Phase Transfer Catalysis

Bibliography of 30/04/2015

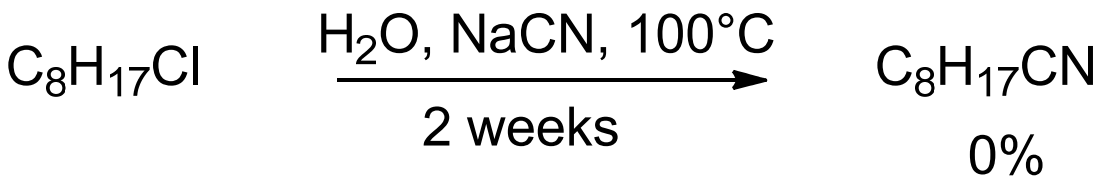
Cecilia Sasso D'Elia

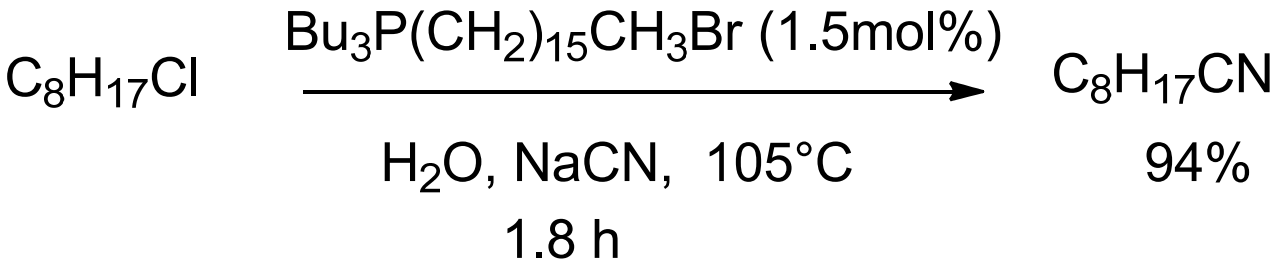
Summary:

- Introduction to PTC:
  - Definition and general mechanisms of action
- Families of catalysts
  - Cinchona alkaloids- derived catalysts: Synthesis, structure, reactivity
  - Maruoka's catalysts: Synthesis, structure, reactivity
  - Tartrate derived catalysts: Synthesis, structure, reactivity
- Applications
- Conclusion and Outlooks

What is PTC?

The term «phase transfer catalysis» has been used to underline the central role of tetraalkylammonium or phosphonium salts in the reaction between two substances located in different immiscible phases

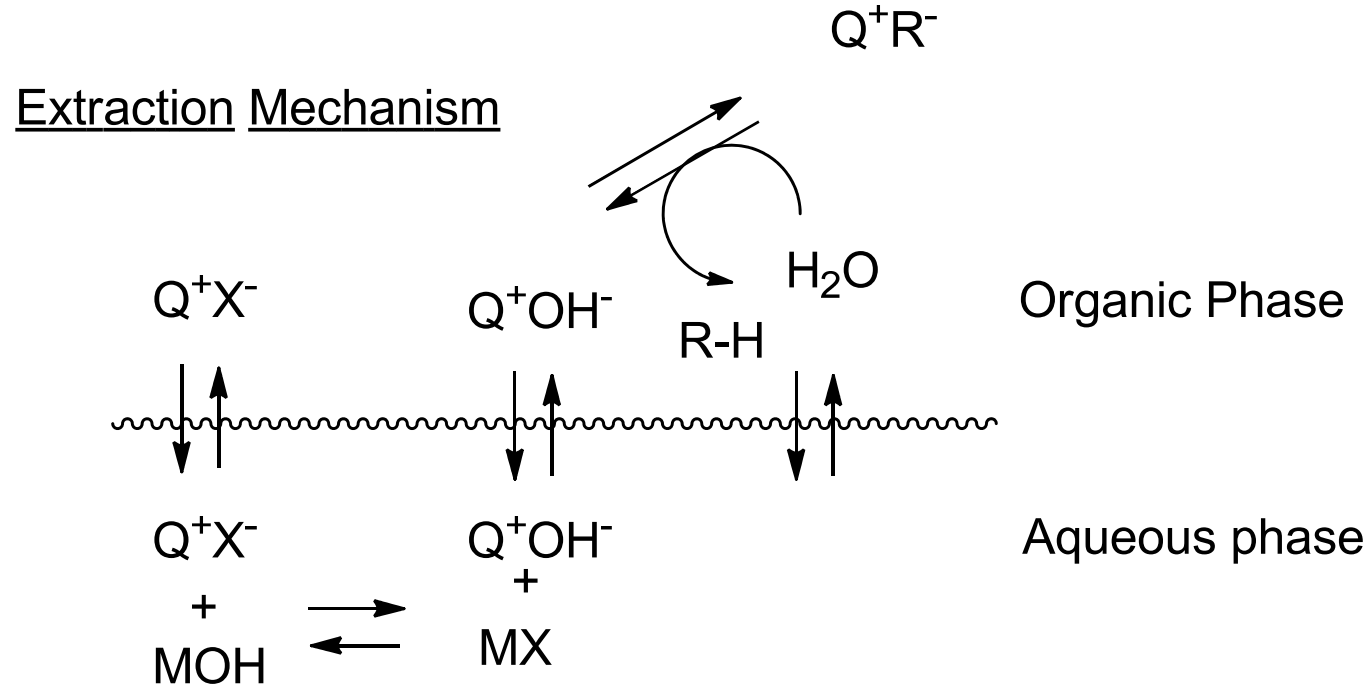




Starks, C.M., *J. Am. Chem. Soc.* **1971**, *93*, 195

How does it work?

Q^+: Phase Tranpher Catalysts



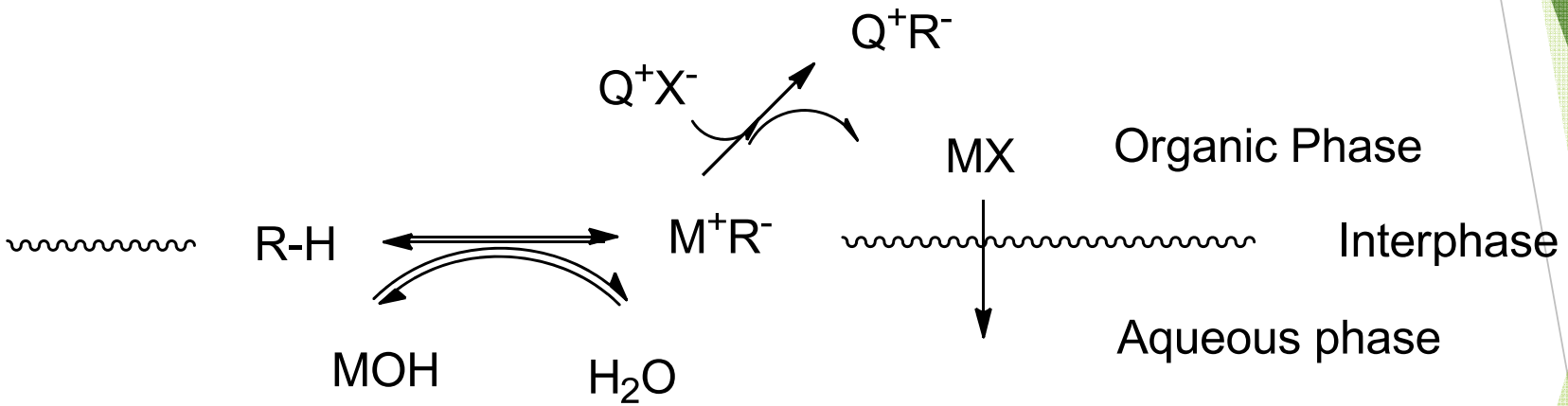
M= Na, K..

Dalko, P. I. Comprehensive Enantioselective Organocatalysis; Wiley-VCH, **2007**

How does it work?

Interfacial Mechanism:

Q^+: Phase Tranpher Catalysts



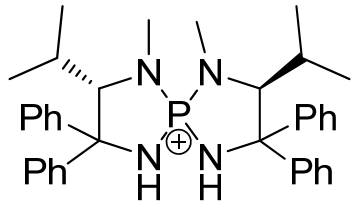
M: Na, K..

Dalko, P. I. Comprehensive Enantioselective Organocatalysis; Wiley-VCH, **2007**

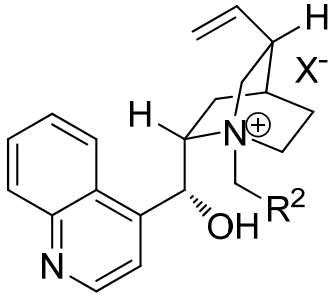
Families of catalysts:

Ammonium catalysts

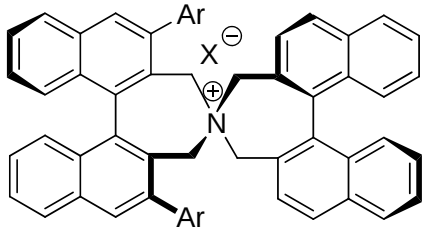
Phosphonium catalysts



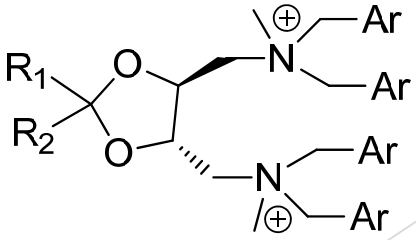
Cinchona alkaloids-derived catalysts



Maruoka's Catalysts



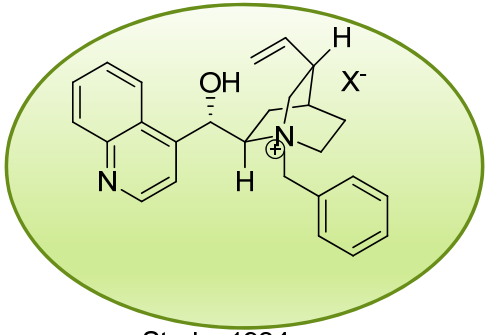
Tartrate- derived catalysts



S. Shirakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 4312

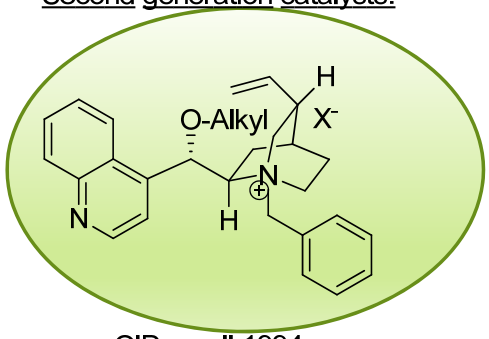
Cinchona alkaloids-derived catalysts:

First generation catalysts:



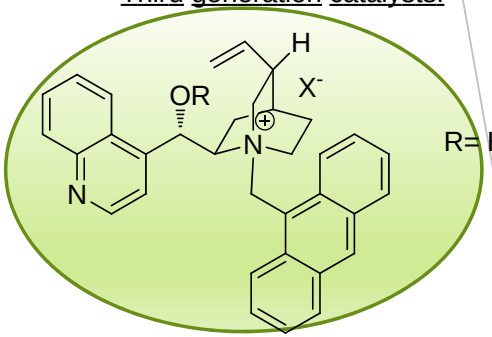
Starks 1984

Second generation catalysts:



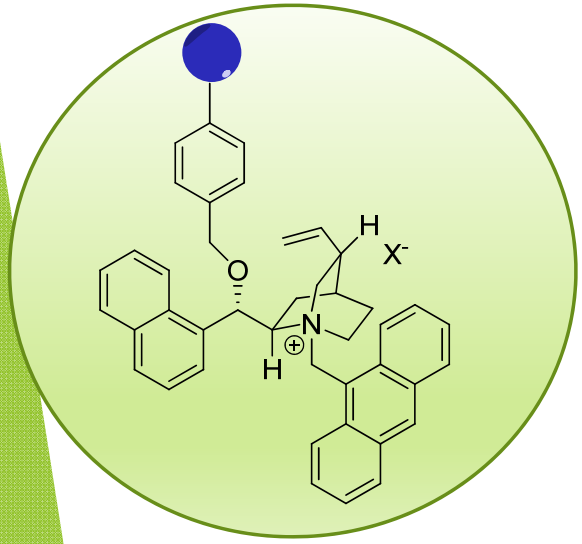
O'Donnell 1994

Third generation catalysts:



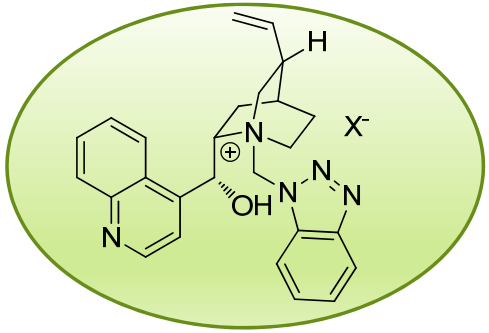
R= H, Metyl, Allyl

Lygo / Corey 1997

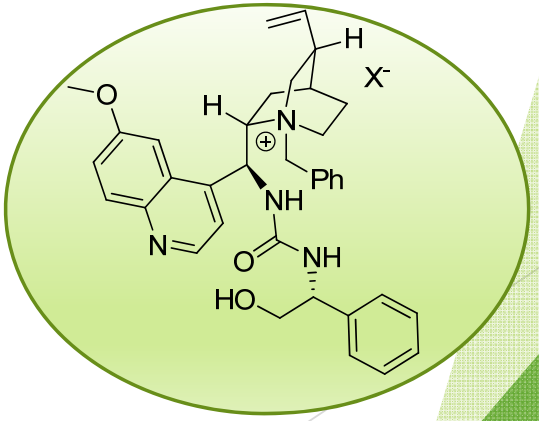


Najera 1999

N+1 generation catalysts

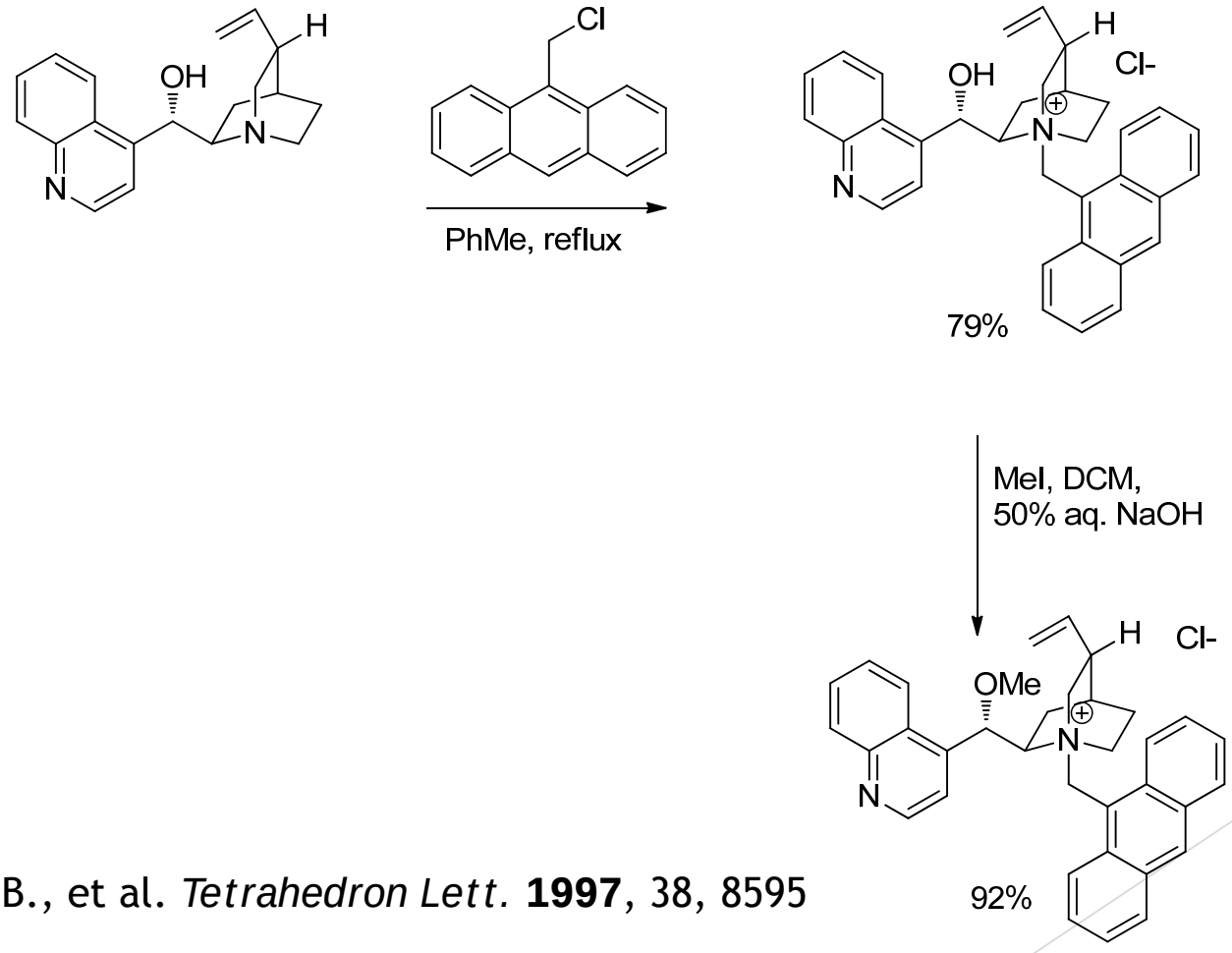


Zang 2009



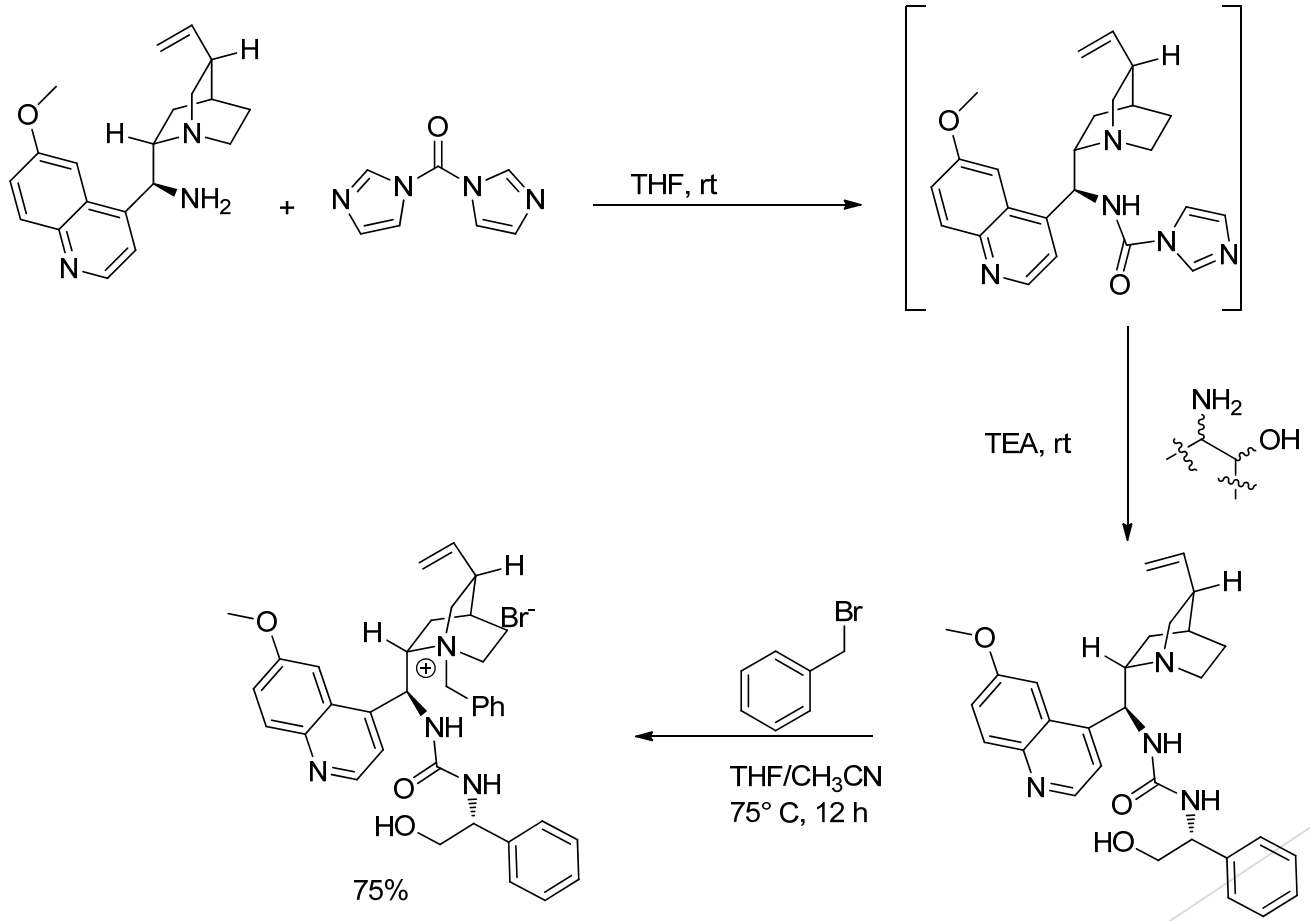
Duan 2014

Synthesis of Cinchona alkaloids-derived catalysts:



Lygo B., et al. *Tetrahedron Lett.* **1997**, 38, 8595

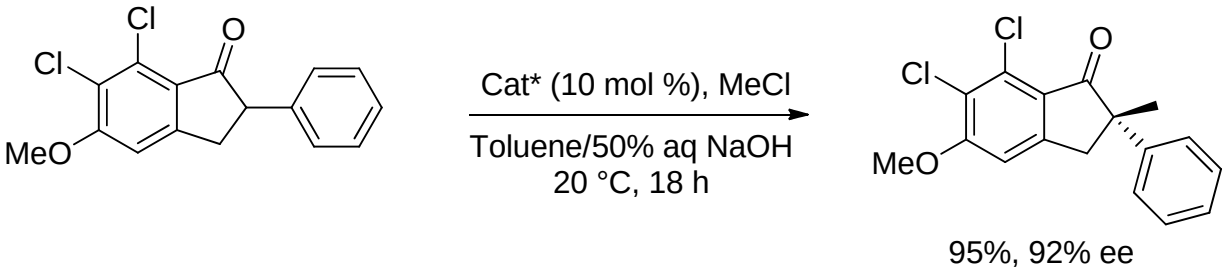
Synthesis of Cinchona alkaloid-derived catalysts:



Duan H. et al., *Org. Lett.* **2014**, *16*, 6432

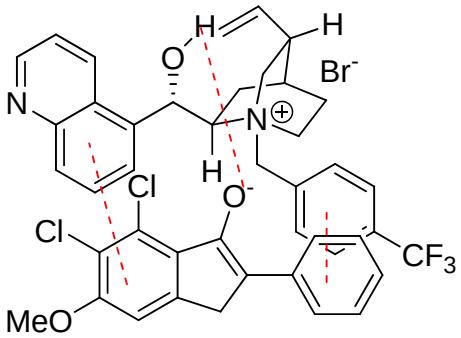
Applications:I Example of PTC

I asymmetric application of PTC



95%, 92% ee

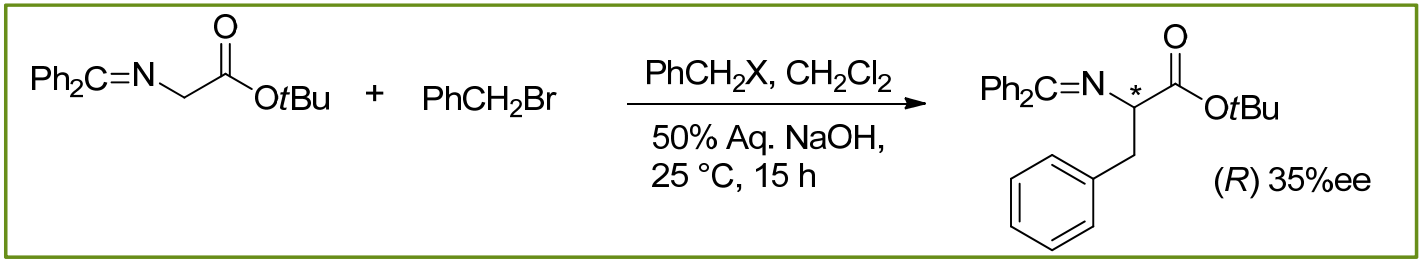
Transition state model

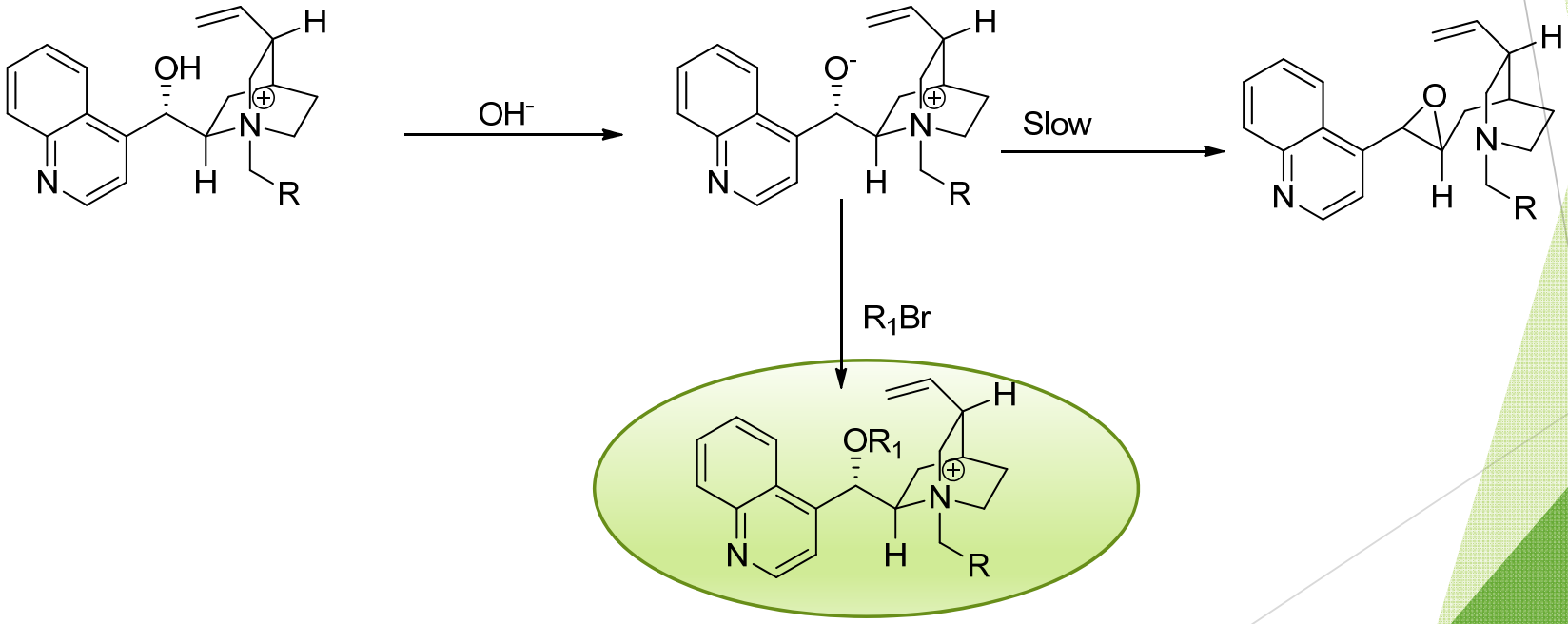


Ulf-H. Dolling, P. Davis, E. J.J Gabrowski., *J. Am. Chem. Soc.* **1984**, *106*, 446

Real transition state model:

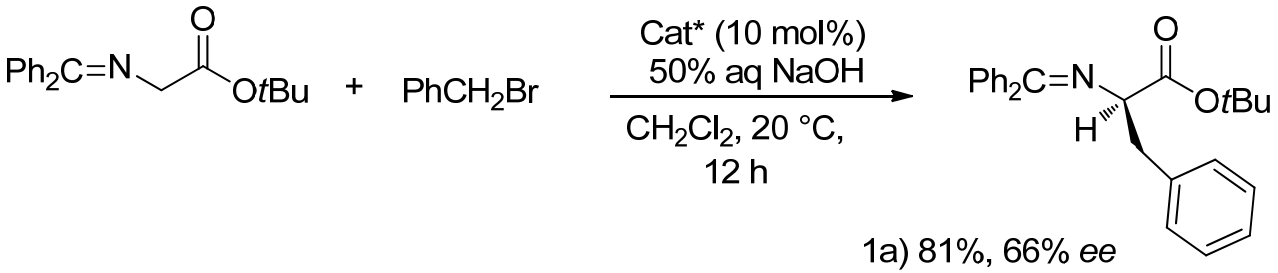
Benchmark reaction for testing catalysts activity



