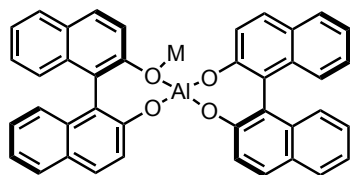
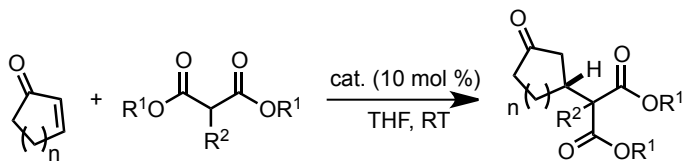
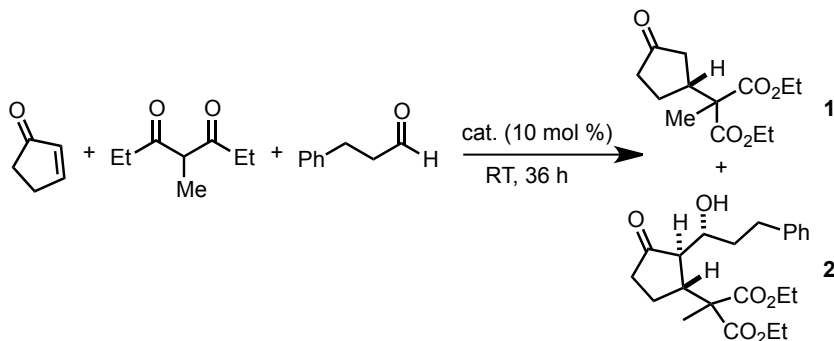


A New Multifunctional Heterobimetallic Asymmetric Catalyst for Michael Additions and Tandem Michael–Aldol Reactions

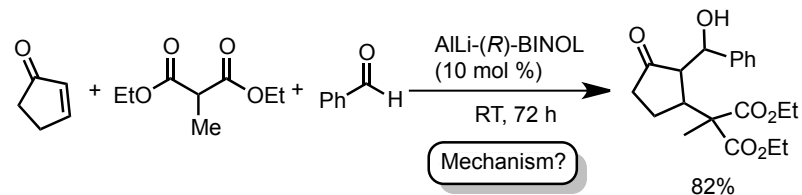
Shibasaki et al; *ACIEE* **1996**, 35, 104–106.



catalyst prepared from LiAlH_4 and (*R*)-BINOL

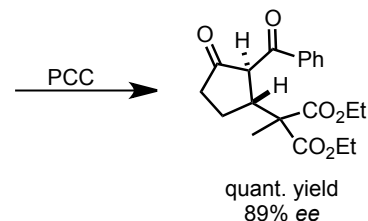


Catalyst	1		2	
	Yield [%]	ee [%]	Yield [%]	ee [%]
AlLi-(<i>R</i>)-BINOL	7	90	64	91
LaLi-(<i>R</i>)-BINOL	46	3	30	–
La-(<i>R</i>)-BINOL	73	86	trace	–
LaNa(<i>R</i>)-BINOL	57	83	trace	–



Mechanism?

82%



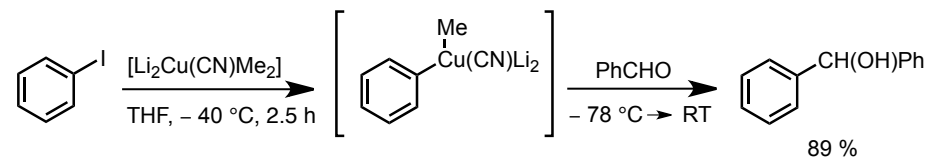
quant. yield
89% ee

Use of LaLi-BINOL, LaNa-BINOL or Li free La-BINOL gave poor results in the three-component coupling reaction.

"This is the first example of a catalytic asymmetric tandem Michael–aldol reaction."

Cuprates as Selective Metalating Reagents for Aromatic Halides

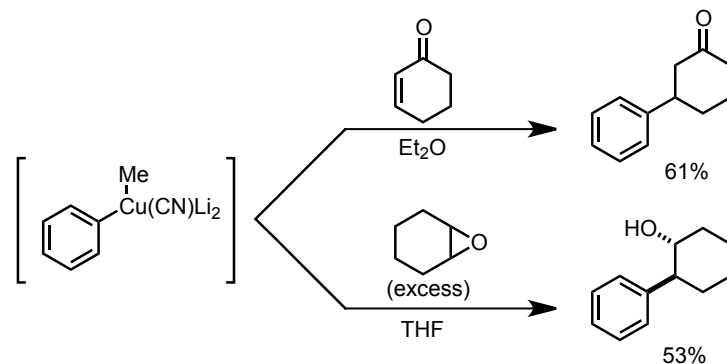
Sakamoto et al; *ACIEE*, **1996**, 35, 736–738.



