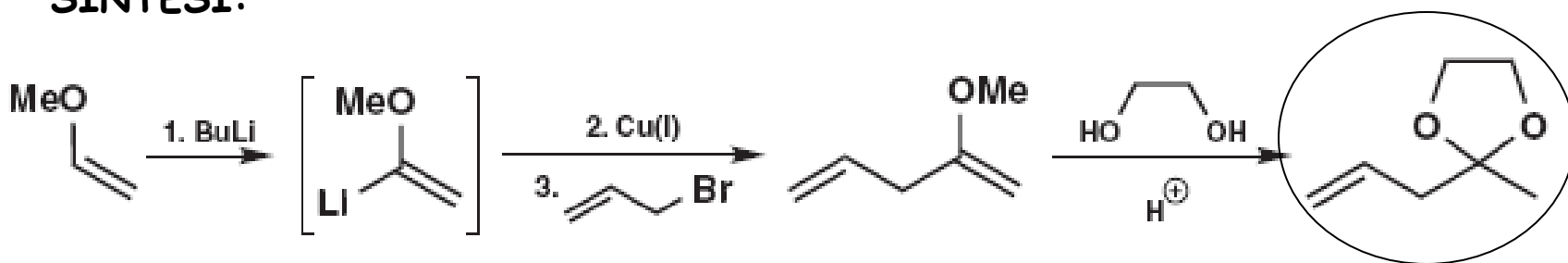


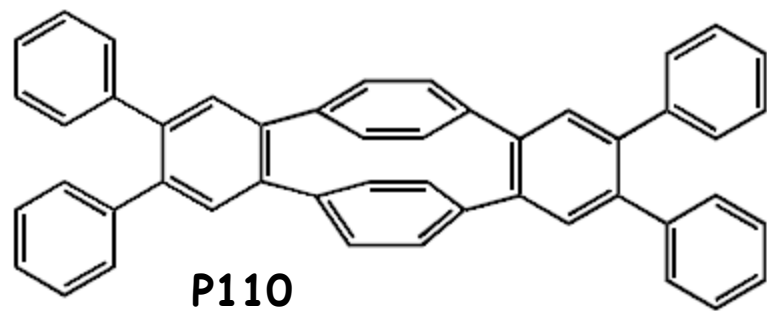
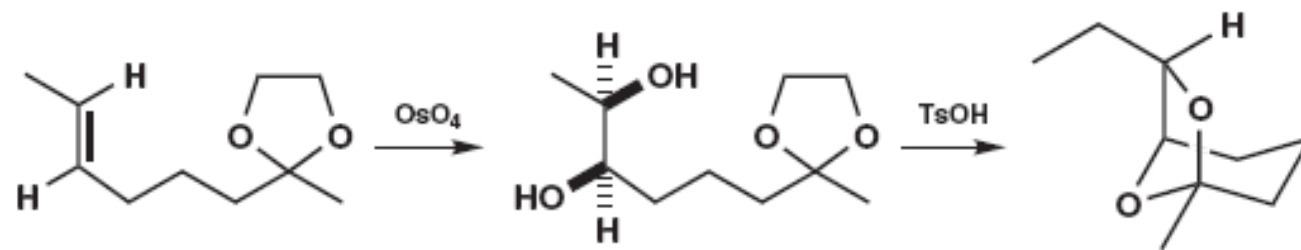




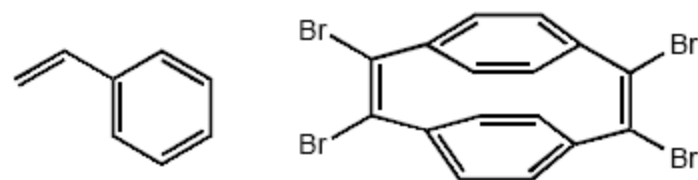
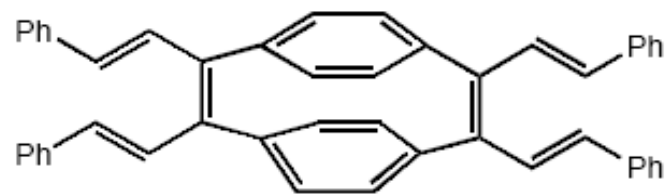


SINTESI:





Angew. Chem. Int. Ed. Engl. **1994**, 33, 2379

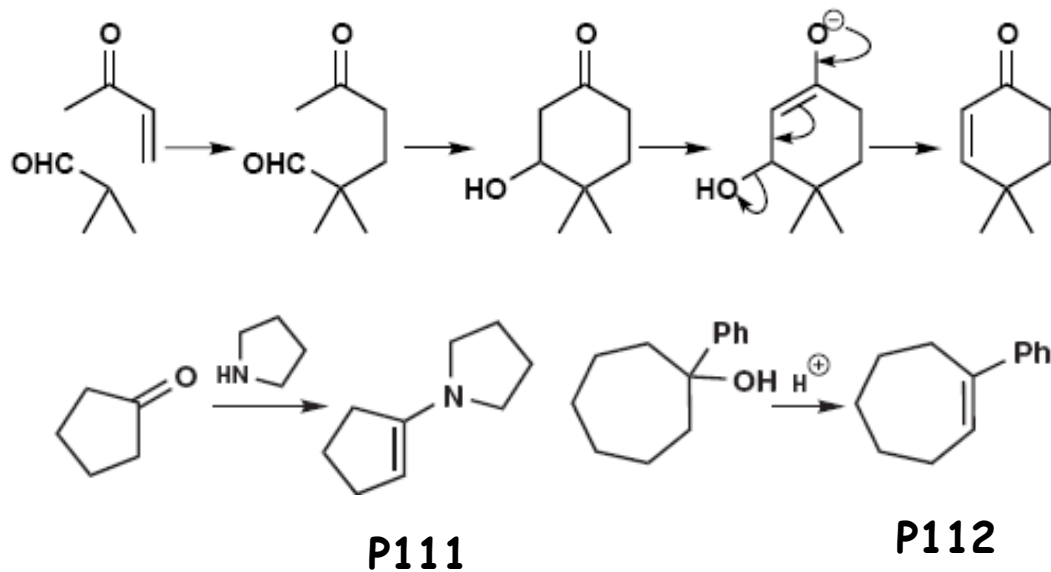


CONTROLLO DELLA STEREOCHIMICA NELLA FORMAZIONE DI DOPPI LEGAMI

Nella formazione di alcheni si possono distinguere i seguenti casi:

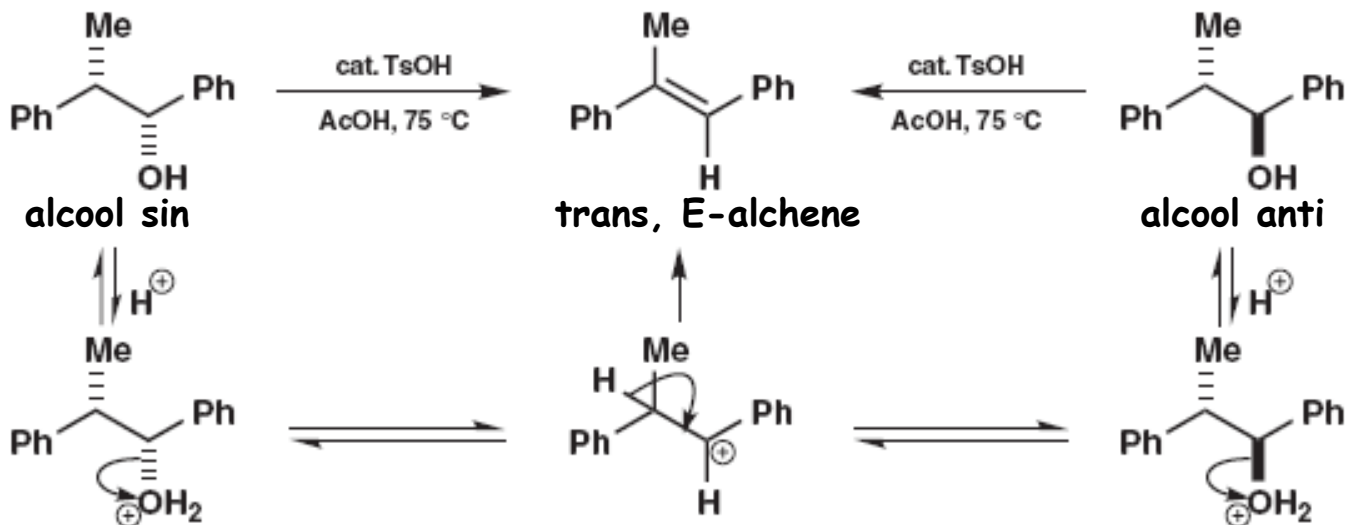
1. Si può formare solo un alchene. Si tratta di solito dell'alchene ciclico cis;
2. I due alcheni (cis e trans) sono in equilibrio: si forma il più stabile, il trans;
3. L'alchene cis si forma in maniera stereoselettiva;
4. La reazione è stereospecifica. La geometria dell'alchene dipende dal meccanismo della reazione e dalla stereochimica del prodotto di partenza.

Esempi di 1.

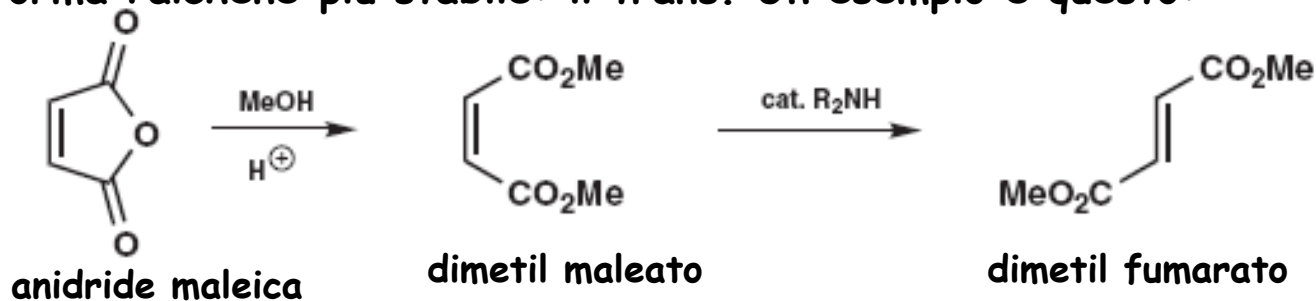


(Si noti che i due prodotti P111 e P112 saranno denominati E!)

Esempi di 2.



Ogniqualevolta si può formare un intermedio con un singolo legame in libera rotazione allora si forma l'alkene più stabile: il trans. Un esempio è questo:



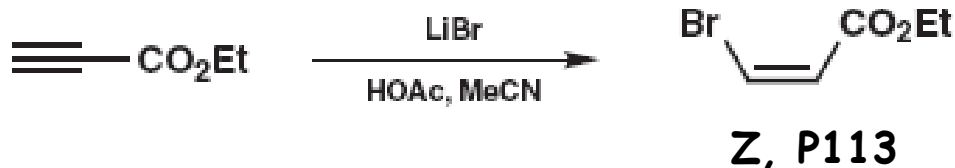
meccanismo:



Esempi di 3.

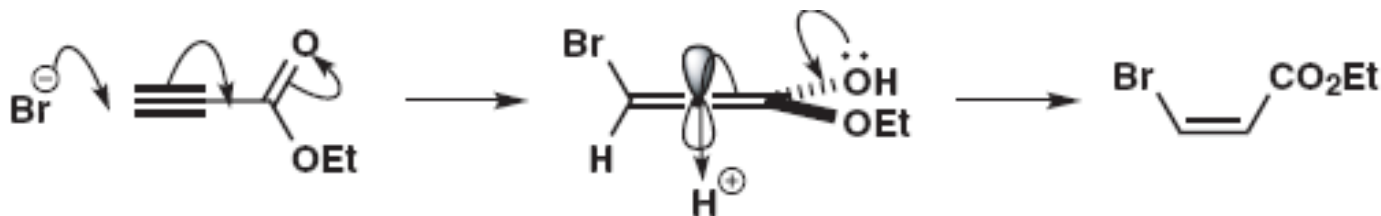
Meno frequenti ma molto importanti!

Addizione di Michael
a un triplo legame

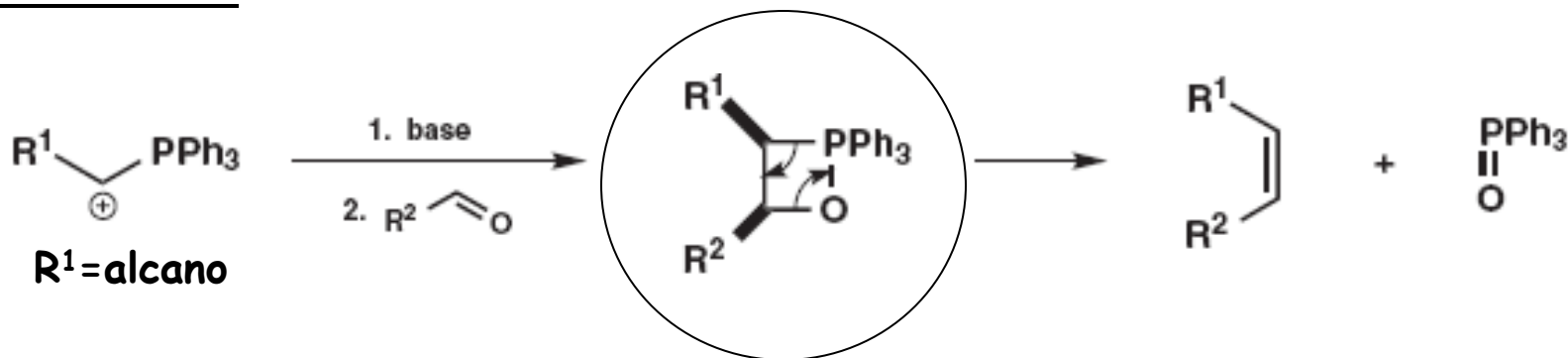


Resa 85%
nessuna traccia
di E!