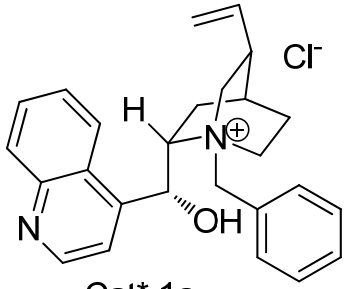


M. J. O'Donnel, S. Wu, J. C. Hoffmann, *Tetrahedron Lett.* **1994**, *50*, 4507

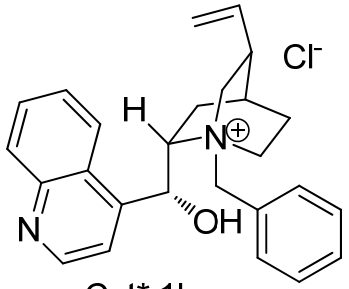
Applications



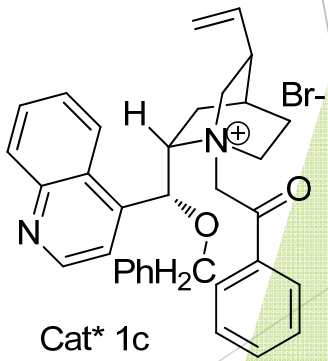
1a) 81%, 66% *ee*
1b) 82% 62% *ee*
1c) 94% 92% *ee*



Cat* 1a



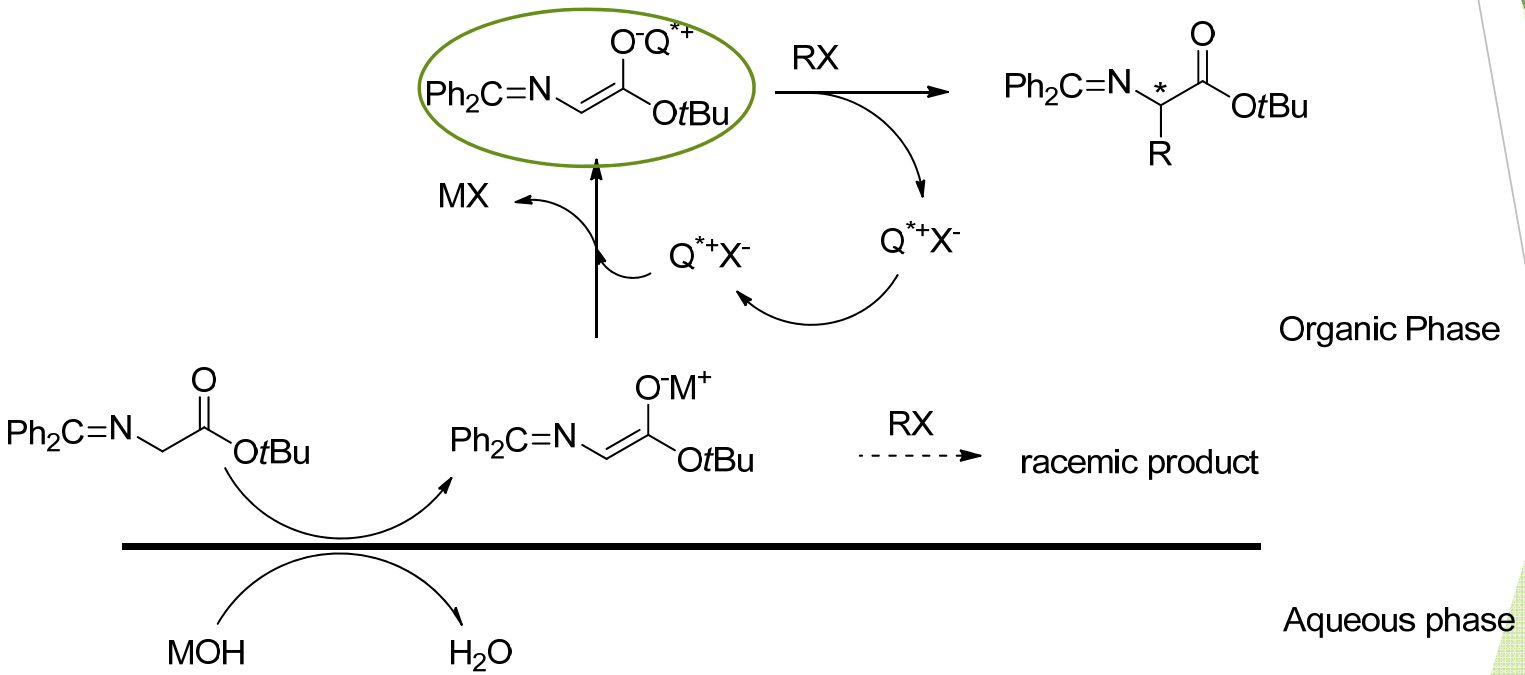
Cat* 1b



Cat* 1c

T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4222

Mechanism of reaction



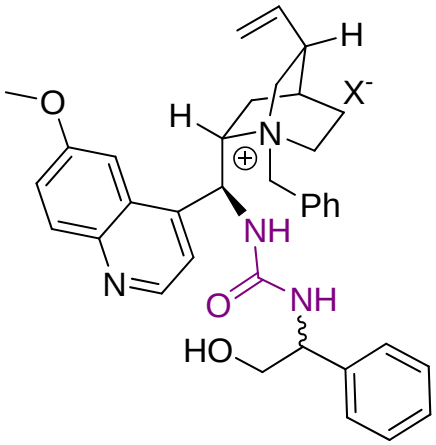
T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4222

Caracteristics of an efficient catalyst

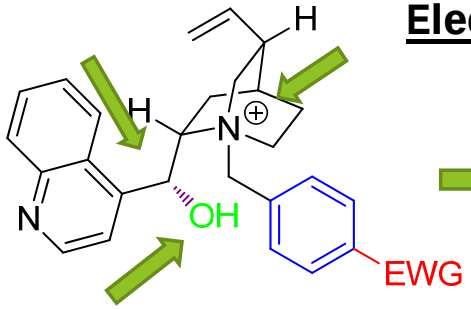
- **Formation of a tight ion pair between the catalyst and the substrate**
- **Shielding one face of the Chinconidinium ion**
- **Not degradate in the reaction conditions**

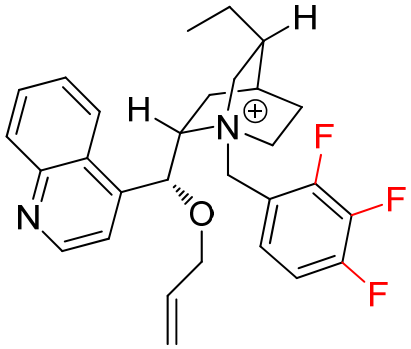
Solutions:

Insertion of a H-bond donor



Electron poor

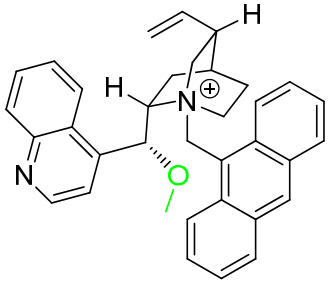


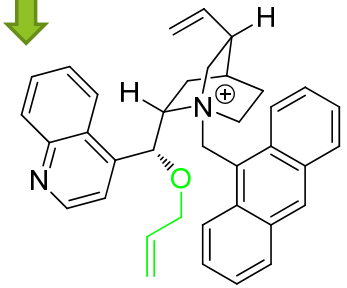


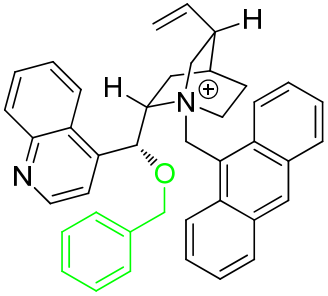
***O*-Alkylation**

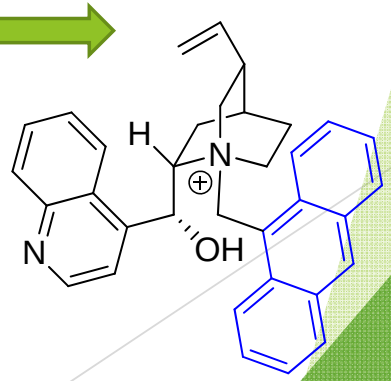
Schielding one face of the catalyst

The alkylation has effect on the reaction rate, enhanching the solubility of the catalyst in organic phase

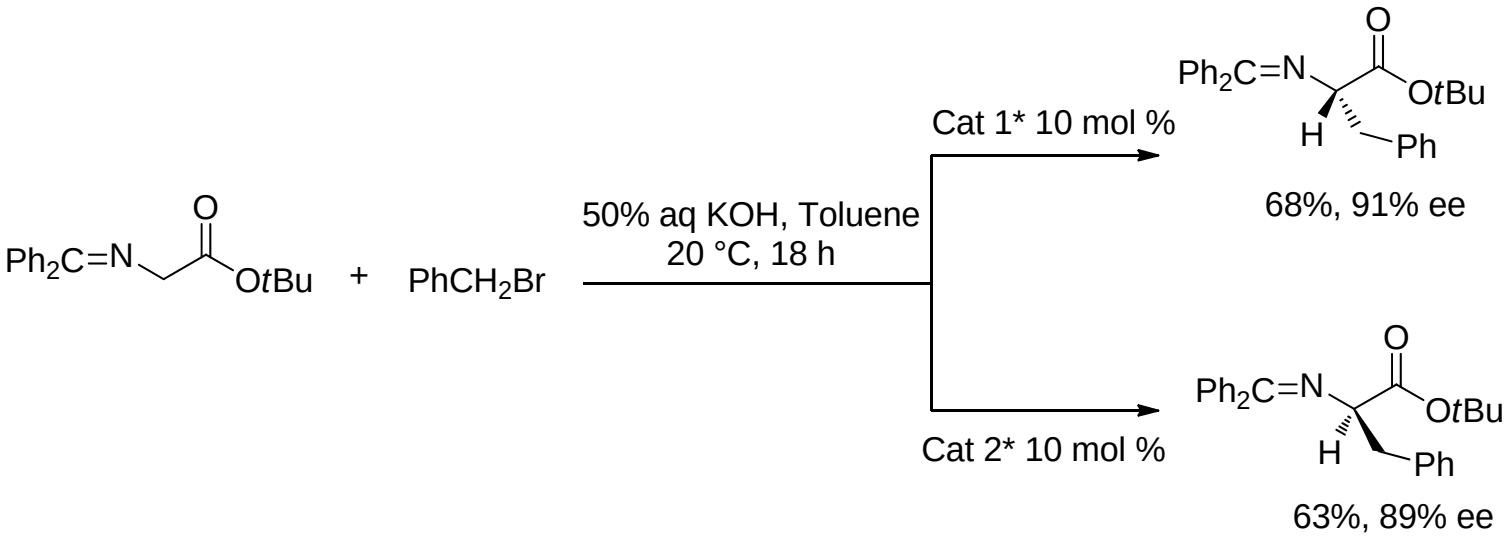




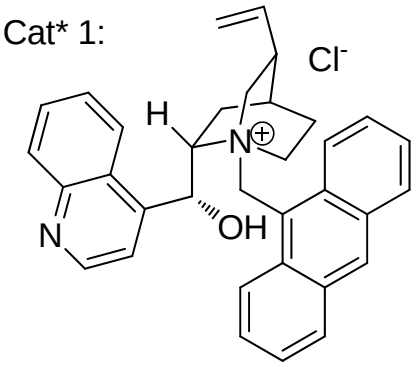




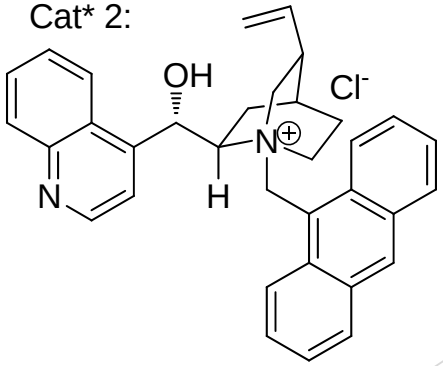
Applications:



Cat* 1:

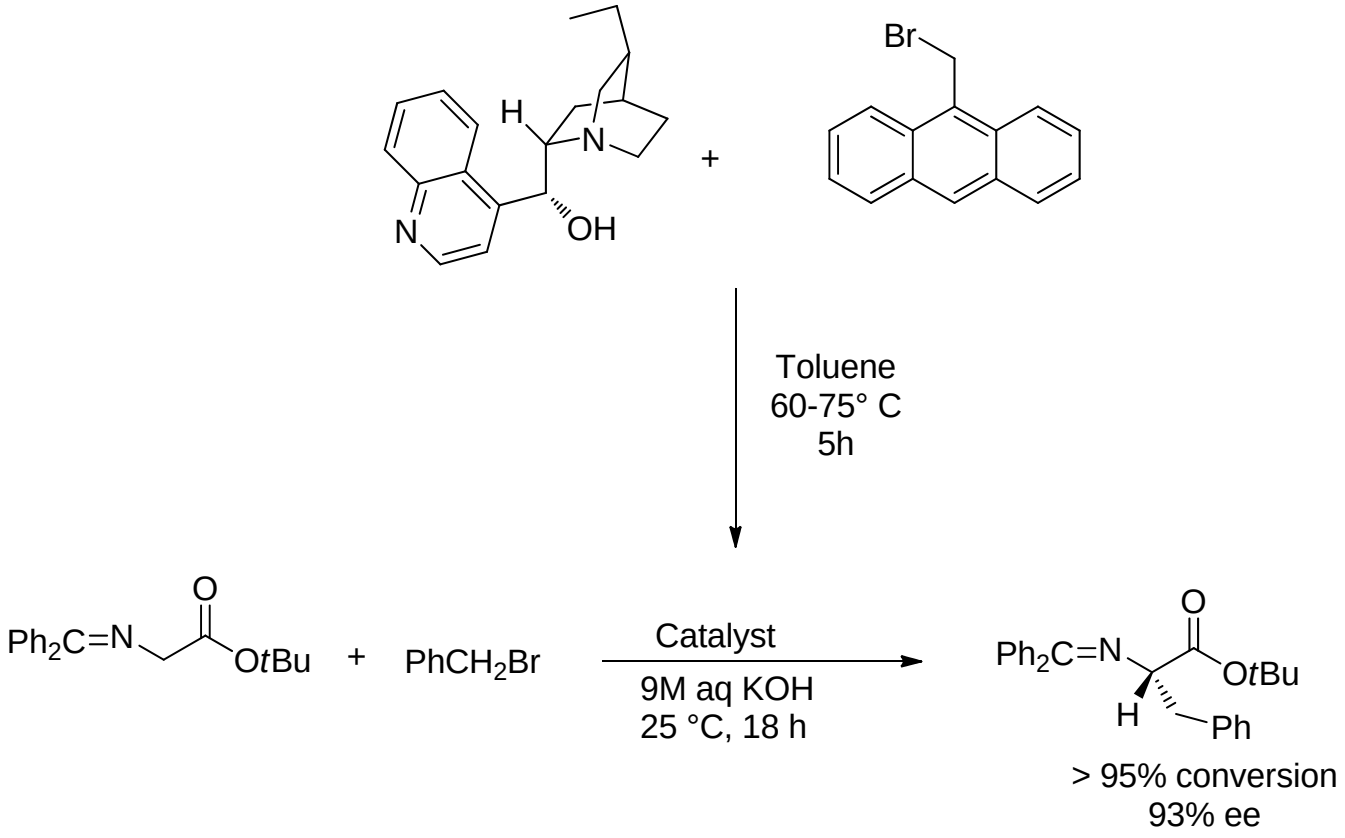


Cat* 2:



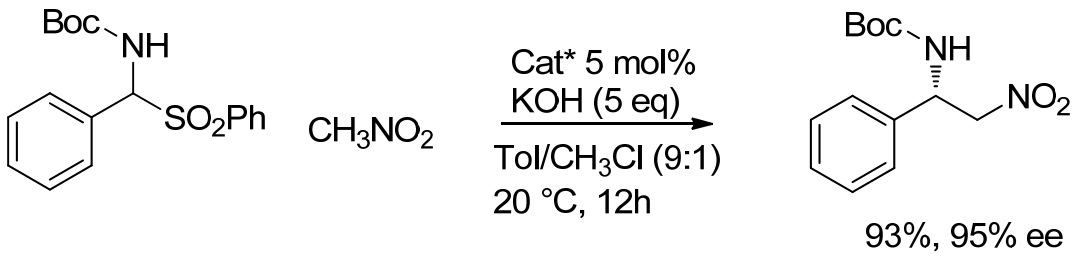
B. Lygo, J. Crosby, T. R. Lowdon, J. A. Peterson, P. G. Wainwright, *Tetrahedron* **2001**, *57*, 2403

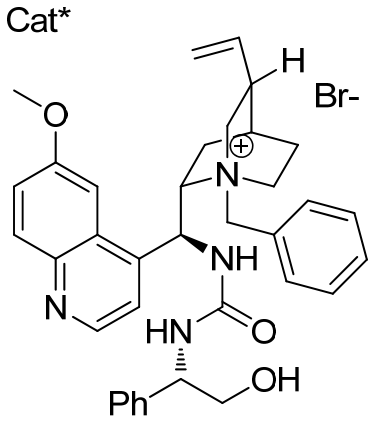
Applications:



B. Lygo, B. I. Andrews, J. Crosby, J. A. Peterson, *Tetrahedron Lett.* **2002**, *43*, 8015

Applications:



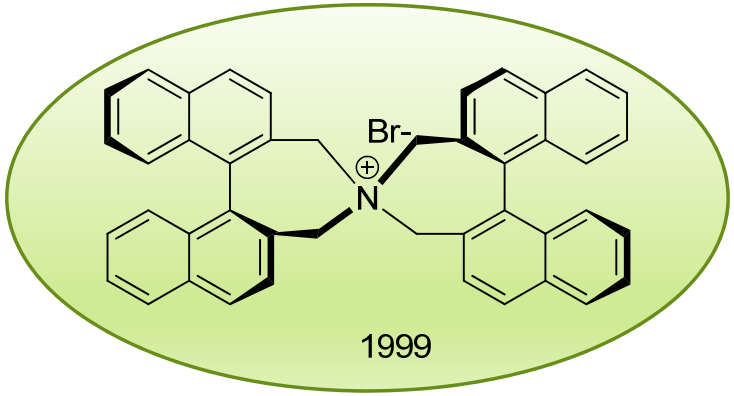


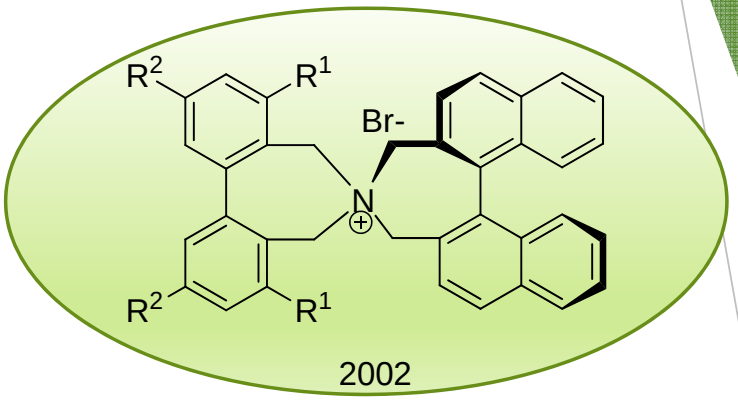
H. Duang et alt, *Org. Lett.* **2014**, *16*, 6432

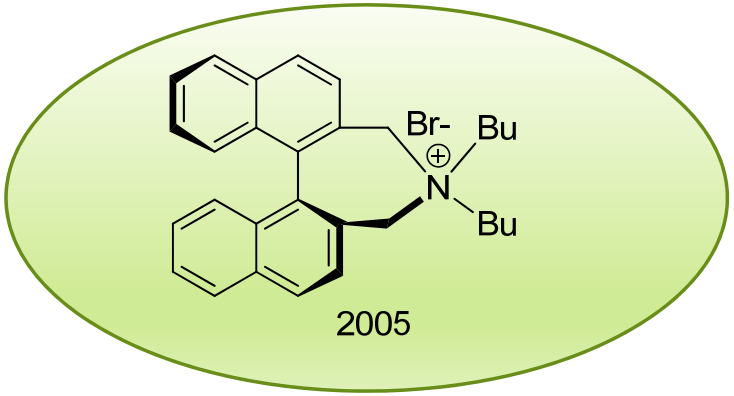
Other factors influencing efficiency of the reactions:

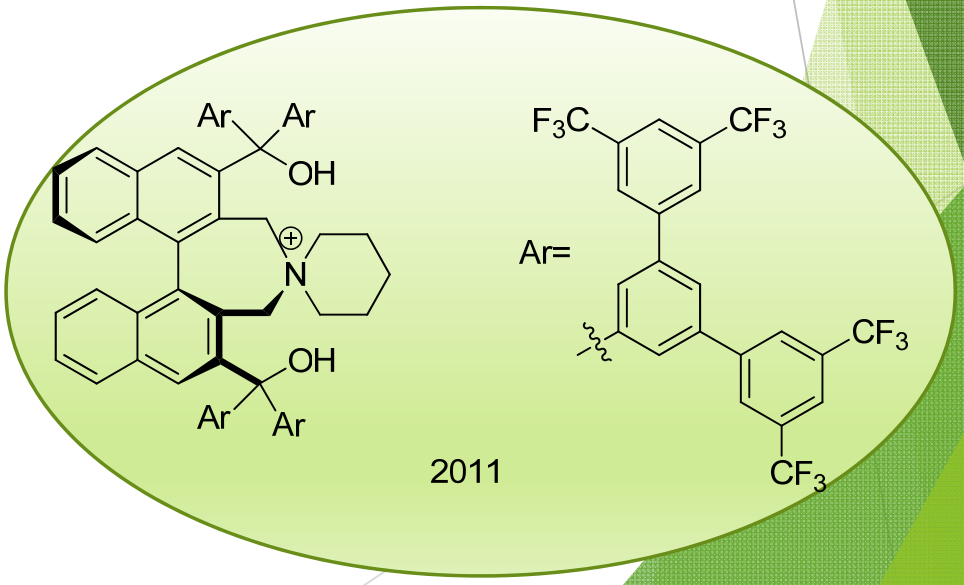
- Role of the solvent: The more apolar the solvent is, the higher the *ee*
- Effect of the counter ion: Chloride and Bromide atoms produce similar effects, while Iodide decrease the ee
- Role of the inorganic base: the choice of inorganic base is strongly depending on the reaction conditions.

Maruoka's Catalysts:

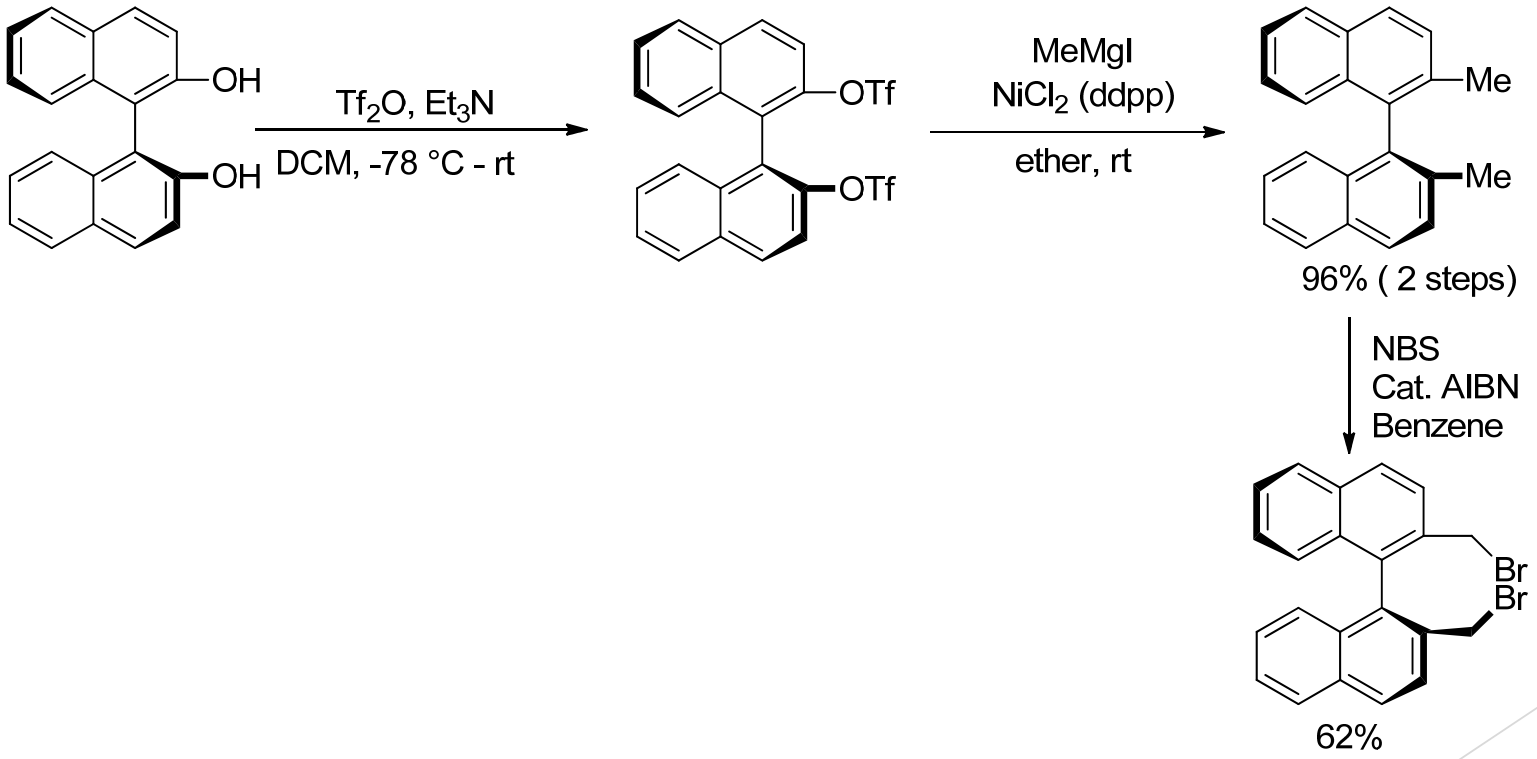






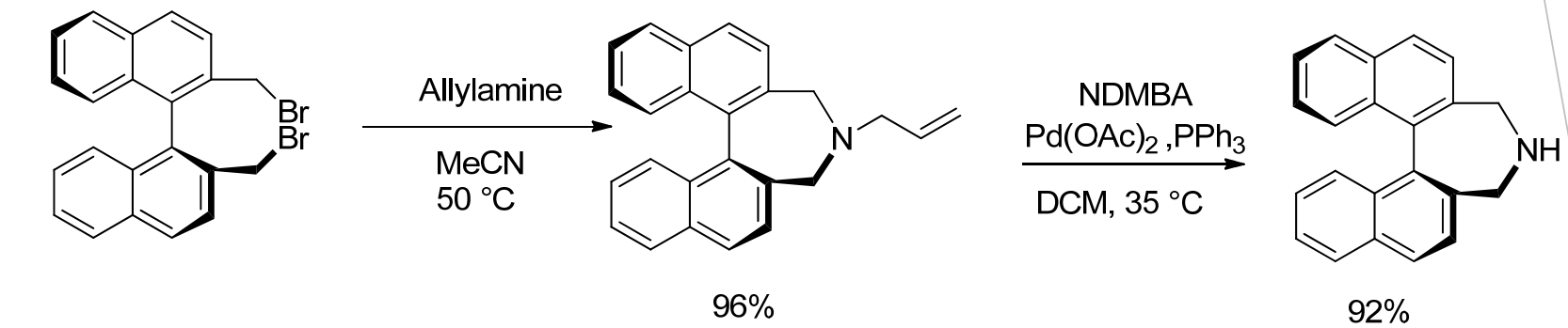


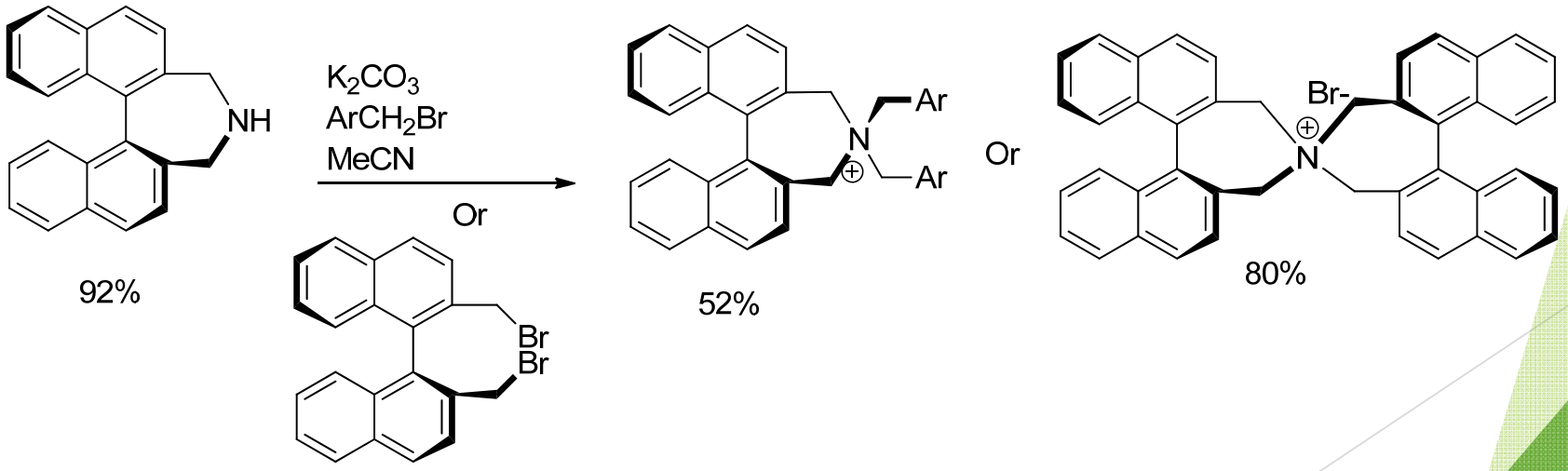
Synthesis of Maruokas catalyst:



T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

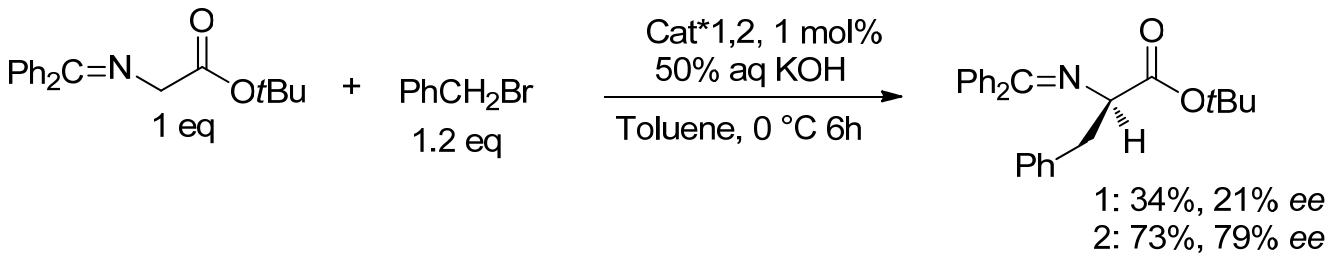
Synthesis of Maruokas catalyst:

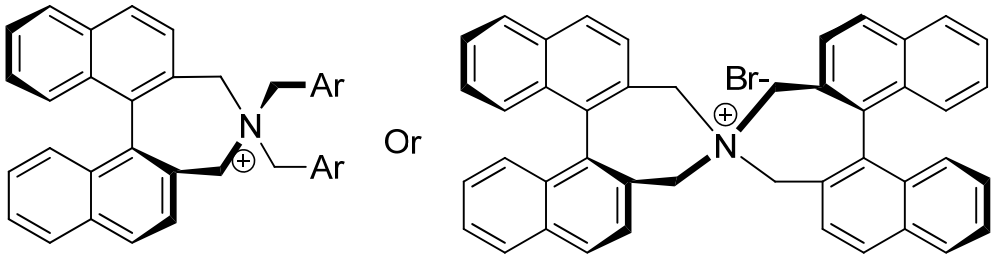




T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

Applications:



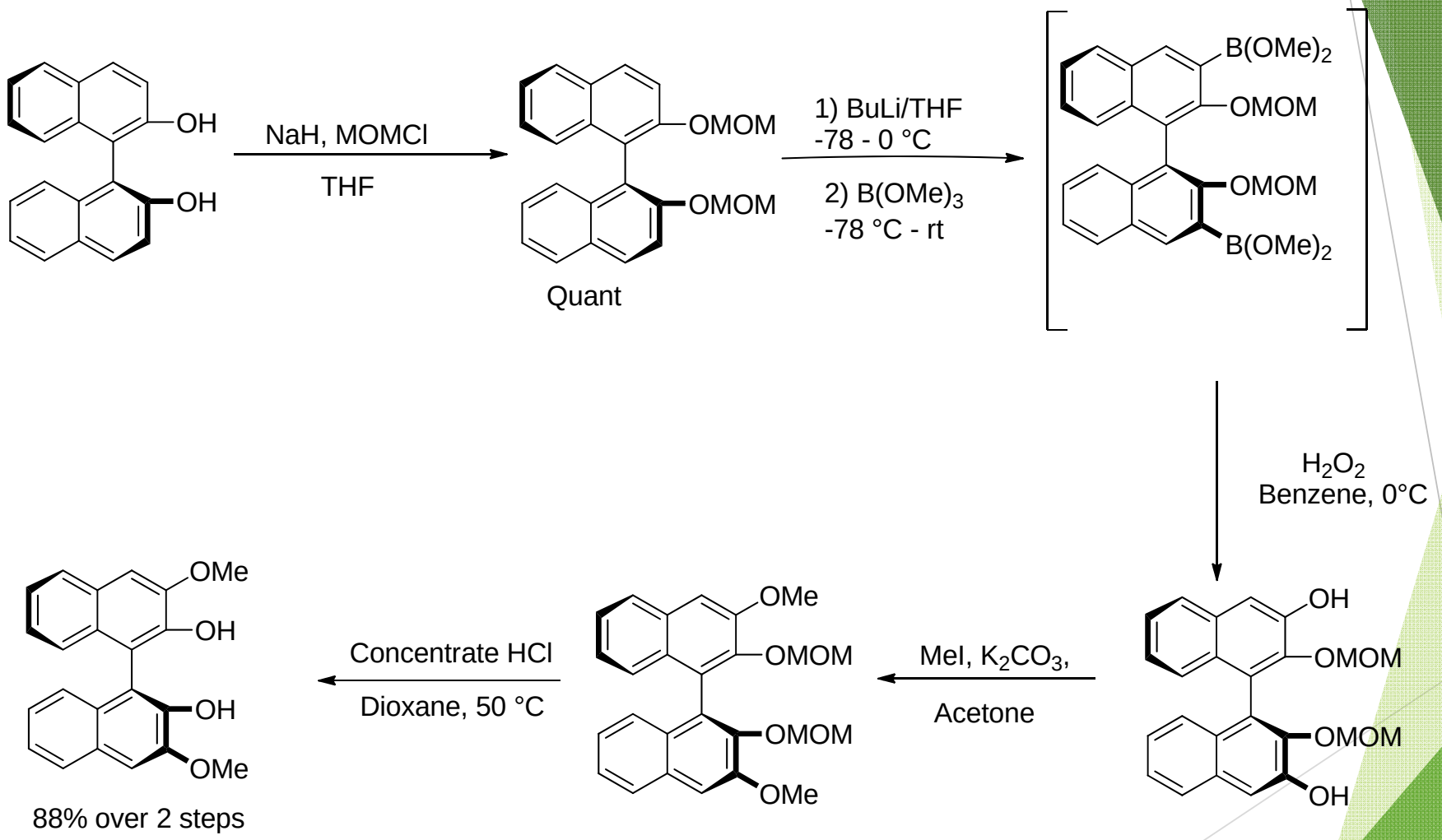


Cat*1 Cat*2

Design of a more constrained catalyst

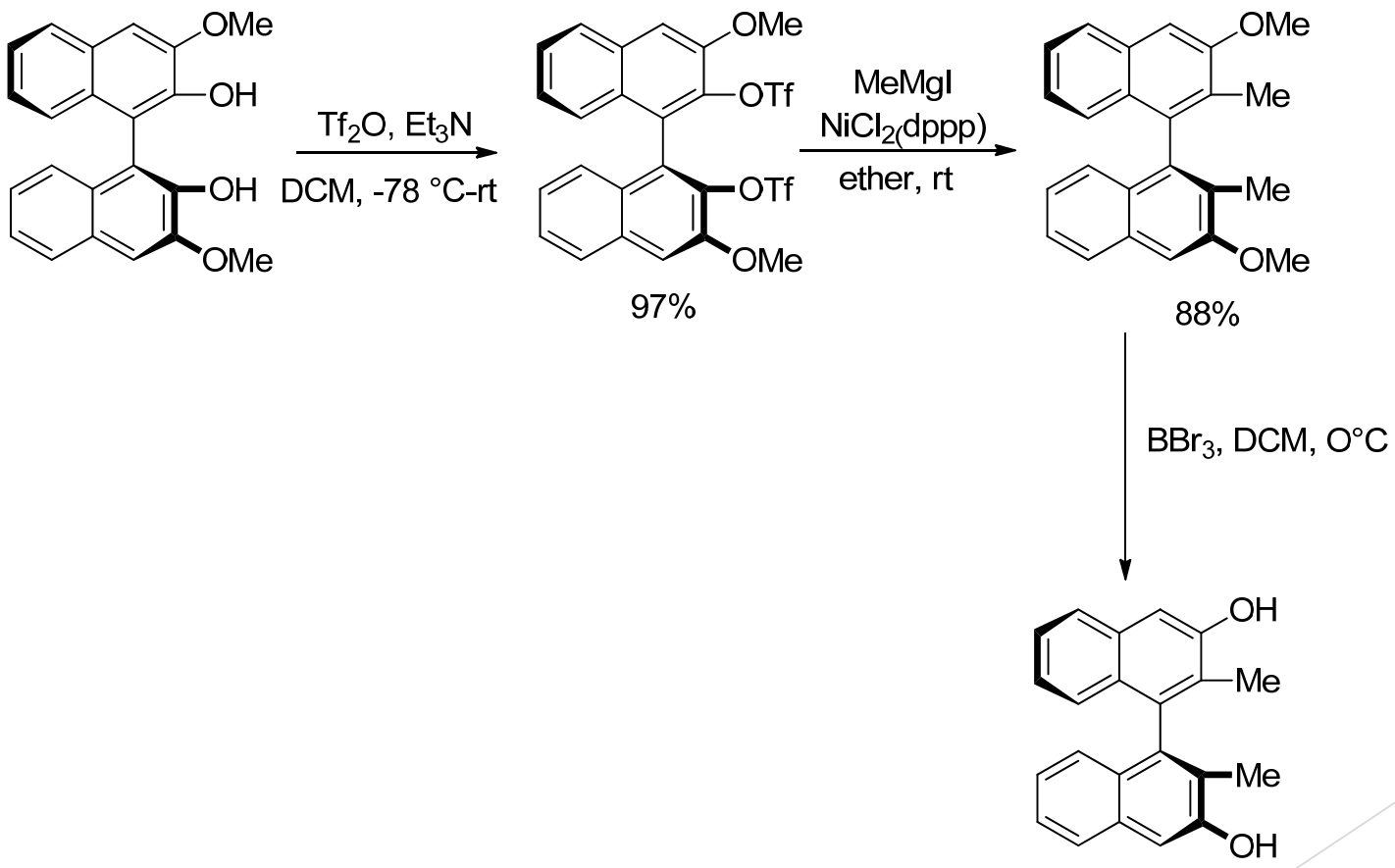
T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

Synthesis of bulkier catalyst



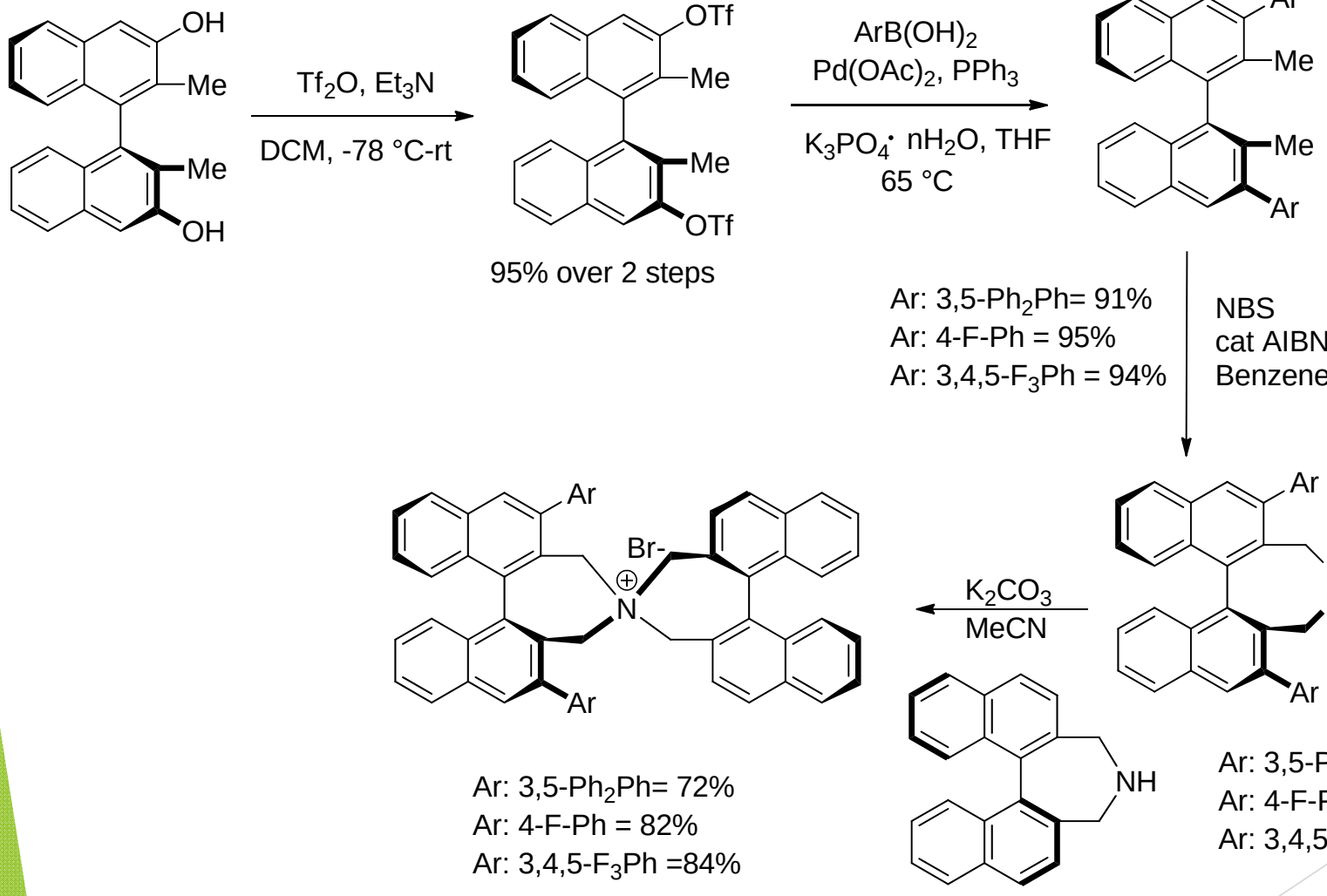
T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

