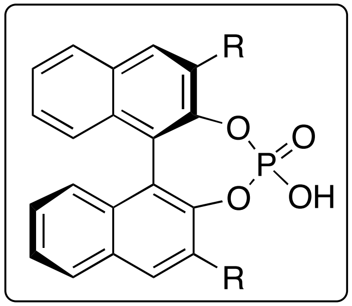
Recent applications of chiral binaphthol-derived phosphoric acid in catalytic asymmetric reactions



1. Seayad, J.; Seayad, A. M.; List, B. *J. Am. Chem. Soc*. **2006**, ASAP.
2. Storer, R. L.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2006**,*128*, 84.
3. Hoffmann, S.; Seayad, A. M.; List, B. *Angew. Chem. Int. Ed.* **2005**, *44*, 7424.
4. Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc*. **2005**,*127*, 15696.
5. Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc*. **2005**,*127*, 9360.
6. Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc*. **2005**,*127*, 11804.
7. Uraguchi, D.; Terada, M. *J. Am. Chem. Soc*. **2004**,*126*, 5356.
8. Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566.
9. Akiyama, T.; Morita, H.; Itoh, J.; Fuchibe, K. *Org. Lett.* **2005**, *7*, 2583.

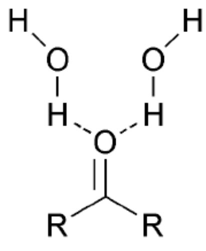
Literature Presentation

Zhenjie Lu

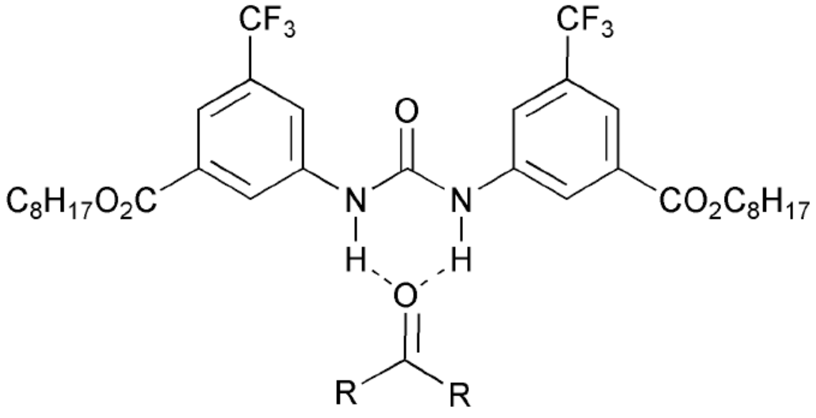
Jan 12, 2006

Introduction

‘Stereoselective chemical transformations perhaps have over emphasized the virtue of metal catalysis but this picture is changing rapidly; fast developing metal-free catalysis with small organic molecules as been described as utilizing “artificial enzymes” or being “enzyme mimetics”.’



Jorgensen's model



Curran's Diarylurea

➢ advantages of using Bronsted acid

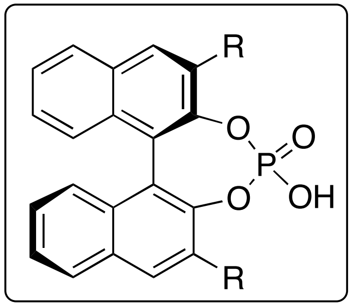
a. Metal-free chiral organocatalysts exhibit catalytic activity by themselves.

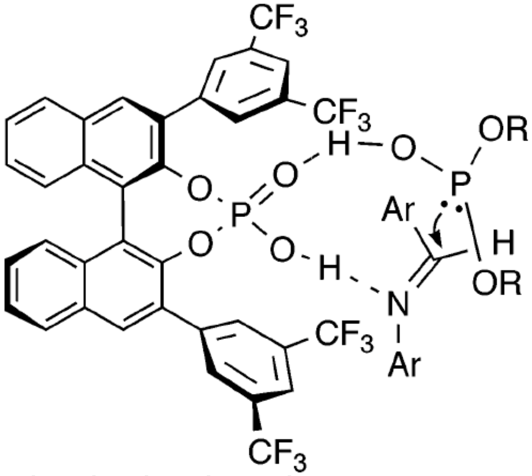
b. Organocatalysts are generally stable in air and easily stored.

c. Chiral Bronsted acid catalysts would electrophilically activate C=O or C=N bond, and cause chiral induction.

Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289.

Chiral Binaphthol-Derived Phosphoric Acid





Plausible hydrophosphonylation mechanism

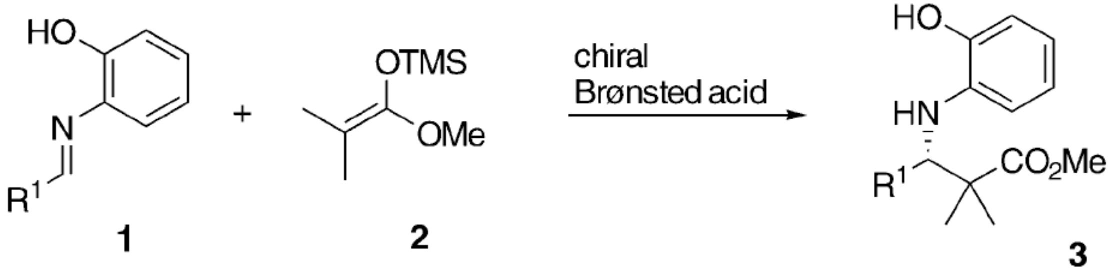
- The tetradentate structure around the phosphorus(V) prevent free rotation at the phosphorus center by formation of a ring structure. This cannot be found in other carboxylic and sulfonic Bronsted acids.

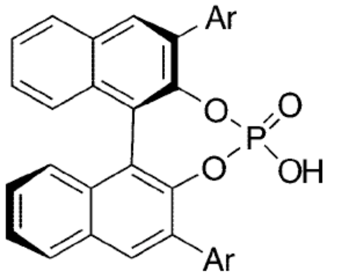
- The appropriate acidity (p*Ka* of diethylphosphate is 1.39) should catch up the substrate through hydrogen bonding without loose ion-pair formation.

- The phosphoryl oxygen should function as a Lewis basic site, and thus a phosphoric acid could function as a bifunctional catalyst.

Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289.