Spiegazione:

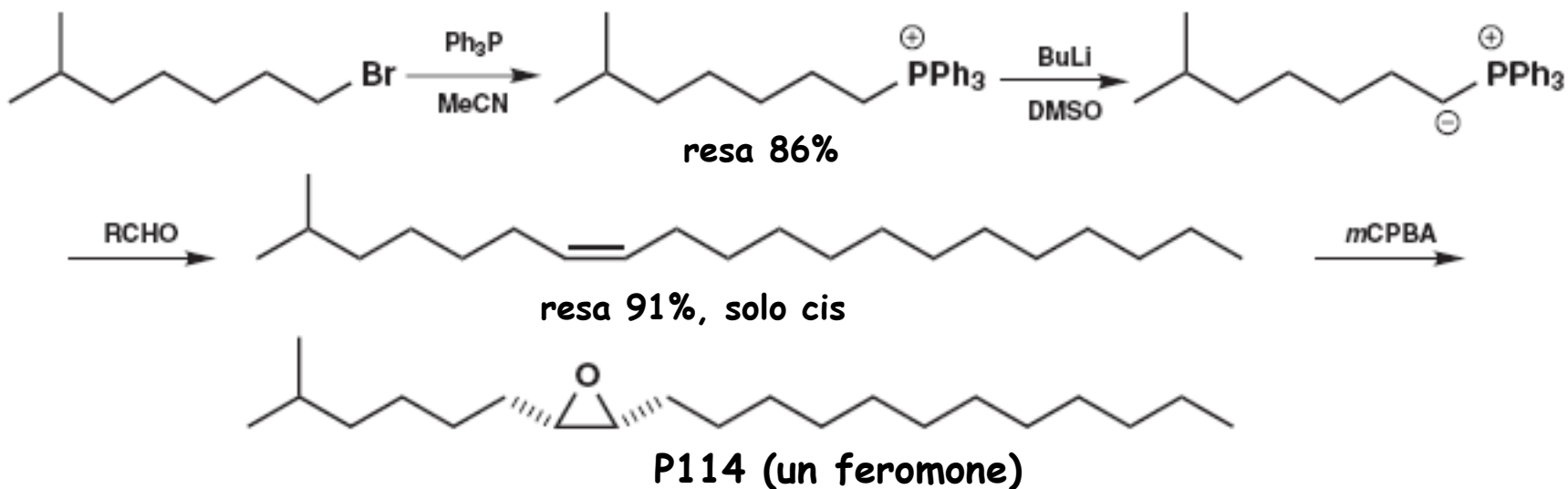


La reazione di Wittig può dare l'alkene cis! In particolare se il sale di fosfonio è poco stabile.

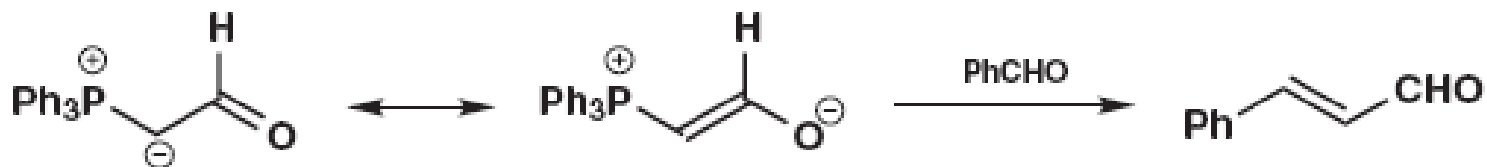
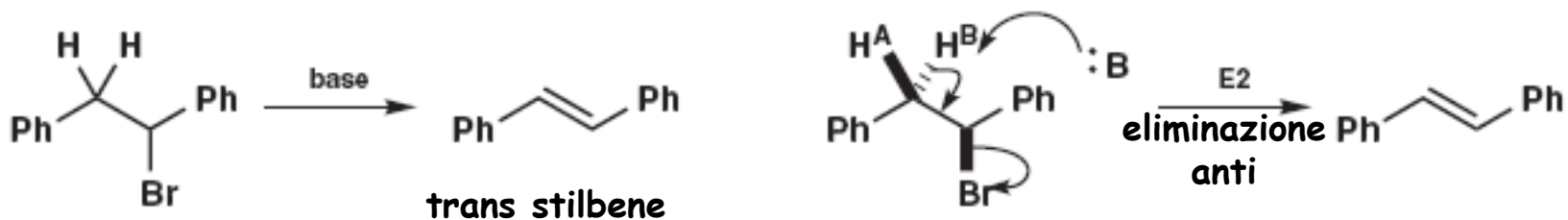


la geometria del doppio legame
dipende dalla velocità dei due
passaggi!

QUINDI NON TUTTE LE WITTIG DANNO PRODOTTI CIS!



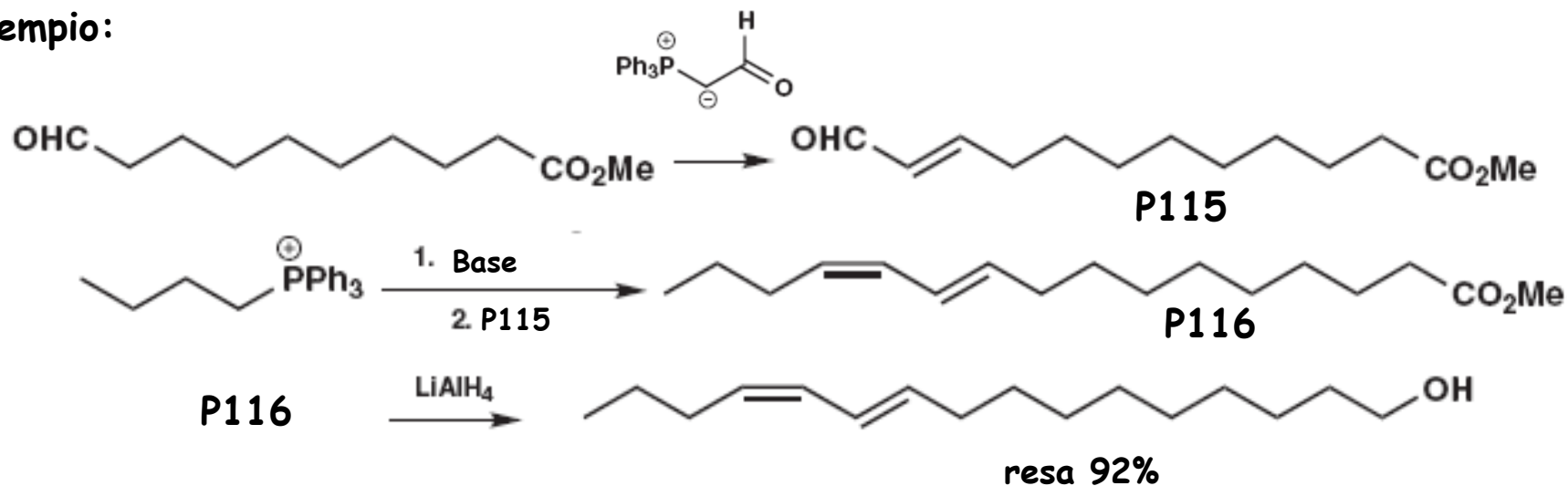
Esempi di 4.



Wittig con sale di fosfonio stabile

QUINDI, A SECONDA DELLE CONDIZIONI, LA REAZIONE DI WITTIG PUO' DARE ALCHENI CIS O TRANS!

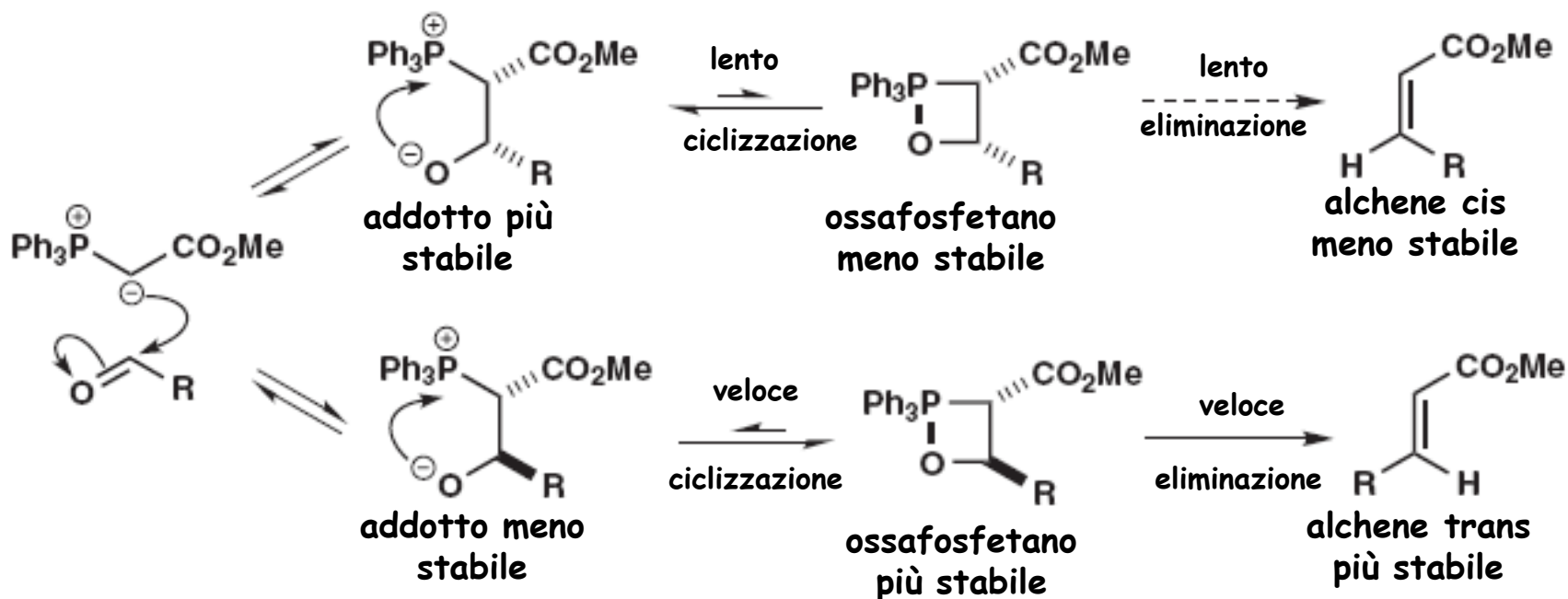
Esempio:



Molto spesso si usano fosfati invece di sali di fosfonio. Queste condizioni vengono chiamate di Horner-Wodsworth-Emmons:



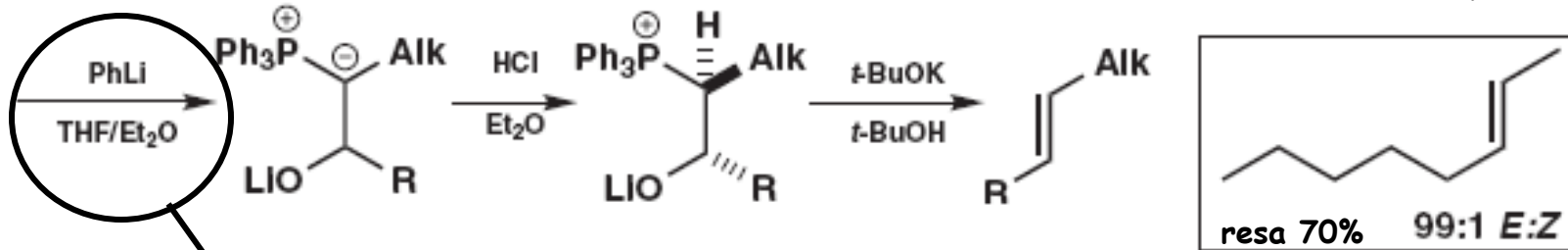
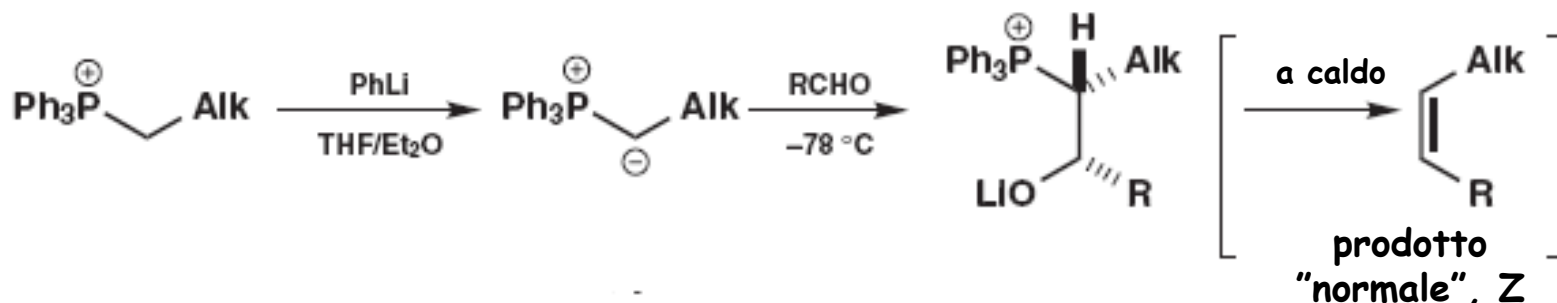
Il meccanismo corretto è probabilmente:



Sulla base di questo meccanismo come suggerireste di condurre la reazione con una ilide poco stabile? (suggerimento: ...bisogna lasciar isomerizzare i due addotti)

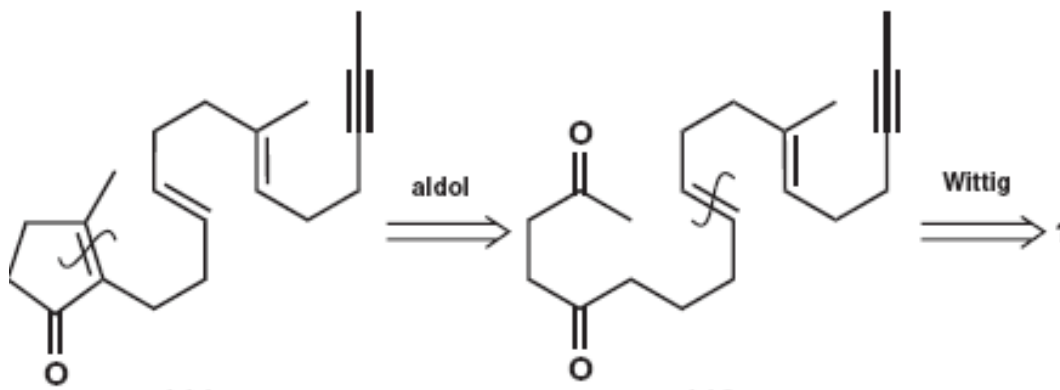
La procedura viene chiamata di Schlosser (o reazione di Wittig-Schlosser)