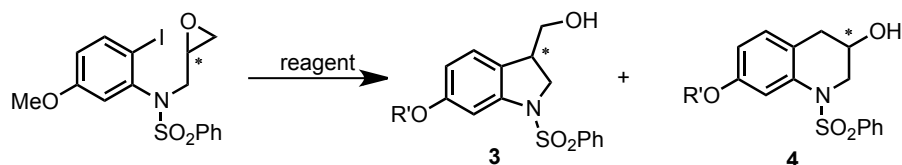
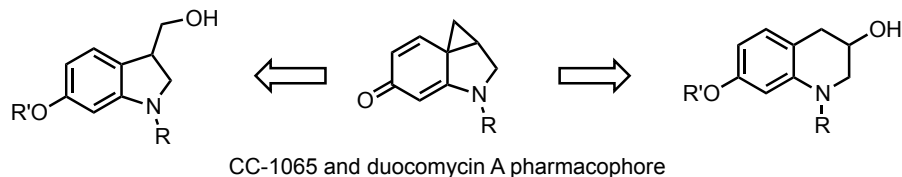
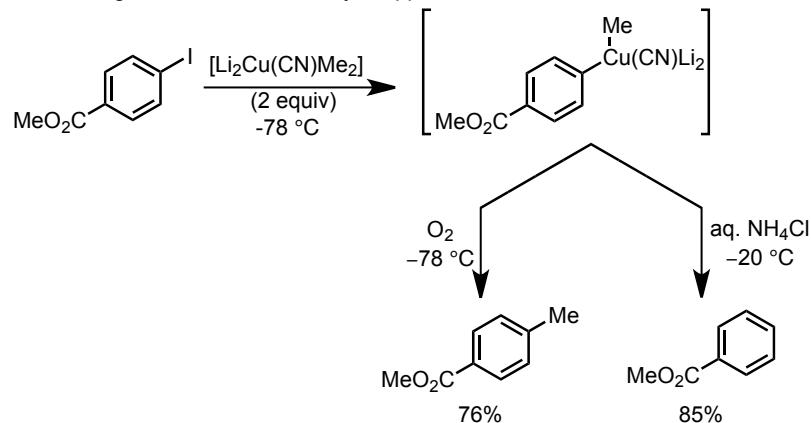
89 %

Functionalized organocupper reagents are typically prepared by transmetalation of functionalized organozincs or direct oxidative addition of activated copper to organic halides.

Modern Organocopper Chemistry; Norbert Krause, Ed.; Wiley-VCH: GmbH, **2002**.



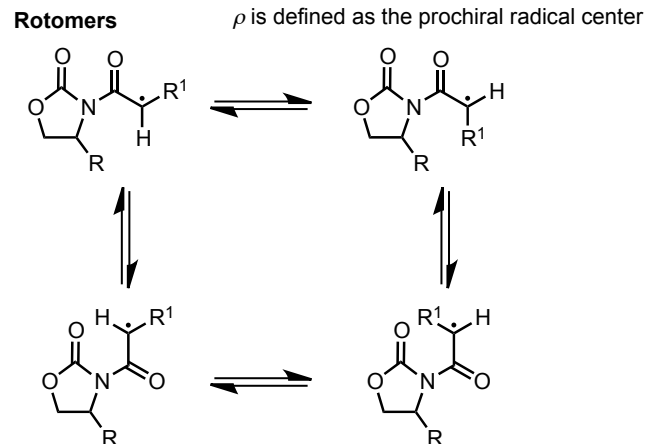
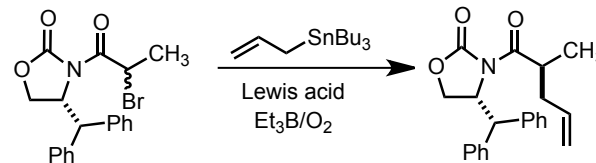
Determining the structure of the aryl-copper intermediate