I. Bronsted Acid Catalyzed Mannich - type Reaction





4a: Ar=H
4b: Ar=C_6H_5
4c: Ar=2,4,6-$Me_3C_6H_2$
4d: Ar=4-$MeOC_6H_4$
4e: Ar=4-$NO_2C_6H_4$

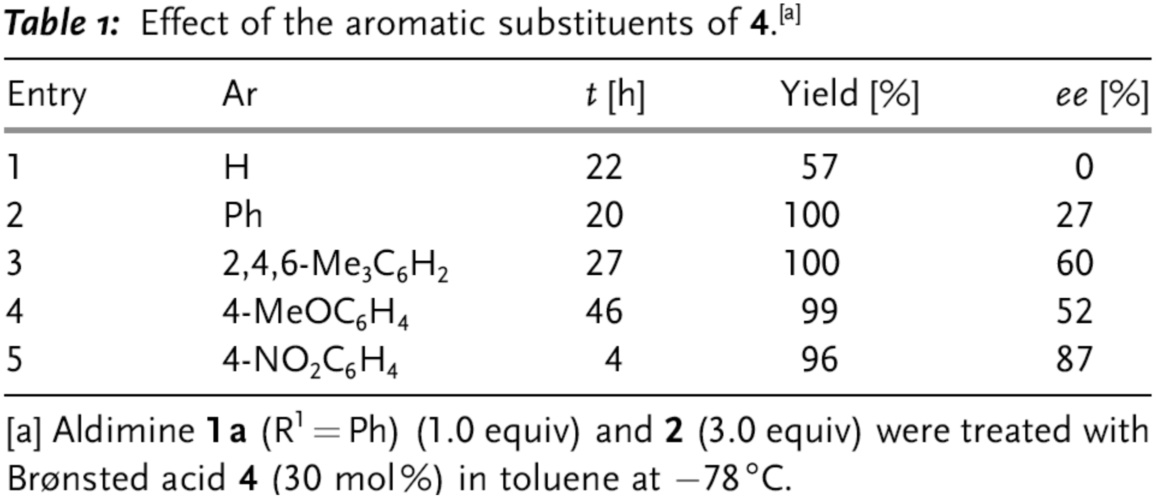


Table 1: Effect of the aromatic substituents of **4**.[a]

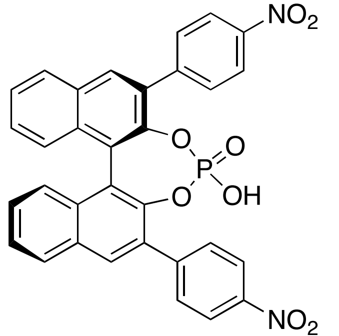
Entry	Ar	*t* [h]	Yield [%]	*ee* [%]
1	H	22	57	0
2	Ph	20	100	27
3	2,4,6-$Me_3C_6H_2$	27	100	60
4	4-$MeOC_6H_4$	46	99	52
5	4-$NO_2C_6H_4$	4	96	87

[a] Aldimine **1a** (R^1 = Ph) (1.0 equiv) and **2** (3.0 equiv) were treated with Brønsted acid **4** (30 mol%) in toluene at −78 °C.

- ❖ Bulky Bronsted acid and aromatic solvent gave better selectivity.

Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566.

I. Bronsted Acid Catalyzed Mannich - type Reaction



Akiyama's catalyst

- Akiyama’s catalyst and results.

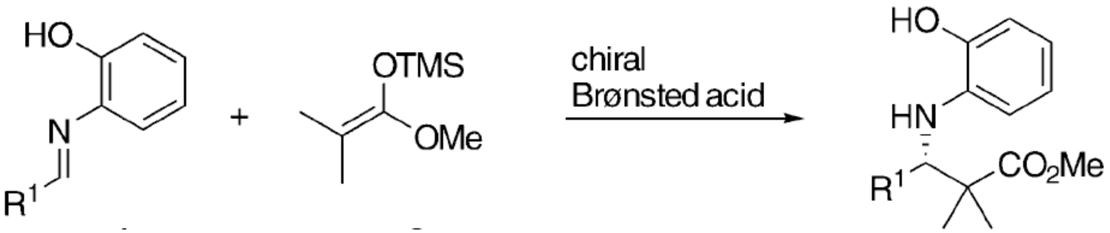


Table 2: Catalytic enantioselective Mannich-type reactions.[a]

Entry	R^1	Product	Yield [%]	*ee* [%]
1	Ph	**3a**	98	89
2	*p*-MeC_6H_4	**3b**	100	89
3	*p*-FC_6H_4	**3c**	100	85
4	*p*-ClC_6H_4	**3d**	100	80

[a] Aldimine **1** (1.0 equiv) and **2** (1.5 equiv) were treated with **4e** (10 mol%) in toluene at −78 °C for 24 h.

Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566.

I. Bronsted Acid Catalyzed Mannich - type Reaction

- Terada's catalyst and results.

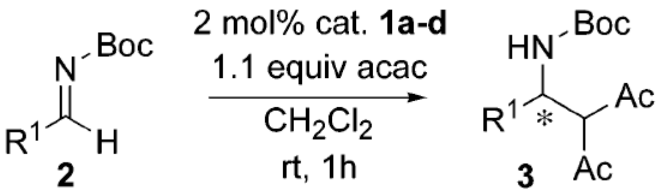
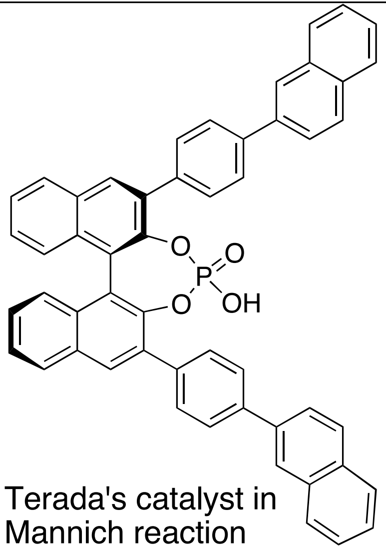


Table 2. The Chiral Phosphoric Acid-Catalyzed Direct Mannich Reactions (Eq 1; Catalyst **1d** Was Used)[a]

entry	R^1	yield[b] (%)	ee[c] (%)
1	4-MeO$-C_6H_4-$	93	90
2	4-Me$-C_6H_4-$	98	94
3	4-Br$-C_6H_4-$	96	98
4	4-F$-C_6H_4-$	94	96
5	2-Me$-C_6H_4-$	94	93
6	1-Naph$-$	99	92

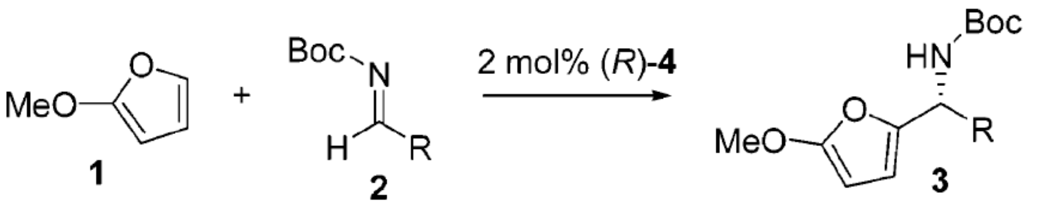
[a] All reactions were carried out on a 0.1 mmol reaction scale. [b] Isolated yield. [c] Enantiomeric excess was determined by HPLC analysis.