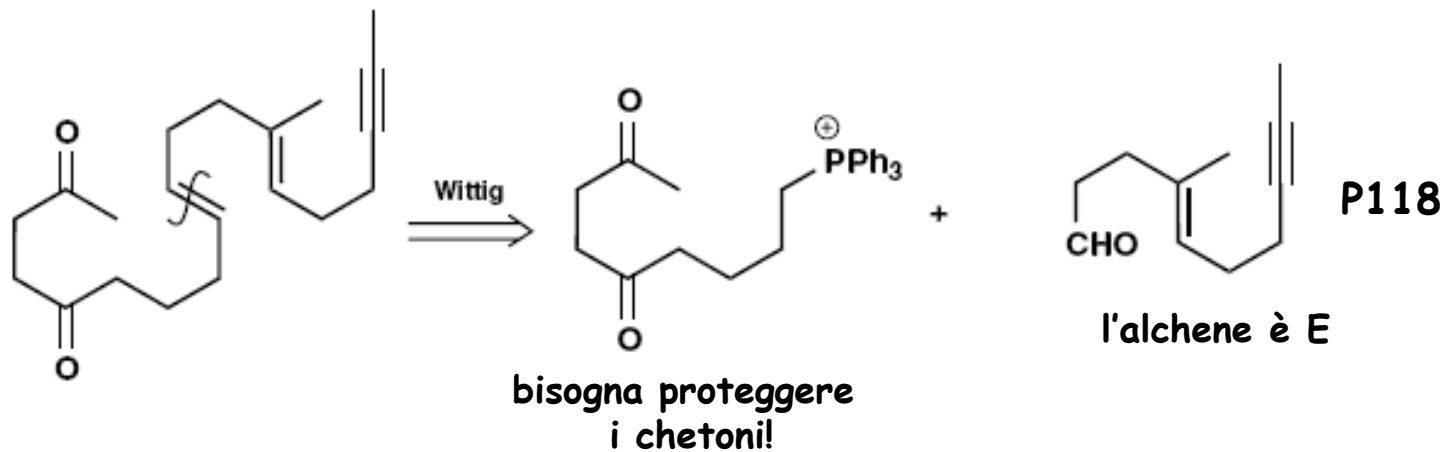
reazione di Wittig-Schlosser:



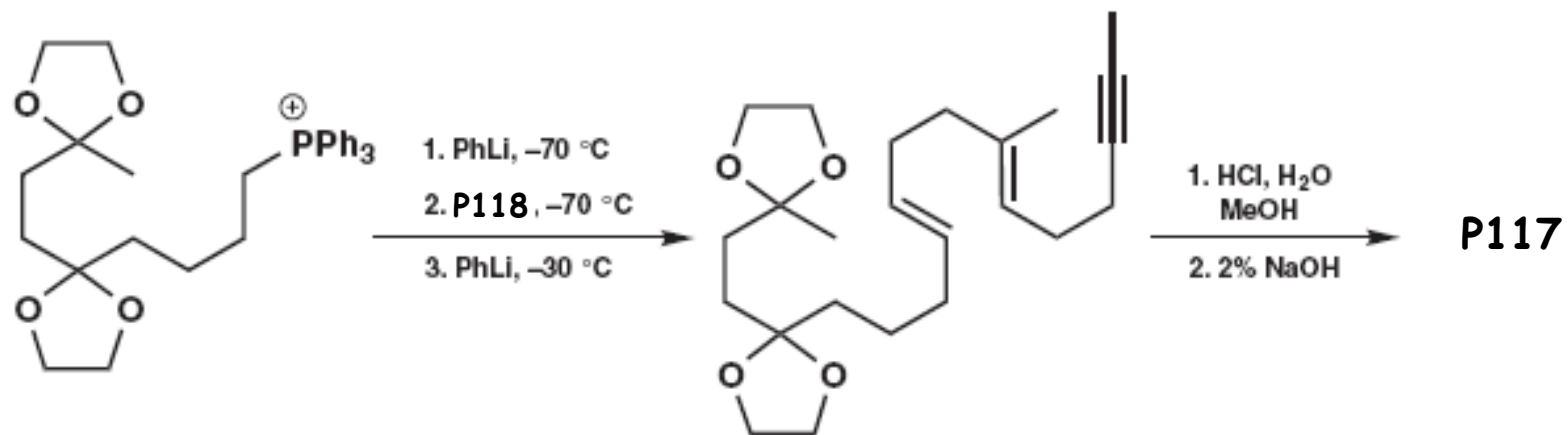
l'aggiunta di un secondo equivalente di base e la bassa temperatura favoriscono la equilibratura dell'addotto verso quello più stabile

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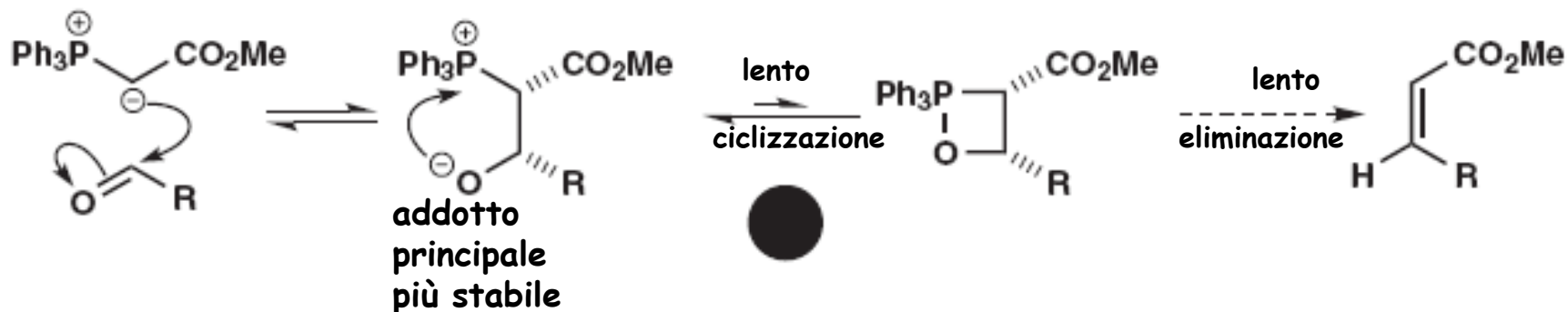


Sintesi:

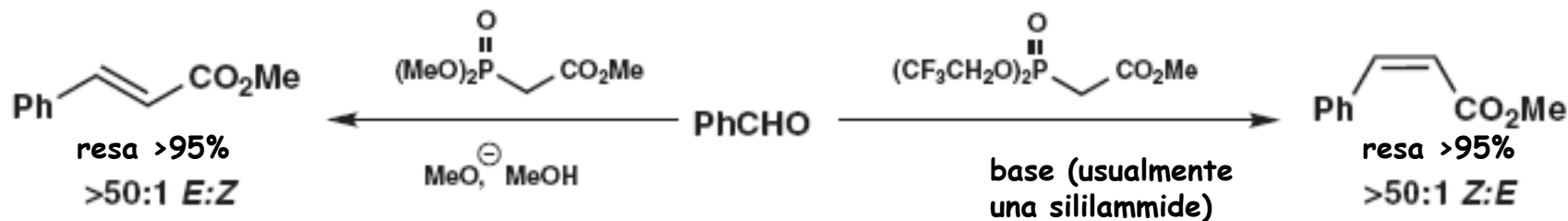


Ora che sappiamo tutto sulla Wittig, possiamo divertirci a giocare un pò. Per esempio che cosa fareste per trasformare una reazione con un sale di fosfonio stabile che dà quindi un alchene E (condizioni di Horner-Wodsworth-Emmons) in un processo che porta alla formazione di un alchene Z?

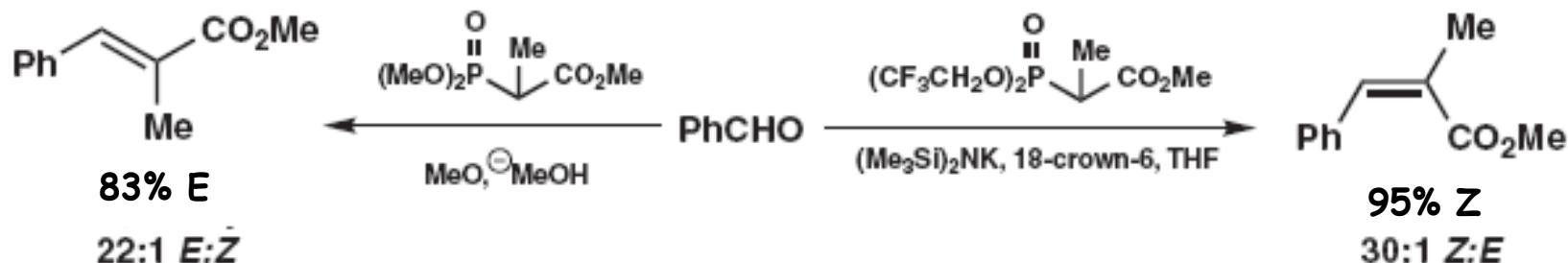
BISOGNA ACCELERARE LA CICLIZZAZIONE DELL'ADDOTTO PIU' STABILE!



E' quello che hanno fatto Still e Gennari usando un gruppo fortemente elettronattrattore sull'atomo di fosforo:



La reazione va molto bene anche per dare alcheni trisostituiti:

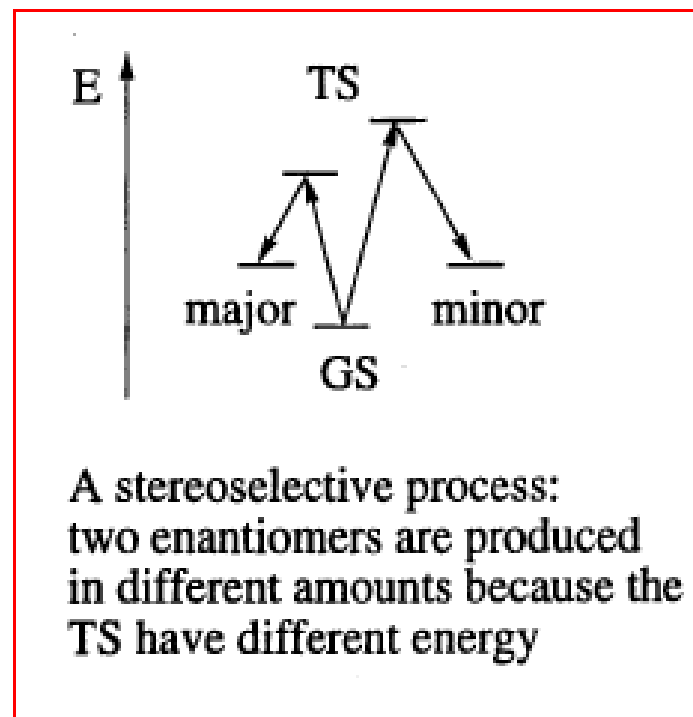
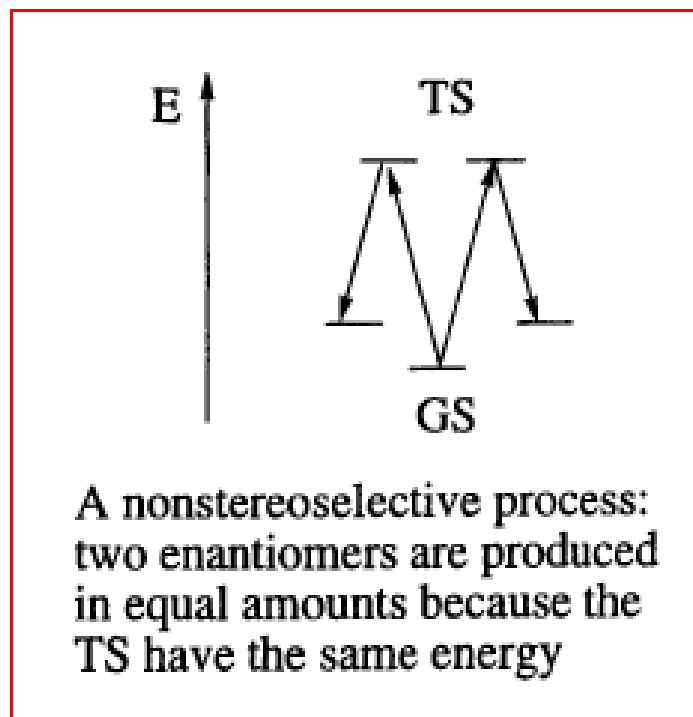


IN CONCLUSIONE LA REAZIONE DI WITTIG (e le sue varianti):

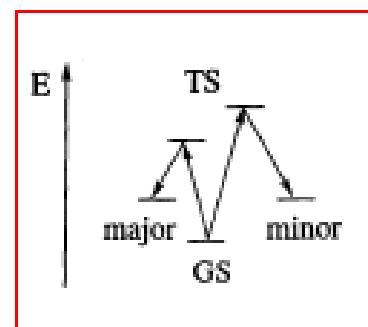
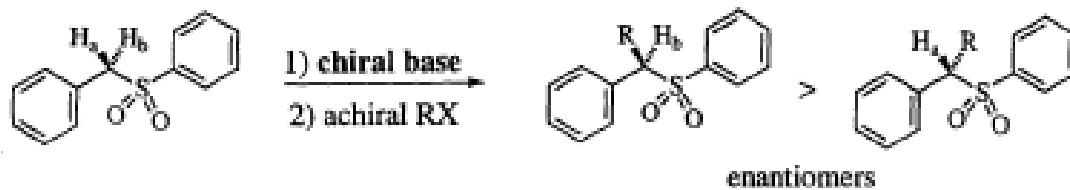
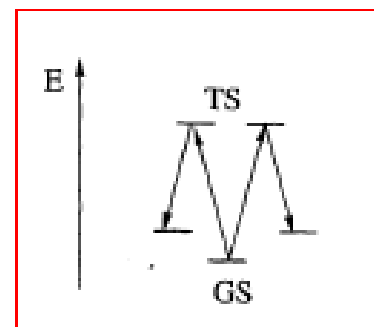
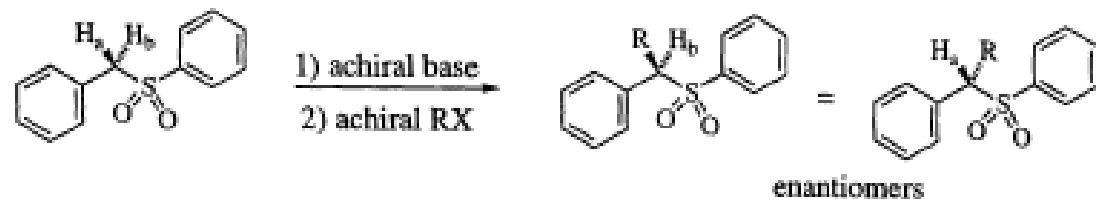
Sale di fosfonio	Condizioni	Alchene	Nome
Poco acido	Temp. ambiente	Z	Wittig
Poco acido	Temp. bassa + 1 equiv base	E	Schlosser
Molto acido	Temp. ambiente	E	Horner- Wodsworth- Emmons
Molto acido (fosfato) con gruppo EWG	Temp. ambiente	Z	Still-Gennari

