

Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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Technische Universität Graz

Übersicht

- Carbonylierungen
 - Essigsäure
 - Hydroformylierung
 - Hydroaminomethylierung
 - Hydrocarboxylierung
 - Carbonylierung von Epoxiden
 - Carbonylierung von Alkylhalogeniden
 - Copolymerisierung von Olefinen und CO
 - Pauson-Khand Reaktion

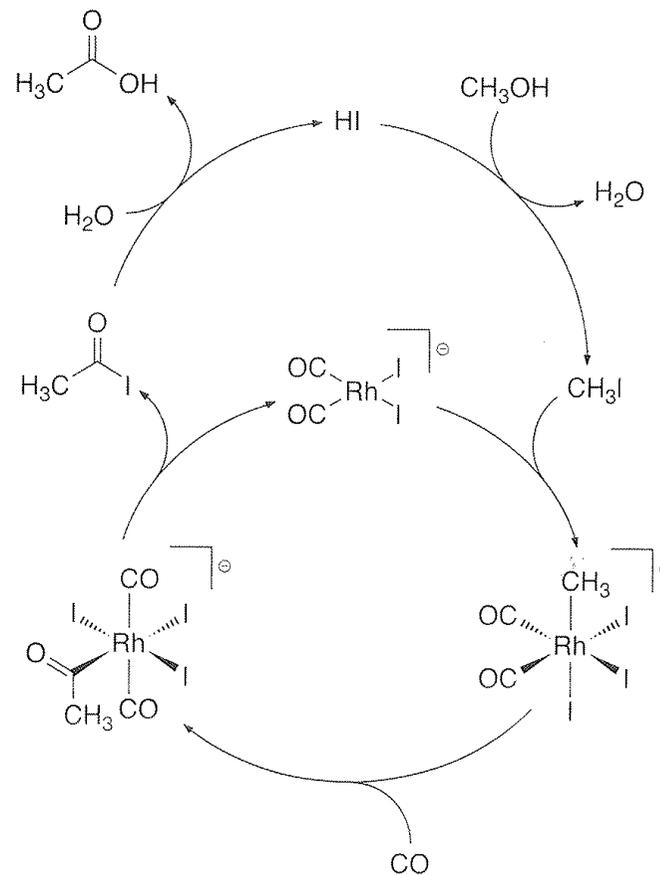
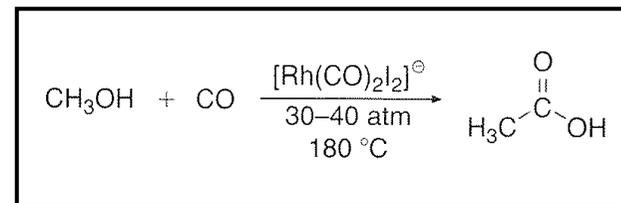
Übersicht

- Kreuzkupplungen
 - Kumada-Corriu
 - Negishi
 - Stille
 - Suzuki
 - Sonogashira
 - Enolatkupplung
 - Mizoroki-Heck
- Mechanismus
 - Homokupplung

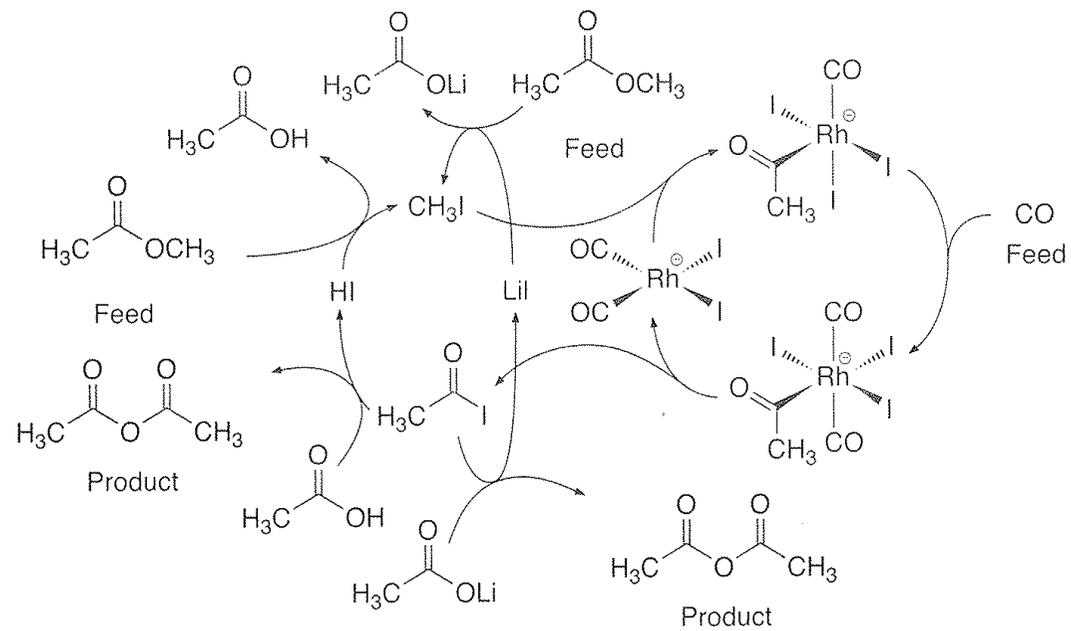
Übersicht

- C-Heteroatomkupplung
 - C-N: Buchwald-Hartwig
- Carbonylierende Kupplung
 - Ketone
 - Formylierung von Alkylhalogeniden
- Kupferkatalyse
 - Ullmann
- Direktarylierung

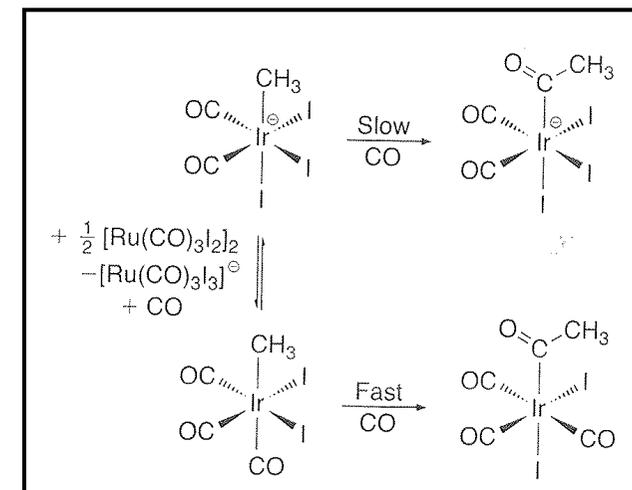
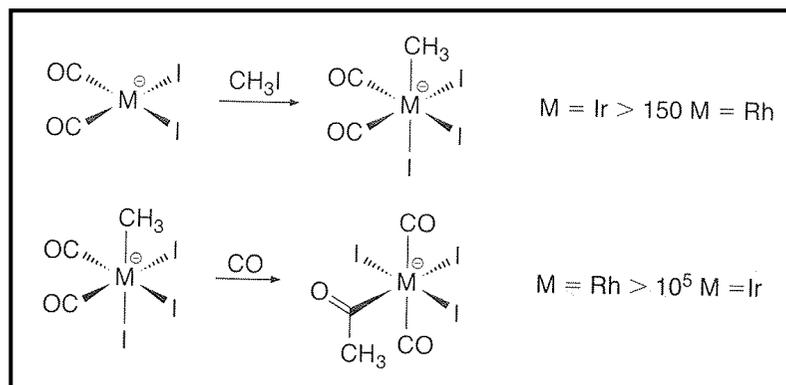
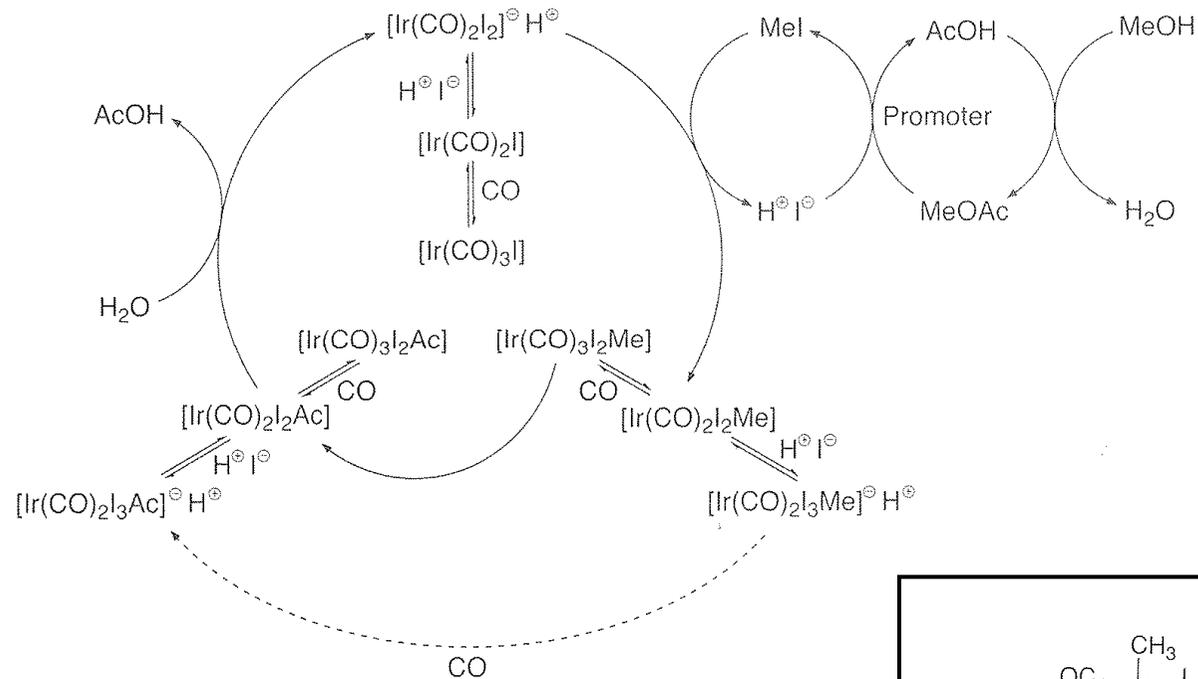
Monsanto-Essigsäure Prozess



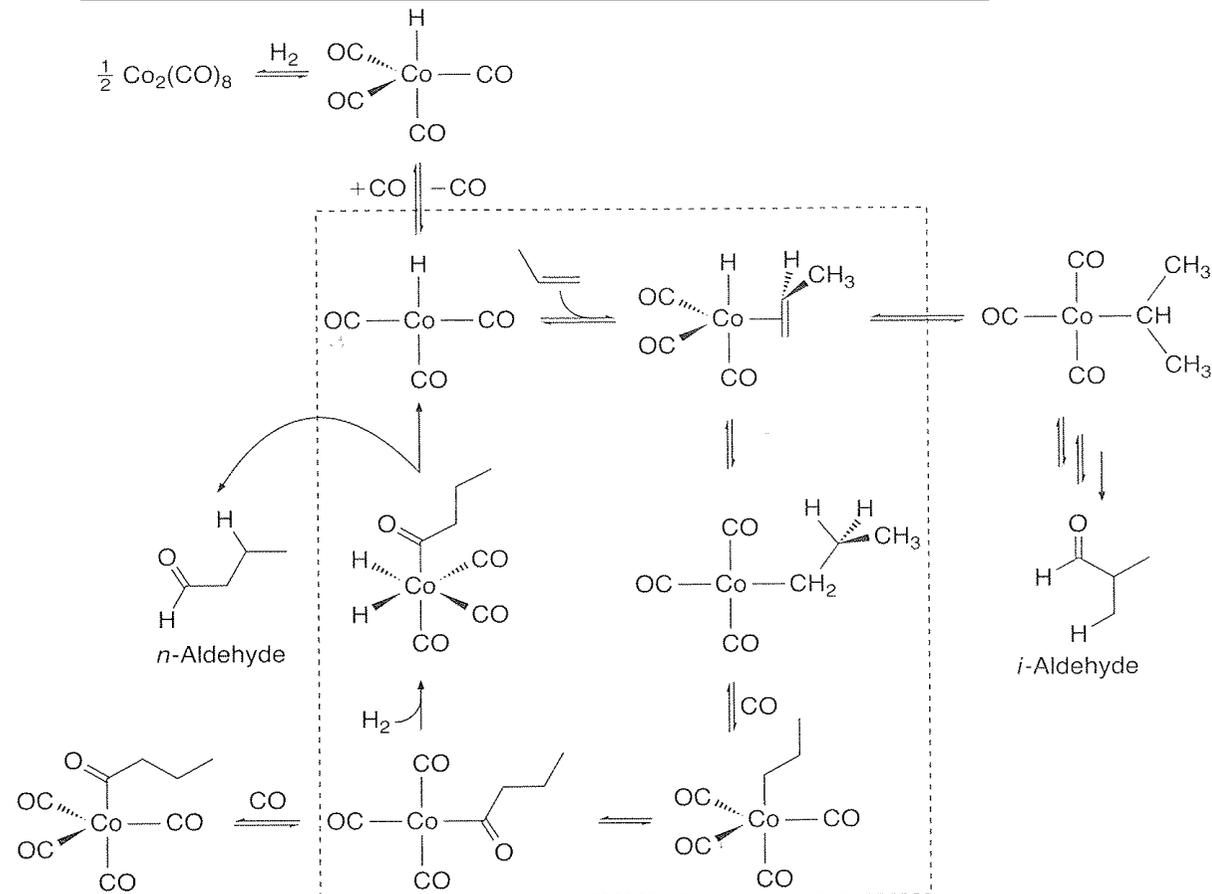
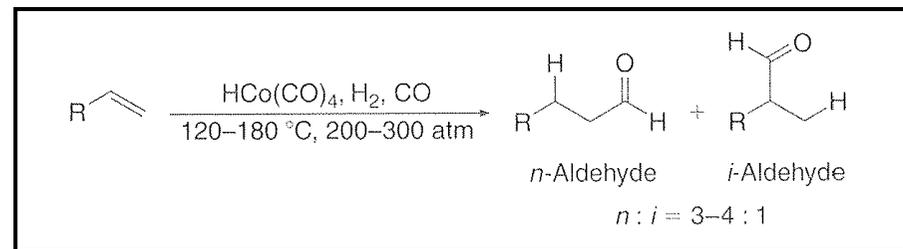
Eastman-Essigsäureanhydrid Prozess