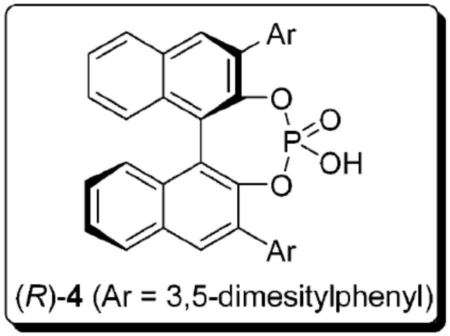


Terada's catalyst in Mannich reaction

Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356.

II. Bronsted Acid Catalyzed Friedel Crafts - type Reactions





(*R*)-**4** (Ar = 3,5-dimesitylphenyl)

Table 2. Organocatalyzed Aza-Friedel−Crafts Reaction of Furan (**1**) with Representative *N*-Boc Aldimine Derivatives (**2**) (Eq 1)[a]

entry	R	yield (%)[b]	ee (%)[c]
1	*p*-MeO-C_6H_4-	95	96
2	*o*-Me-C_6H_4-	84	94
3	*m*-Me-C_6H_4-	80	94
4	*p*-Me-C_6H_4-	96	97
5	*o*-Br-C_6H_4-	85	91
6	*m*-Br-C_6H_4-	89	96
7	*p*-Br-C_6H_4-	86	96
8	*p*-Cl-C_6H_4-	88	97
9	*p*-F-C_6H_4-	82	97
10	1-naphthyl-	84	86
11	2-naphthyl-	93	96
12	2-furyl-	94	86
13[d]	Ph-	95	97

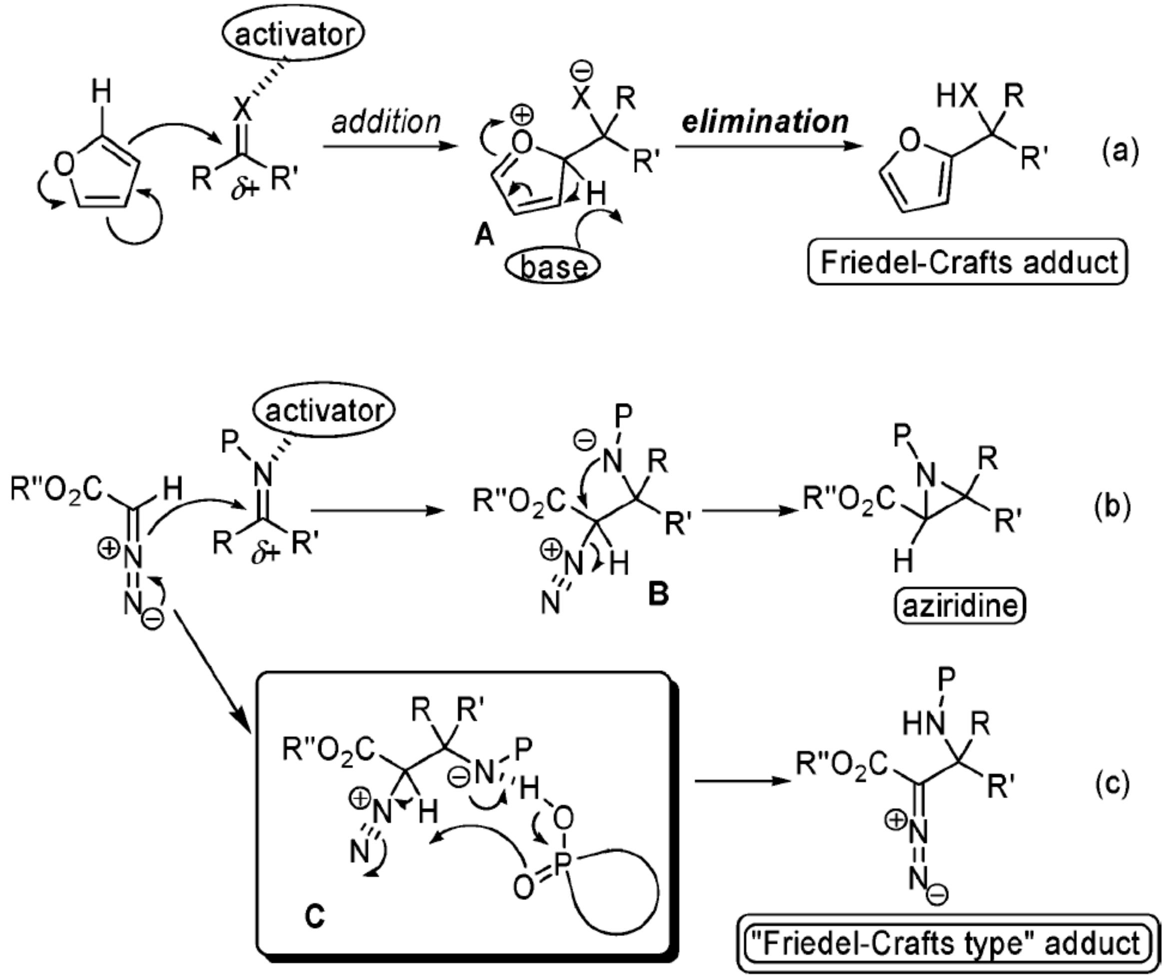
[a] 0.1 M in $(CH_2Cl)_2$ at -35 °C for 24h.

❖ Halogenated solvent gave better results than ethereal or aromatic solvents. (87% yield, 97% ee vs. 70% yield, 83% ee in THF or 88% yield, 83% ee in toluene.)

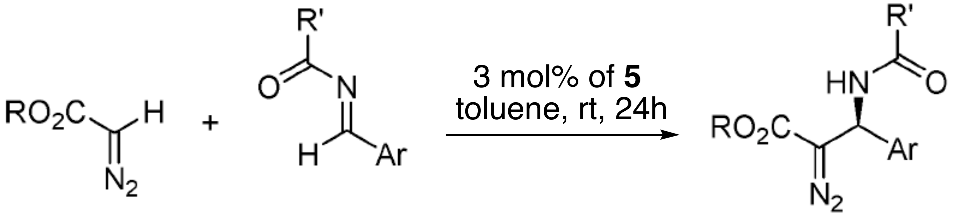
Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc.* **2005**, *127*, 11804.