Reagent	Temperature	3 Yield [%] (ee [%])	4 Yield [%] (ee [%])
n-BuLi	-90 °C	43 (93)	0
[Li ₃ ZnMe ₃ (SCN) ₂]	-78 °C	72 (90)	15(91)
[Li ₃ Cu(CN)Me ₃]	-78 °C	0	73(92)

Reversed regioselectivity with use of Cu

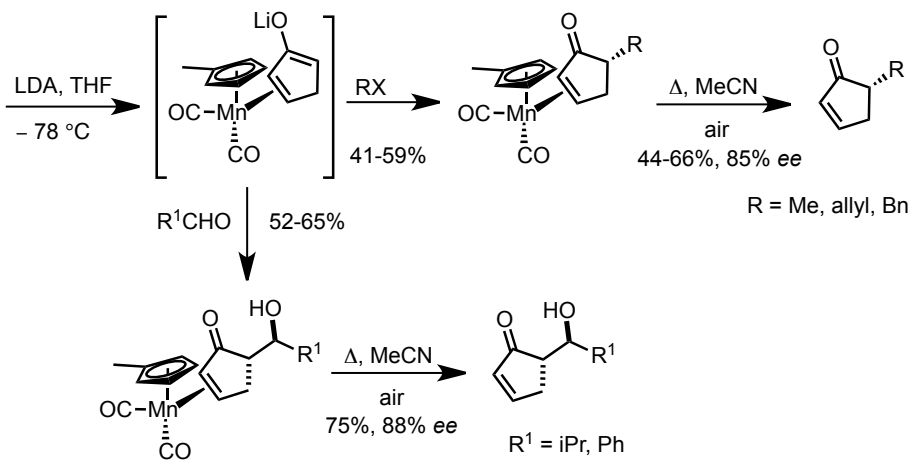
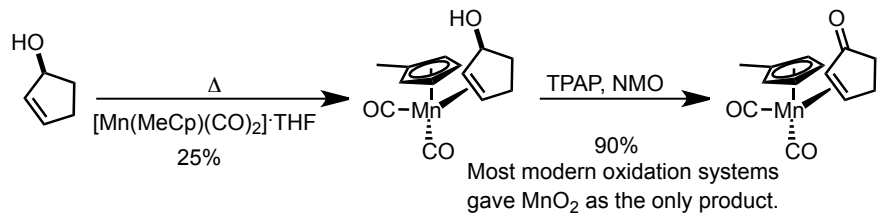
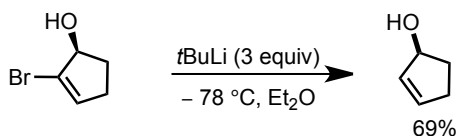
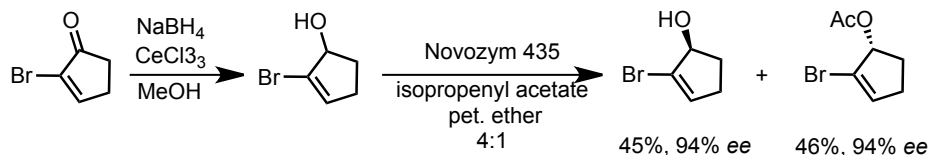
Acyclic Stereocontrol in Radical Reactions: ρ -Selectivity with Oxazolidinone Auxiliaries

Sibi et al; *ACIEE*, 1996, 35, 190-192.For a discussion on acyclic stereocontrol in free-radical reactions see:
Acc. Chem. Res. 1991, 24, 296-304.

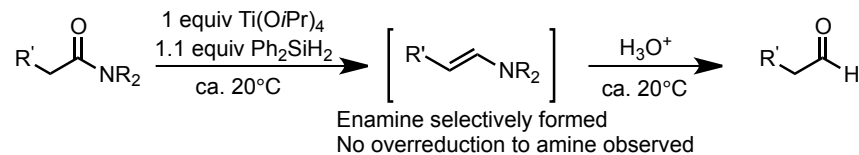
Lewis Acid	Conditions	Yield [%]	Ratio (RS:RR)
none	-78 °C, CH ₂ Cl ₂ , 3 h	93	1:1.8
MgBr ₂	-78 °C, CH ₂ Cl ₂ , 2 h	94	≥100:1
Yb(OTf) ₃	-78 °C, Et ₂ O, 2 h	91	16:1
Sc(OTf) ₃	-78 °C, Et ₂ O, 2 h	94	≥100:1

"These experiments present the first examples of the use of scandium triflate in radical reactions."