INDUZIONE ASIMMETRICA

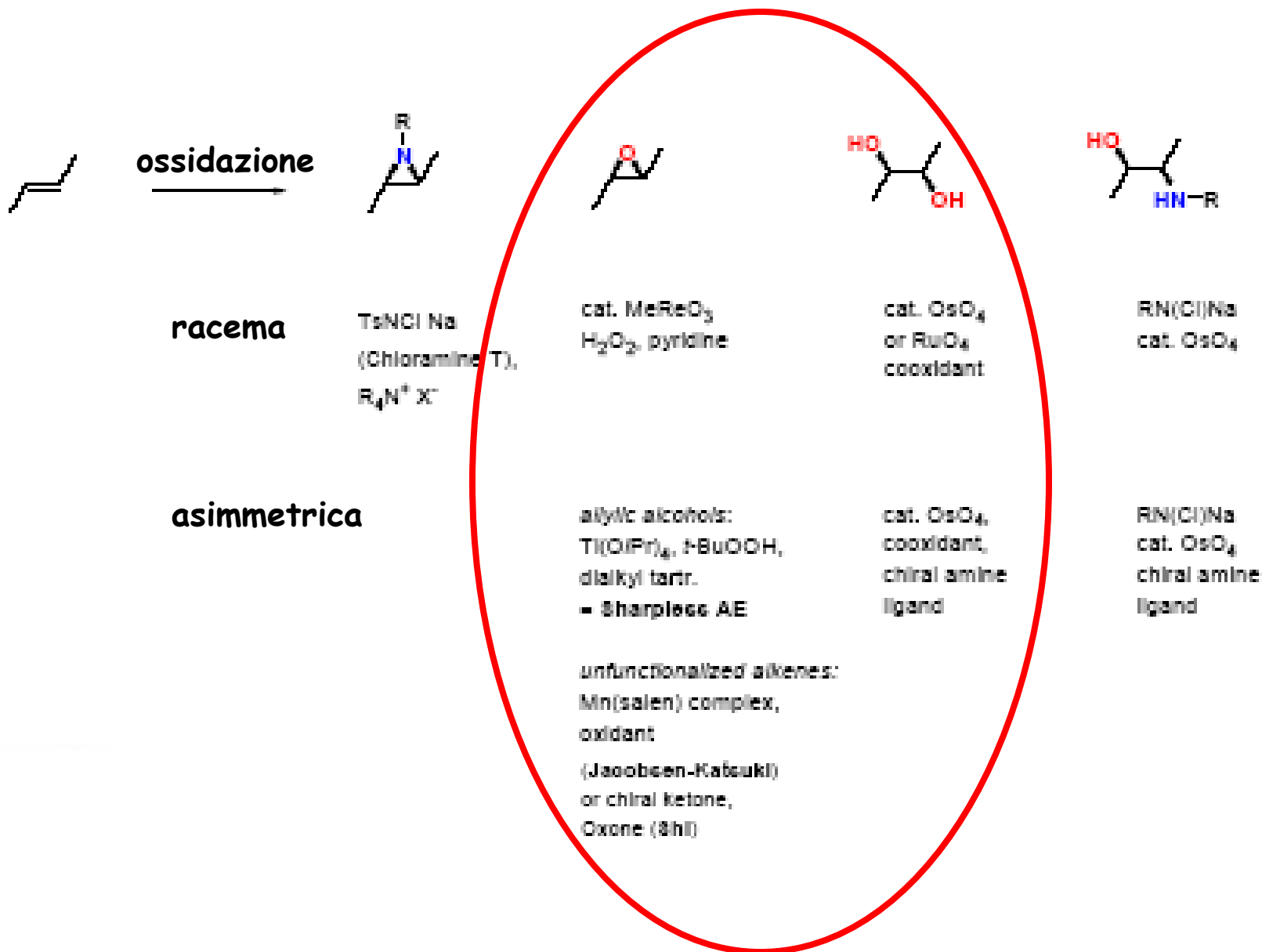
Bisogna differenziare i due stati di transizione|



ESEMPI:

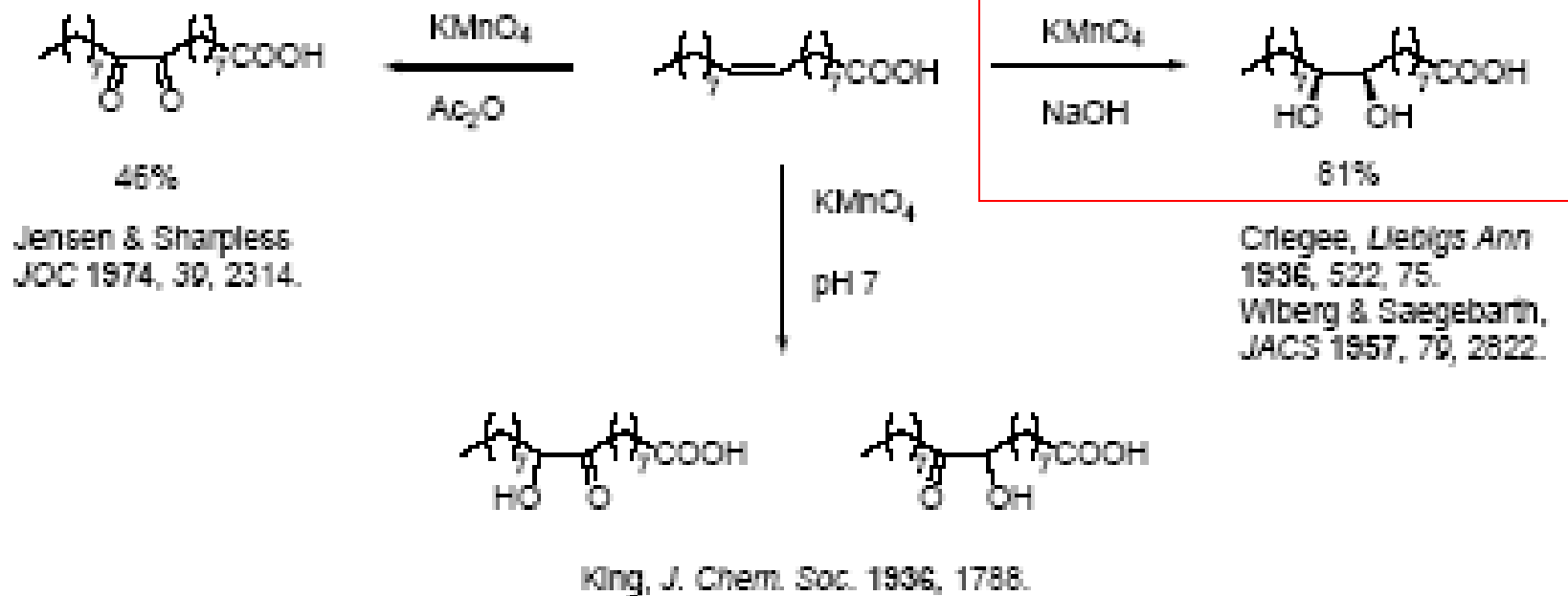


FUNZIONALIZZAZIONE DEGLI ALCENI MEDIANTE OSSIDAZIONE

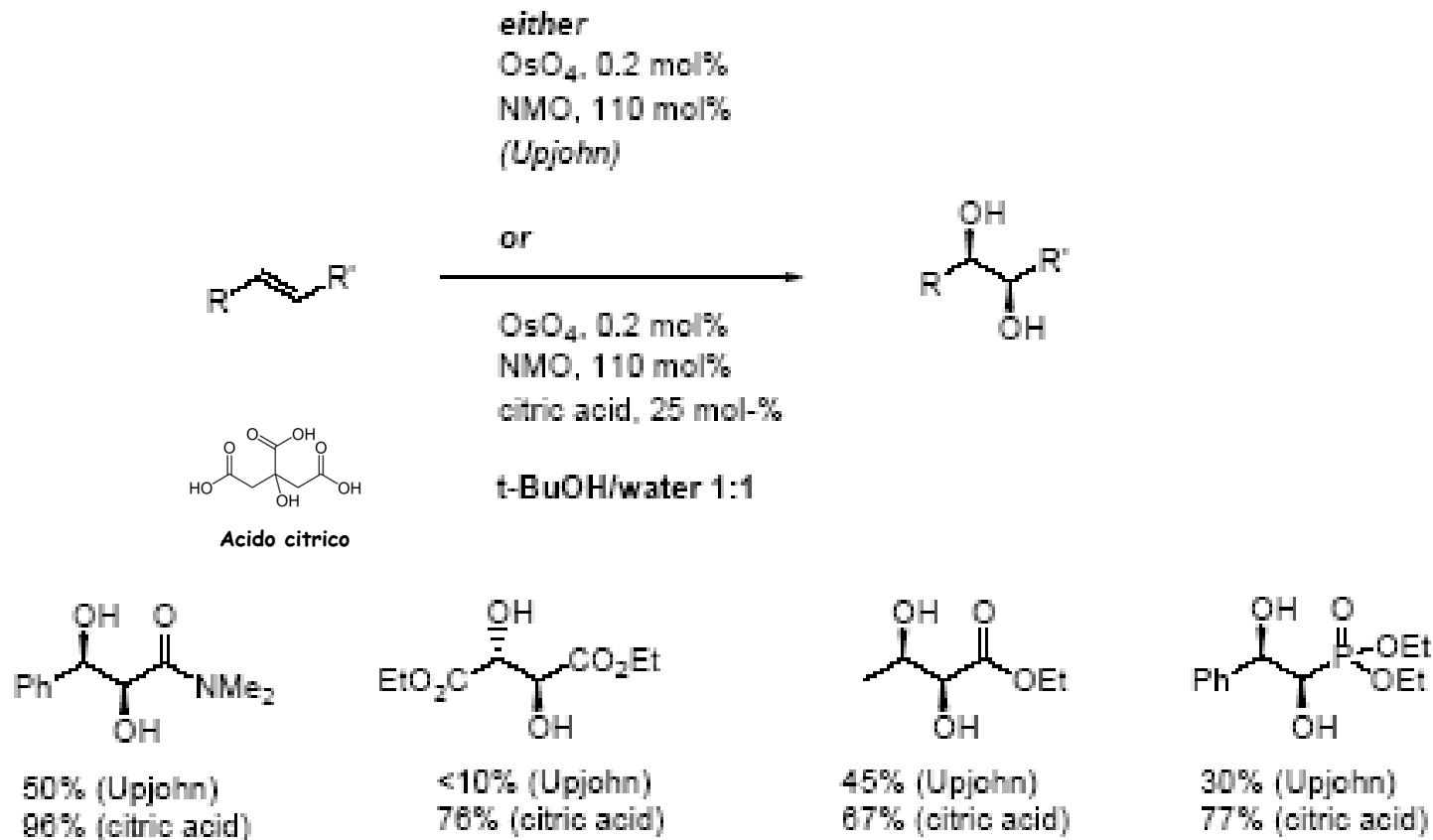


OSSIDAZIONI CON PERMANGANATO

Early work: Wagner, *J. Russ. Phys. Chem. Soc.* 1895, 27, 219.

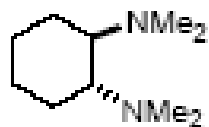


L'AGGIUNTA DI ACIDO CITRICO (SHARPLESS) AUMENTA DI MOLTO LE RESE



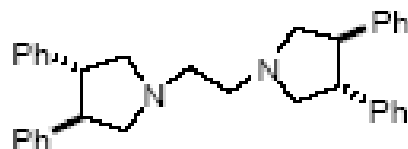
Dupau, Epple, Thomas, Fokin, Sharpless
Adv. Synth. Catal. 2002, 344, 421

USO DI AMMINE CHIRALI COME LEGANTI: SINTESI ASIMMETRICA



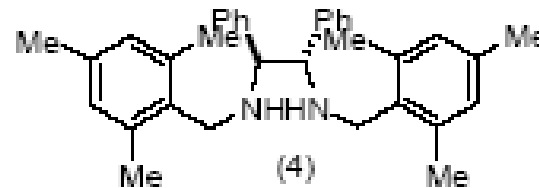
(2)

Snyder



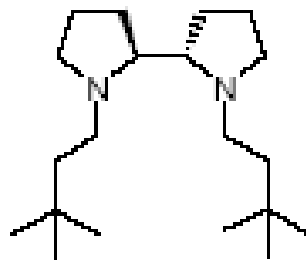
(3)

Tomioka



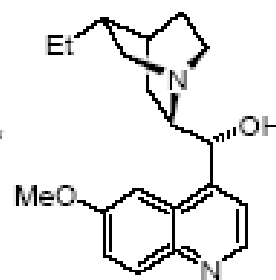
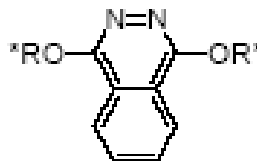
(4)

Corey



(5)

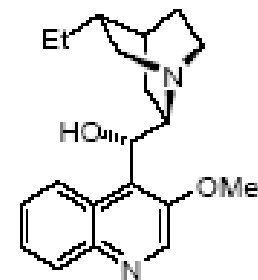
Hirama



(DHQ)₂PHAL

(6)