II. Bronsted Acid - Catalyzed Friedel Crafts - type Reactions

Scheme 1. Mechanism for Friedel–Crafts Alkylations and Reaction Modes of Diazoacetate with Imine



II. Bronsted Acid - Catalyzed Friedel Crafts - type Reactions



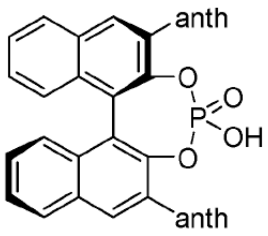
1a: R = Et

1b: R = ^{t}Bu

2

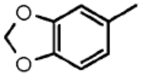
3a: R = Et

3b: R = ^{t}Bu



(*R*)-**5** (anth = 9-anthryl)

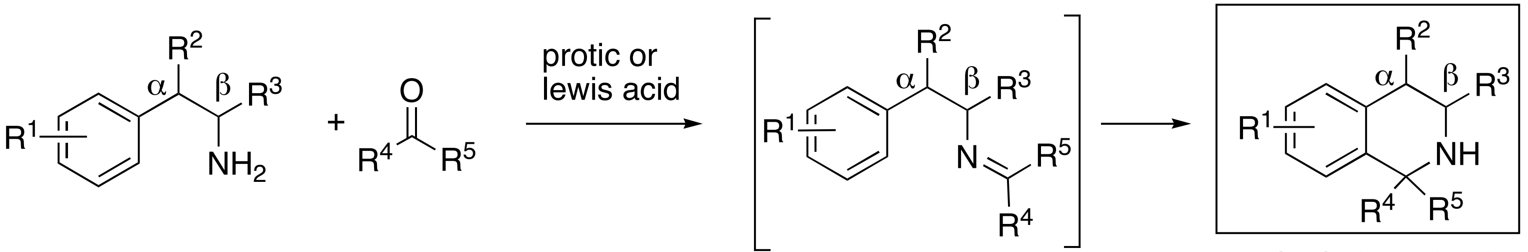
Table 2. Organocatalyzed Direct Alkylation of *tert*-Butyl Diazoacetate (**1b**) with Representative Aldimine Derivatives (**2**) (Eq 1, R′ = *p*-Me_2N-C_6H_4, **1b**, and (*R*)-**5** Were Used)[a]

entry	Ar	yield (%)[b]	ee (%)[c]
1	*p*-F-C_6H_4-	74	97
2	*p*-Ph-C_6H_4-	71	97
3	*p*-Me-C_6H_4-	74	97
4	*p*-MeO-C_6H_4-	62	97
5[d]	*o*-F-C_6H_4-	89	91
6	*o*-MeO-C_6H_4-	85	91
7	*m*-F-C_6H_4-	84	93
8[d]		75	95

Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc.* **2005**, *127*, 9360.

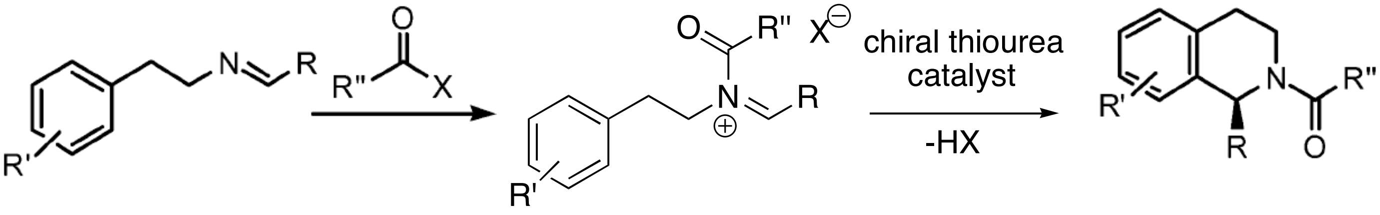
II. Bronsted Acid Catalyzed Friedel Crafts - type Reactions: Pictet-Spengler Reaction

Pictet-Spengler Reaction:

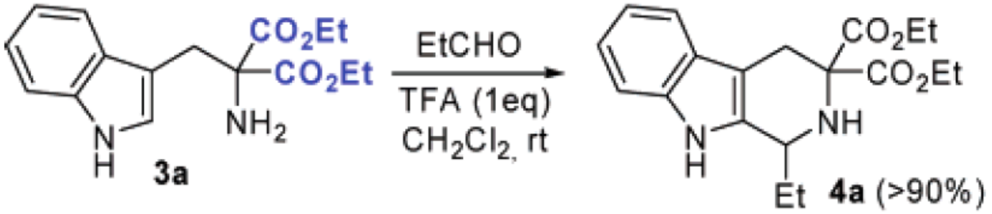


tetrahydroisoquinoline

- Jacobsen's approach



- List's approach



3a **4a** (>90%)

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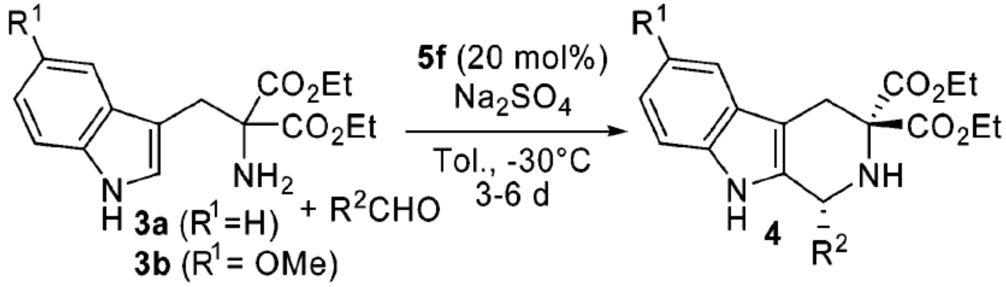
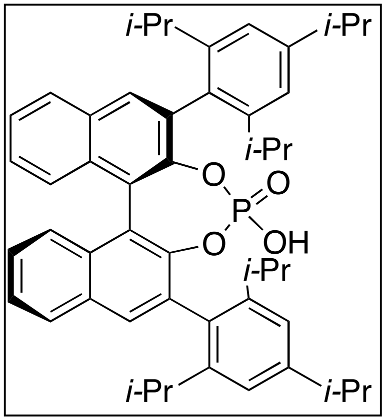
1) Taylor, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 10558.
2) Seayad, J.; Seayad, A. M.; List, B. *J. Am. Chem. Soc.* **2006**, ASAP.

