Asymmetric Counteranion-Directed Catalysis (ACDC)

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Outlines

Outlines

Background

nature chemistry

REVIEW ARTICLE

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The progression of chiral anions from concepts to applications in asymmetric catalysis

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Background

Born in 1971 in Tercelra, Azores, Portugal, but soon moved to Canada.

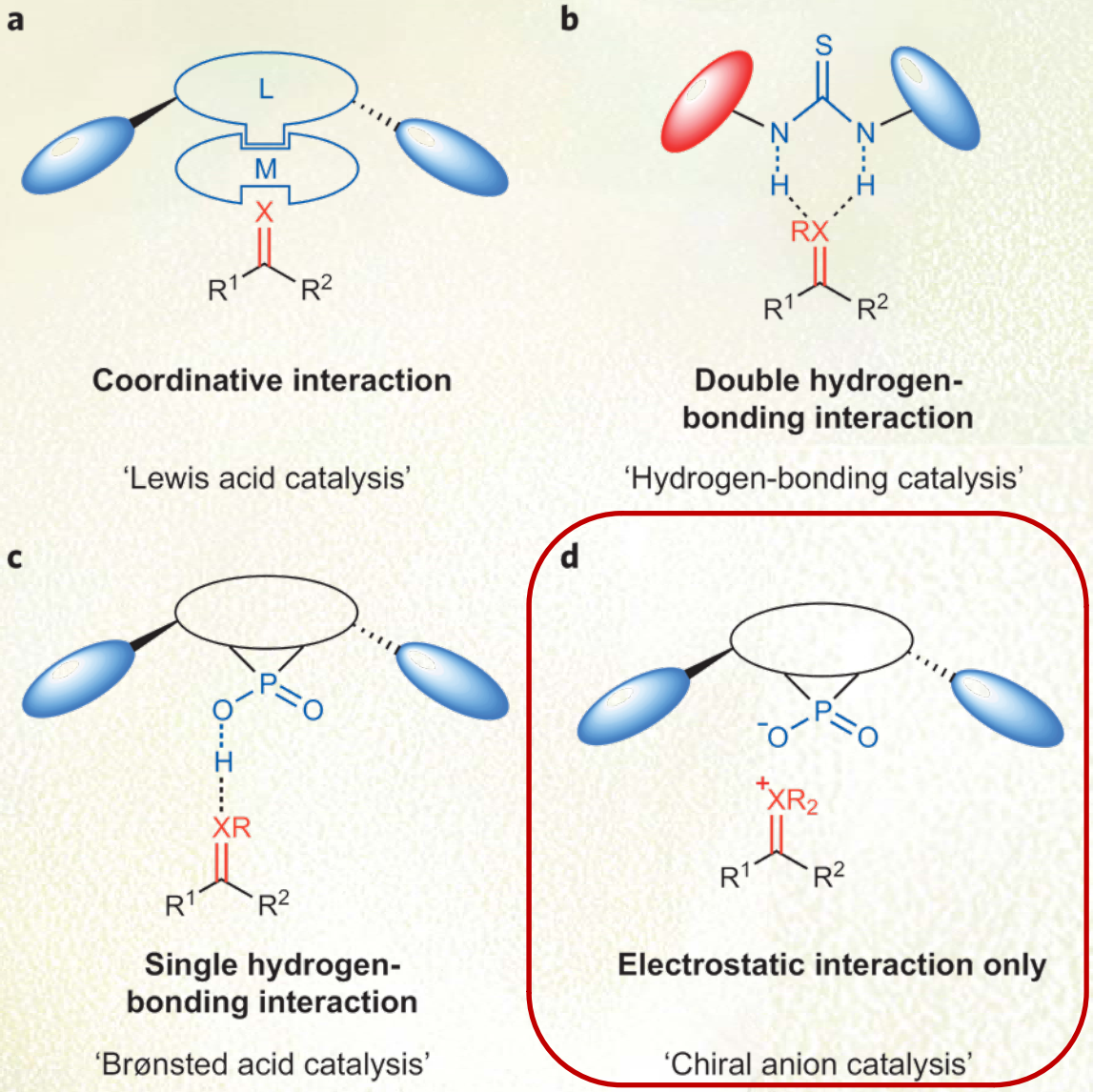
Majored in Chemistry and Biochemistry and went on to obtain a M.Sc. in Organic Chemistry While at the University of Toronto.

Pursued Ph.D. with Prof. Barry Trost at Stanford and a post-doctoral appointment with Prof. Robert Grubbs at Caltech.

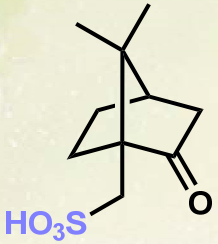
Currently is the Chevron Professor of Chemistry at UC Berkeley.

Pro. F Dean Toste

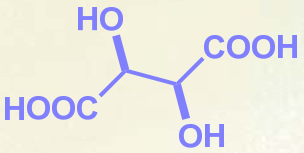
Representative Asymmetric Activation Modes



The Progression of ACDC: Early Use of Chiral Anion



1



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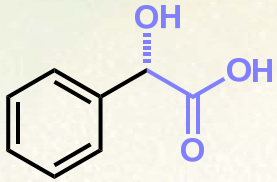
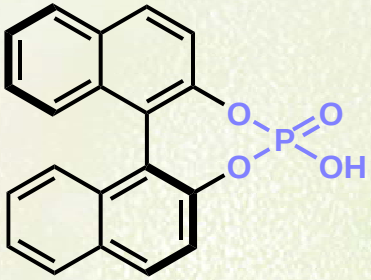


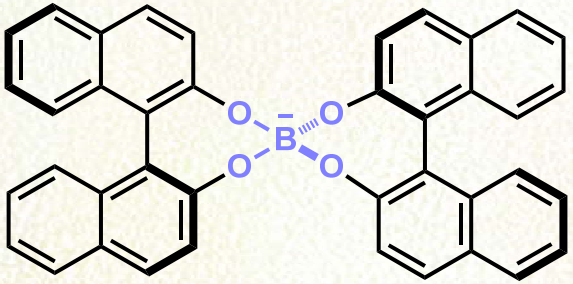
3

Resolve basic compound



4

Determine the enantioenrichment



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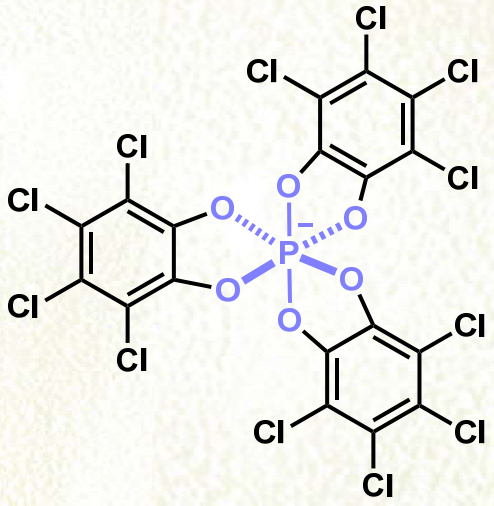


6

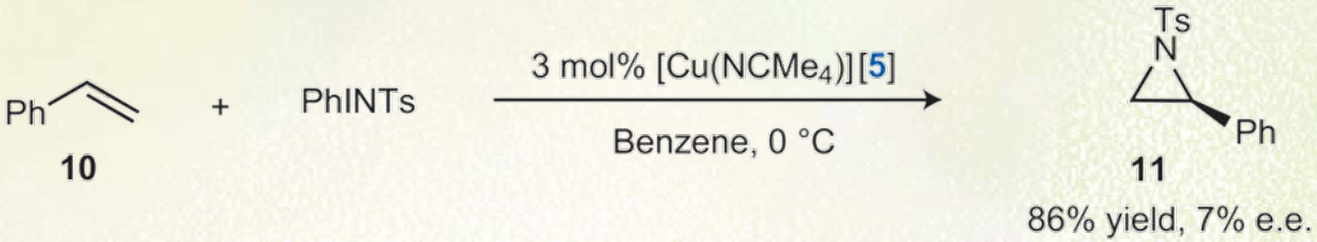
Chiral anion catalysis mode

Favarger, F. *et al., Tetrahedron Lett.* **1998**. *39,* 4825.