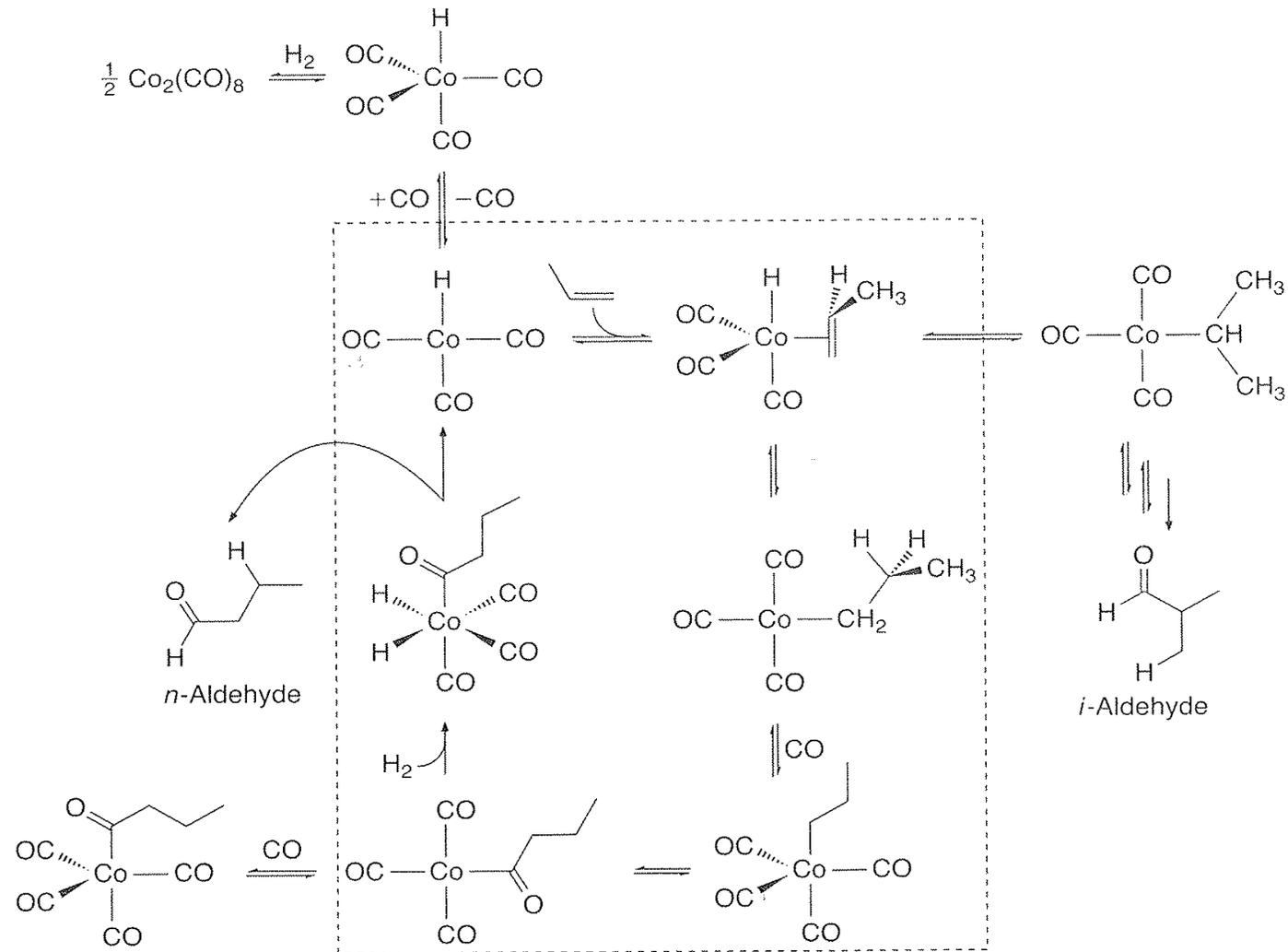
BP-Cativa Prozess



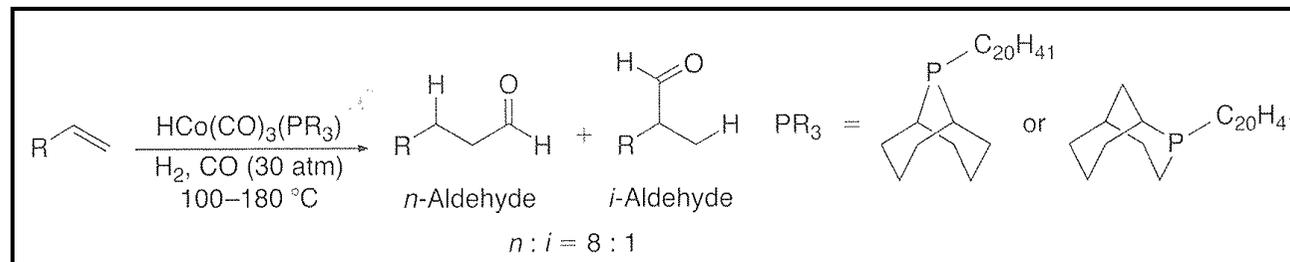
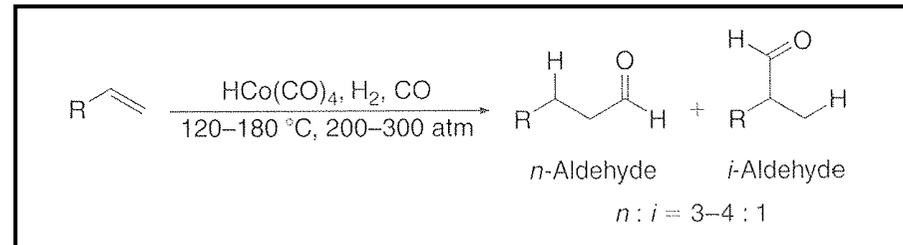
Hydroformylierung



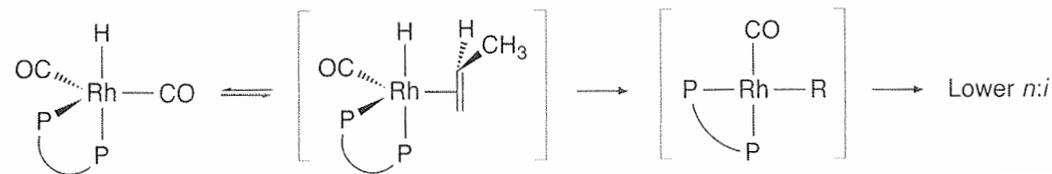
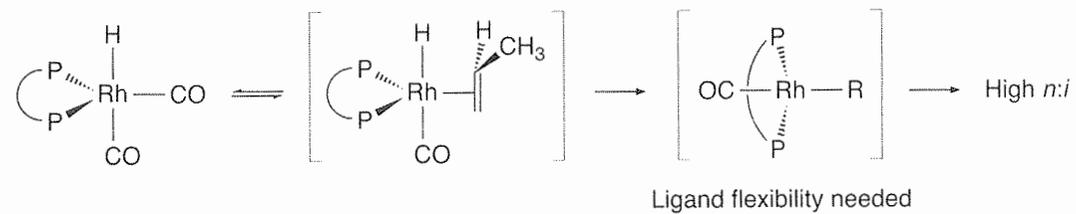
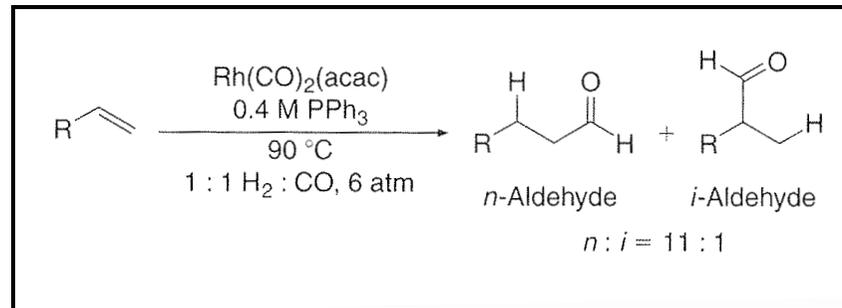
Hydroformylierung: $(\text{CO})_4\text{CoH}$

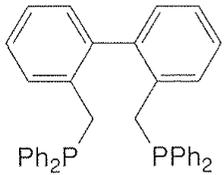
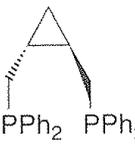
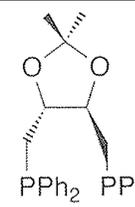
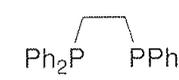


Hydroformylierung: *n*:*i*-Selektivität

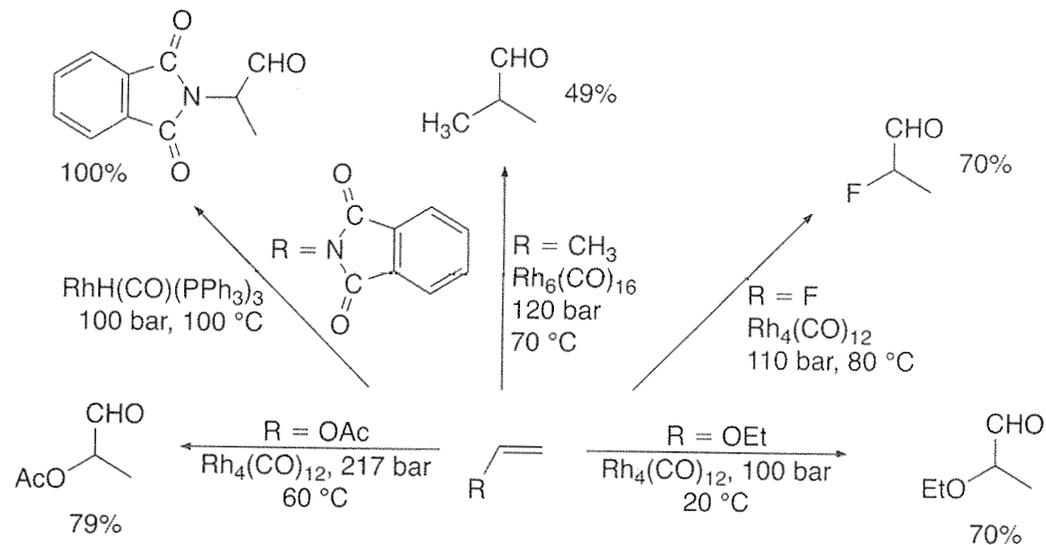
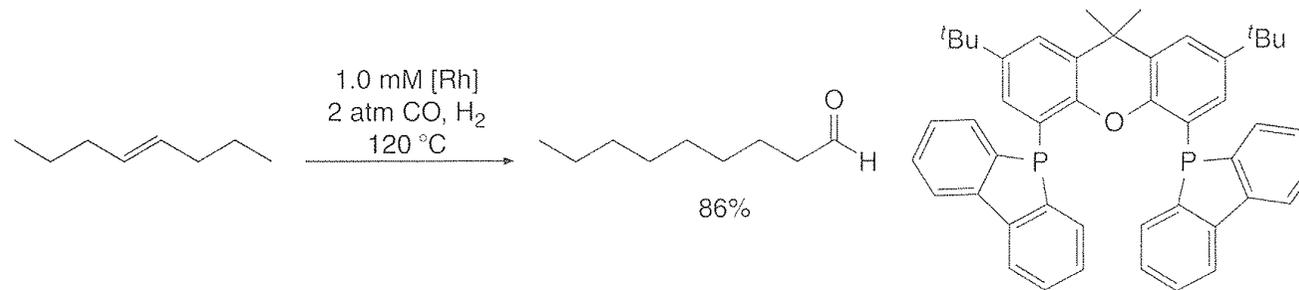