II. Bronsted Acid Catalyzed Friedel Crafts - type Reactions: Pictet-Spengler Reaction



Entry	R^1	R^2	Yield [%][a]	*ee* [%][b]
1	OMe	Et	96	90
2	H	Et	76	88
3	OMe	*n*-Pr	98	88
4	OMe	*n*-Bu	90	87
5	H	*n*-Bu	91	87
6	OMe	*i*-Bu	96	80
7	OMe	Bn	85	72
8	H	Bn	58	76
9	OMe	*i*-Pr	85	81
10[c]	OMe	Cy	64	94
11	OMe	2-pentyl	50	84
12[d]	OMe	*p*-O_2N-C_6H_4	98	96
13[d]	H	*p*-O_2N-C_6H_4	60	88
14[d]	OMe	*p*-NC-C_6H_4	60	80
15[d]	H	*p*-NC-C_6H_4	40	89
16[d]	OMe	Ph	82	62

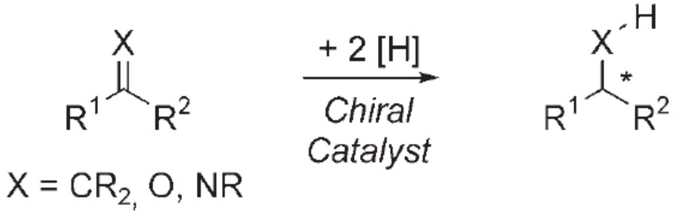


5 List's catalyst

This reaction tolerates aromatic aldehydes (at -10°C in CH_2Cl_2) (entry 12-16).

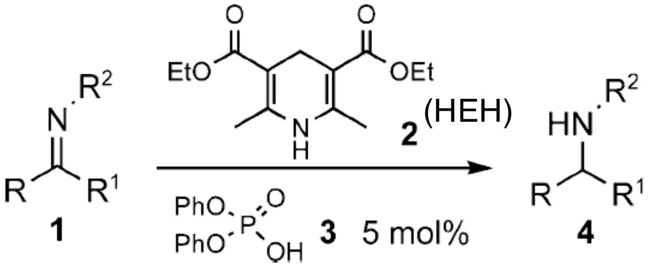
Seayad, J.; Seayad, A. M.; List, B. *J. Am. Chem. Soc.* **2006**, ASAP.

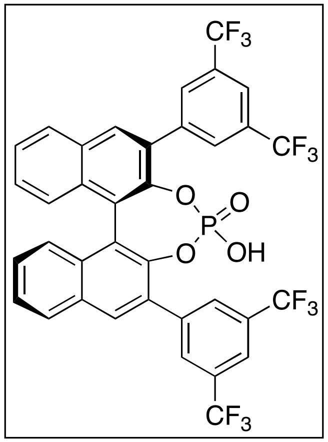
III. Bronsted Acid Catalyzed Reductive Amination



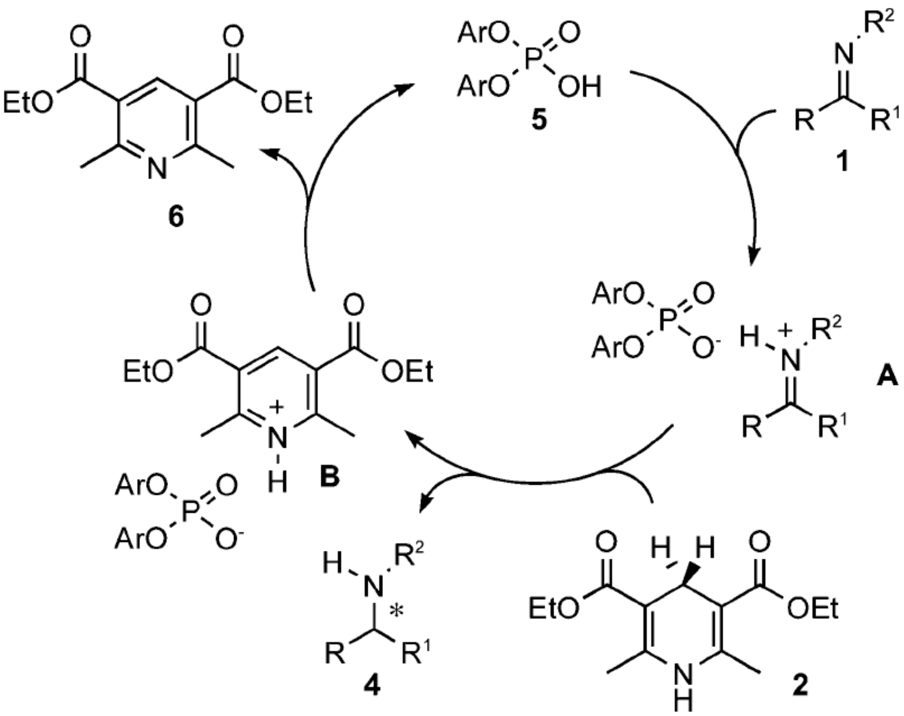
Catalytic asymmetric hydrogenation to imine is limited.

- Rueping's approach:





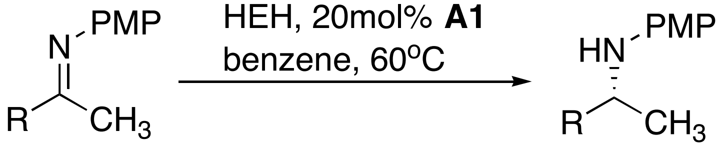
- Proposed mechanism



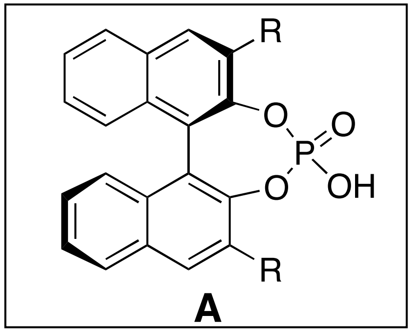
Rueping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. *Org. Lett.* **2005**, *7*, 3781.

III. Bronsted Acid Catalyzed Reductive Amination

- Rueping's approach:



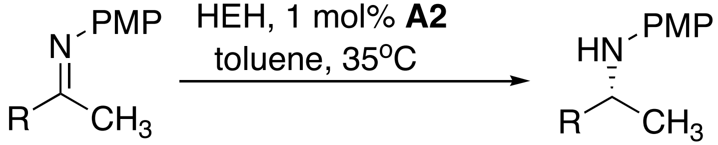
R = Ar, 46-91% yield, 70-82% ee.



A

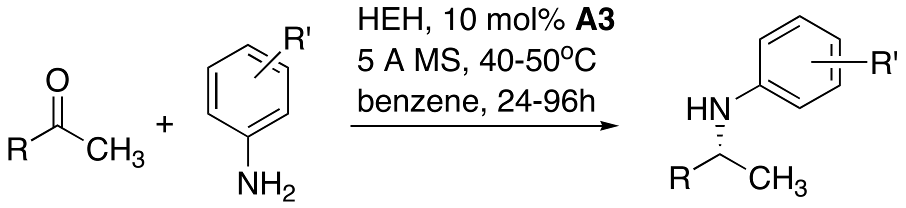
Rueping's A1: R = 3,5-(CF_3)-phenyl
List's A2: R = 2,4,6-(*i*-Pr)-phenyl
MacMillan's A3: R = $SiPh_3$

- List's approach:



R = Ar, *i*-Pr, 80-98% yield, 80-93% ee.
One example that from ketone to a deprotected amine (R = Ph, 75% overall yield, 88% ee).