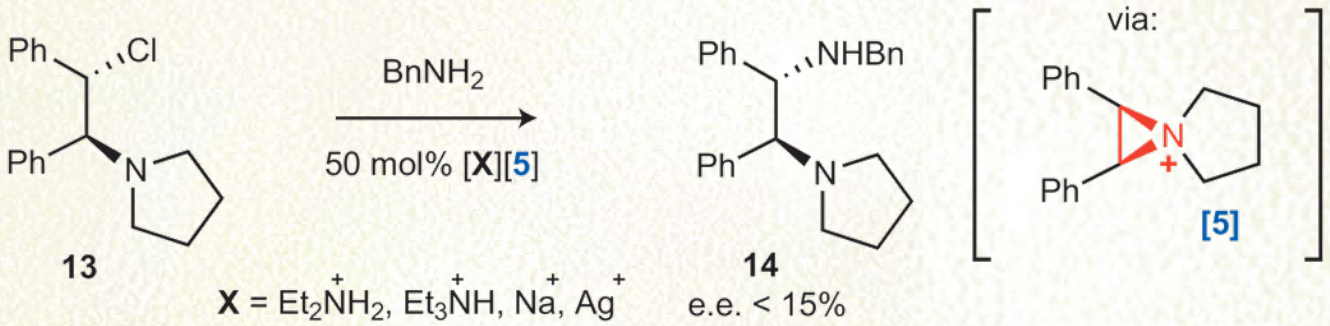
Yamamoto, H. *et al., J. Am. Chem. Soc.* **1994**. *116,* 10520

The Progression of ACDC: Chiral Non-Coordinating Anion

1. Copper(I)-catalysed aziridination



2. Ring-opening of *meso*-aziridinium ions

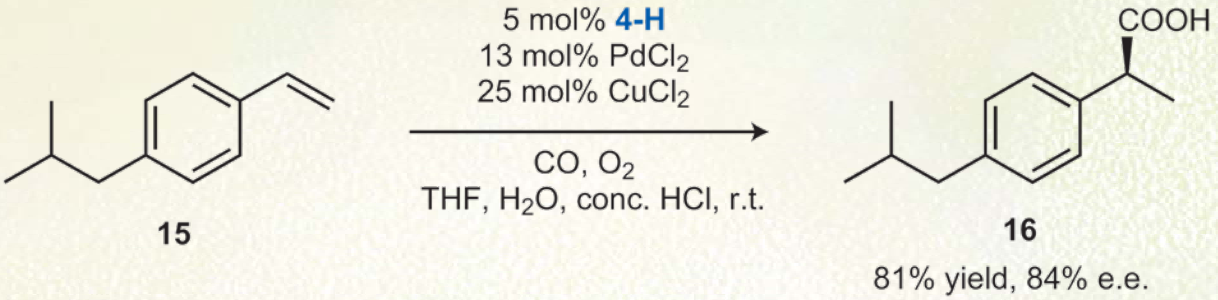


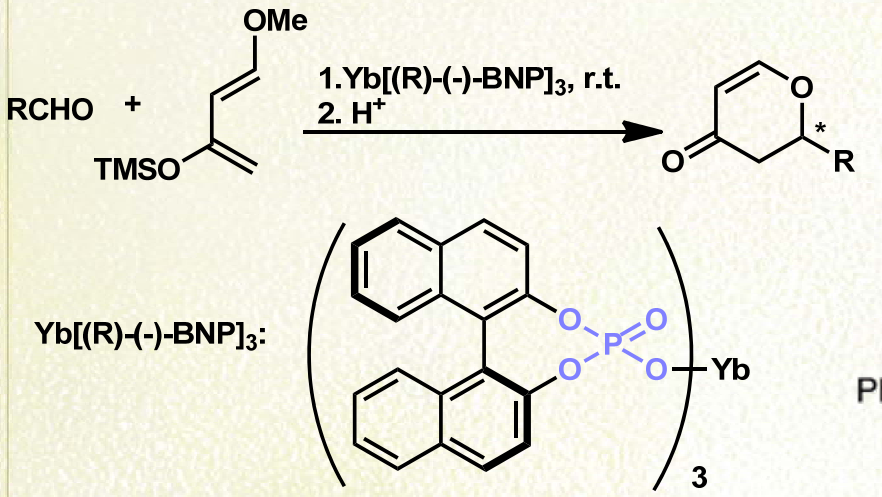
Points: chiral anions can be used for asymmetric catalysis reaction. new asymmetric counteranion is need.

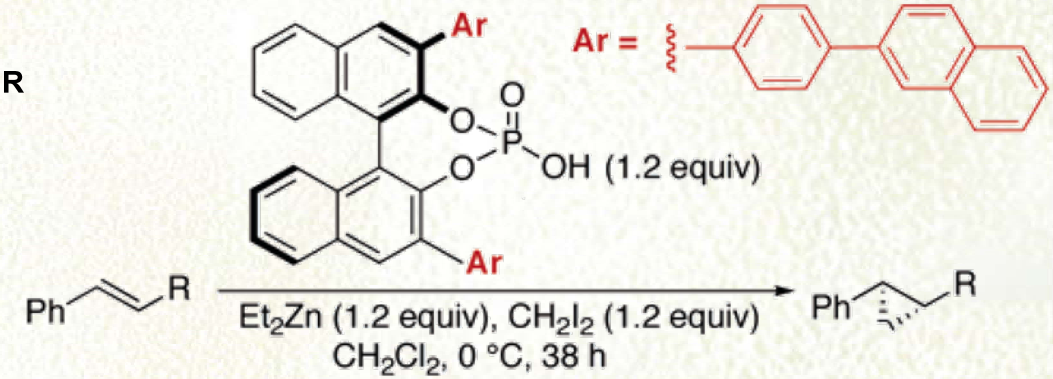
Arndtsen, B. A. *et al., Org. Lett.* **2000**. *2*, 4165.
Nelson, A. *et al., Tetrahedron.* **2003.** *14,* 1995.