Hydroformylierung: Rh-Katalyse

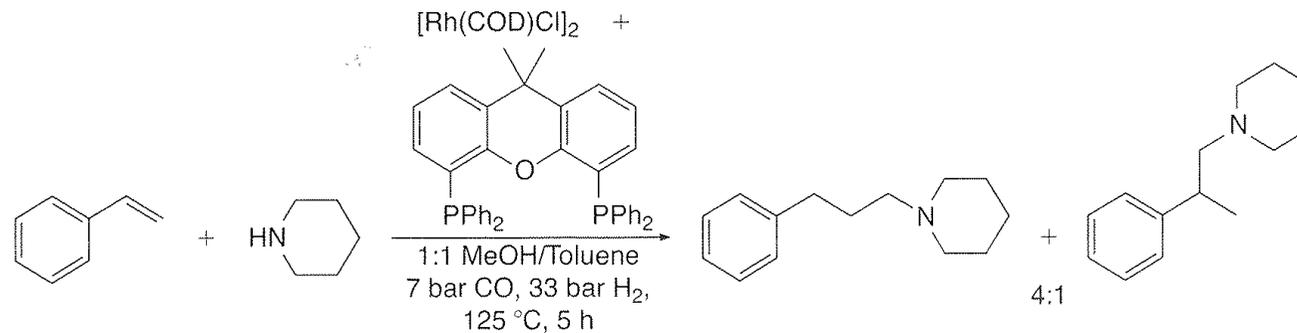
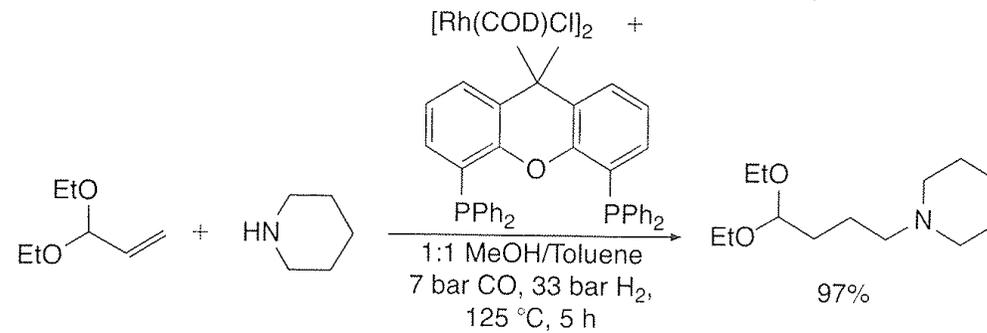
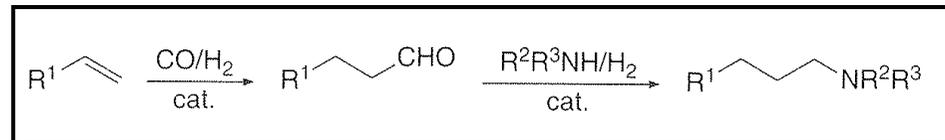


				
Ph ₂ P	PPh ₂	PPh ₂	PPh ₂	
PPh ₂	PPh ₂	PPh ₂	PPh ₂	
BISBI	diop	diop	dppe	
Bite angle	113°	107°	102°	85°
<i>n</i> : <i>i</i> aldehyde	66	12	8.5	2.1

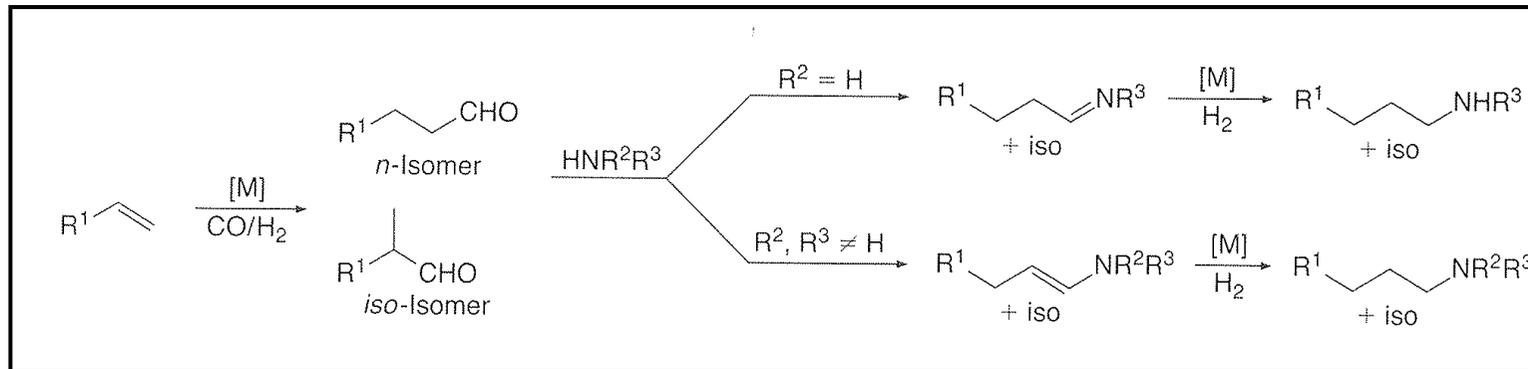
Hydroformylierung: Interne Alkene und EWGs



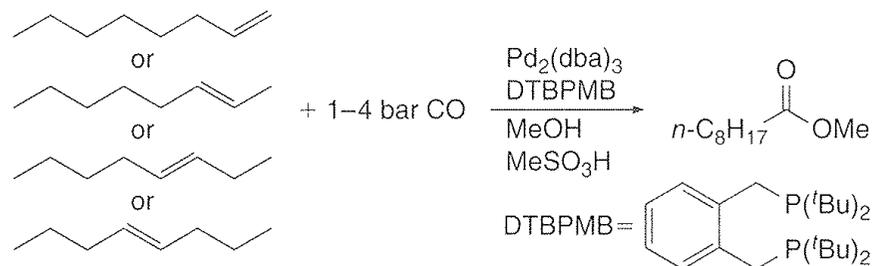
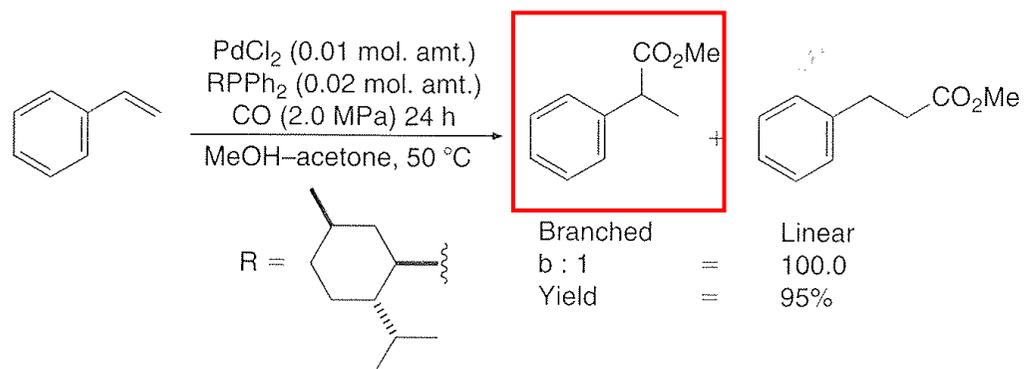
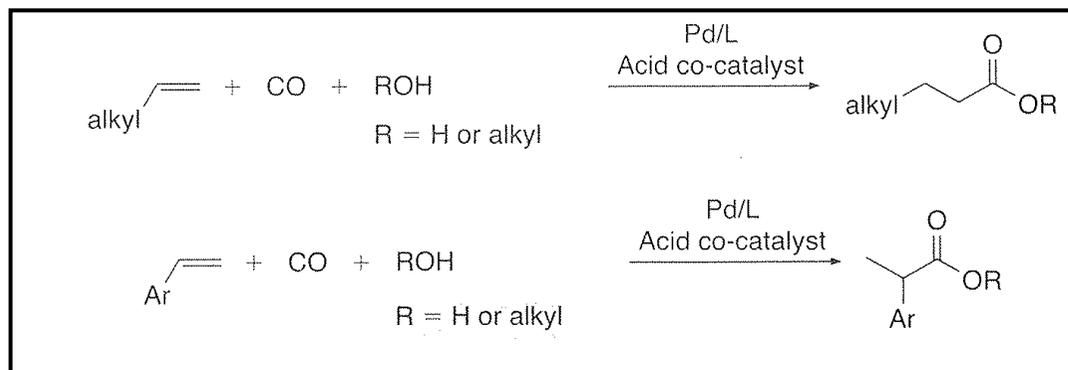
Hydroaminomethylierung



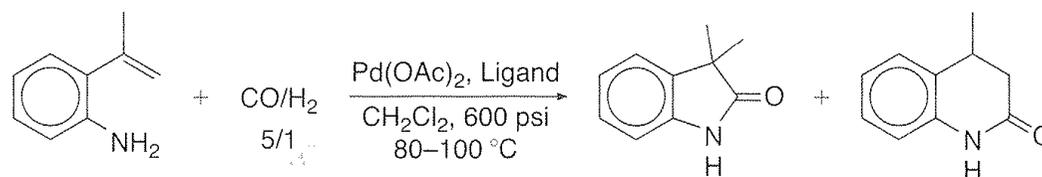
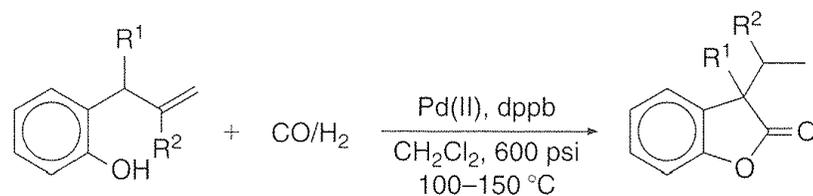
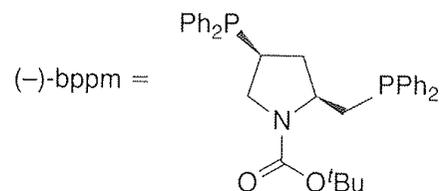
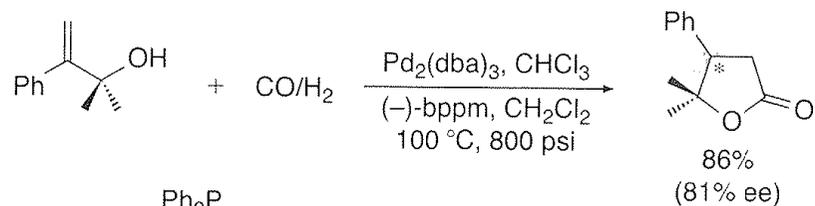
Hydroaminomethylierung