- MacMillan's approach:

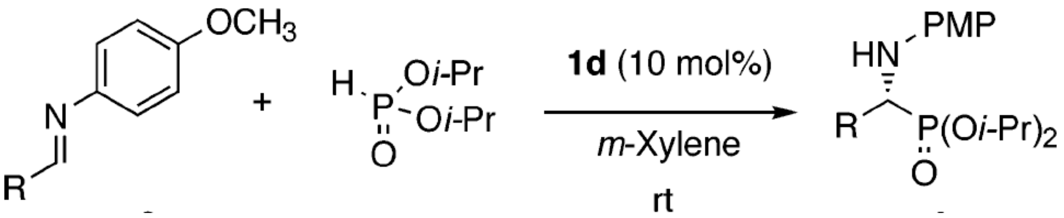


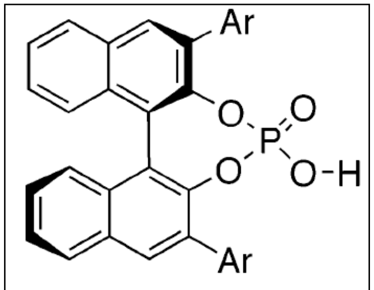
R = Ar, R'= OMe, 60-87% yield, 83-95% ee.
R = alkyl, R'= OMe, 49-75% yield, 81-94% ee.
R = Ar, R'= aryl, 55-92% yield, 91-95% ee.

---

1) Rueping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. *Org. Lett.* **2005**, *7*, 3781.
2) Hoffmann, S.; Seayad, A. M.; List, B. *Angew. Chem. Int. Ed.* **2005**, *44*, 7424.
3) Storer, R. L.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84.

IV. Bronsted Acid Catalyzed Hydrophosphonylation





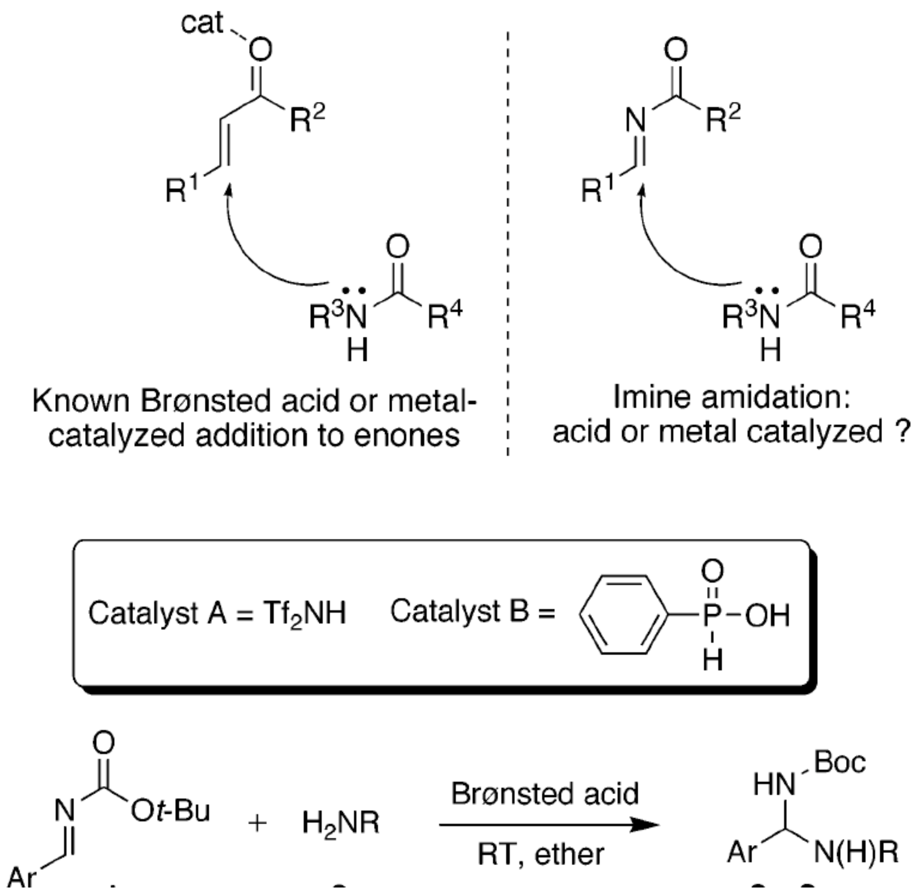
1d; Ar=3,5-$(CF_3)_2C_6H_3$

entry	R	time (h)	yield (%)	ee (%)
1	C_6H_5	24	84	52
2	o-$CH_3C_6H_4$	46	76	69
3	o-$NO_2C_6H_4$	24	72	77
4	$C_6H_5CH{=}CH$	101	92	84
5	p-$CH_3C_6H_4CH{=}CH$	170	88	86
6	p-$ClC_6H_4CH{=}CH$	145	97	83
7	o-$CH_3C_6H_4CH{=}CH$	171	80	82
8	o-$ClC_6H_4CH{=}CH$	70	82	87
8	o-$NO_2C_6H_4CH{=}CH$	49	92	88
10	o-$CF_3C_6H_4CH{=}CH$	46	86	90
11	1-naphthyl-$CH{=}CH$	168	76	81

[a] 2.0 equiv of diisopropyl phosphite was employed.

Akiyama, T.; Morita, H.; Itoh, J.; Fuchibe, K. *Org. Lett.* **2005**, *7*, 2583.