The Progression of ACDC: Chiral Phosphate Anion

1. Combination of metal and phosphoric acid catalyst





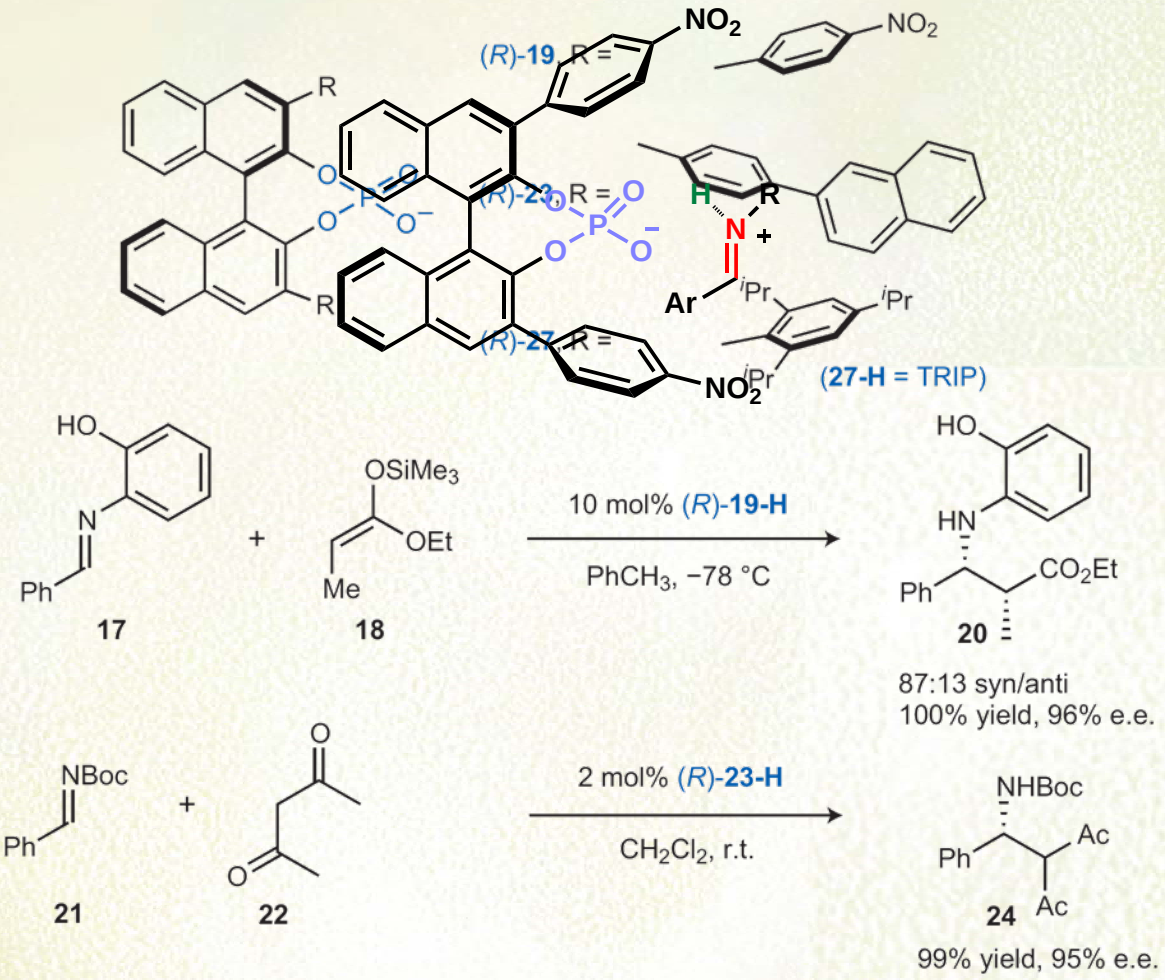


Inanaga, J. *et al., Synlett.* **1997**. *1,* 79

Charette, A. B. *et al., J. Am. Chem. Soc.* **2005**. *127,* 12440

The Progression of ACDC: Chiral Phosphate Anion

2. Defined as Brønsted Acid Catalysts

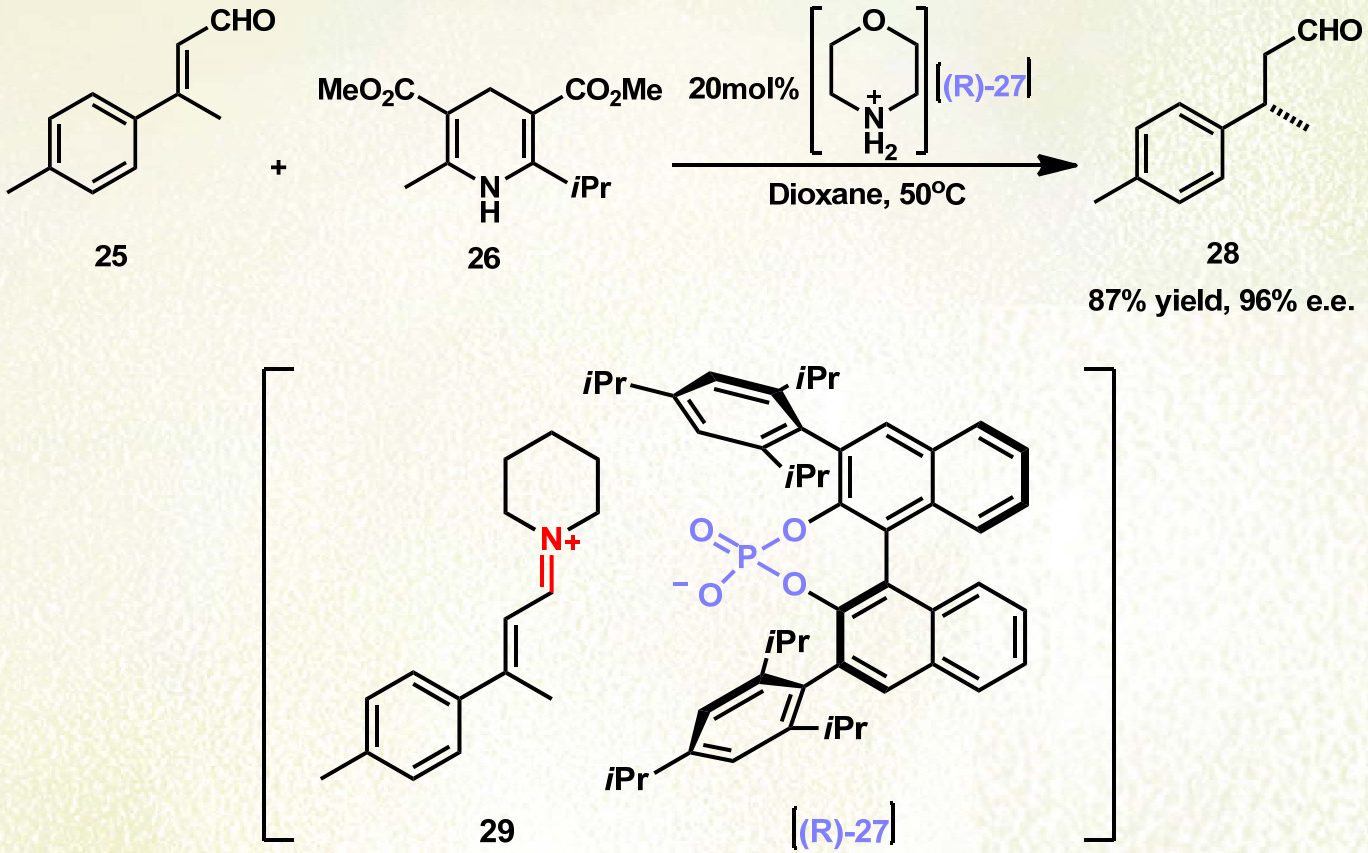


Akiyama, T. *et al., Angew. Chem. Int. Ed.* **2004**. *43,* 1566

Terada, M.*et al., J. Am. Chem. Soc.* **2004**. *126,* 5356

The Progression of ACDC: Chiral Phosphate Anion

3. Work as counteranion, give birth to ACDC



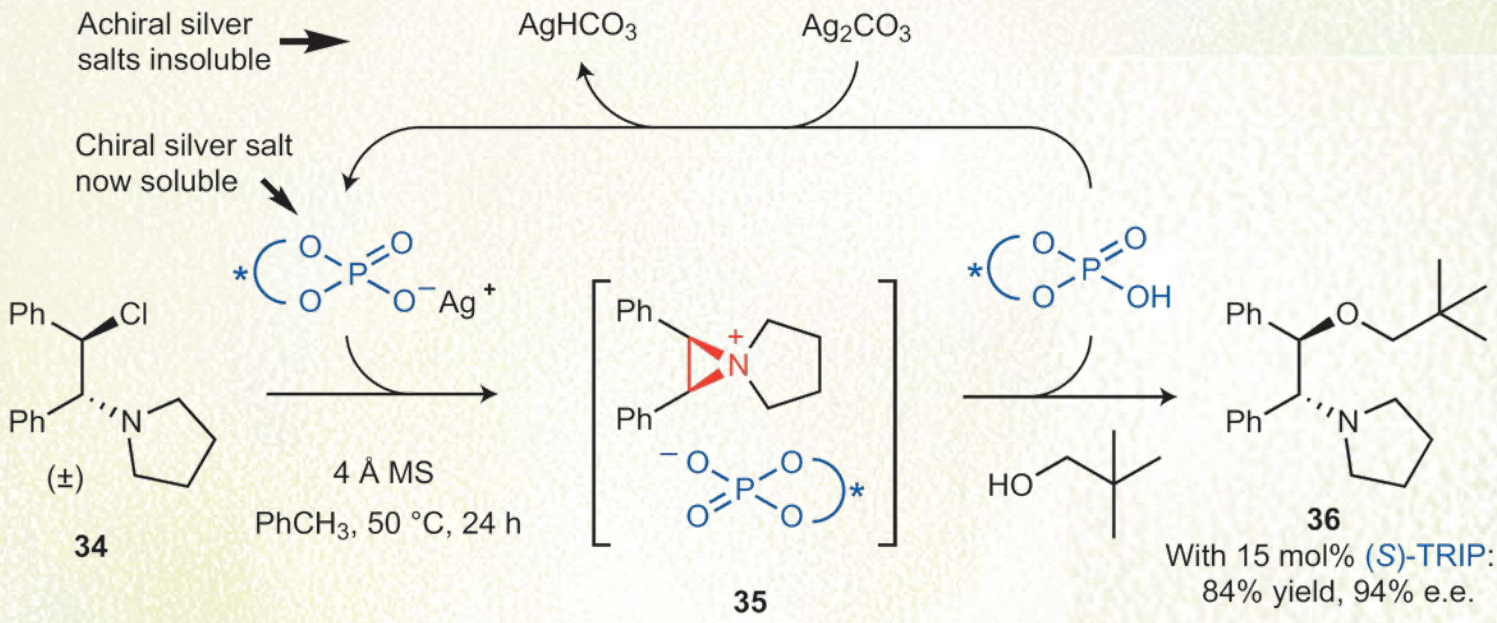
List, B. *et al., Angew. Chem. Int. Ed.* **2006**. *45,* 4193

Outlines

Application: Derived from Brønsted Acid Catalysts