Synthesis of bulkier catalyst



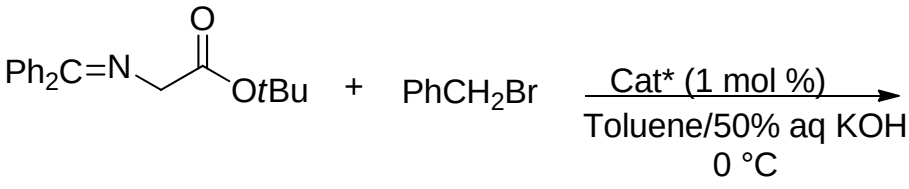
T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

Synthesis of bulkier catalyst

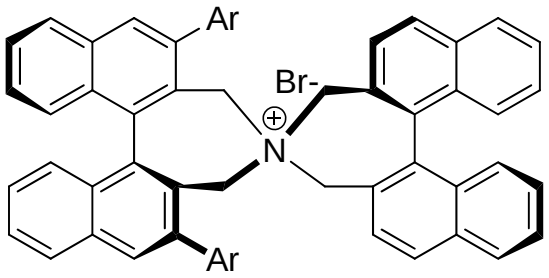


T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

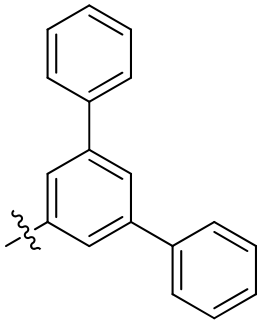
Applications



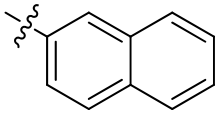
1a) 91%, 98% *ee*
1b) 91% 94% *ee*



1a) Ar: 3,5 diphenilphenil



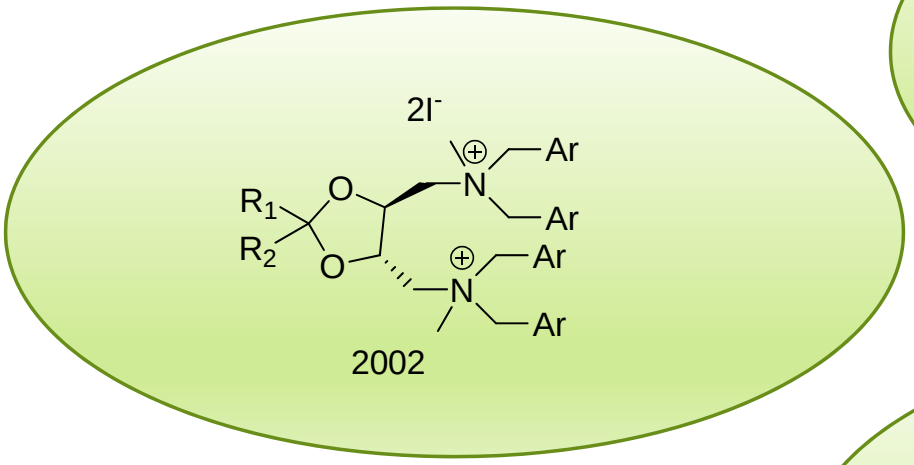
1b) Ar: B-Naphty

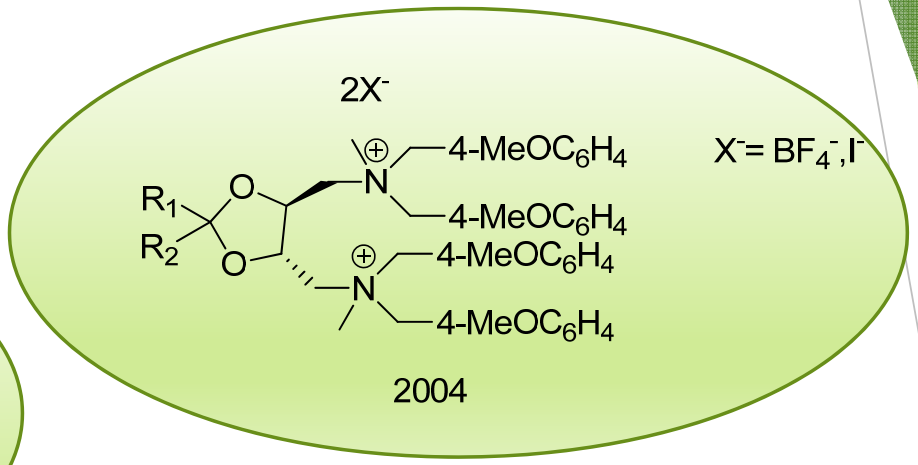


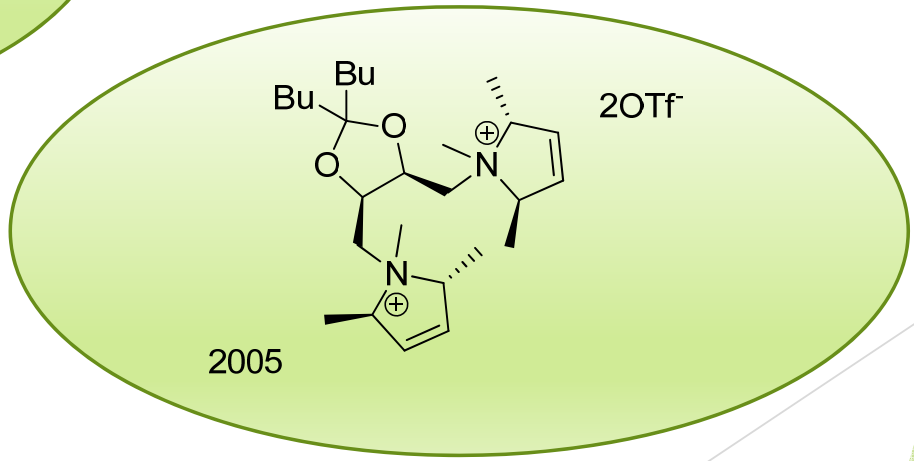
- The more apolar the solvent, the better
- No counterion effect recognised

T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

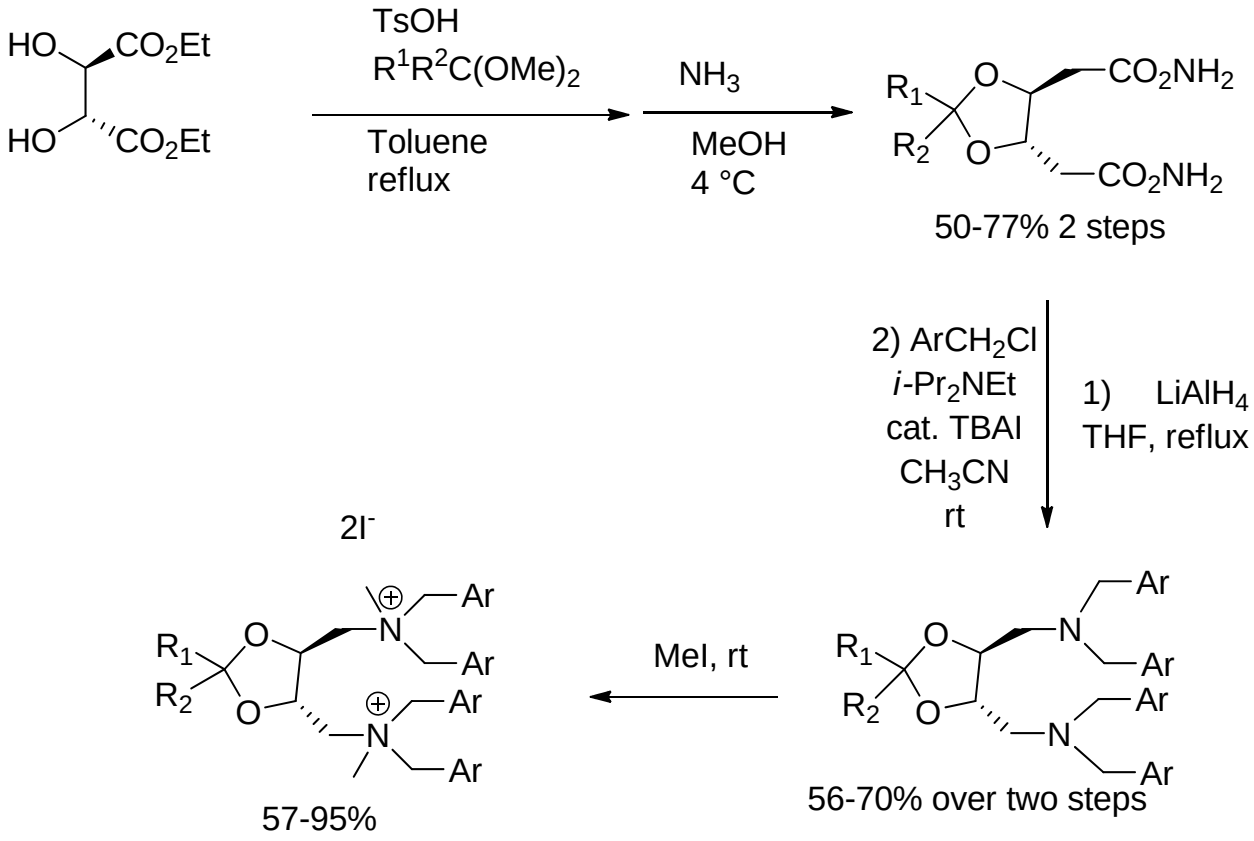
Tartrate-derived catalysts







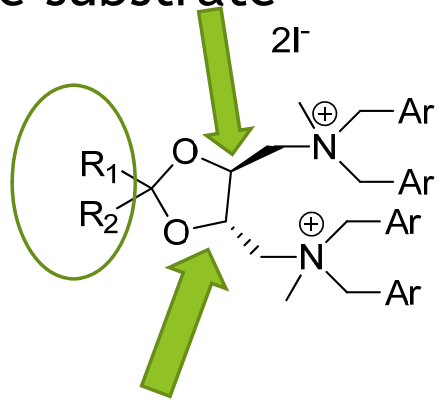
Sinthesys of tartrate-derived catalyst:



T. Shibuguchi, Y. Fukuta, Y. Akachi, A. Sekine, T. Oshima, M. Shibasaki, *Tetrahedron Lett.* **2002**, *43*, 9539

Characteristics of this catalyst:

Importance of the spacer between the two ions to complex the substrate

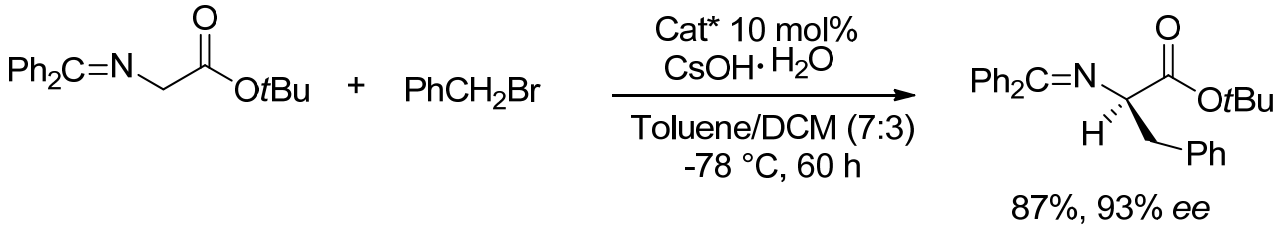


Easy to variate the substituents

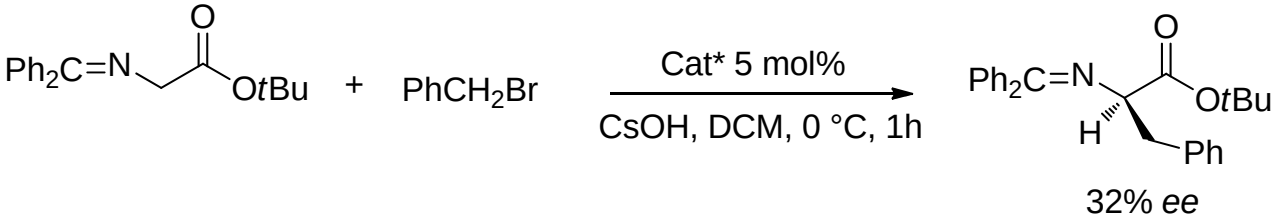
Easy access both the enantiomers

→ Strong counter ion effect: the harder the counterion (BF_4^- better than I^-) the higher the solubility in organic solvents, the more efficient the reaction

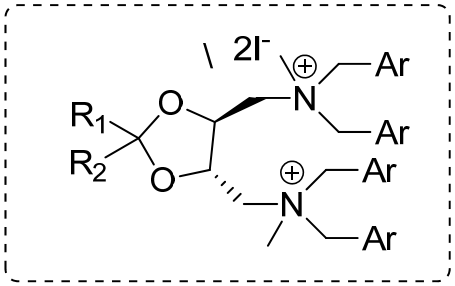
Applications:

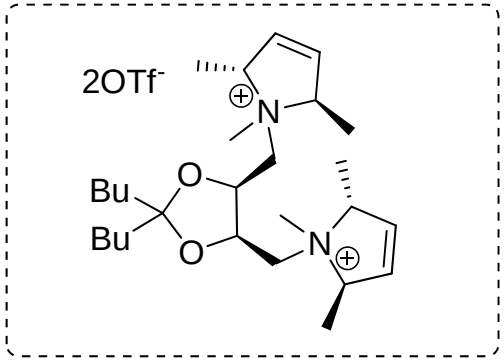


87%, 93% *ee*



32% *ee*

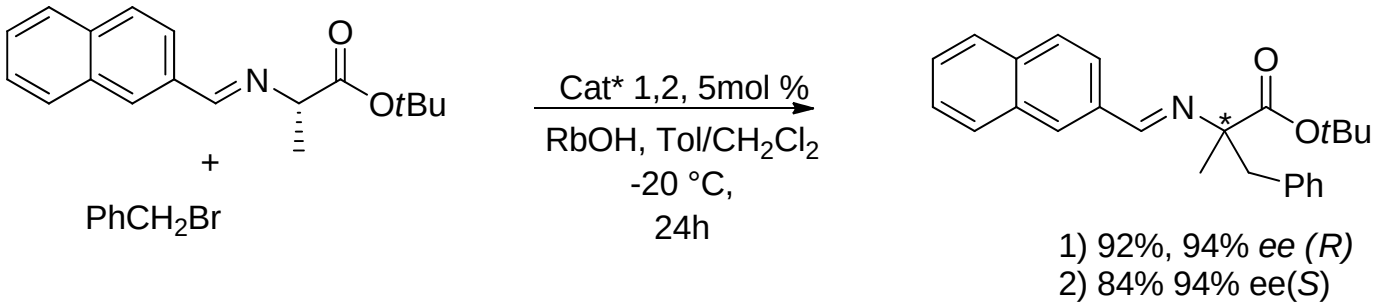




T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003,** *125*, 5139

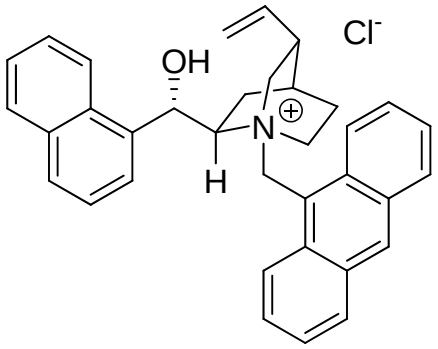
Other Applications of PT Catalysts

Synthesis of α,α-Dialkyl α- Amino Acids

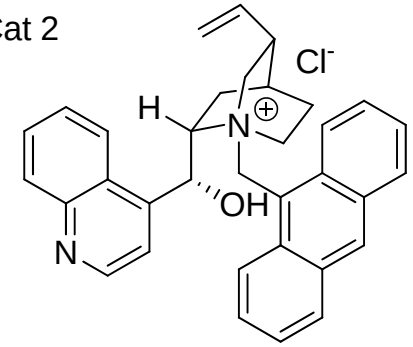


1) 92%, 94% *ee (R)*
2) 84% 94% ee(*S*)

Cat 1

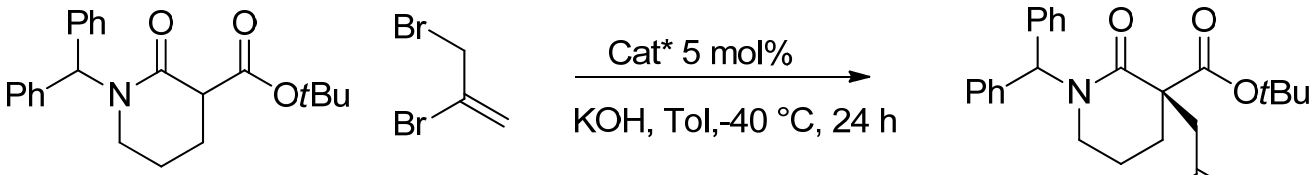


Cat 2



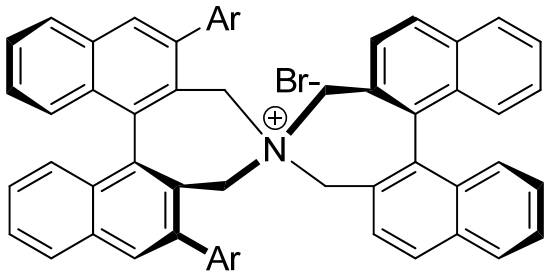
S.-s Jew, B.-S. Jeong, J.-H Lee, M.-S. Yoo, Y.-J.Lee, B.-s Park, M. G. Kim, H. g. Park, *J. Org. Chem.* **2003**, *68*, 4514

Other Applications of PT Catalysts

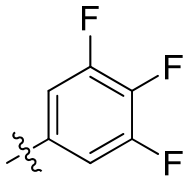


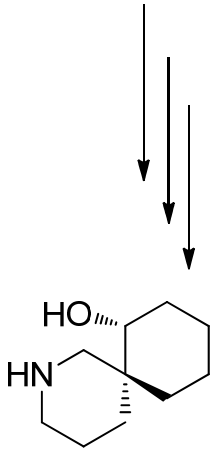
95%, 98% *ee*

Cat*



Ar:

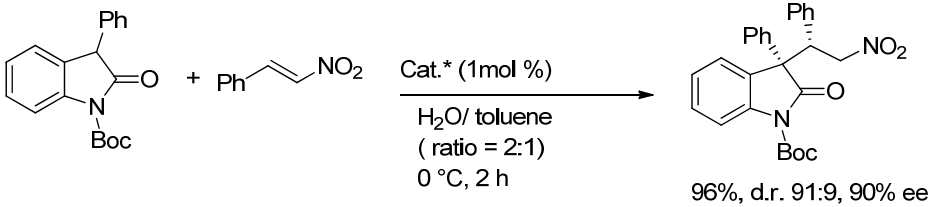


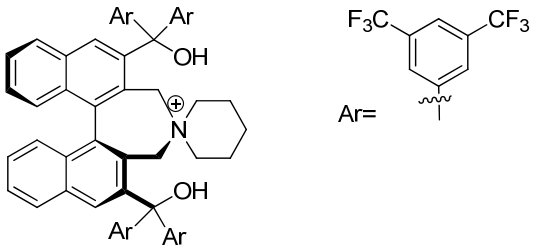


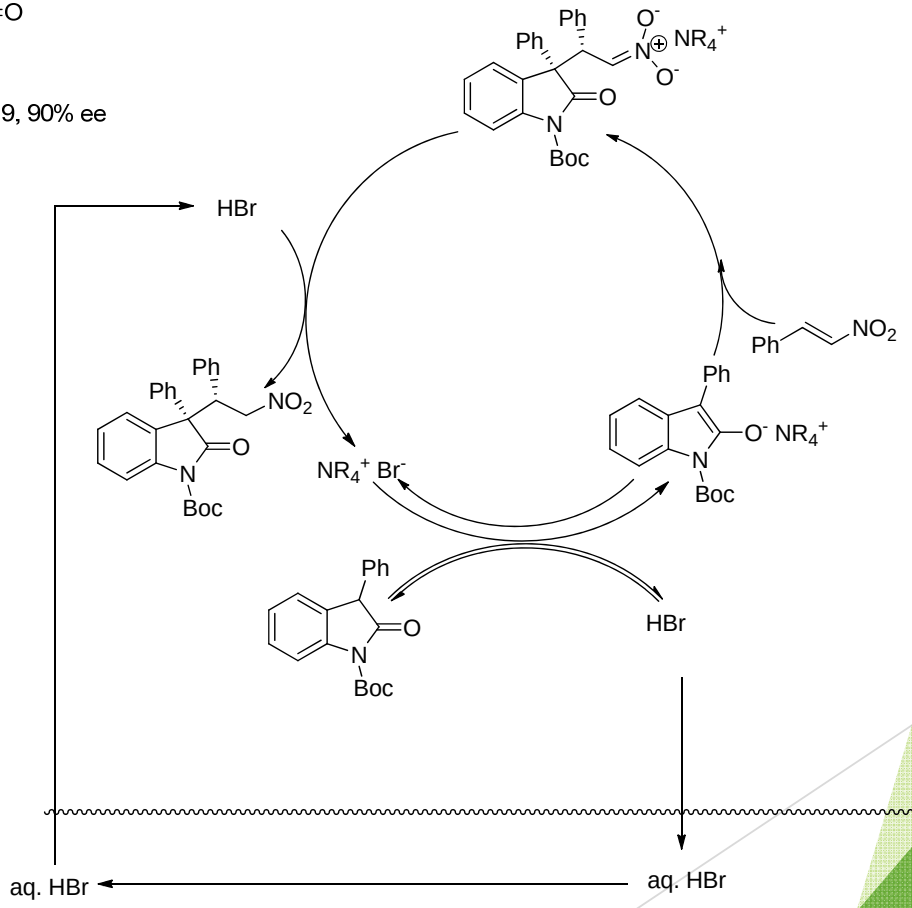
(-)- isonitramine

T. Ooi, T. Miki, K. Fukumoto, K. Maruoka, *Adv. Synth. Catal.* **2006**, *348*, 1539

Base free conjugate addition

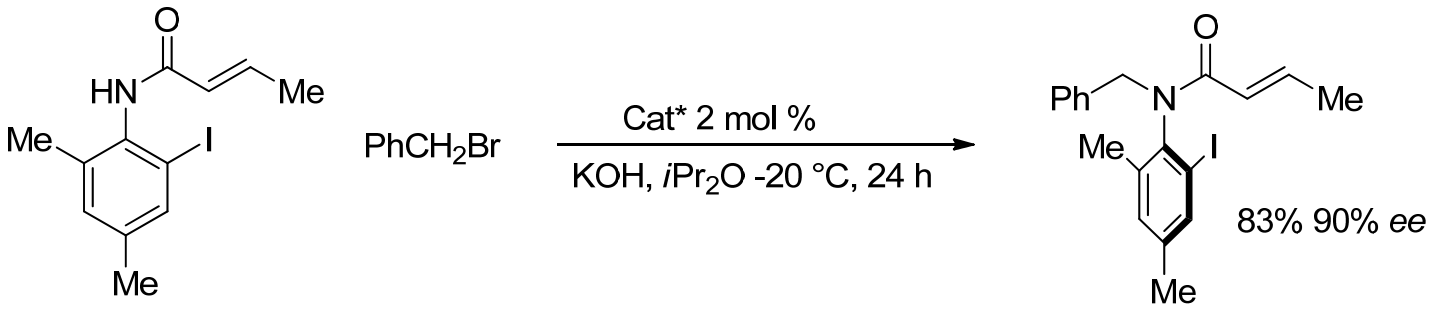


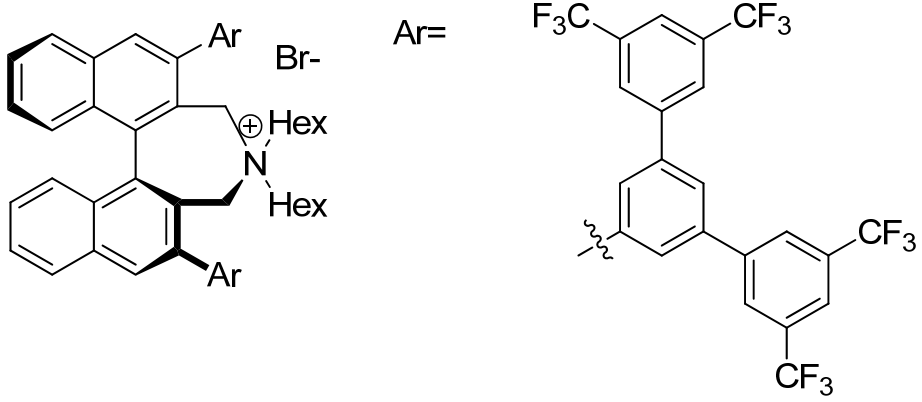




S. Shirakawa, L. Wang, R. He, S. Arimitsu, K. Maruoka *Chem. Asian. J.* **2014**, *9*, 1586

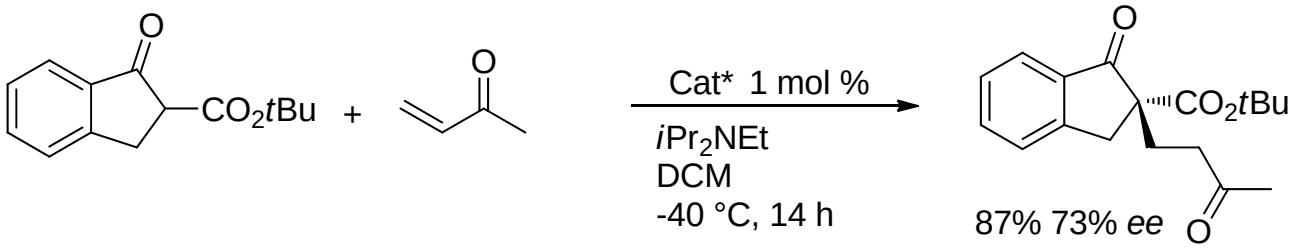
C-N Bond formation

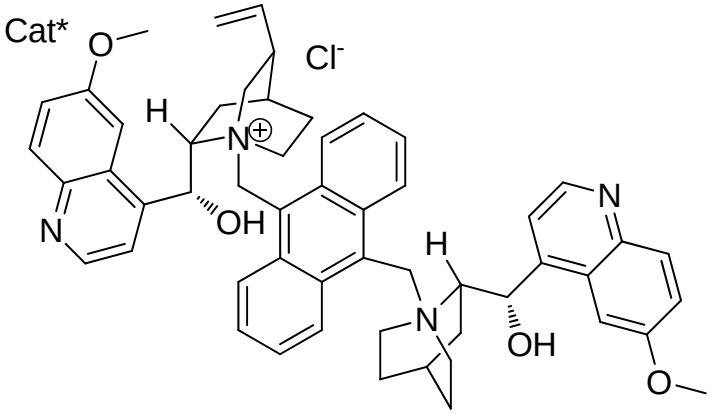




S. Shirakawa, K. Liu, k. Maruoka, *J. Am. Chem. Soc.*, **2012**, *134*, 916

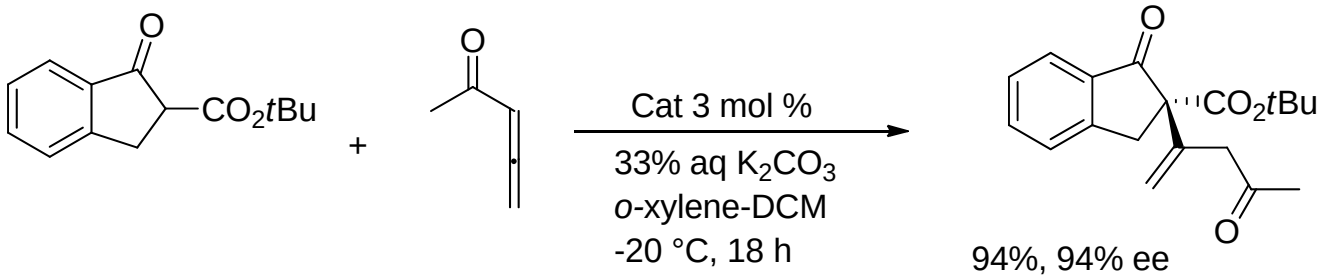
Conjugate addition

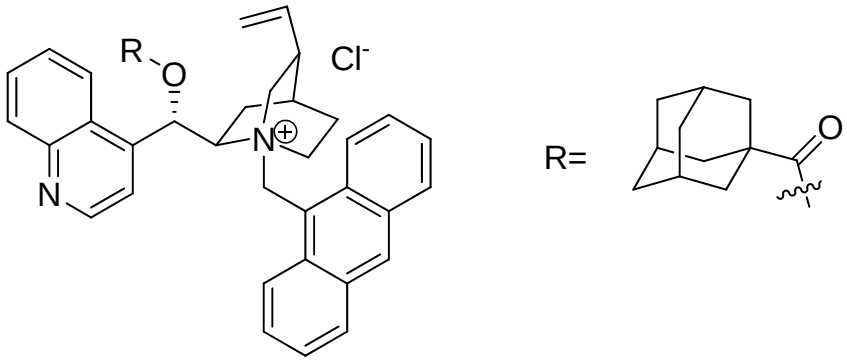




S. Tarì, R. Chichilla, C. Nàjera, *Tetrahedron Asymm.* **2009**, *20*, 2651

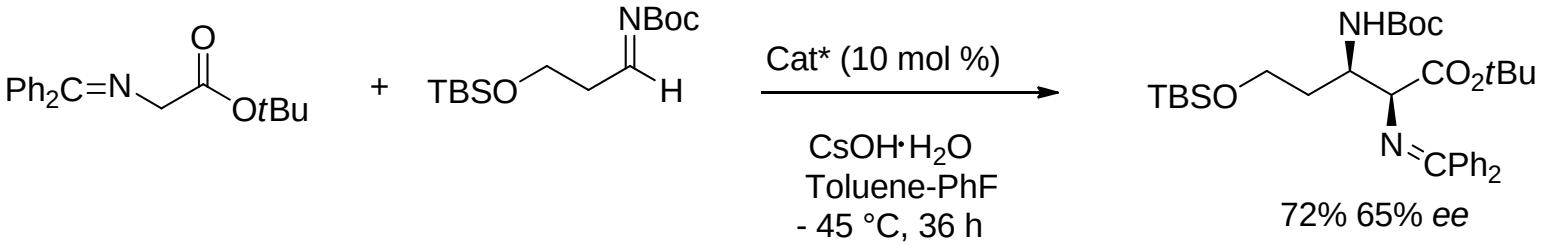
Conjugate addition:



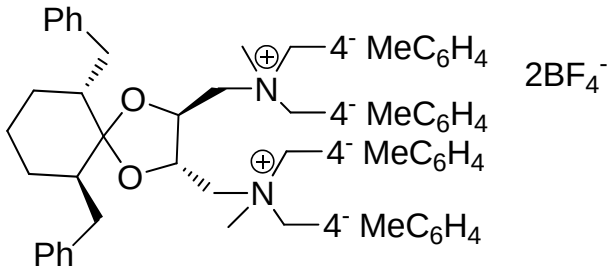


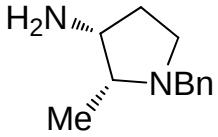
J. Aleman, E. Reyes, B. Richter, J. Overgaard, K. A. Jorgensen *Chemm. Commun.* **2007**, 3291

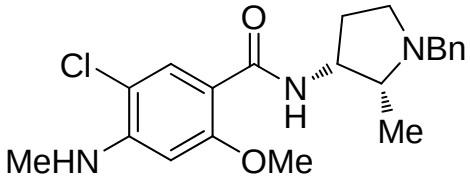
Mannich Reaction



72% 65% *ee*



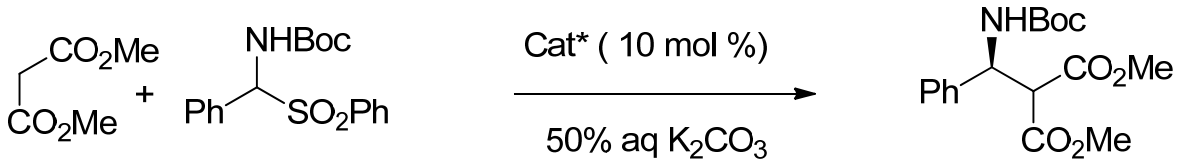




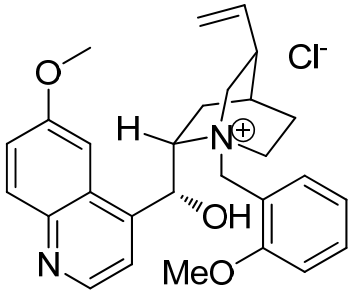
(+)-nemonapride

T. Shibuguchi, H. Mihara, A. Kuramochi, T. Oshima, M. Shibasaki, *Chem. Asian J.* **2007**, *2*, 794

Mannich Reactions

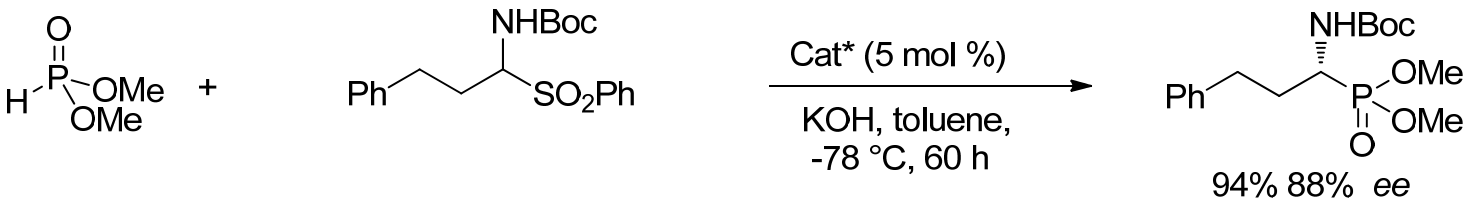


Cat*

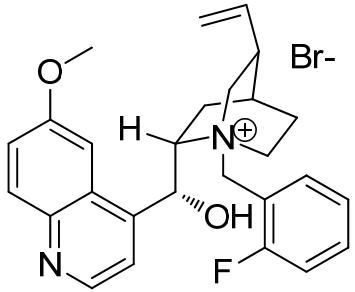


F. Fini, L. Bernardi, R. P. Herrera, D. Pettersen, A. Ricci, V. Sgarzani, *Adv. Synth. Catal.* **2006**, *348*, 2043

C–P Bond Formation

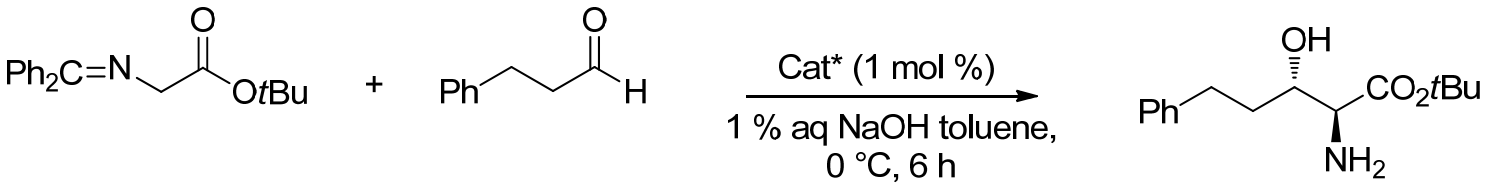


Cat*

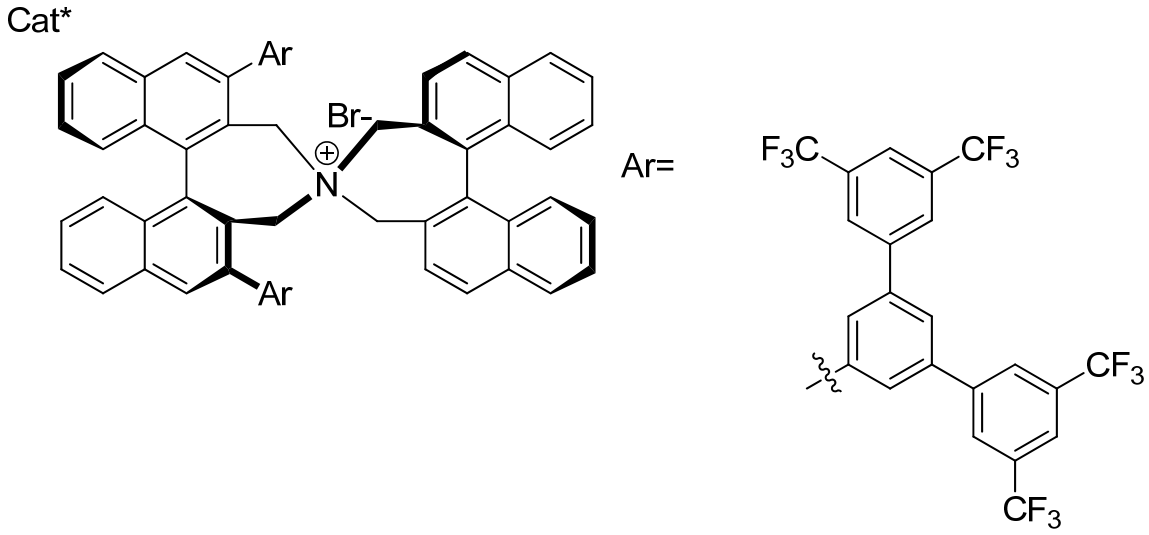


F. Fini, G. Micheletti, L. Bernardi, D. Pettersen, M. Fochi, A. Ricci *Chemm. Comm.* **2008**, 4345

Aldol Reaction

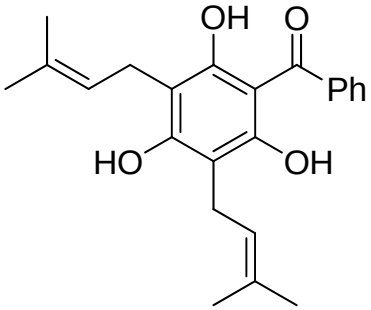


90%, dr:28: 72
-90% *ee*

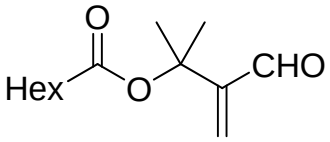


T. Ooi, M. Taniguchi, M. Kamenada, K. Maruoka, *Angew. Chem. Int. Ed.* **2002**, *41*, 4542

Alkylative dearomatization/annulation

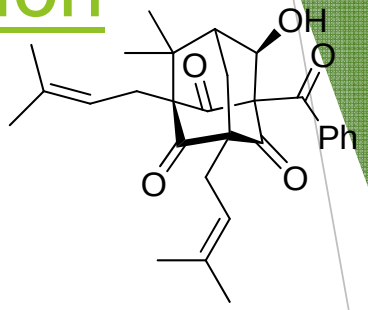


+



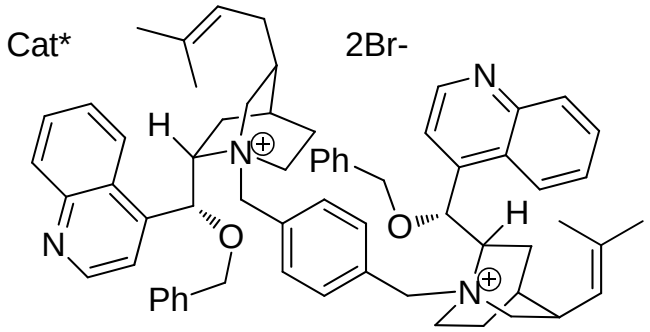
Cat* (25 mol %)

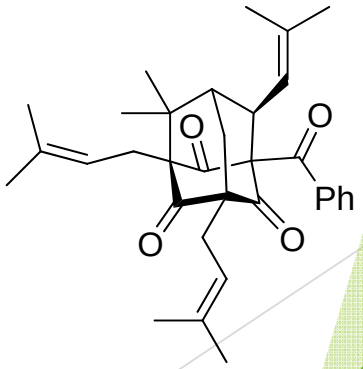
$CsOH\ H_2O$, -50 °C, 10 h



71% 90% *ee*

Cat*

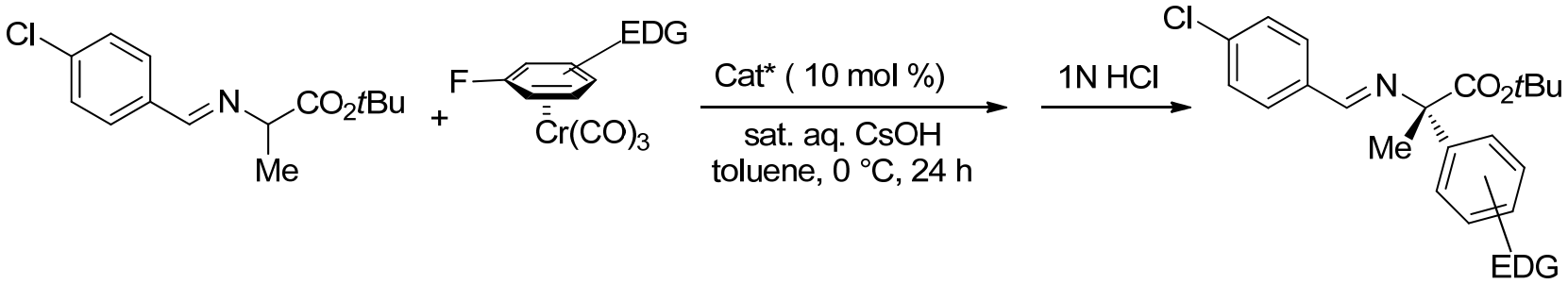




(-)-hyperibone K

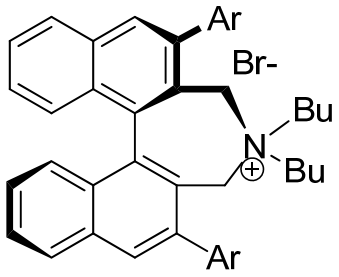
J. Qui, A. B. Beeler, Q. Zhang, J. A. Porco, Jr. *J. Am. Chem. Soc.* **2010,** *132*, 13642

Aromatic Nucleophilic Substitution

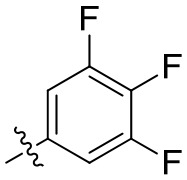


EDG: H, 70%, 97 %*ee*
p-Me 71% 98%*ee*

Cat*



Ar=



S. Shirakawa, K. Yamamoto, K. Maruoka *Angew. Chem. Int. Ed.*, **2015**, *54*, 838

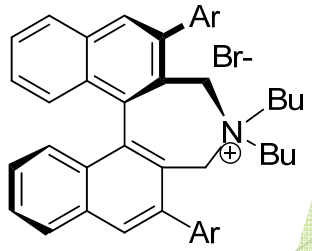
Conclusion and Outlook

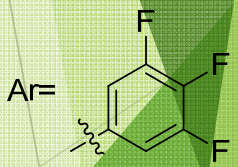
Qualities of the method

- Versatile methodology which can be applied with mild conditions
- Easy to scale up → Appealing for industrial applications

Drawbacks of the methodology

- Some of the designed catalyst are extremely expensive, or difficult to synthesize





250 € 50 mg

Design of new catalysts applicable to a wide range of reactions

Thanks for your attention!