Sharpless

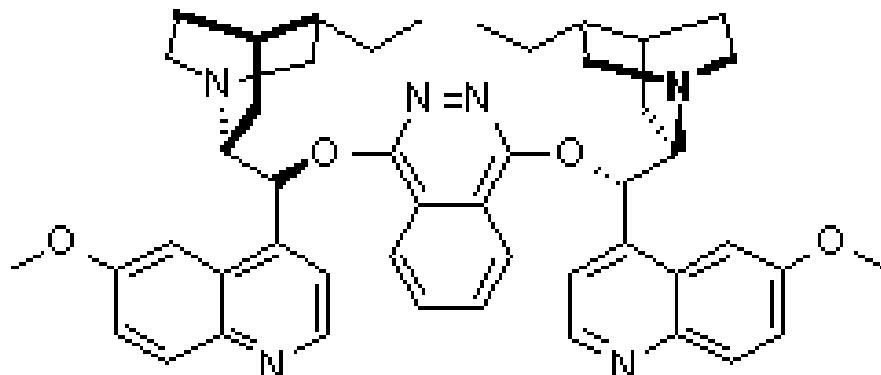


(DHQD)₂PHAL

LEGANTI DI SHARPLESS

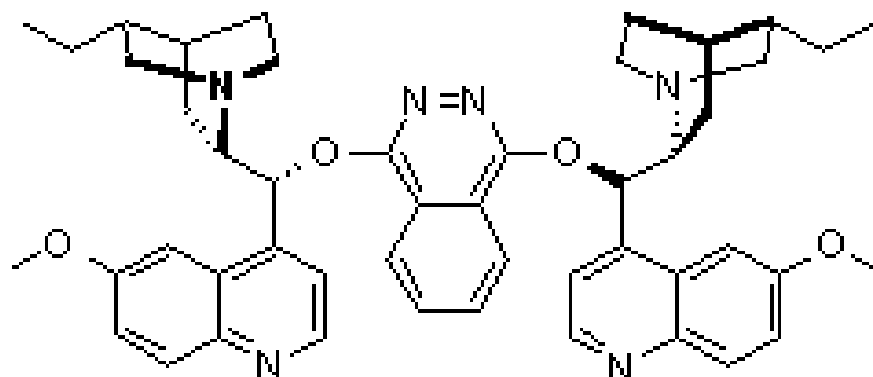
AD-mix- β :

$K_2OsO_2(OH)_4$ (cat), K_2CO_3 , $K_3Fe(CN)_6$, $(DHQD)_2PHAL$ (cat):

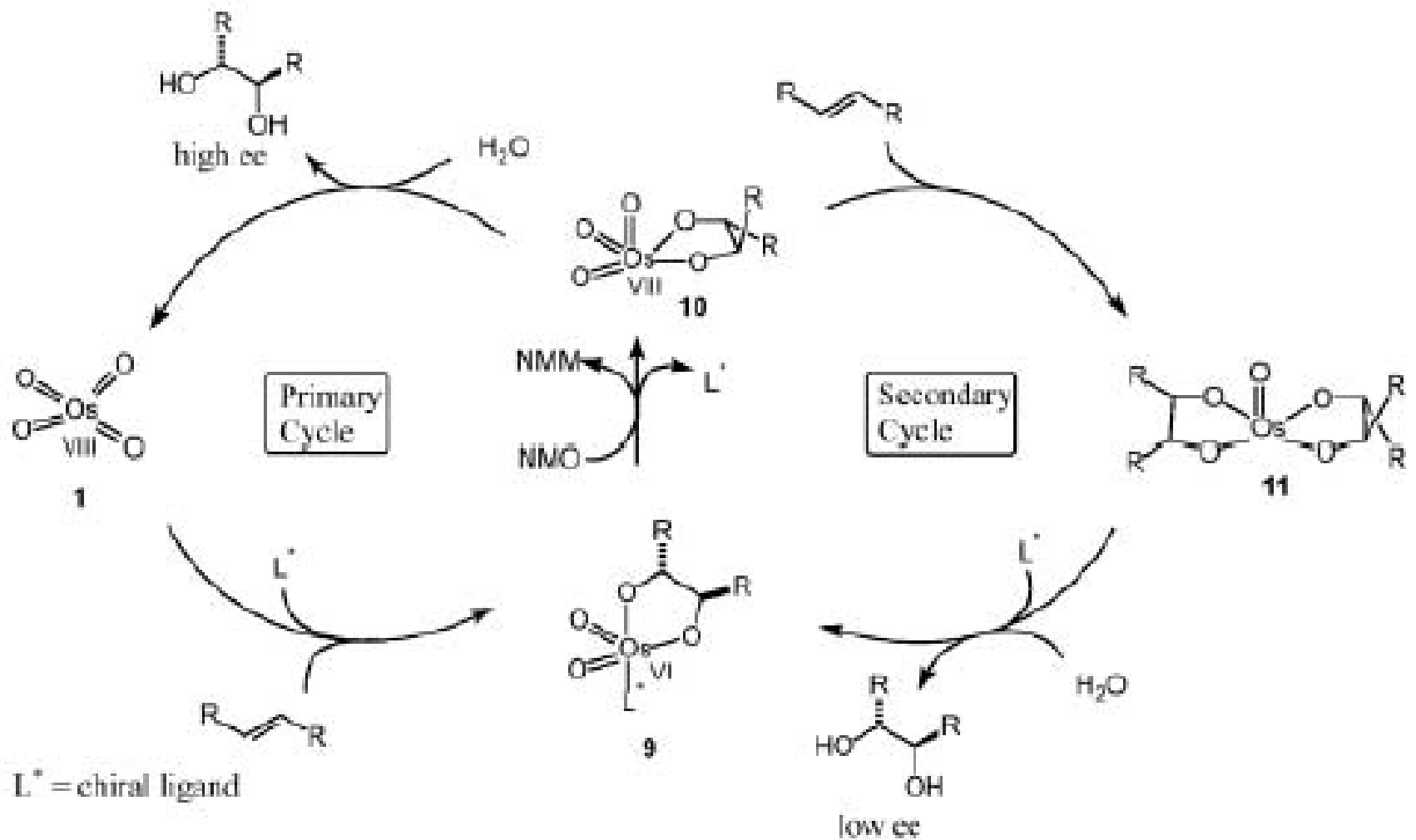


AD-mix- α :

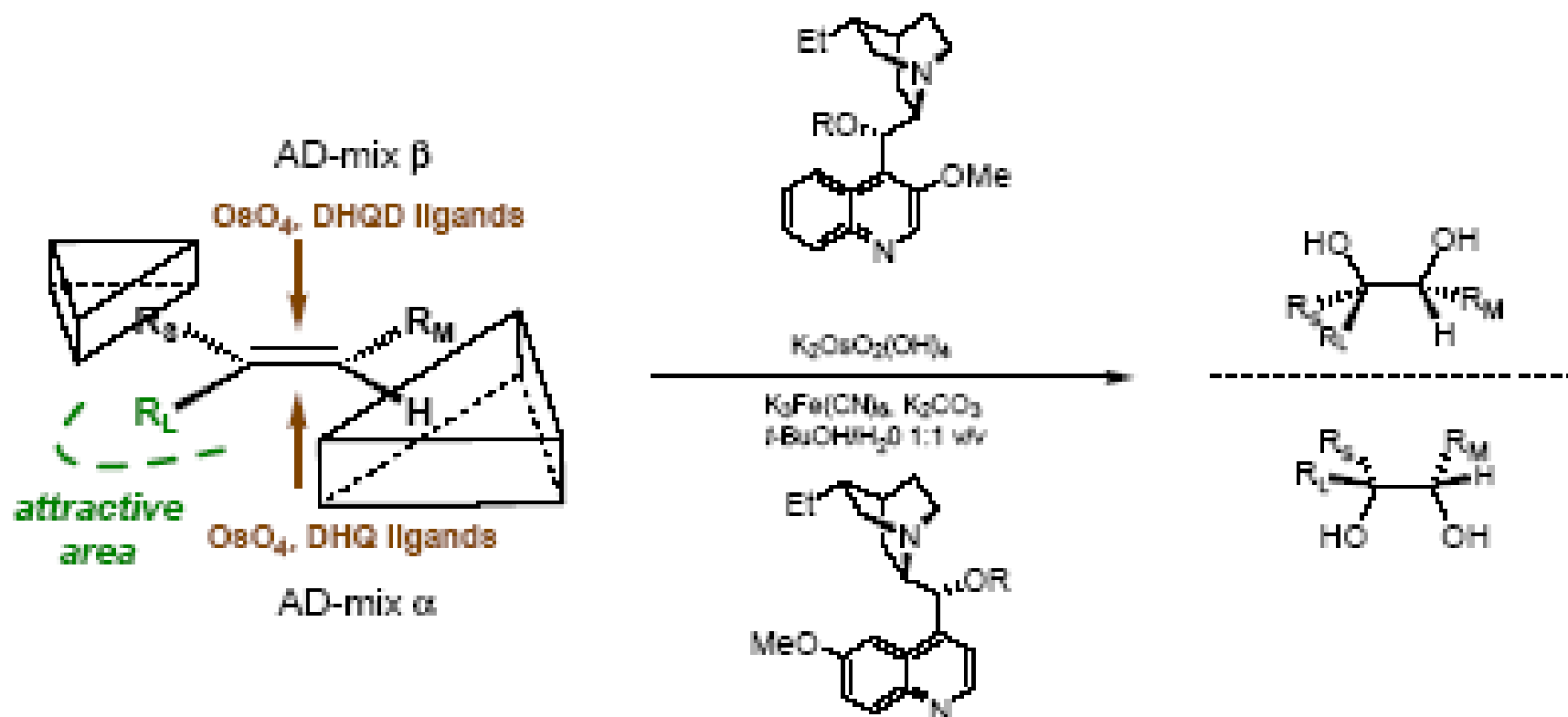
$K_2OsO_2(OH)_4$ (cat), K_2CO_3 , $K_3Fe(CN)_6$, $(DHQ)_2PHAL$ (cat):



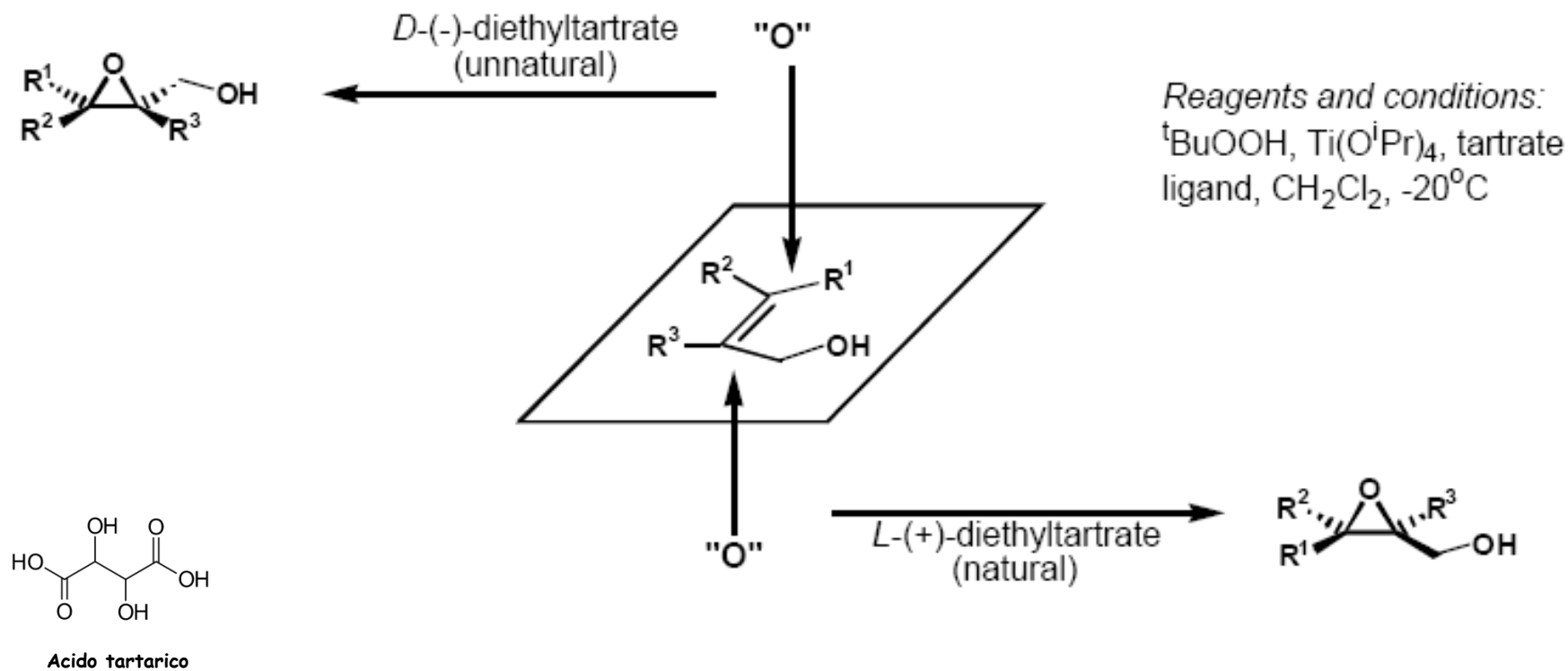
CICLO CATALITICO



FATTORI CHE INFLUENZANO L'ENANTIOSELETTIVITA'

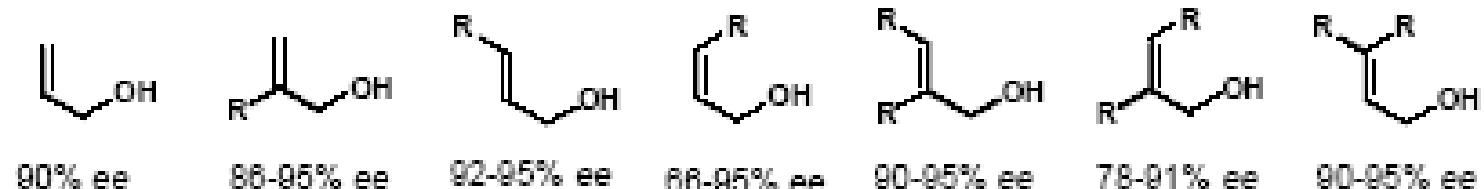


EPOSSIDAZIONE ASIMMETRICA DI KATSUKI-SHARPLESS DEGLI ALCOLI ALLILICI



INFLUENZA DELLA STRUTTURA DELL'OLEFINA SULL'ENANTIOSELETTIVITA'

- **Effetto della struttura dell'olefina:**

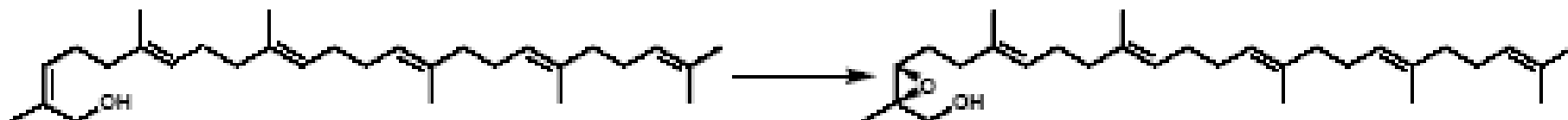


- **Compatibilità con gruppi funzionali:**

Reaction tolerates acetals, alkynes, alcohols, aldehydes, amides, azides, carbamates, epoxides, esters, ethers, hydrazides, ketones, nitriles, nitro, olefins, pyridines, silyl ethers, sulfones, sulfoxides, tetrazoles, ureas