Goal: Using substrates in which hydrogen bonding with the catalyst would be mechanistically improbable.

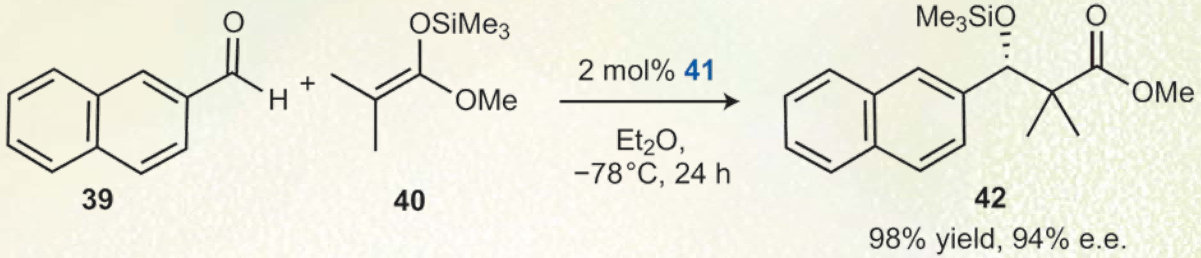
1. Conversion of β-chloro tertiary amine

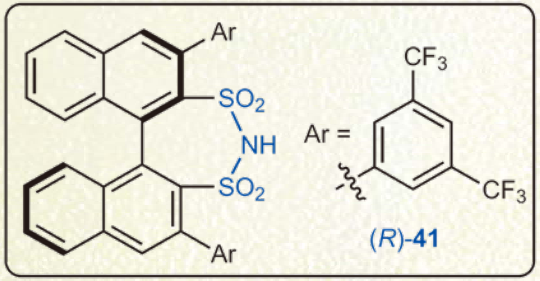


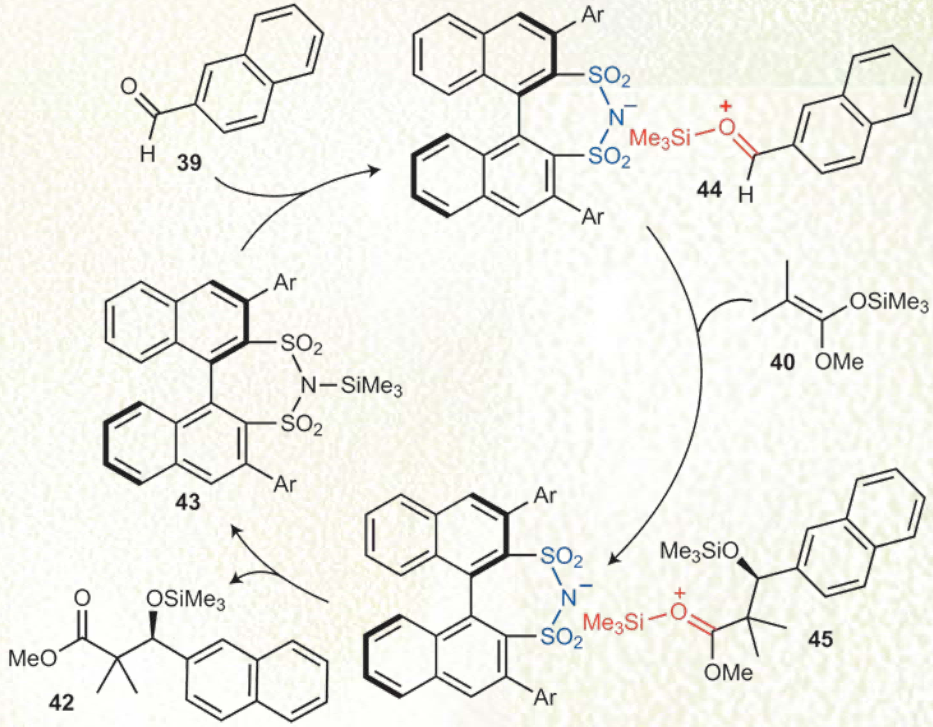
Toste, F. D. *et al., J. Am. Chem. Soc.* **2008**. *130,* 14984.

Application: Derived from Brønsted Acid Catalysts

2. Mukaiyama aldol reaction







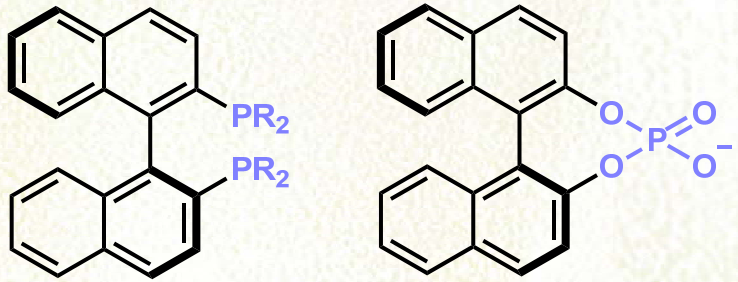
List, B. *et al., Angew. Chem. Int. Ed.* **2009**. *48,* 4363.

Application: Metal Catalysis with Chiral Counteranion

Goal: Inducing asymmetry by using chiral ions that interact with a metal only through electrostatic interactions, rather than using chiral ligands that coordinate tightly to the metal.

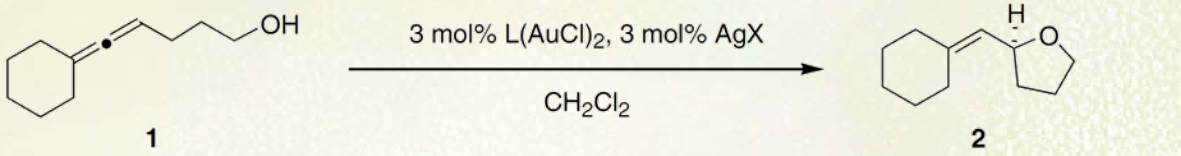
Comparison between chiral ligand and chiral counteranion!