Hydrocarboxylierung und -veresterung



Hydrocarboxylierung und -veresterung



Ligand = PCy₃
dppb

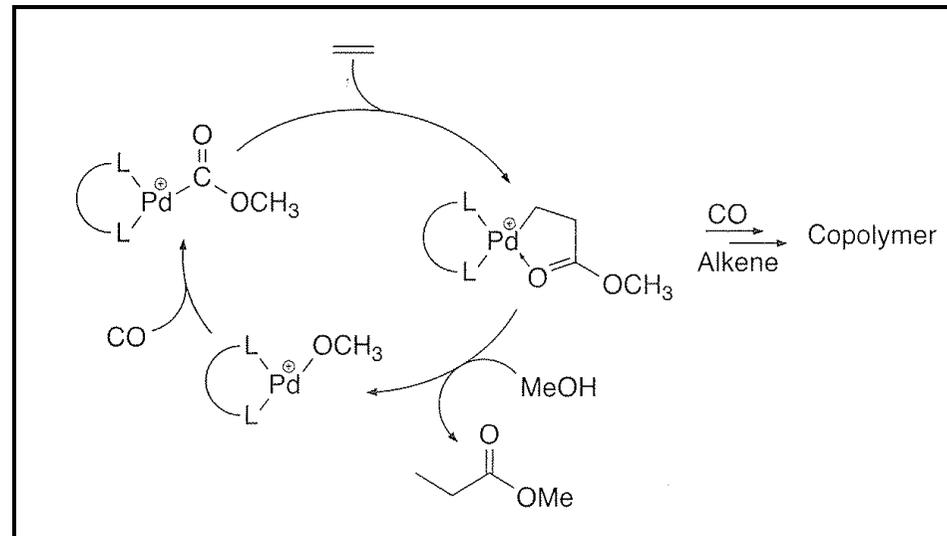
95% yield
75% yield

100
0

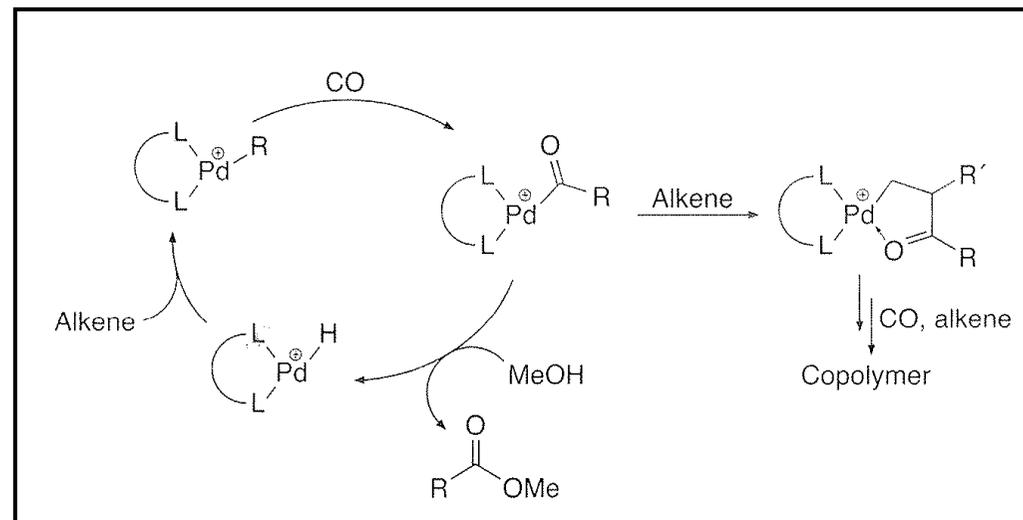
0
100

Hydrocarboxylierung und -veresterung

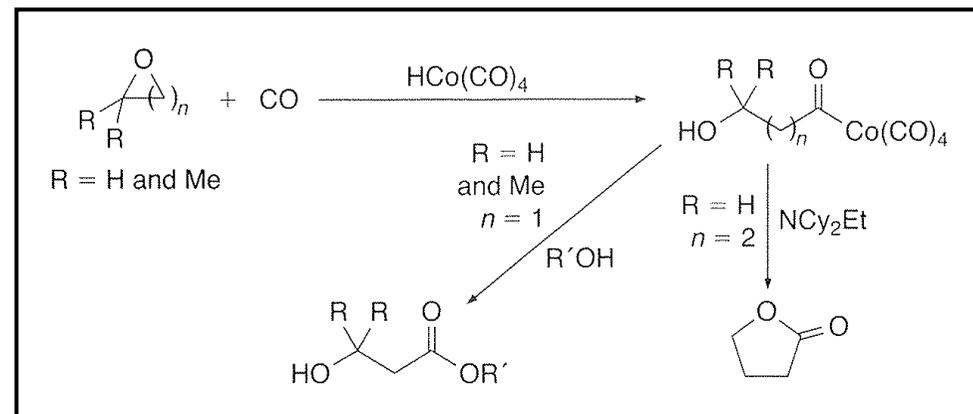
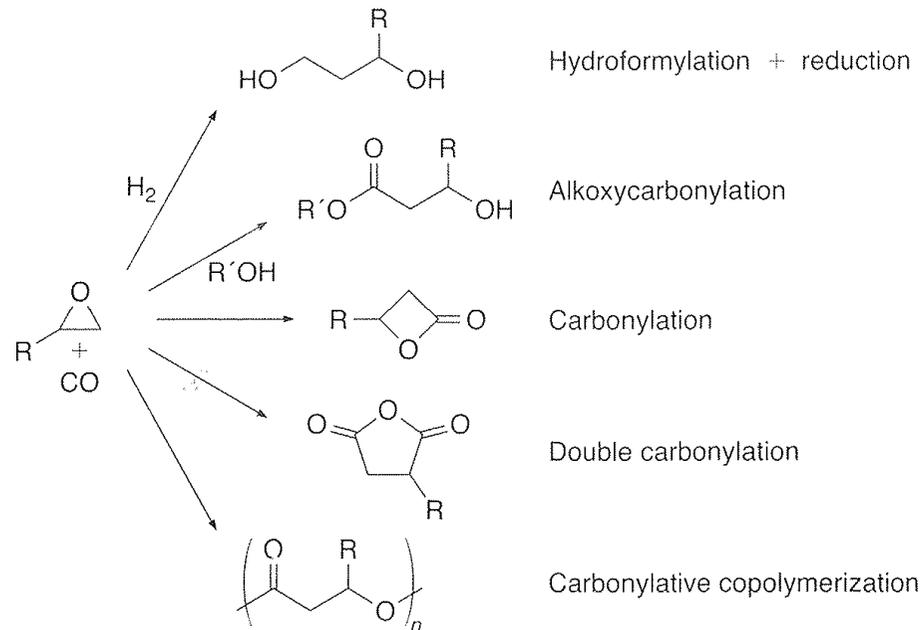
Alkoxid Kreislauf



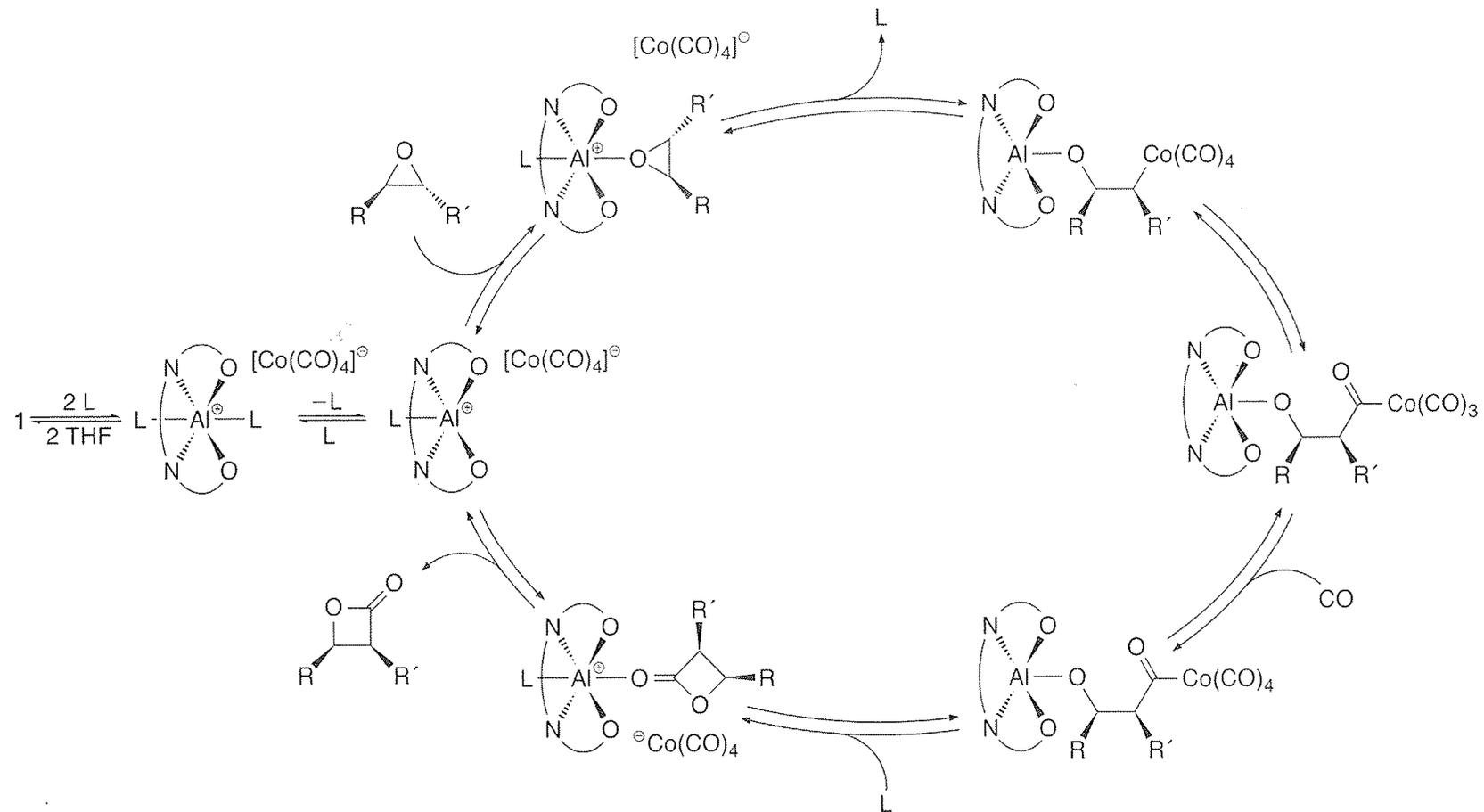
Hydrid Kreislauf



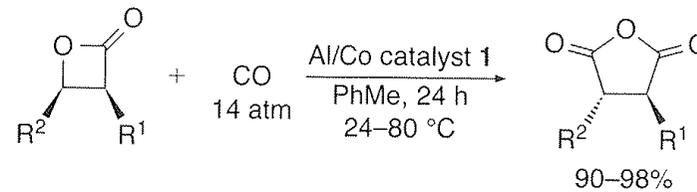
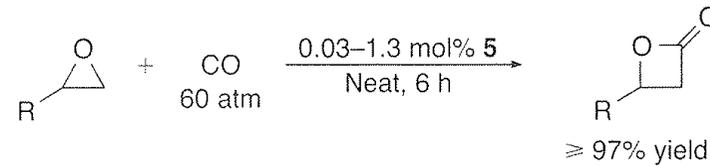
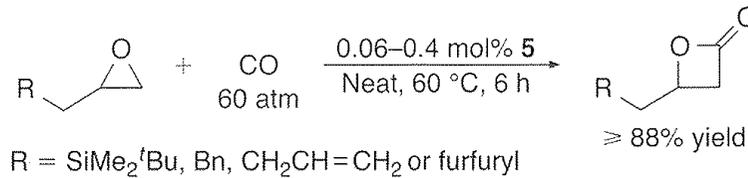
Epoxidcarbonylierung