V. Bronsted Acid Catalyzed Imine Amidation

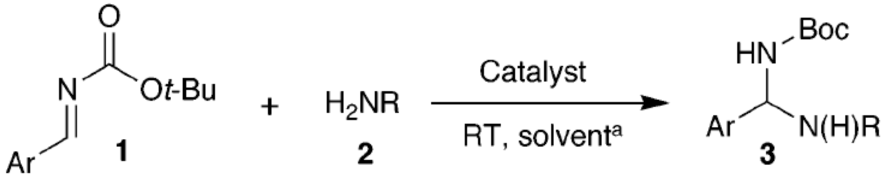


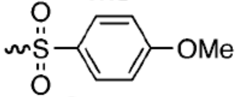
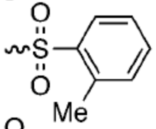
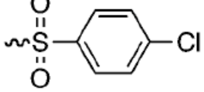
Scheme 1. The Catalytic Amidation of Enones and Imines

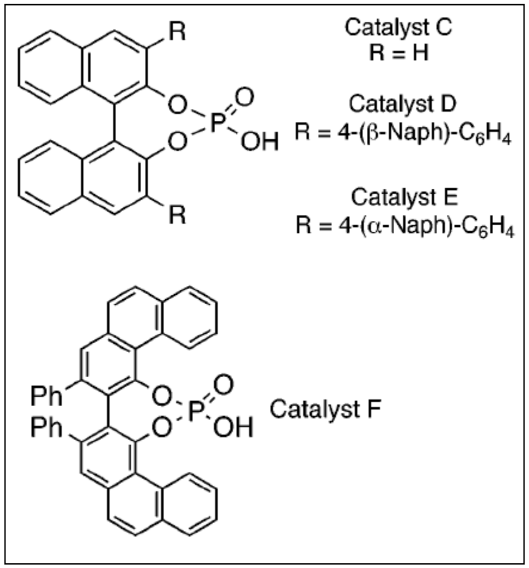
catalyst A: 91-99% yield, catalyst B: 91-99% yield.

Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15696.

Bronsted Acid - Catalyzed Imine Amidation



Entry[a]	Ar	R	mol% Acid[b]	Time	Yield and ee **3**
1	Ph	Ts	5 mol% C	16 h	**3a** = 95%, **<5% ee**
2	Ph	Ts	4 mol% D	20 h	**3a** = 96%, **60% ee**
3	Ph	Ts	5 mol% E	24 h	**3a** = 99%, **71% ee**
4	Ph	Ts	5 mol% F	1 h	**3a** = 95%, **94% ee**
5	Ph	Ms	5 mol% F	1 h	**3b** = 86%, **93% ee**
6	Ph		5 mol% F[c]	1 h	**3p** = 89%, **91% ee**
7	Ph		20 mol% F[c]	50 h	**3q** = 80%, **73% ee**
8	Ph		20 mol% F[d]	15 h	**3r** = 98%, **95% ee**
9	4-ClC_6H_4	Ts	10 mol% F	17 h	**3s** = 88%, **94% ee**
10	4-BrC_6H_4	Ts	10 mol% F[d]	13 h	**3t** = 96%, **92% ee**
11	4-$CF_3C_6H_4$	Ts	10 mol% F[d]	20 h	**3u** = 99%, **99% ee**
12	4-$MeOC_6H_4$	Ts	10 mol% F[d]	17 h	**3v** = 92%, **90% ee**
13	2-thienyl	Ts	10 mol% F[d]	17 h	**3w** = 94%, **87% ee**



Catalyst C
R = H

Catalyst D
R = 4-(β-Naph)-C_6H_4

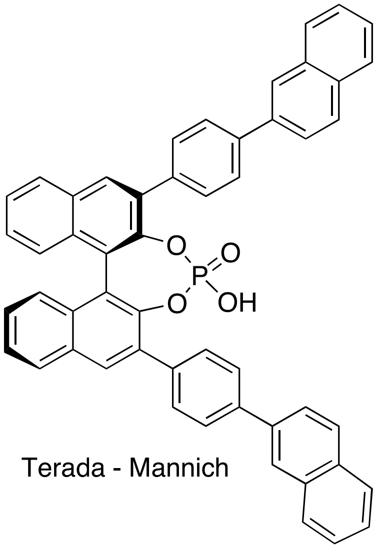
Catalyst E
R = 4-(α-Naph)-C_6H_4

Catalyst F

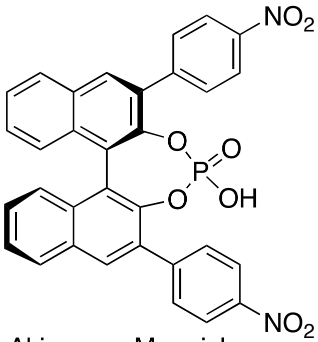
Toluene was used as solvent in entry 8-13.

Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15696.