Comparison between chiral phosphine and chiral phosphate!

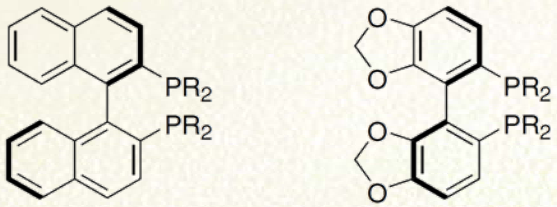


Application: Metal Catalysis with Chiral Counterions

1. Intramolecular hydroalkoxylation of allenes



1 2

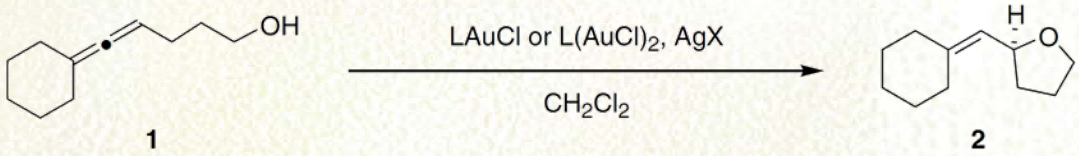


3, R = Ph
4, R = 3,5-$(CH_3)_2$-C_6H_3

5, R = 3,5-*t*-Bu_2-4-(CH_3O)-C_6H_2

L = **3**, X = BF_4^-	52% yield, 6% ee
L = **4**, X = BF_4^-	68% yield, 0% ee
L = **5**, X = BF_4^-	79% yield, 2% ee
L = **4**, X = 4-(NO_2)-C_6H_3-CO_2^-	89% yield, 8% ee

Benzene for the highest enantioselectivities



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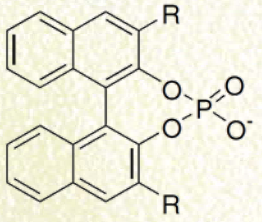


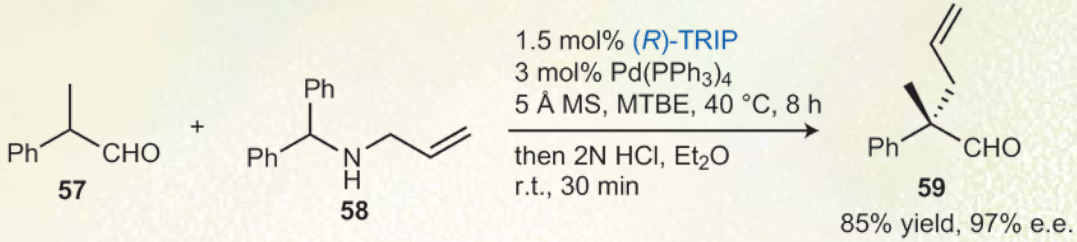
6, R = 2,4,6-*i*-Pr_3-C_6H_2

L = Ph_3P (5 mol%), X = (*R*)-**6** (5 mol%)	89% yield, 48% ee
L = dppm (2.5 mol%), X = (*R*)-**6** (5 mol%)	76% yield, 65% ee

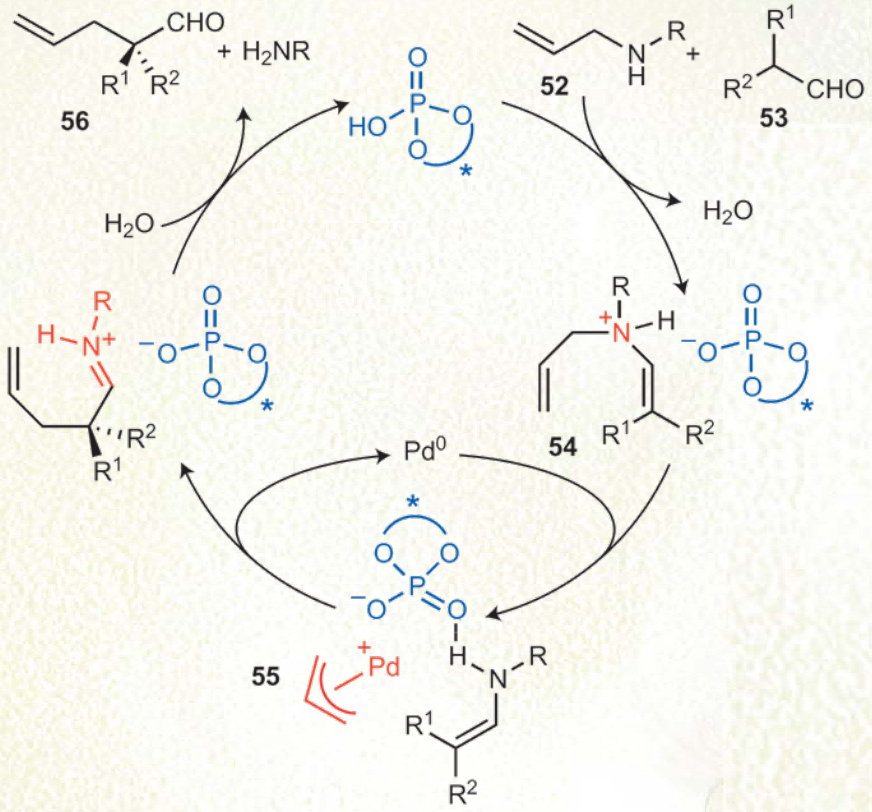
Toste, F. D. *et al.*, *Science* **2007**. *317*, 496