Epoxidcarboxylierung

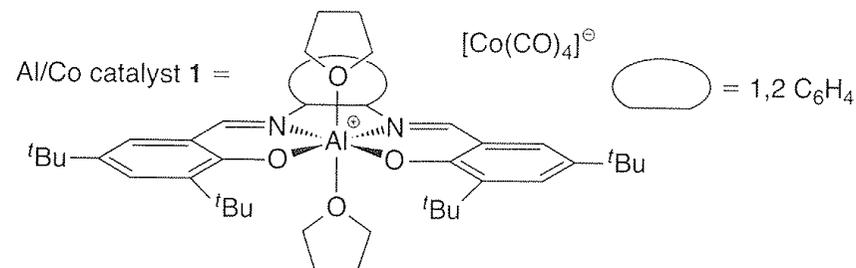


Epoxidcarboxylierung

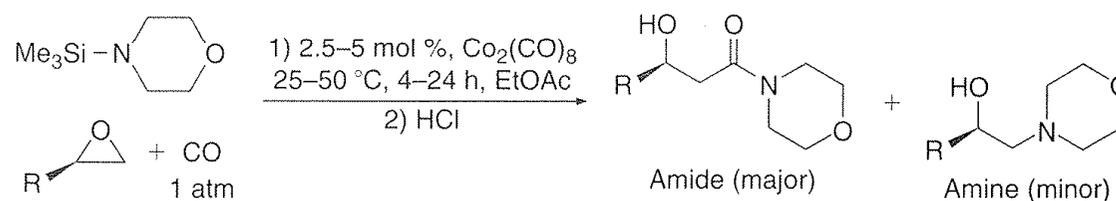
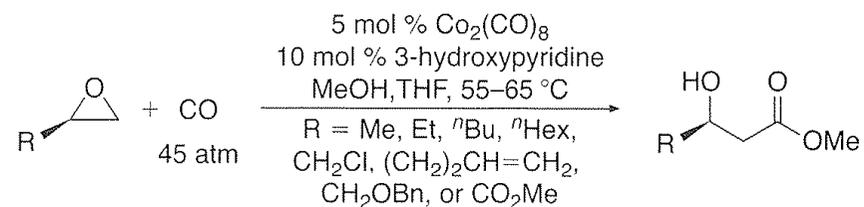
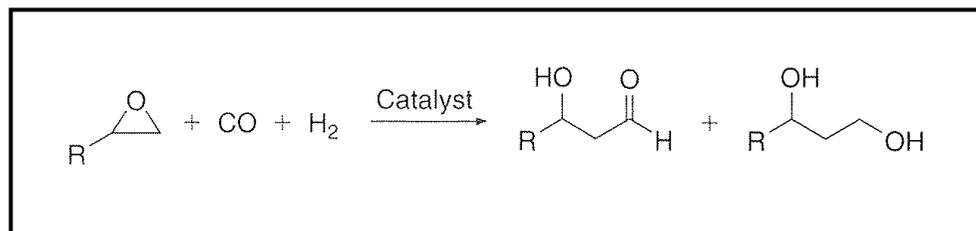


$\text{R}^1 = \text{H or Me}$

$\text{R}^2 = \text{H, Me, Et, decyl, CH}_2\text{O}^n\text{Bu, CH}_2\text{OSiMe}_2^t\text{Bu or (CH}_2\text{)}_2\text{CH=CH}_2$

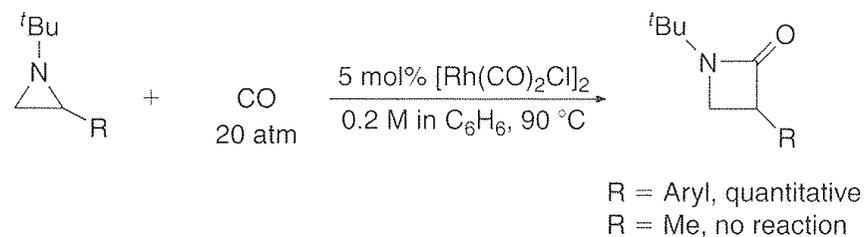
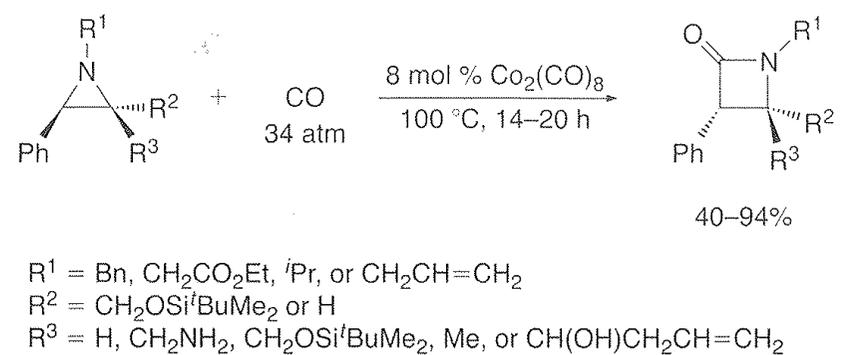
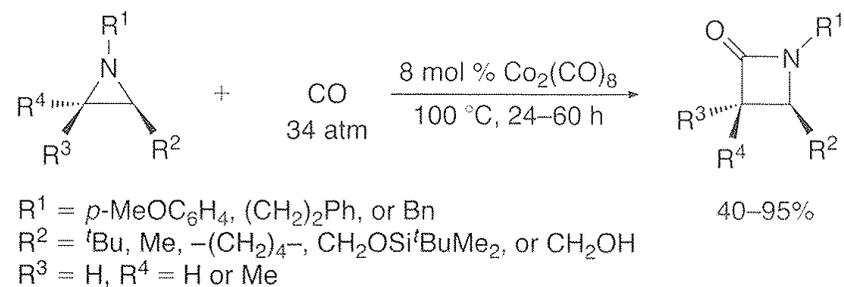


Ringöffnende Epoxidcarboxylierung

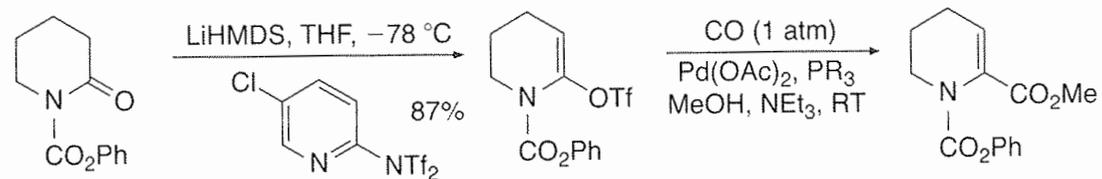
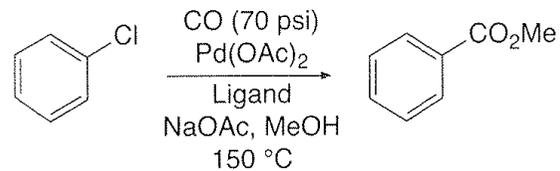
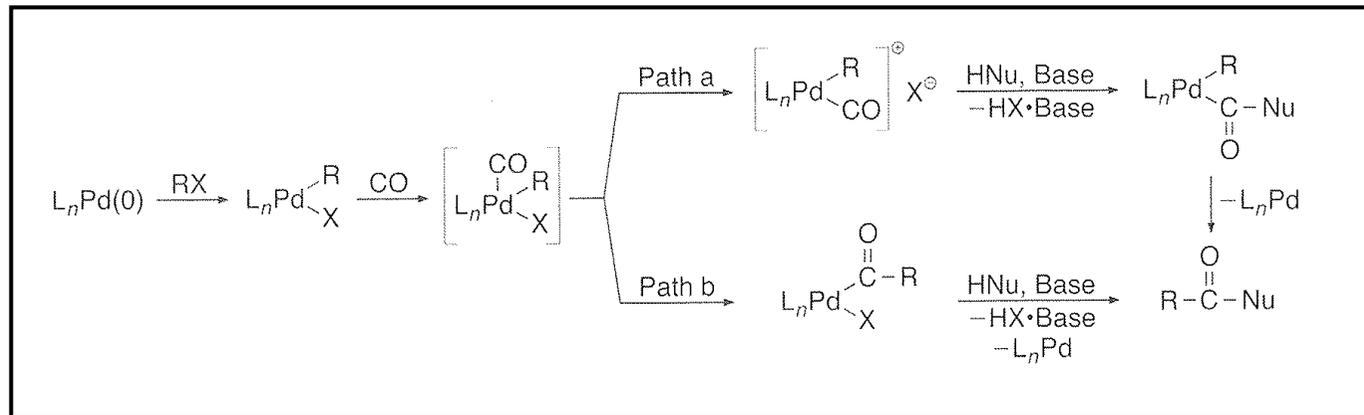


R = Me, Et, ⁿBu, CH₂Cl, (CH₂)₂CH=CH₂,
CH₂OⁱPr, CH₂OBn, or CH₂OC(O)ⁿPr

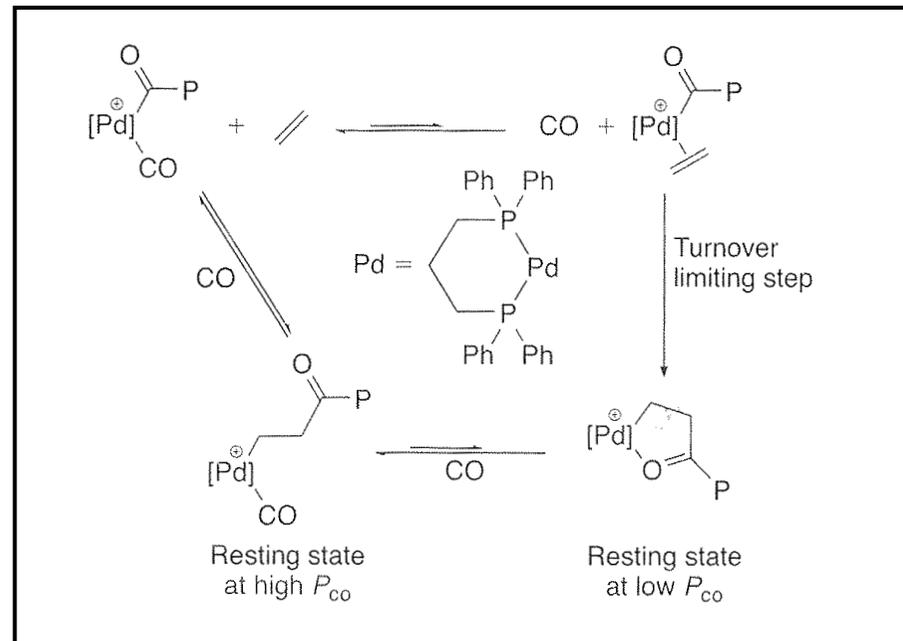
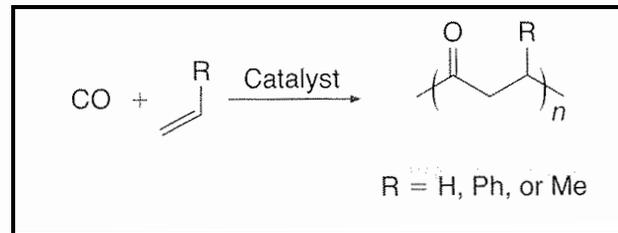
Aziridincarbonylierung



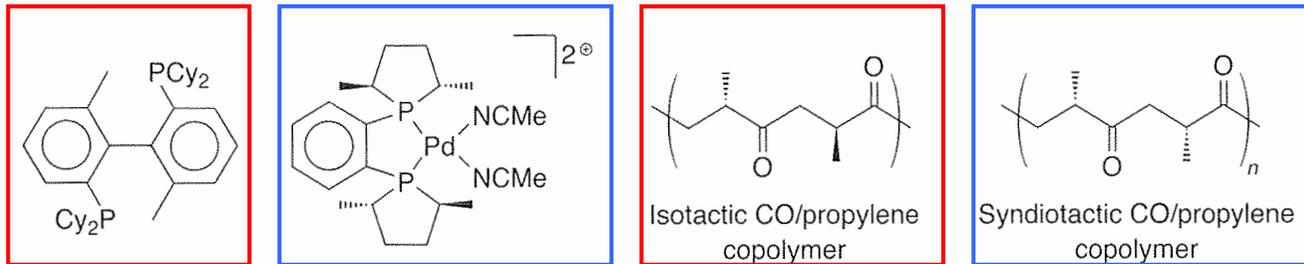
Carbonylierung von organischen Halogeniden