**Diastereoselective C–C Bond Formation with
Nonracemic Planar-Chiral η^2 -Manganese Complexes**
Schnizer et al; *ACIEE* 1996, 35, 1678–1680.



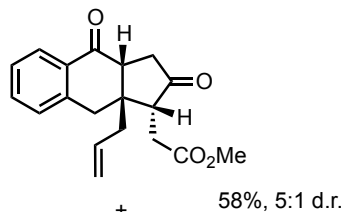
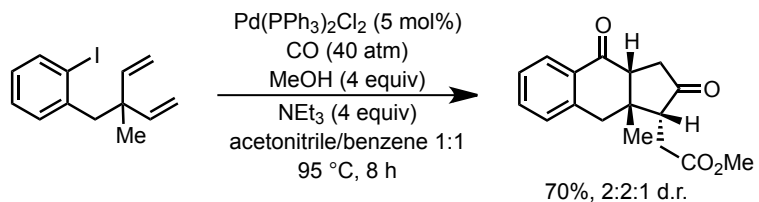
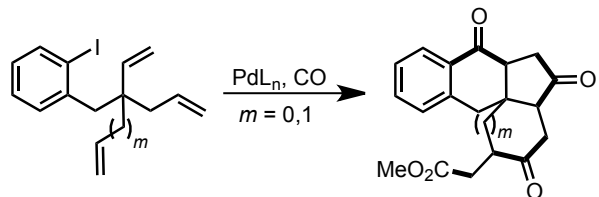
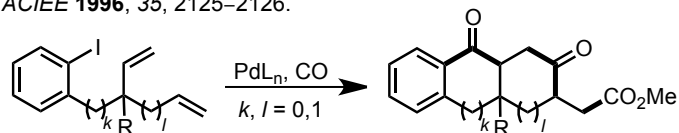
A Mild General Procedure for the One-Pot Conversion of Amides to Aldehydes
Buchwald et al; *ACIEE* 1996, 35, 1678–1680.



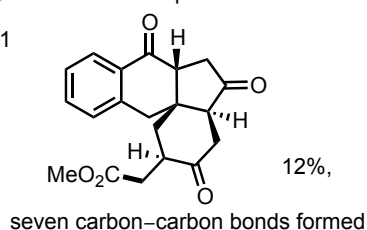
Amide	Product	Yield [%]
		74
		90
		71
		50
		80

Acid sensitive compounds worked up with THF and wet silica gel

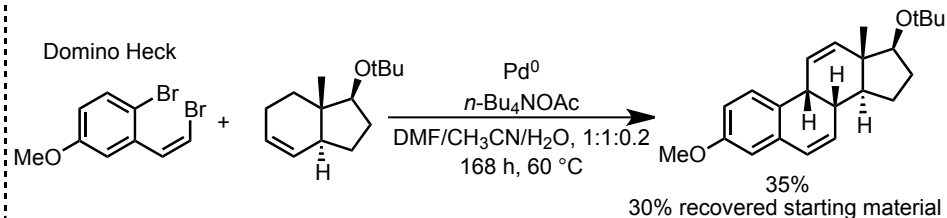
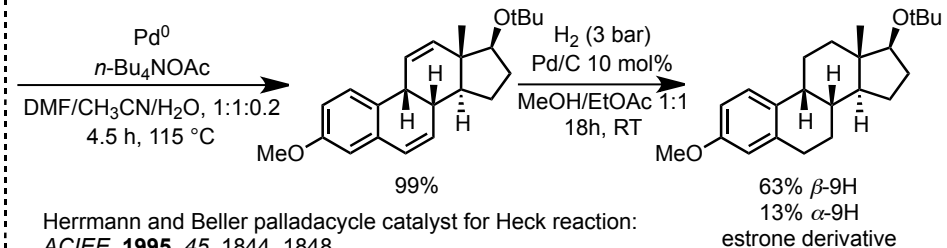
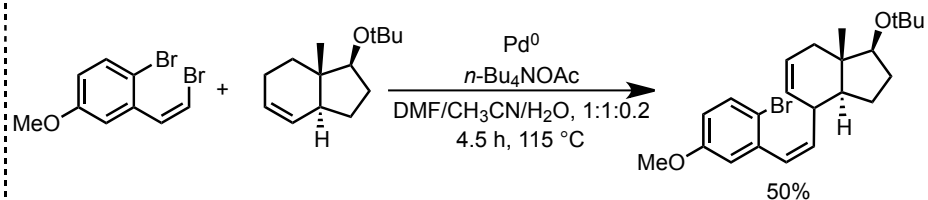
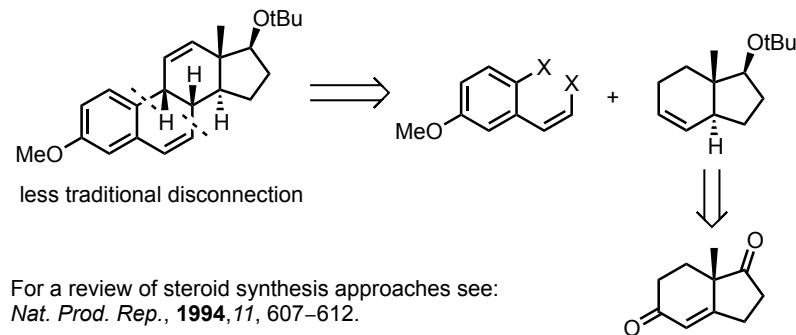
Palladium-Catalyzed Carbonylative Cyclization Cascades with Iododienes and -trienes
Negishi et al; *ACIEE* **1996**, 35, 2125–2126.