Application: Metal Catalysis with Chiral Counterions

2. Tsuji–Trost reaction



quaternary allylated stereocenter

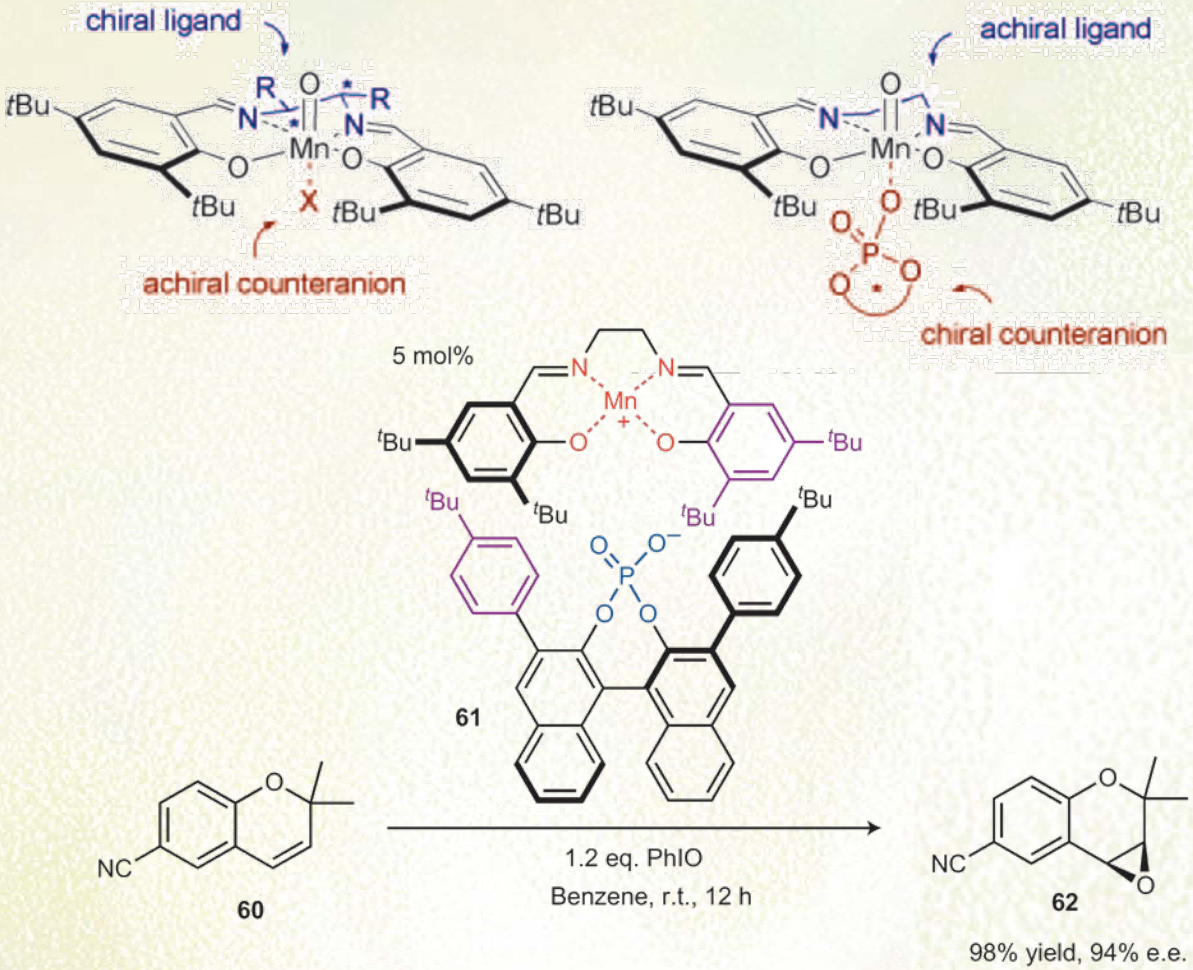


chiral enammonium phosphate salt

List, B. *et al., J. Am. Chem. Soc.* **2007**. *129,* 11336

Application: Metal Catalysis with Chiral Counterions

3. Jacobsen–Katsuki epoxidation

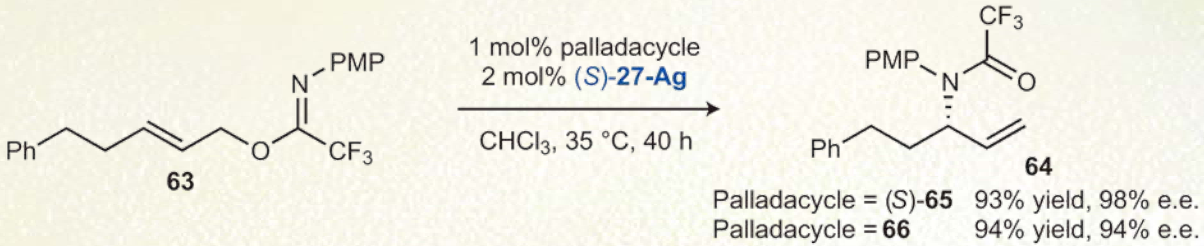


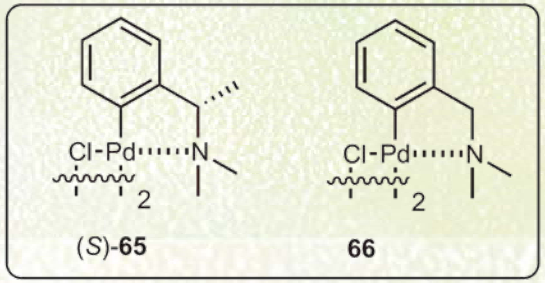
List, B. *et al., Angew. Chem. Int. Ed.* **2010**. *49,* 628**.**

Application: Metal Catalysis with Chiral Counterions

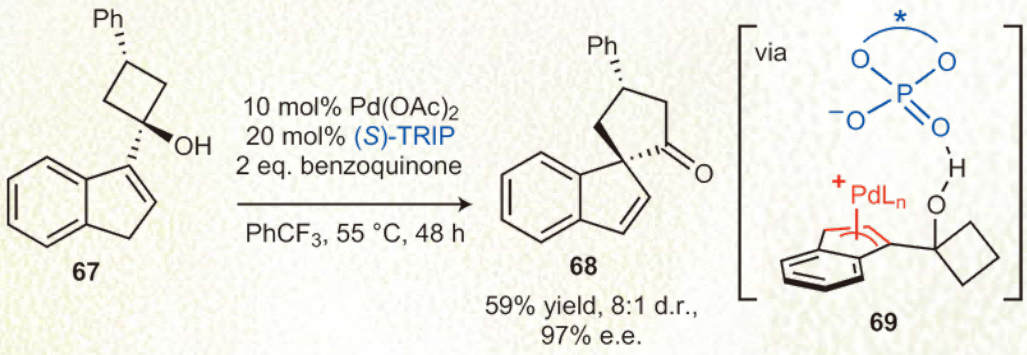
4. Other breakthroughs

Overman rearrangement





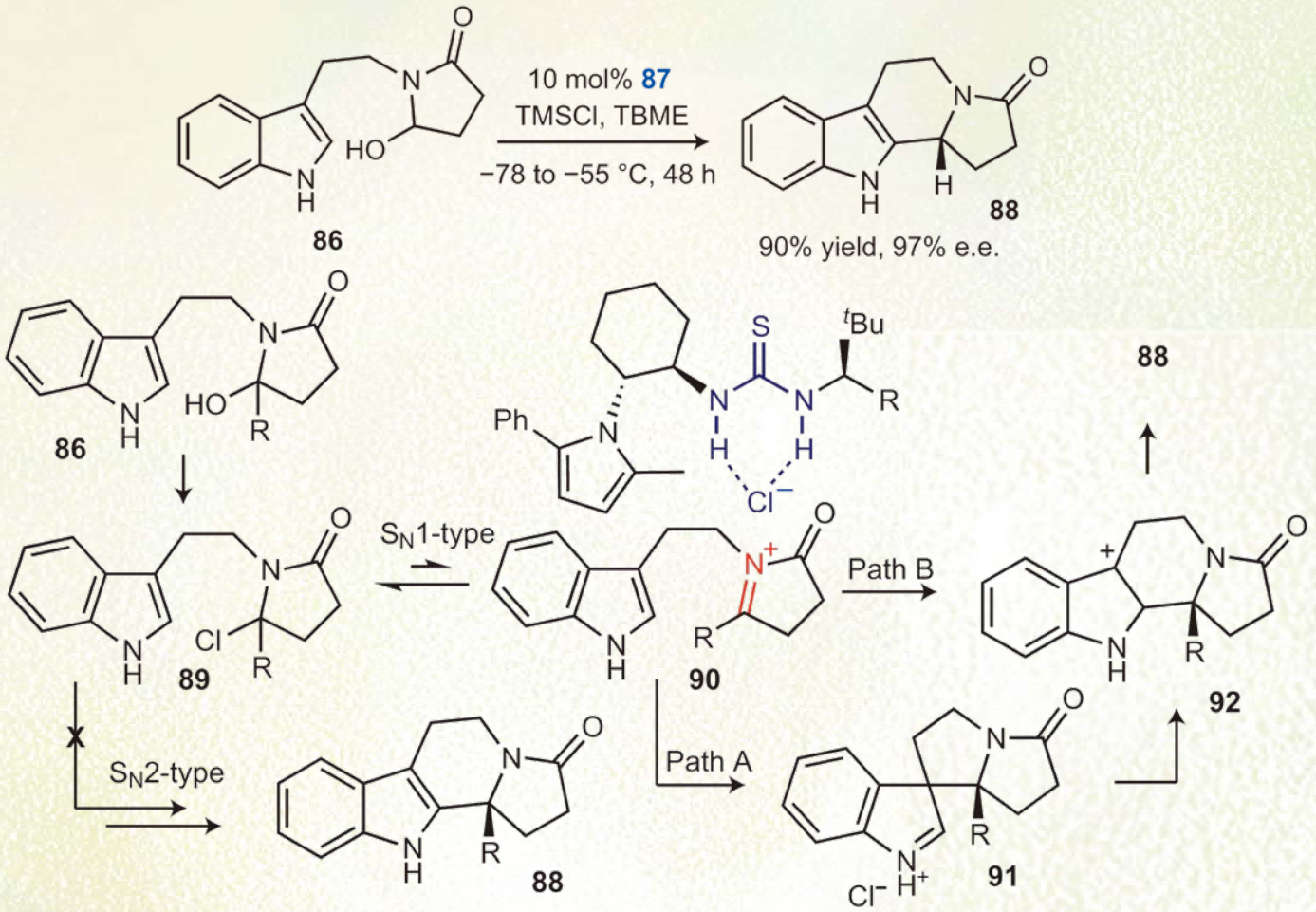
Semi-Pinacol rearrangement



List, B. *et al., Angew. Chem. Int. Ed.* **2011**. *50*, 9752.
Rainey, T. J. *et al., J. Am. Chem. Soc.* **2012**. *134*, 3615