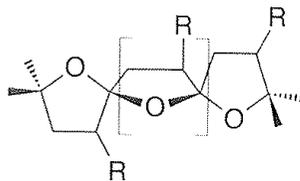
Copolymerisierung von CO und Olefinen



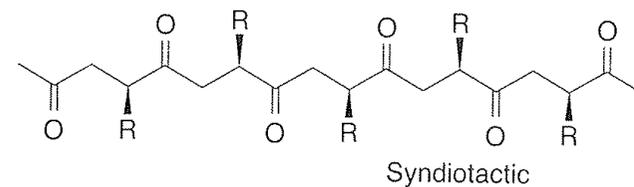
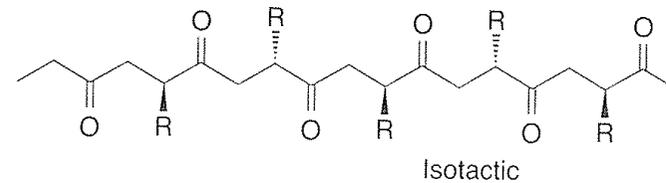
Copolymerisierung von CO und Propen



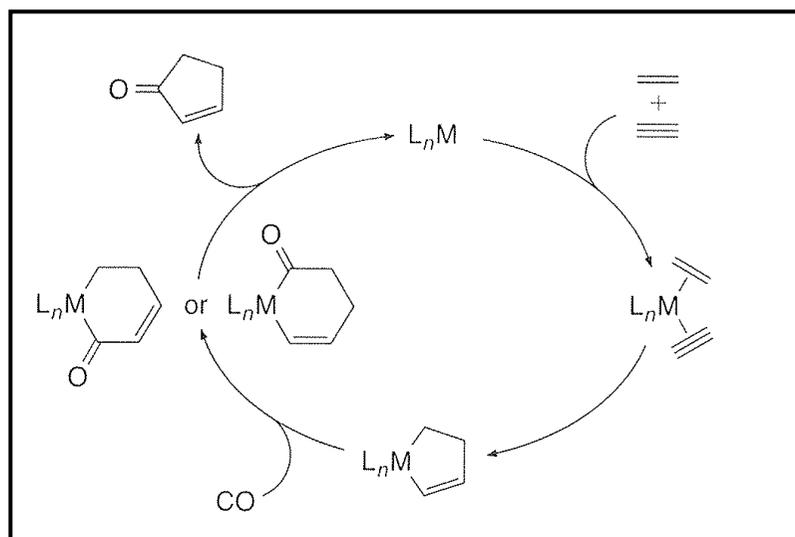
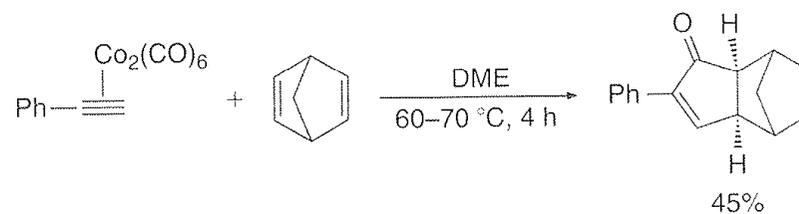
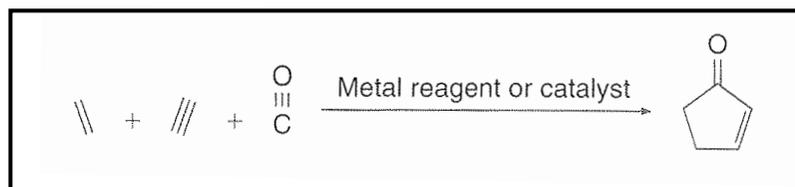
Biaryl bisphosphine reported by Consiglio and catalyst reported by Sen for the copolymerization of carbon monoxide and propene to form syndiotactic CO/propylene copolymer.



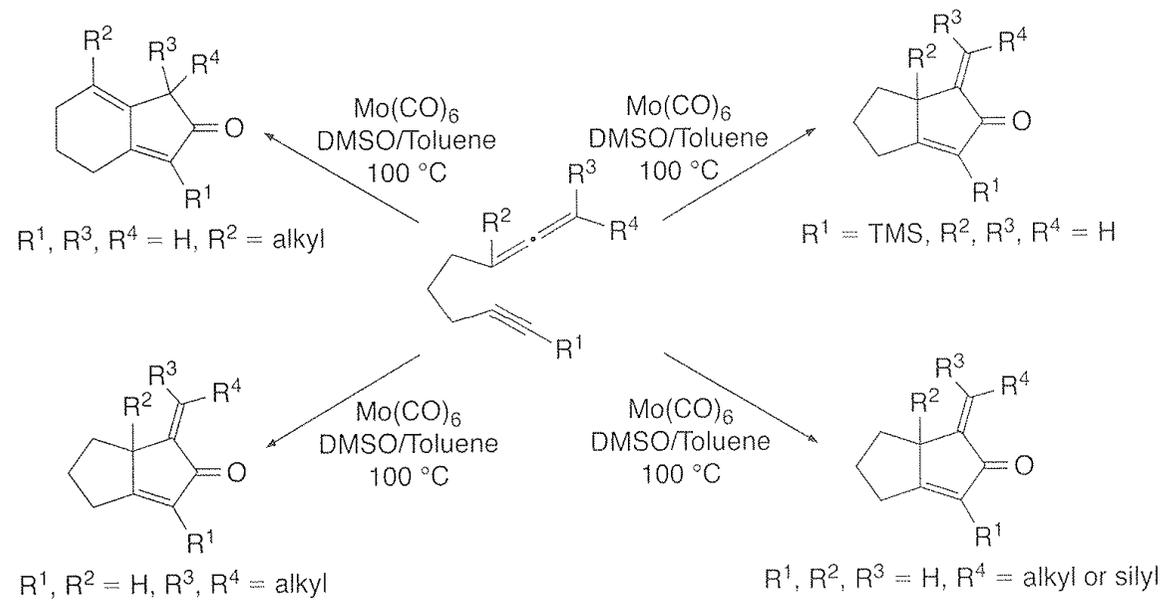
Ketal structure of the copolymer of CO and propene formed in the absence of protic component.



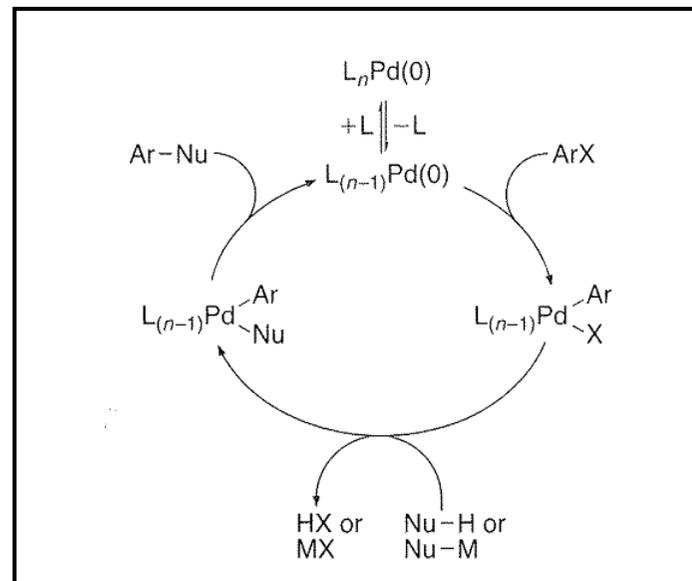
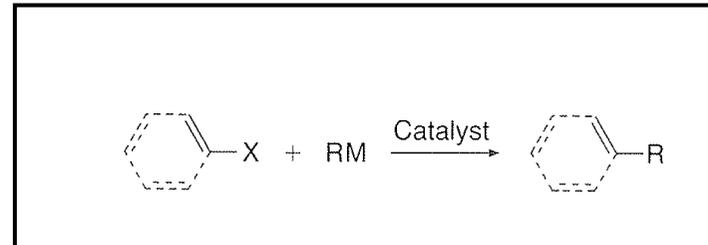
Pauson Khand Reaktion