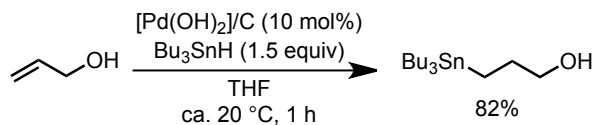


For a review on cascades in total synthesis see:
ACIEE, **2006**, 45, 7134–7186.



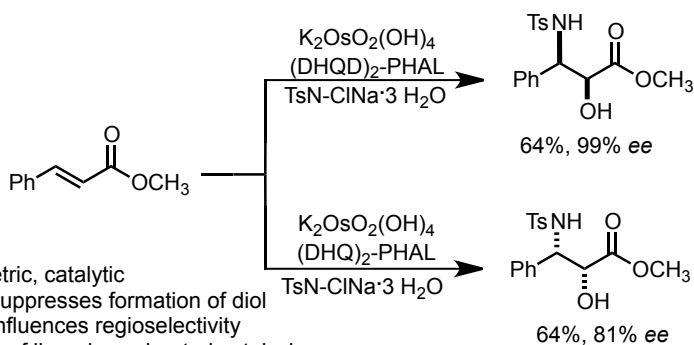
Stereoselective Synthesis of Steroids with the Heck Reaction
Tietze et al; *ACIEE* **1996**, 35, 2259–2261.



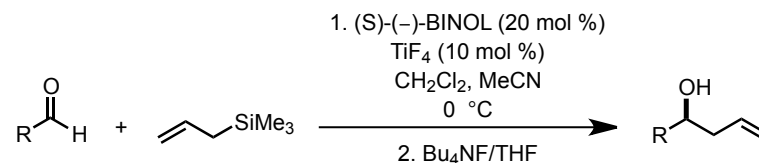
Heterogenous Palladium-Catalyzed Regioselective Hydrostannation of AlkenesLautens et al; *ACIEE* 1996, 35, 1329–1330.

Alkene	Product	Yield [%]
		96
		94
		94

Use of Pearlman's catalyst as a Pd source gave superior yields compared to homogeneous Pd catalyst systems.

Catalytic Asymmetric Aminohydroxylation (AA) of OlefinsSharpless et al; *ACIEE* 1996, 35, 451–454.

- Asymmetric, catalytic
- Ligand suppresses formation of diol
- Ligand influences regioselectivity
- Example of ligand accelerated catalysis

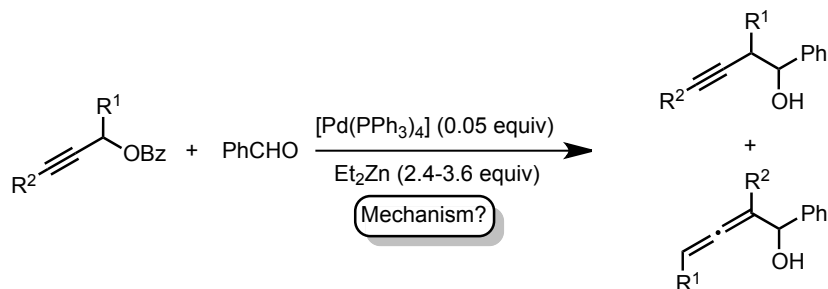
Catalytic, Enantioselective Additions of Allylsilanes to Aldehydes:**Generation of a Novel, Reactive Ti^{IV} Complex from TiF₄**Carreira et al; *ACIEE* 1996, 35, 2365–2363.