Application: Hydrogen-Bonding Catalysts

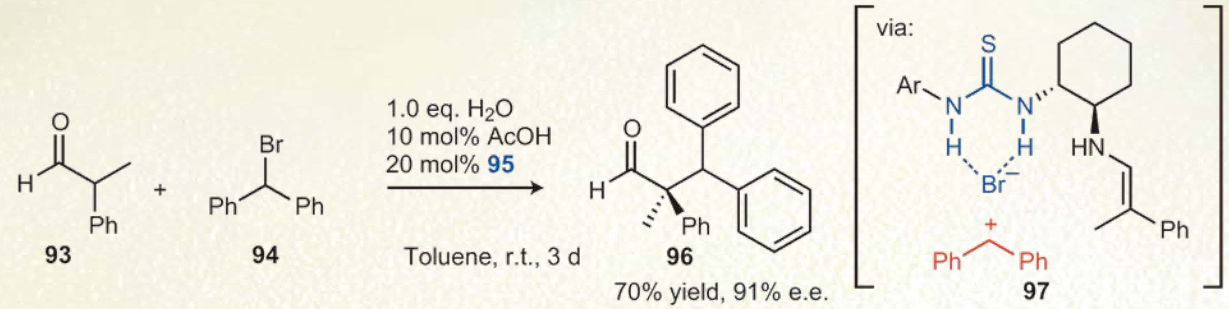
1. Asymmetric Pictet–Spengler

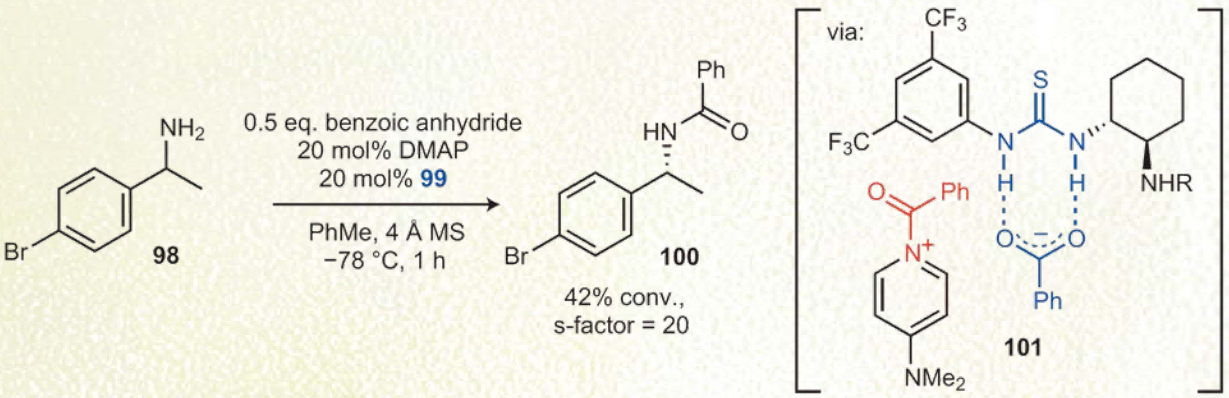


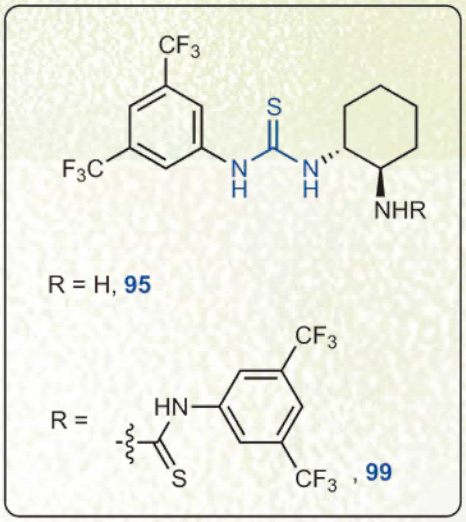
Jacobsen, E. N. *et al., J. Am. Chem. Soc.* **2007**. *129*, 13404.