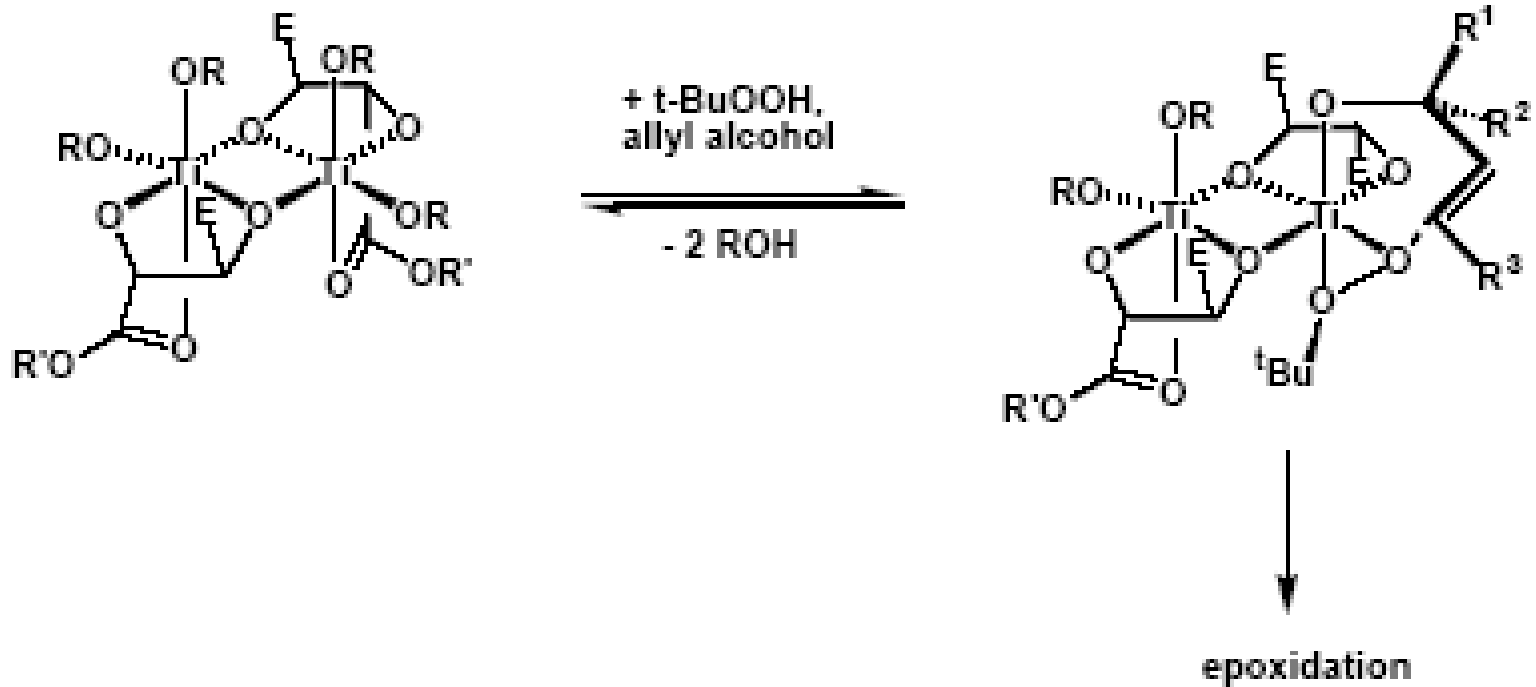
Reaction *does not tolerate*: amines, carboxylic acids, phenols, thiols, phosphines

- **viene ossidato solo l'alchene in posizione allylica**

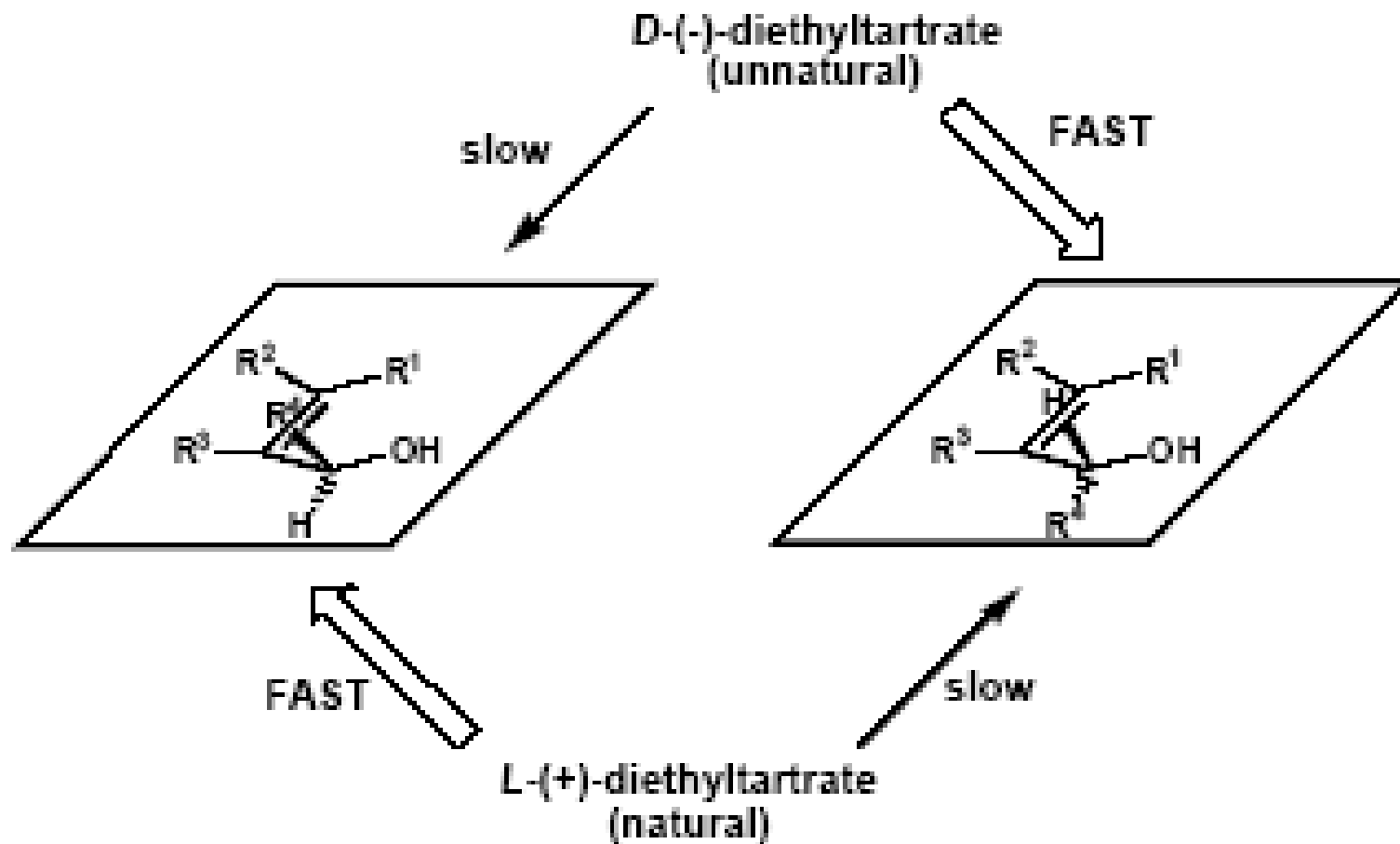


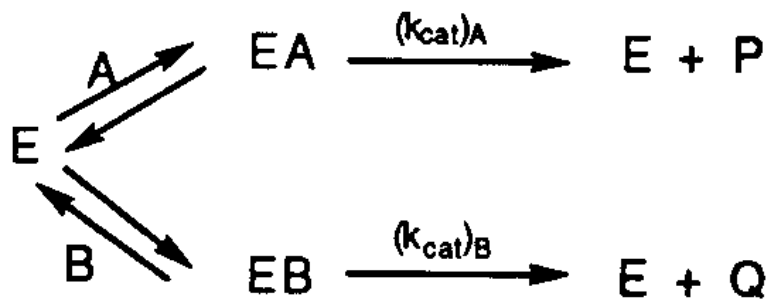
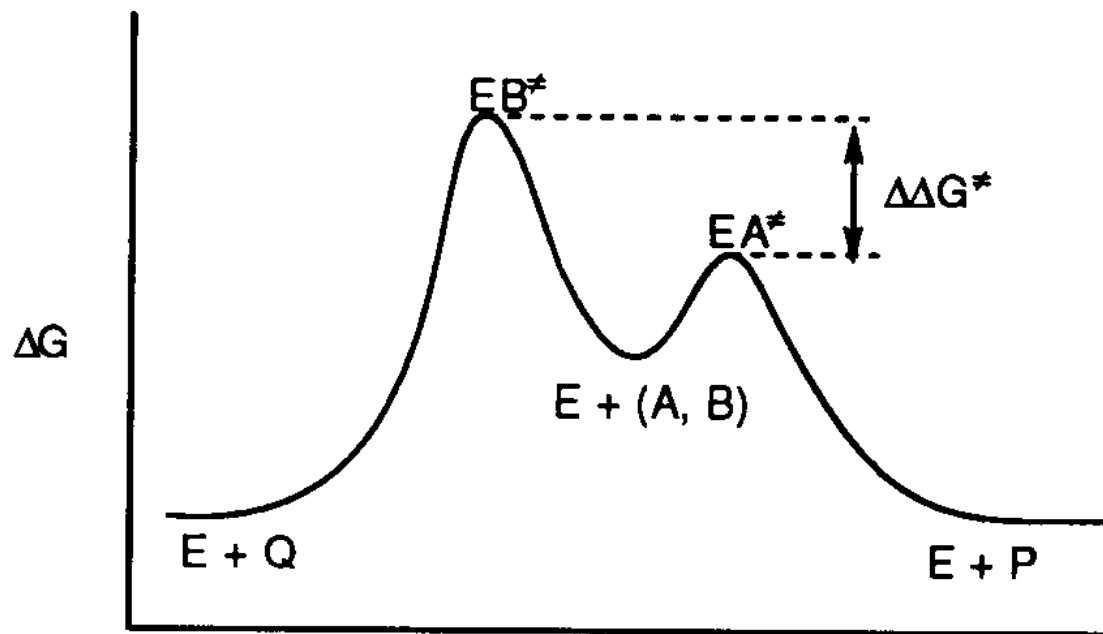
J. Am. Chem. Soc., 1988, 110, 4818

SI RITIENE CHE LA SPECIE CATALITICAMENTE ATTIVA
SIA UN DIMERO

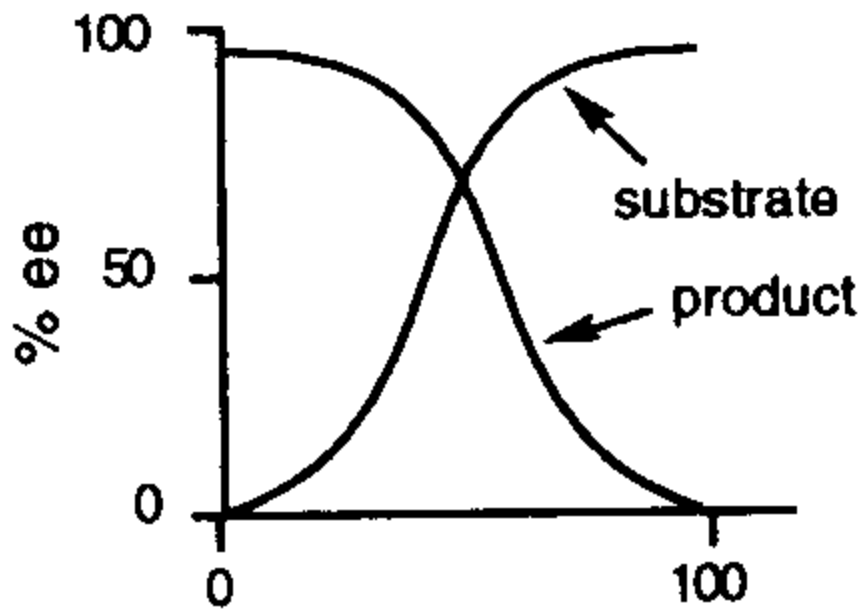
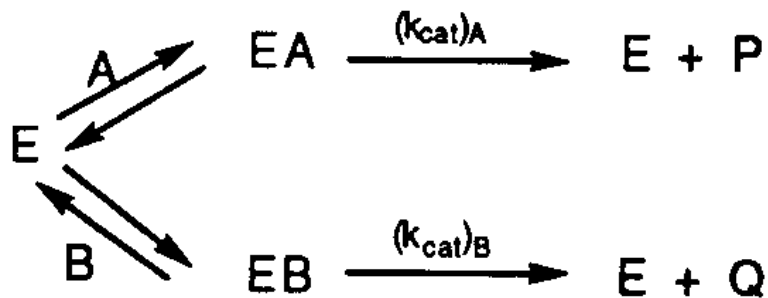