Aldehyde	t [h]	Yield [%]	ee [%]
	4	90	94
	20	93	84
	20	92	93
	20	81 [a]	74
	4	85	80

[a] Based on 25% recovered aldehyde

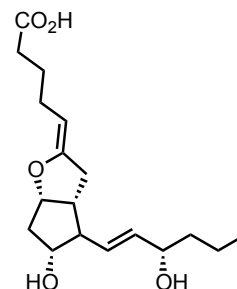
Propargylation of Carbonyl Compounds by Umpolung of Propargylpalladium Complexes with Diethylzinc

Tamaru et al; *ACIEE* **1996**, 35, 878–880.

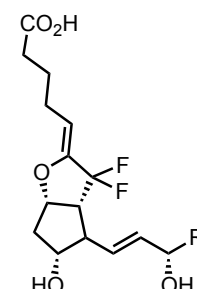


Synthesis of Novel Difluoroprostacyclin Derivatives: Unprecedented Stabilizing Effect of Fluorine Substituents

Matsumura et al; *ACIEE* **1996**, 35, 1019–1021.



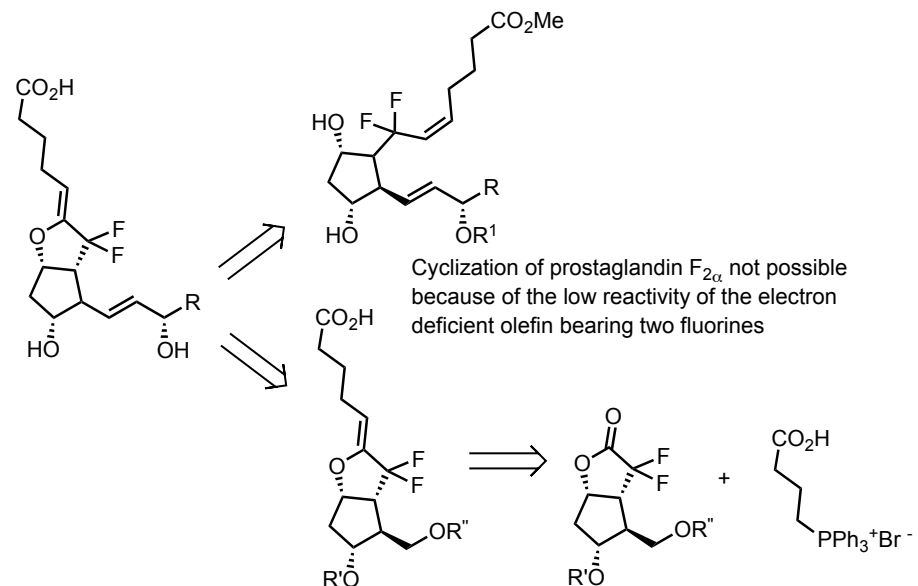
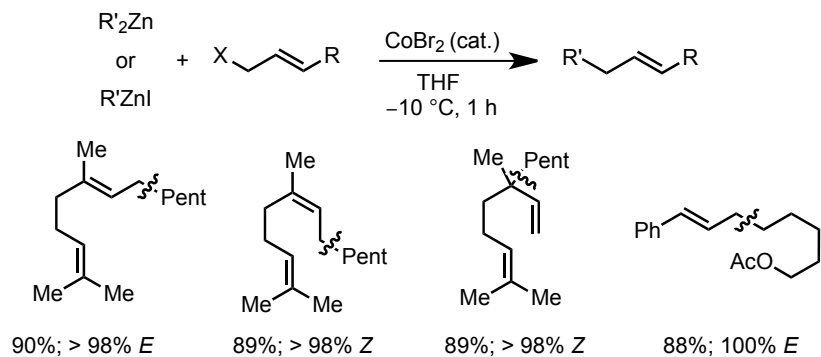
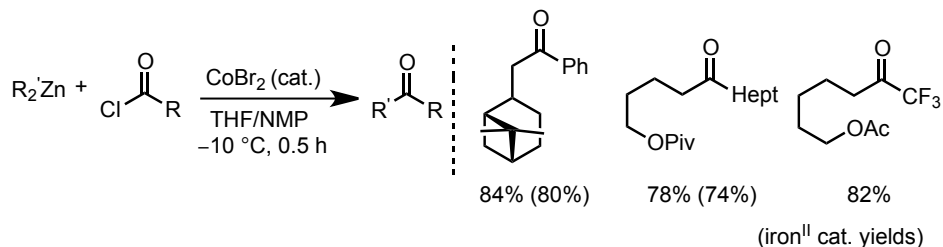
prostacyclin
half life of 76 seconds