Application: Hydrogen-Bonding Catalysts

2. Other breakthroughs



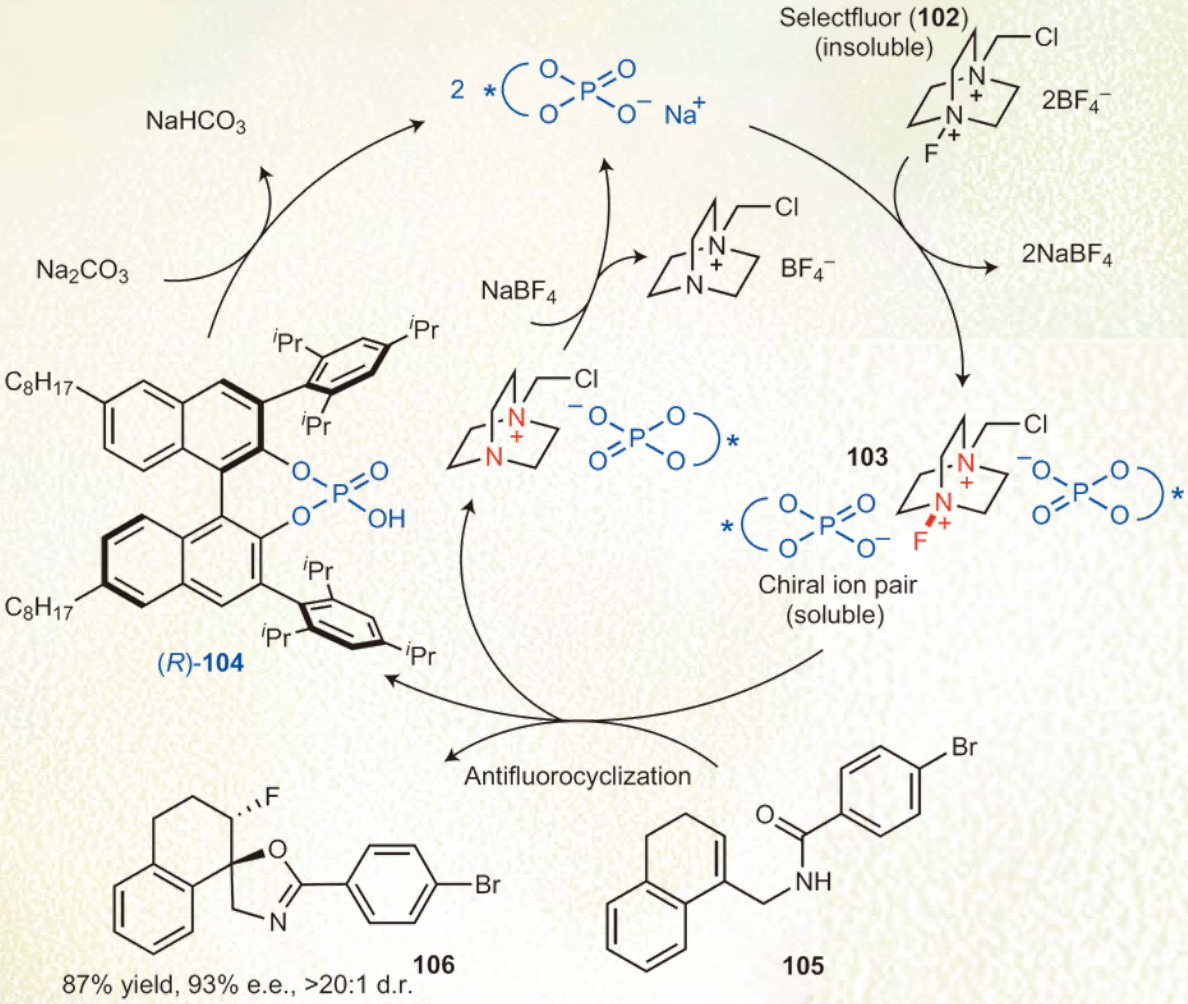




Jacobsen, E. N. *et al., J. Am. Chem. Soc.* **2010**. *132*, 9286.
Seidel, D. *et al., J. Am. Chem. Soc.* **2010**. *132*, 13624.

Application: Phase-Transfer Catalysis

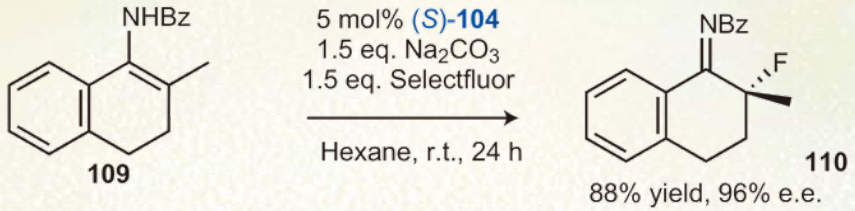
1. Fluorocyclization of enol ether

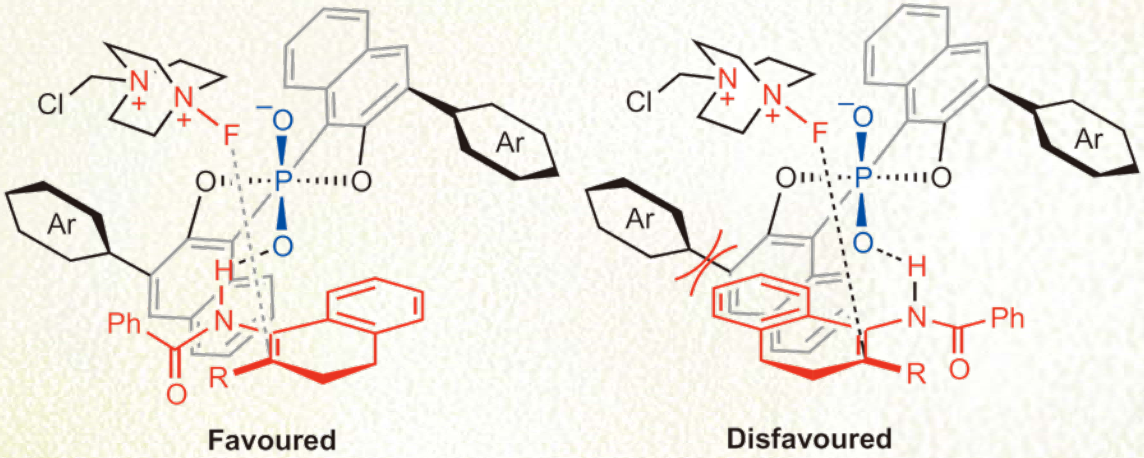


Toste, F. D. *et al., Science*. **2011**. *334*, 1681.

Application: Phase-Transfer Catalysis

2. Fluorination of cyclic enamide

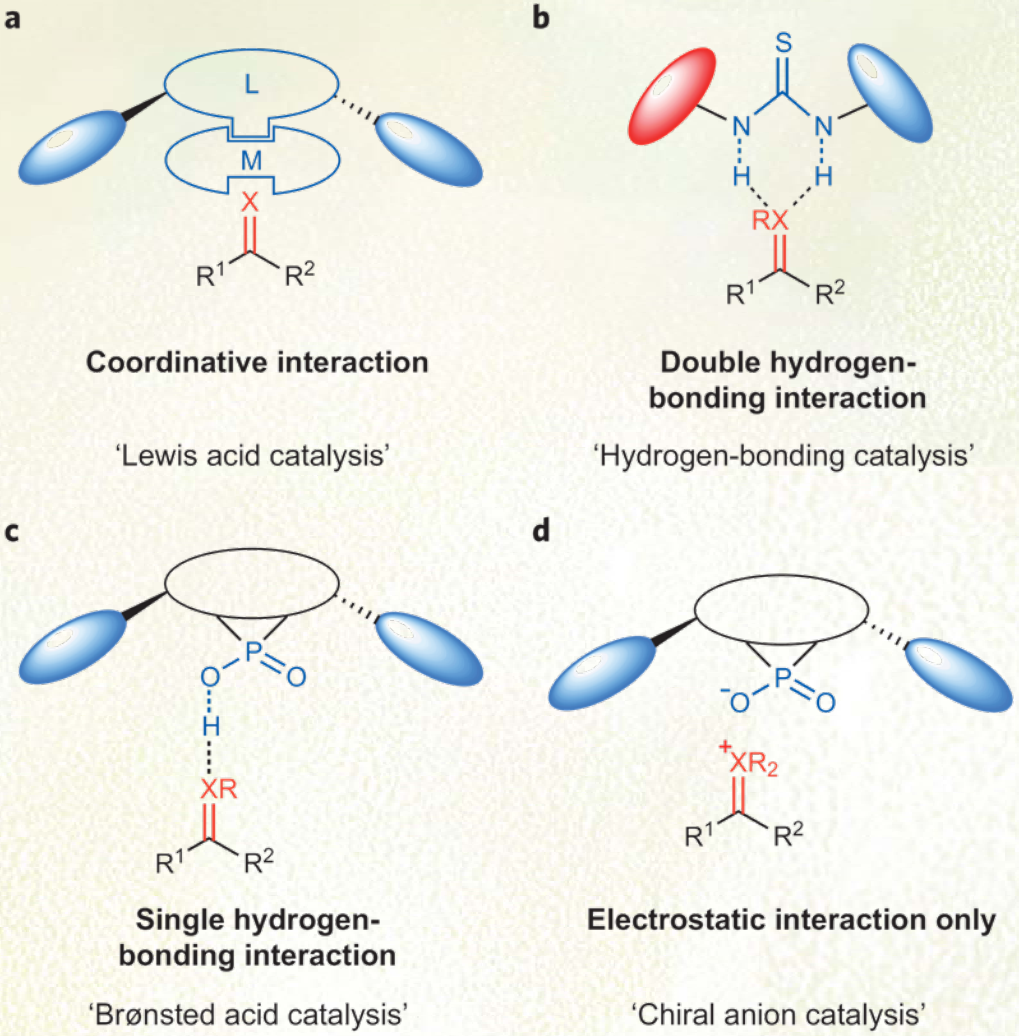




Toste, F. D. *et al., J. Am. Chem. Soc.* **2012.** *34,* 8376.

Outlines

Summary


a
L
M
X
R1
R2
Coordinative interaction
'Lewis acid catalysis'
b
S
N
N
H
H
RX
R1
R2
Double hydrogen-bonding interaction
'Hydrogen-bonding catalysis'
c
P
O
O
H
XR
R1
R2
Single hydrogen-bonding interaction
'Brønsted acid catalysis'
d
P
O
O
+XR2
R1
R2
Electrostatic interaction only
'Chiral anion catalysis'

Acknowledgment

- **Prof. Huang**
- **All members here**

Thanks for your attention!