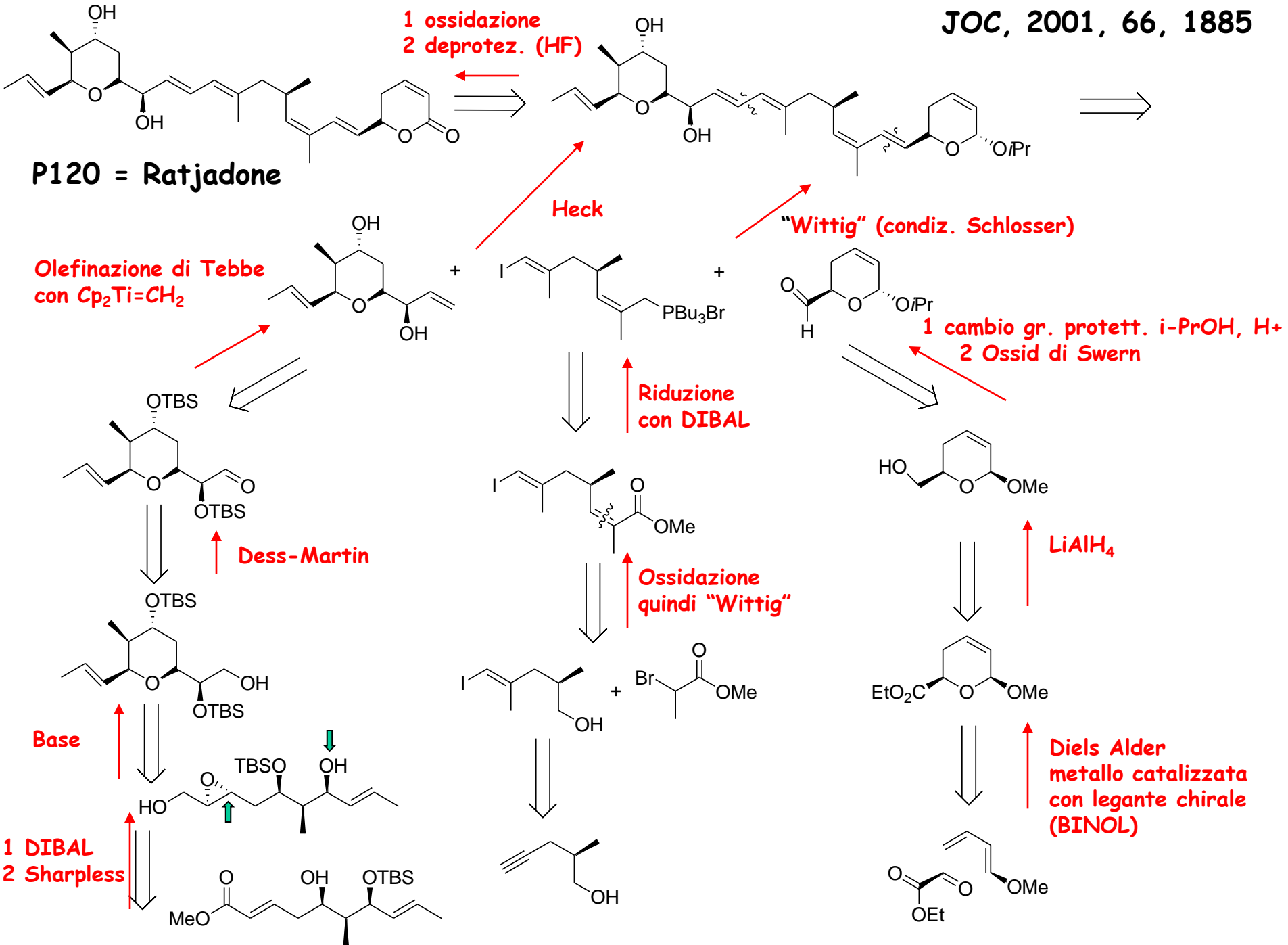
L'OSSIDAZIONE PUO' ESSERE CONDOTTA MEDIANTE RISOLUZIONE CINETICA A PARTIRE DA UN ALCOL ALLILICO CHIRALE



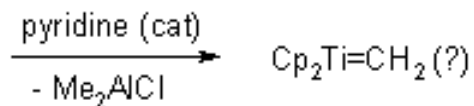
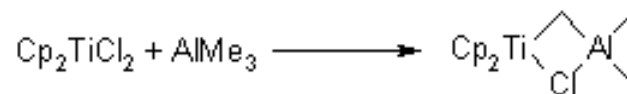


Processo Irreversibile

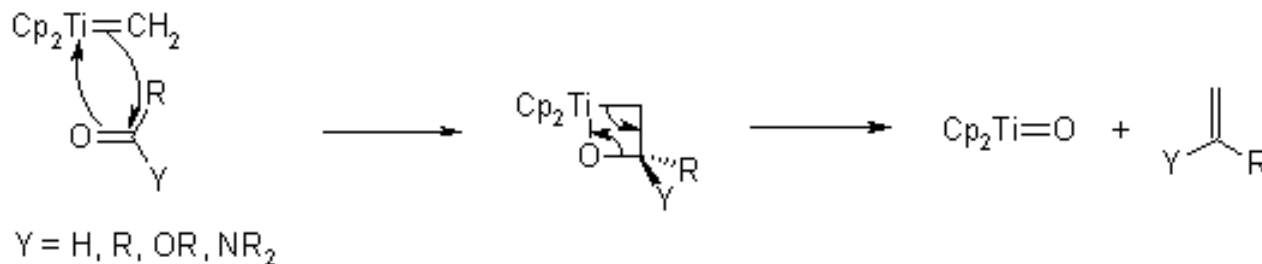




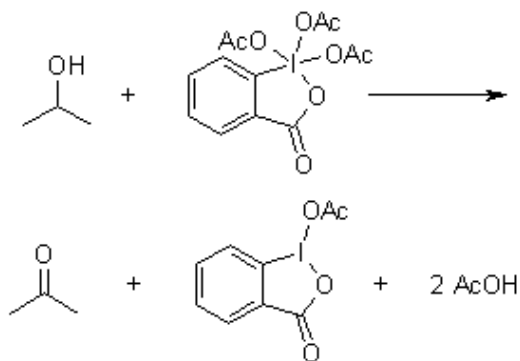
Olefinazione di Tebbe



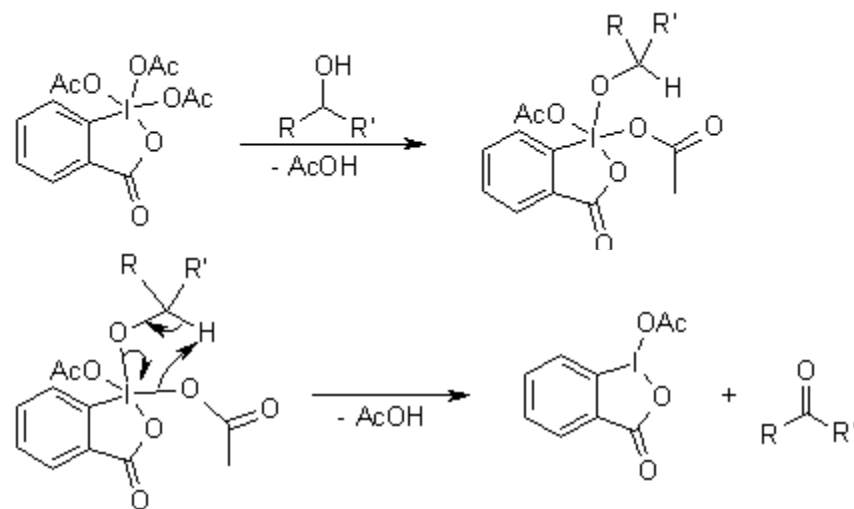
Meccanismo:



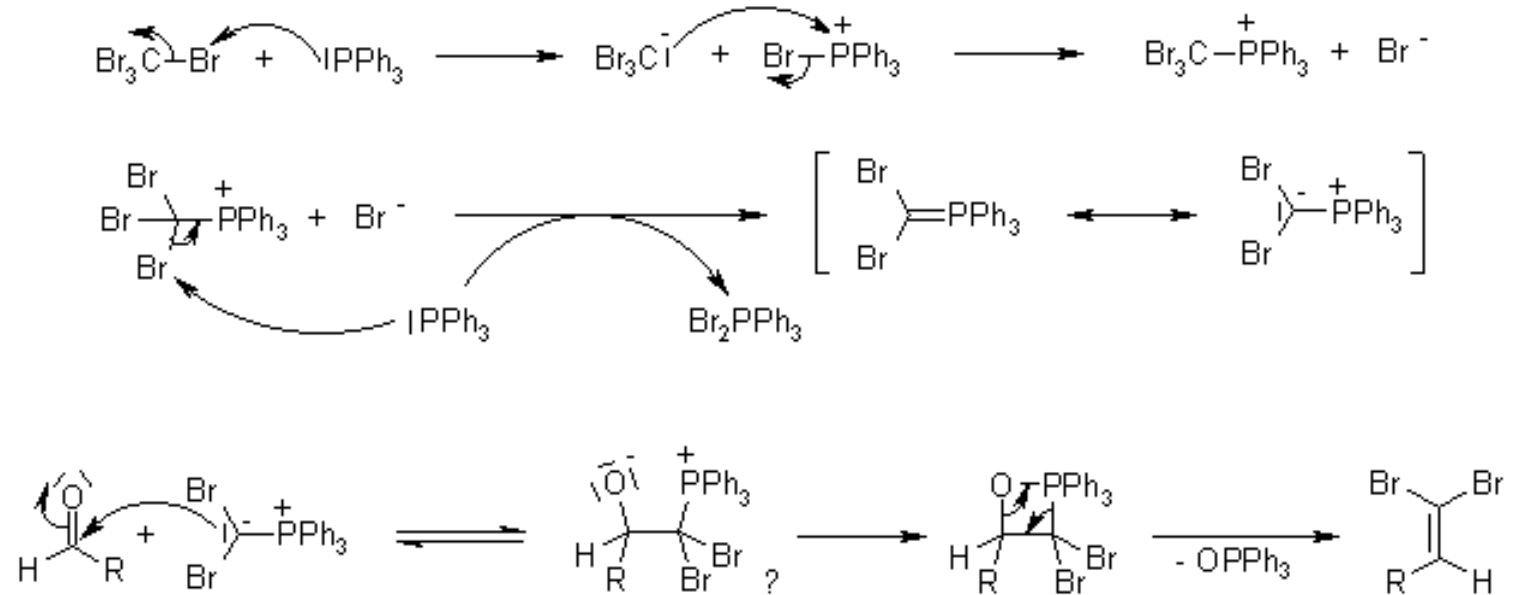
Periodinano di Dess Martin (ossidazione di alcoli a chetoni o aldeidi)



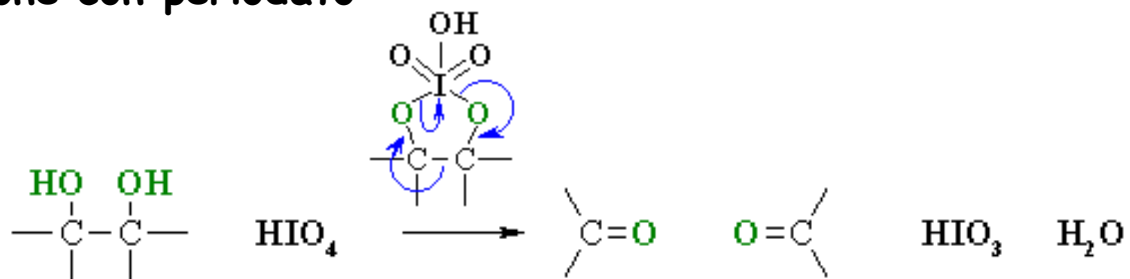
Meccanismo:



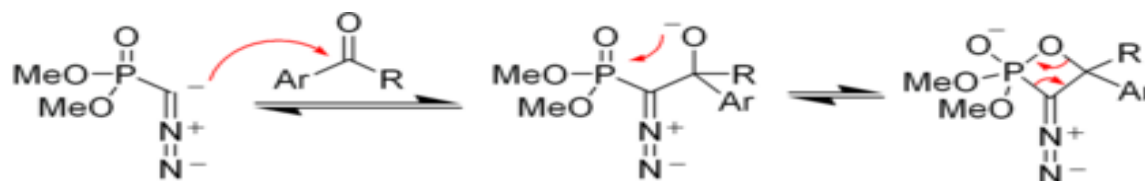
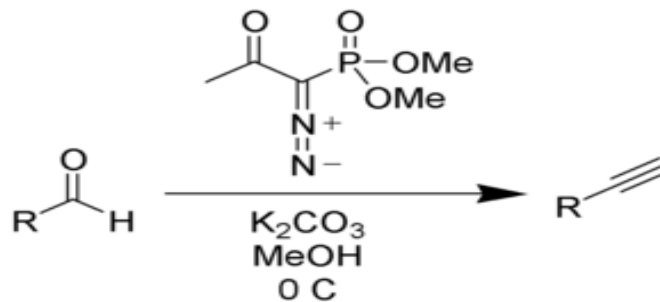
Reazione di Corey-Fuchs (tipo Wittig)