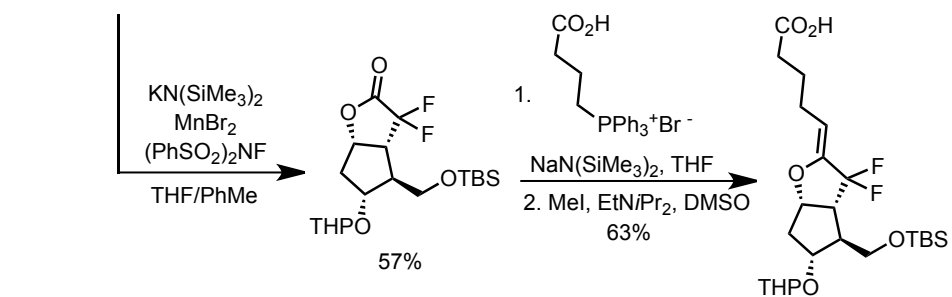
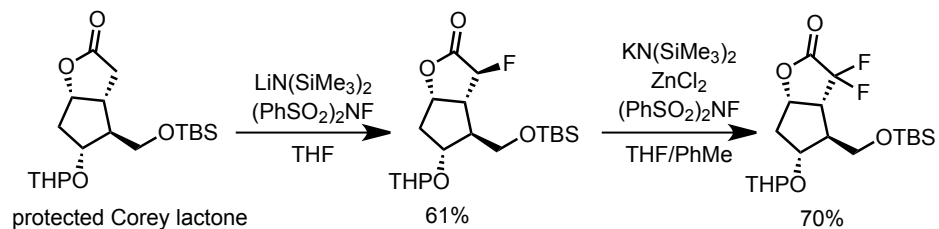


The electron withdrawing effect of the fluorine atoms prevents the hydrolysis of the acid labile vinyl ether.

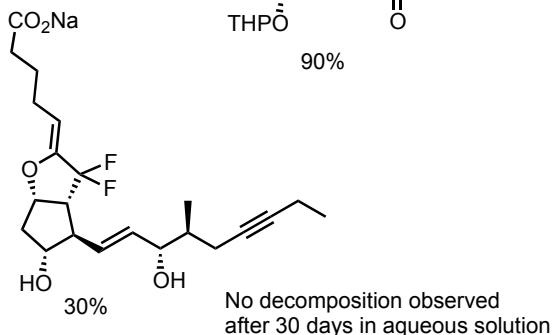
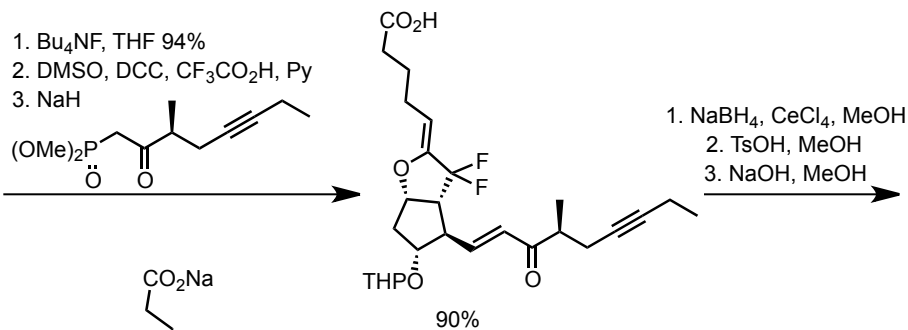
New Cobalt- and Iron-Catalyzed Reactions of Oganozinc Compounds

Knochel et al; *ACIEE* **1996**, 35, 1700–1701.





1. Bu₄NF, THF 94%
2. DMSO, DCC, CF₃CO₂H, Py
3. NaH



Syntheses not covered today