Pauson Khand Reaktion mit Allenen

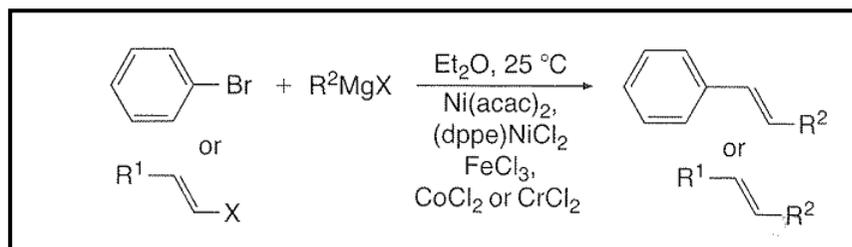


Kreuzkupplungen

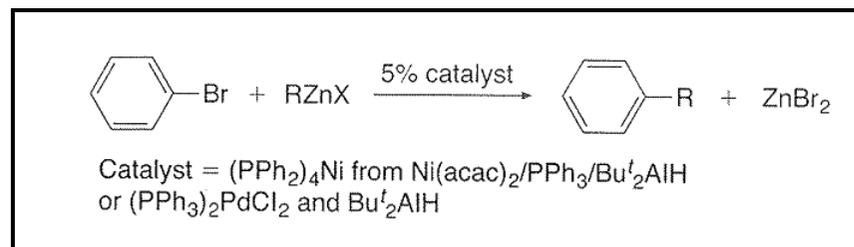


Kreuzkupplungen

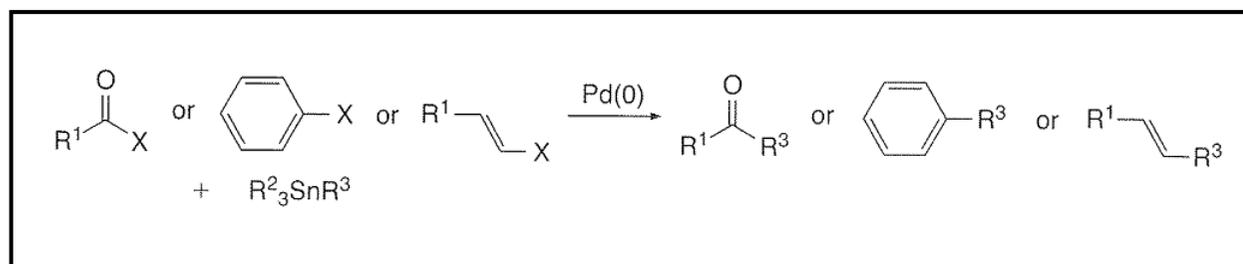
Kumada-Corriu



Negishi

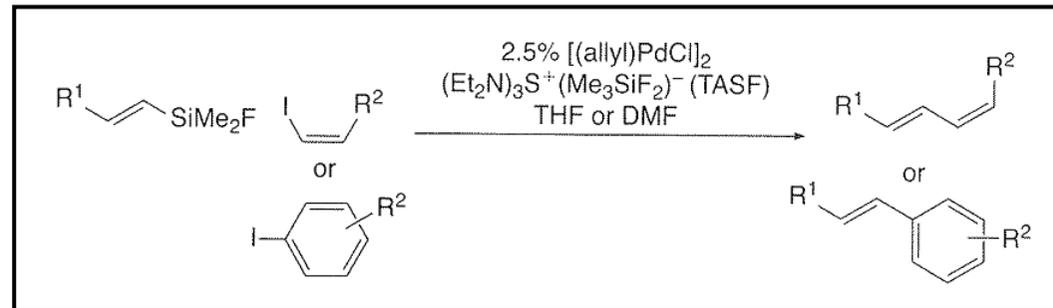


Stille

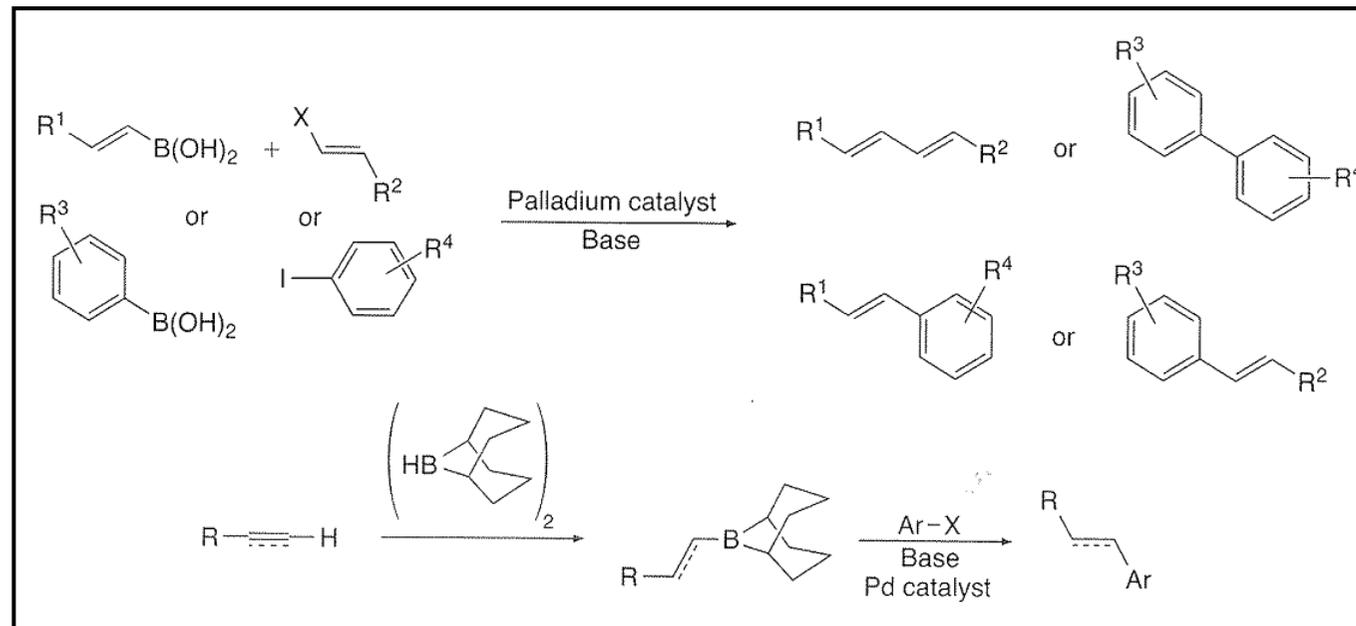


Kreuzkupplungen

Hiyama-Tamao

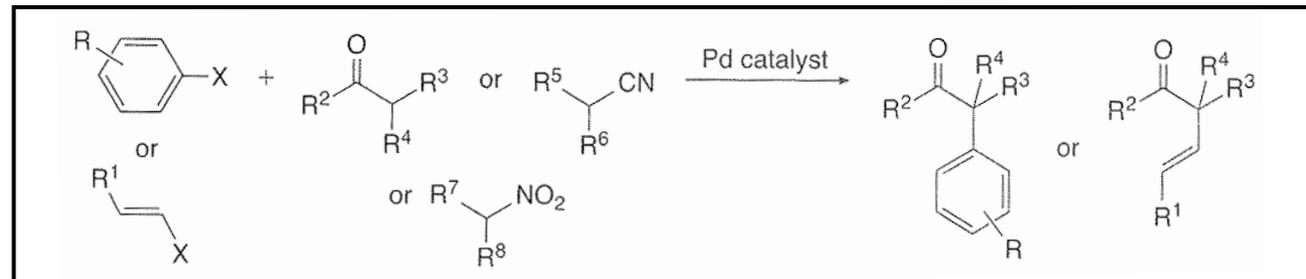
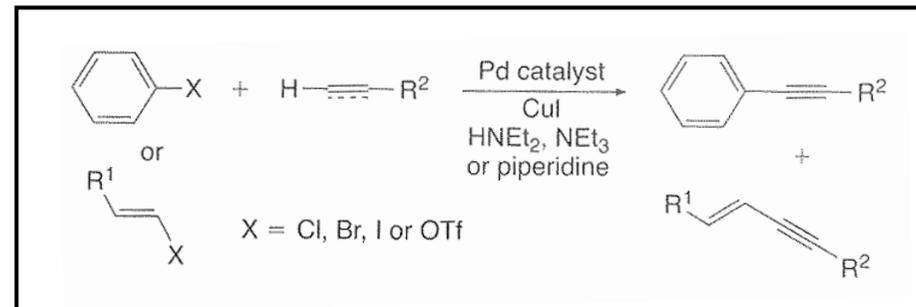


Suzuki

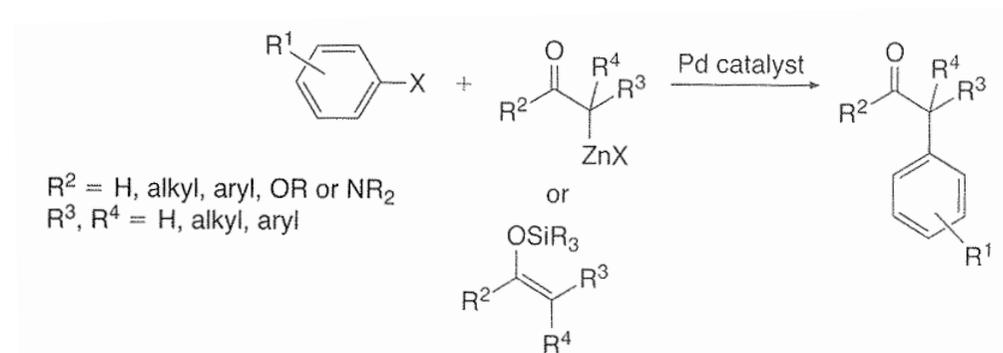


Kreuzkupplungen

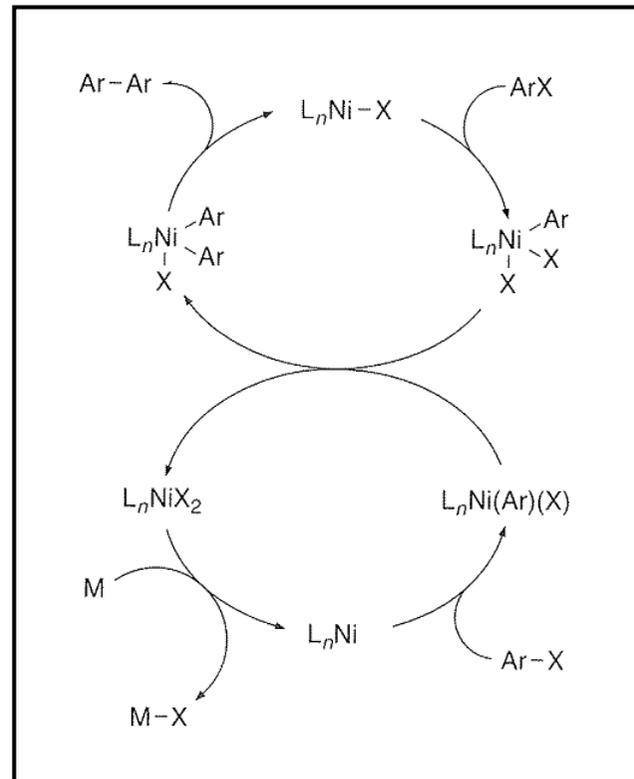
Sonogashira



Enolatkupplung

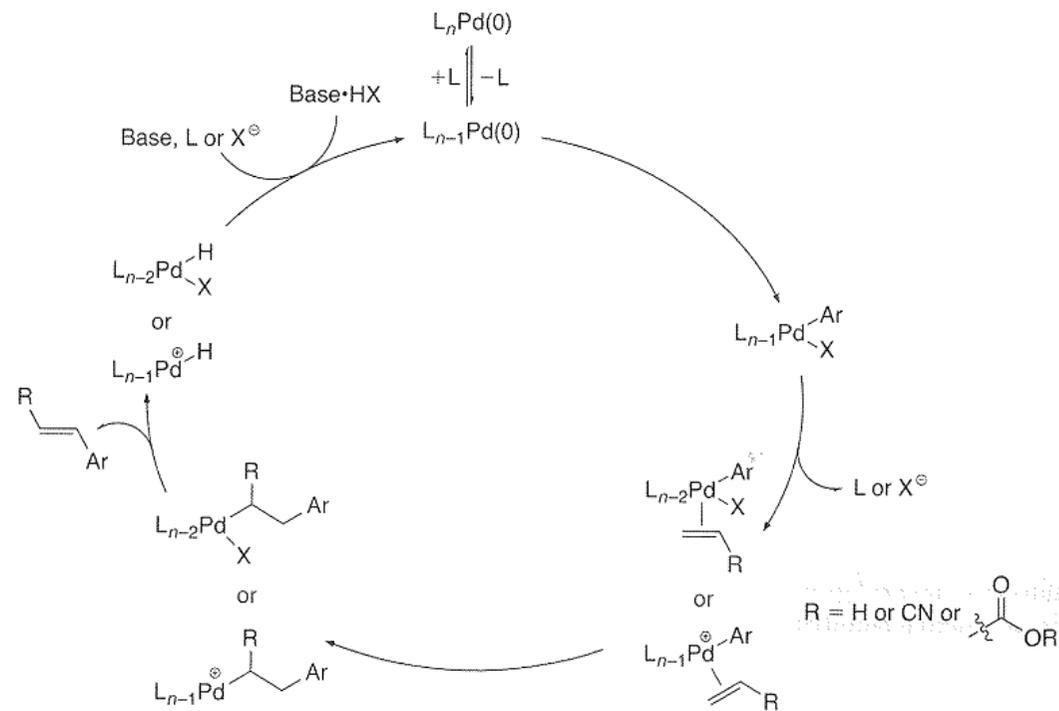
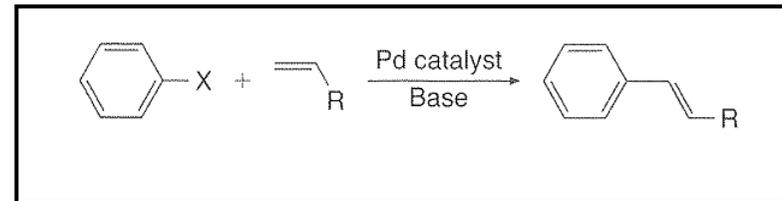


Homokupplungen

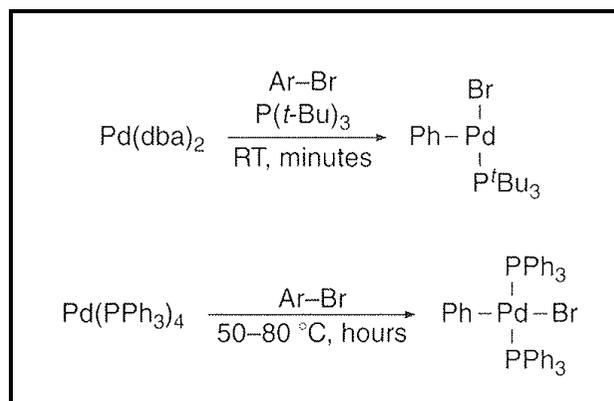


Kreuzkupplungen

Mizoroki-Heck



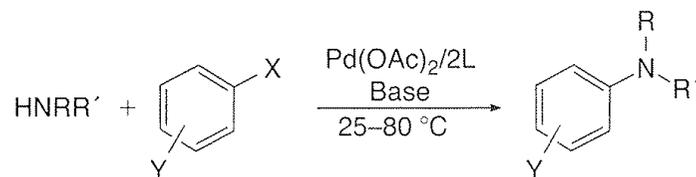
Kreuzkupplungen: Ligandeneffekte



Sterically hindered ligands **accelerate oxidative addition** because they favor generation of the unsaturated intermediate that reacts with the aryl halide, and they **accelerate reductive elimination** because reductive elimination reduces the steric congestion of the palladium(II) species created by the hindered ligands. Moreover steric hindrance can even **accelerate transmetalation** in some cases. Steric hindrance of a monophosphine ligand can accelerate transmetalation in the Stille reaction by increasing the concentration of the unsaturated palladium intermediate that reacts with the organotin reagent.