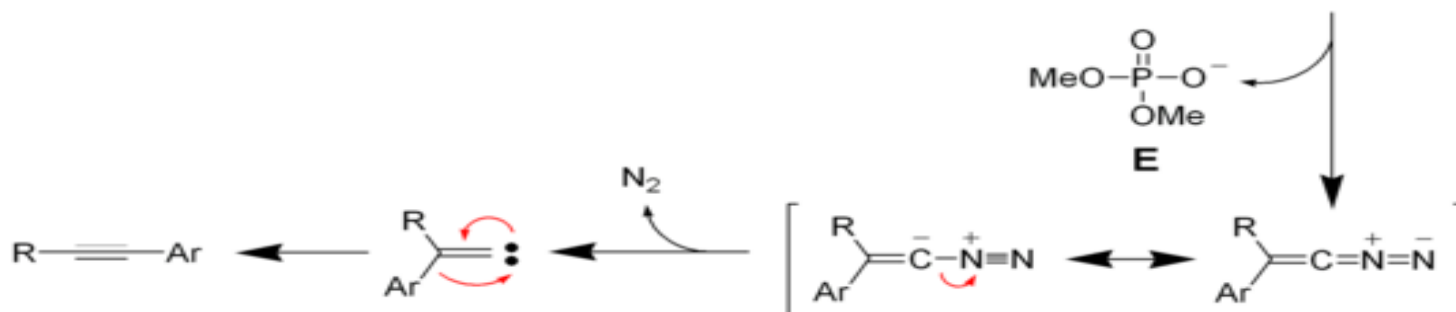
Ossidazione con periodato

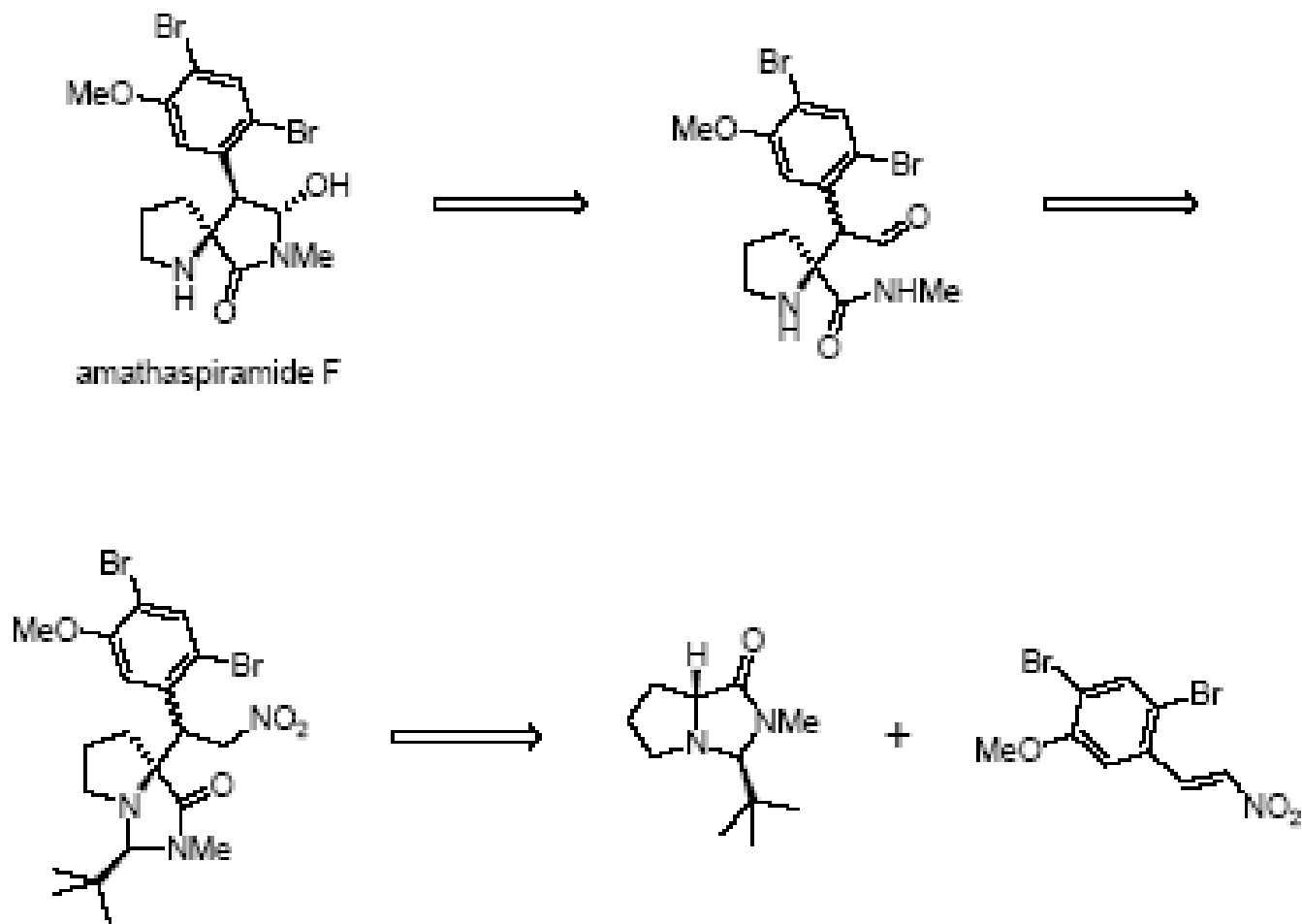


Reazione di Gilbert



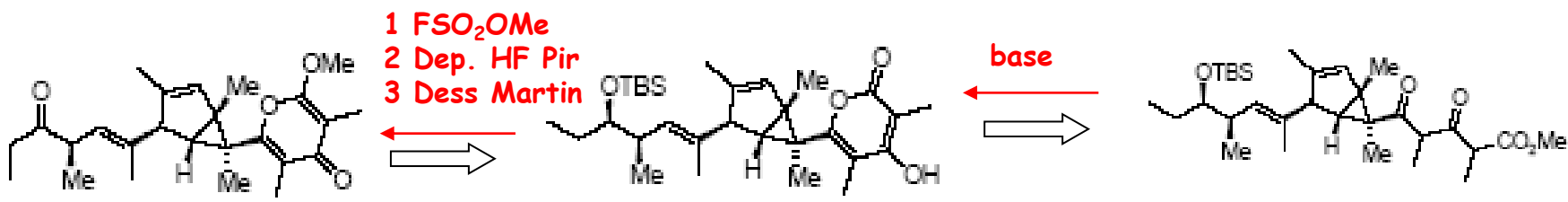
Anche se Ar=H



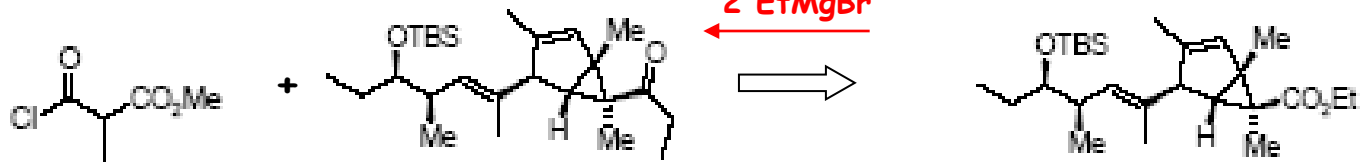


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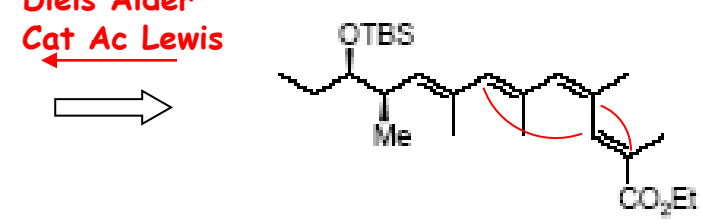
crispatene



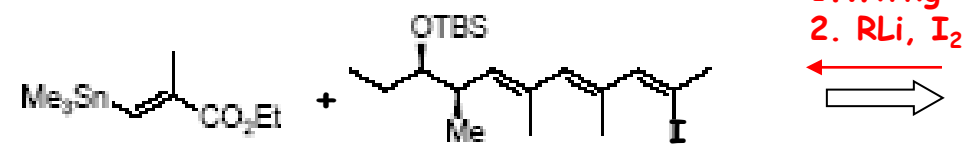
Base forte
3 equiv



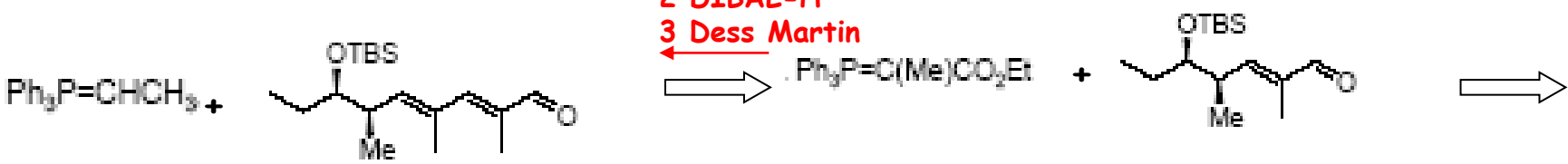
Diels Alder
Cat Ac Lewis



Stille



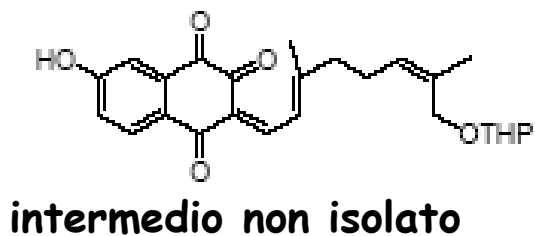
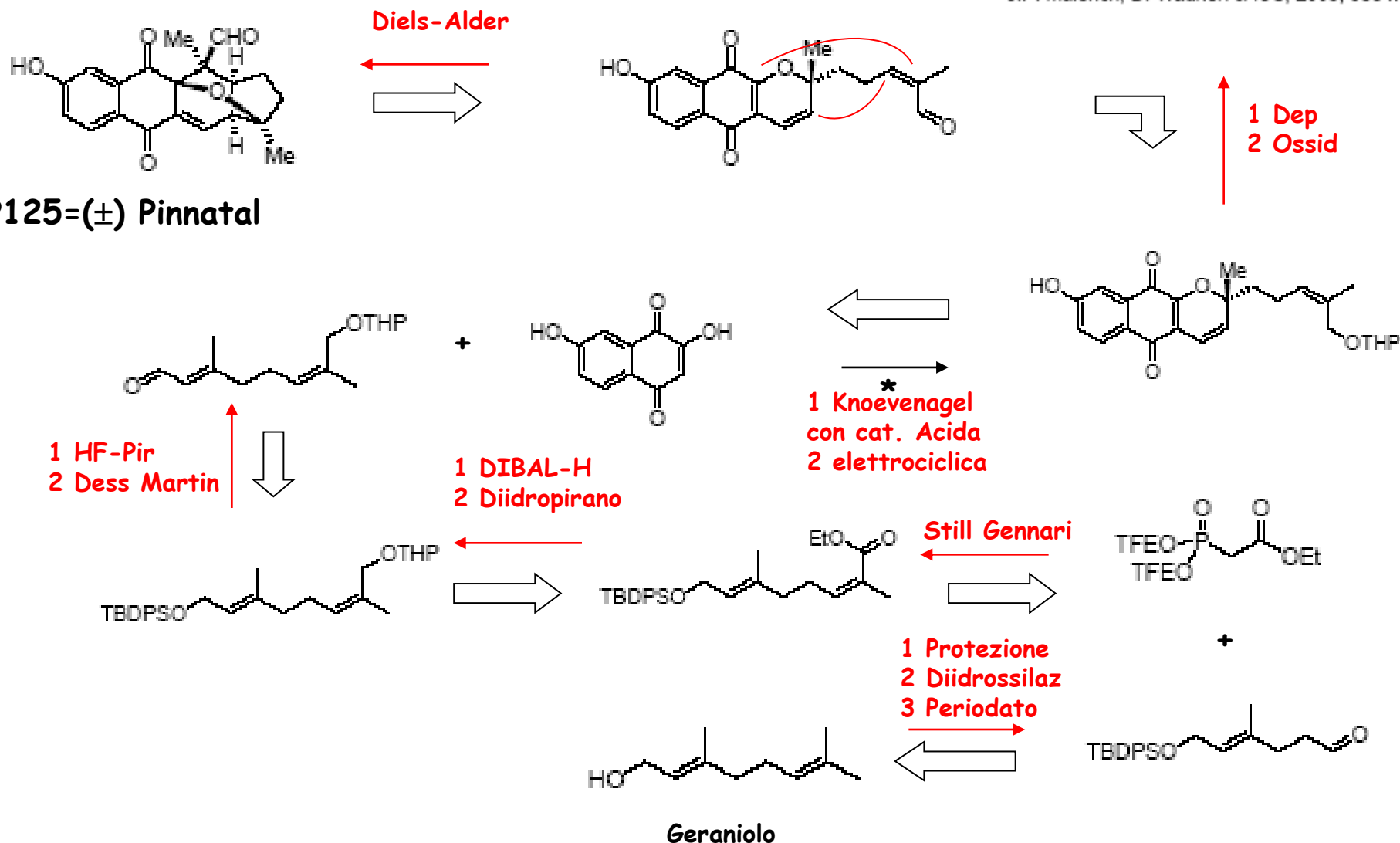
1 Wittig
(Horner-Wodsworth-Emmons)
2 DIBAL-H*
3 Dess Martin

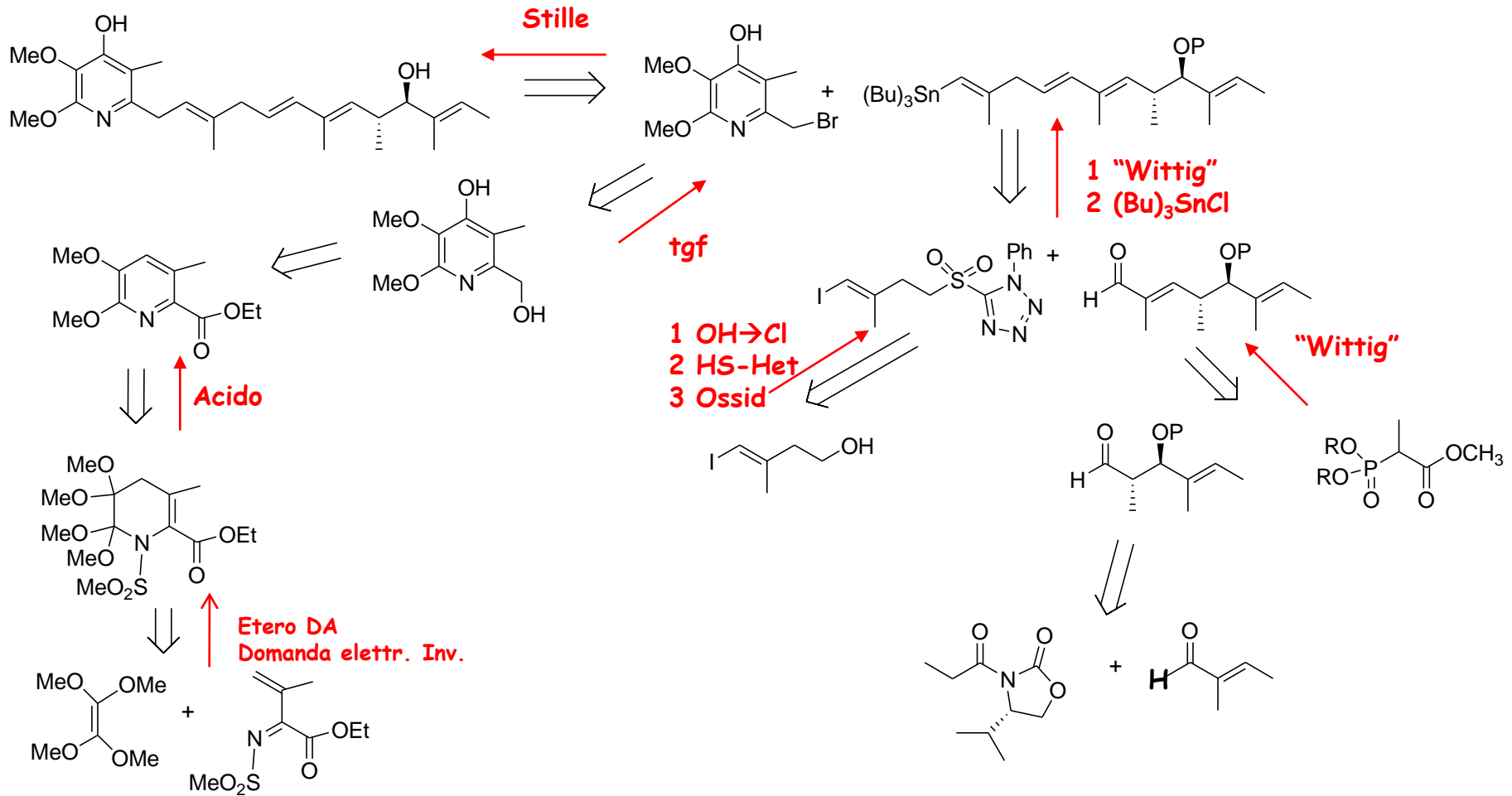


*DIBAL-H:
COOR → HCO
CH=C-COOR → CH=C-C-OH

continuare....

P125=(±) Pinnatal





(±)-Stenine P127