Kreuzkupplungen: C-X Bindungsbildung

Buchwald-Hartwig



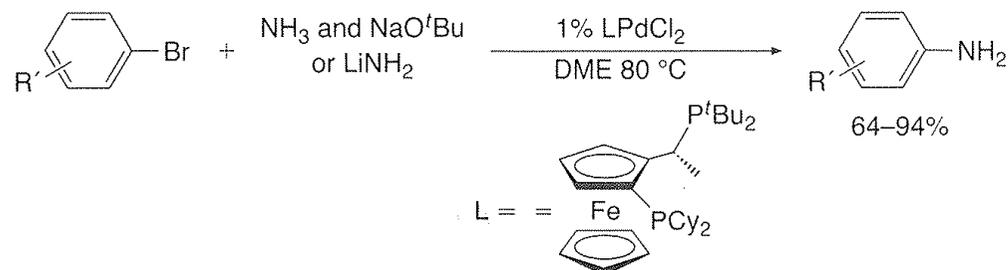
X = Cl, Br, I, OTf, or OTs

L = Hindered monodentate ligands:

P(*o*-tolyl)₃, P(*t*-Bu)₃, Ph₅FcP(*t*-Bu)₂ (Q-phos), heterocyclic carbenes, (Biaryl)PR₂,
 –OP(*t*-Bu)₂, and Verkade's proazaphosphatranes

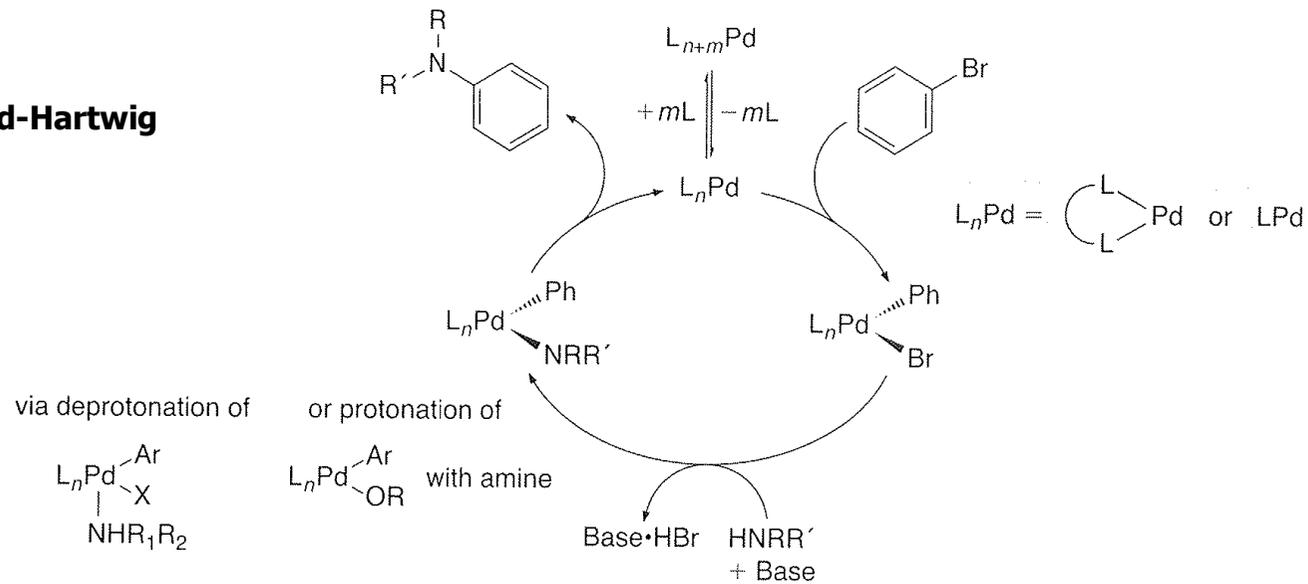
L = Chelating bidentate ligands:

dppf, BINAP, Xantphos, and Josiphos ligands

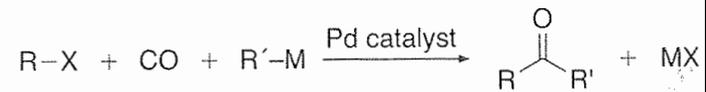


Kreuzkupplungen: C-X Bindungsbildung

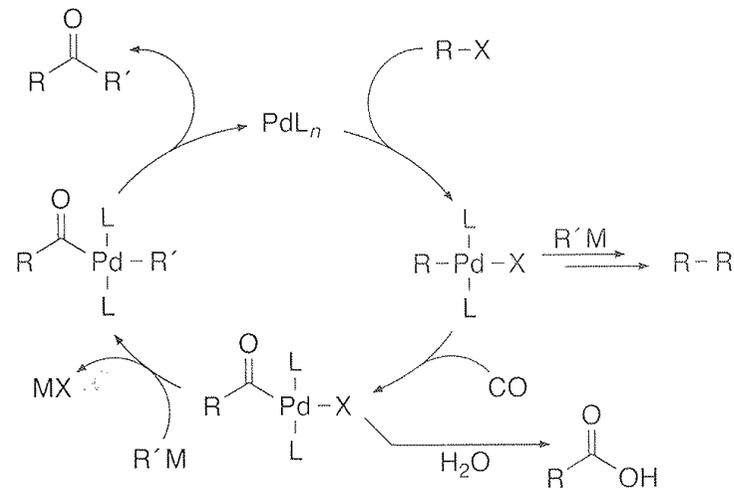
Buchwald-Hartwig



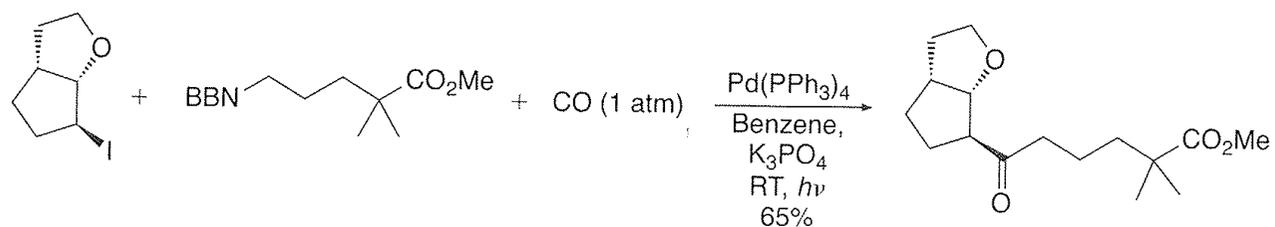
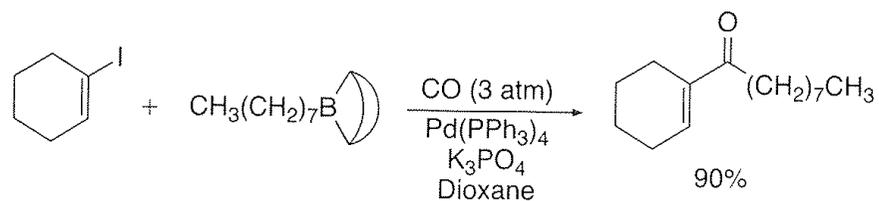
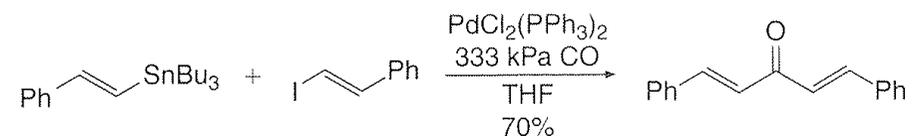
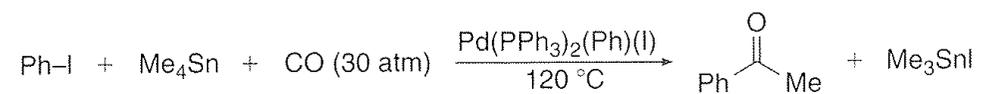
Kreuzkupplungen: Carbonylierung -> Ketonen



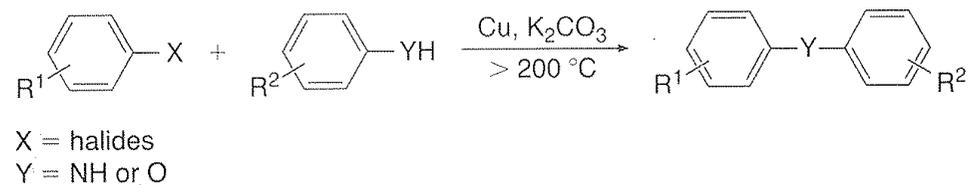
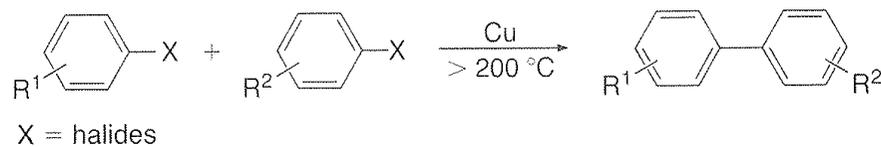
R = Ar, vinyl, benzyl, or alkyl
M = SnR''₃, BR''₂, or ZnX



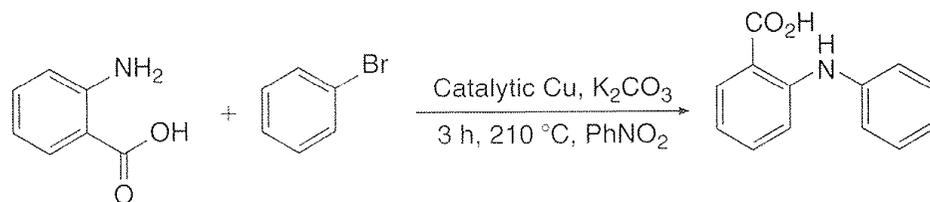
Kreuzkupplungen: Carbonylierung -> Ketonen



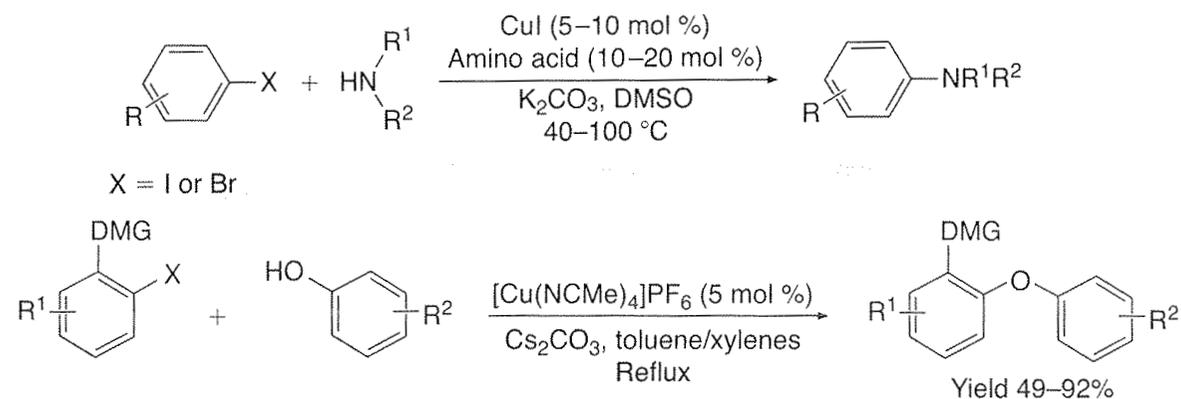
Kupfer vermittelte Kupplungen



Ullmann



Kupfer vermittelte Kupplungen

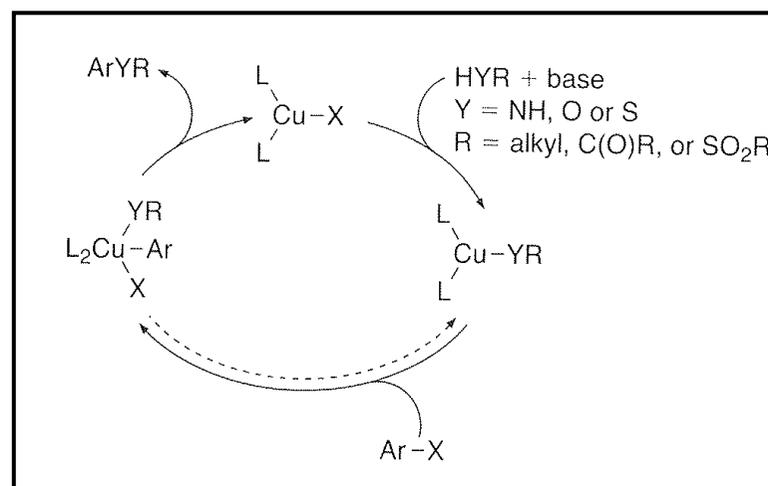


X = I, Br, or Cl

DMG = C(O)NH_{Et}, C(O)NEt₂, SO₂NH_{Et}, or SO₂NEt₂

R₁ = H, Me, or OMe

R₂ = H, Me, F, OMe, or CONEt₂



Direktarylierung