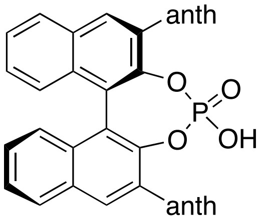
Conclusion



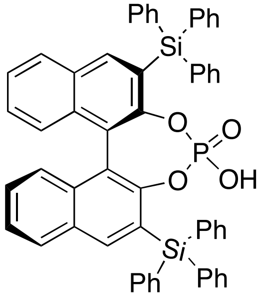
Terada - Mannich



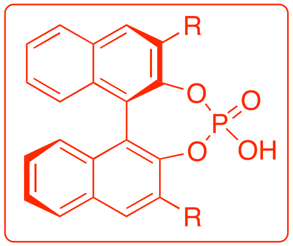
Akiyama - Mannich

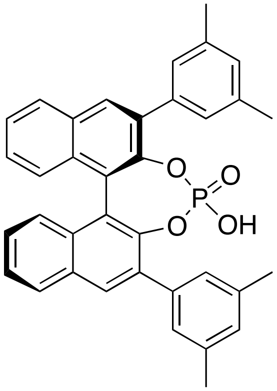


Terada - alkylation of diazoester

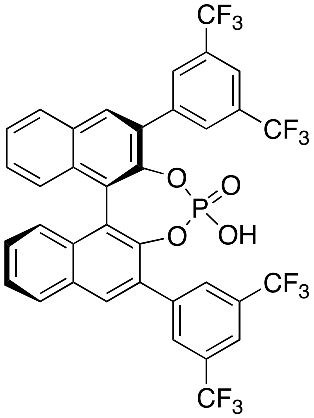


MacMillan - amination

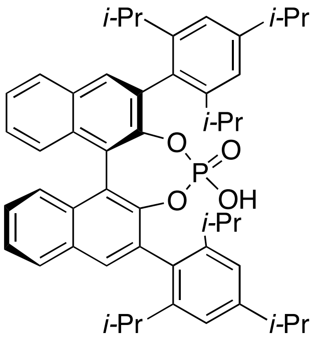




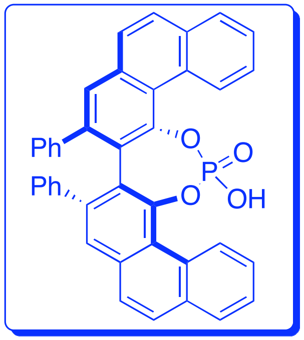
Terada - aza-Friedel-Crafts



Rueping - amination and
Akiyama - hydrophosphonylation



List - Pictet-Spengler
and amination



Antilla -imine amidation

Bronsted Acid - Catalyzed Mannich-type Reaction- Deastereoselectivity

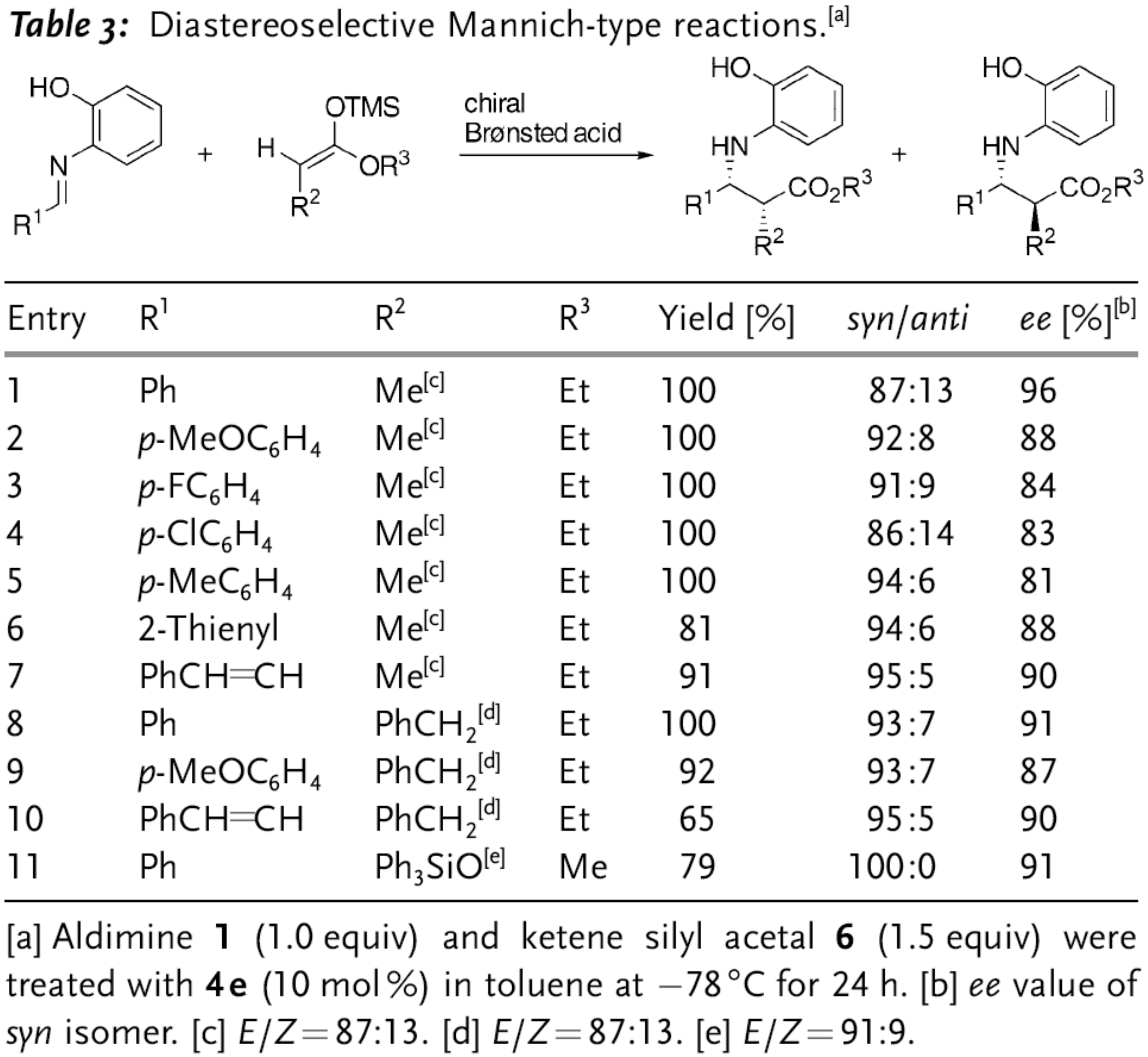
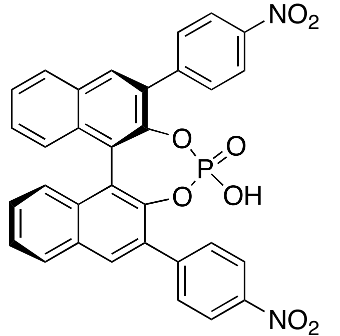


Table 3: Diastereoselective Mannich-type reactions.[a]

Entry	R^1	R^2	R^3	Yield [%]	*syn*/*anti*	*ee* [%][b]
1	Ph	Me[c]	Et	100	87:13	96
2	*p*-$MeOC_6H_4$	Me[c]	Et	100	92:8	88
3	*p*-FC_6H_4	Me[c]	Et	100	91:9	84
4	*p*-ClC_6H_4	Me[c]	Et	100	86:14	83
5	*p*-MeC_6H_4	Me[c]	Et	100	94:6	81
6	2-Thienyl	Me[c]	Et	81	94:6	88
7	PhCH=CH	Me[c]	Et	91	95:5	90
8	Ph	$PhCH_2$[d]	Et	100	93:7	91
9	*p*-$MeOC_6H_4$	$PhCH_2$[d]	Et	92	93:7	87
10	PhCH=CH	$PhCH_2$[d]	Et	65	95:5	90
11	Ph	Ph_3SiO[e]	Me	79	100:0	91

[a] Aldimine **1** (1.0 equiv) and ketene silyl acetal **6** (1.5 equiv) were treated with **4e** (10 mol%) in toluene at −78 °C for 24 h. [b] *ee* value of *syn* isomer. [c] *E*/*Z*=87:13. [d] *E*/*Z*=87:13. [e] *E*/*Z*=91:9.

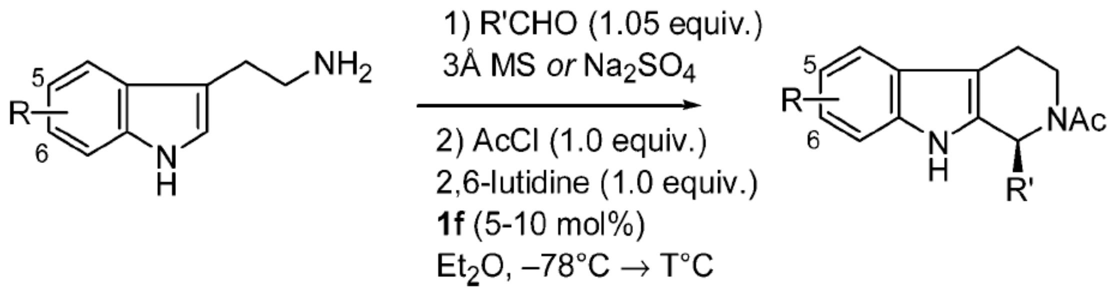


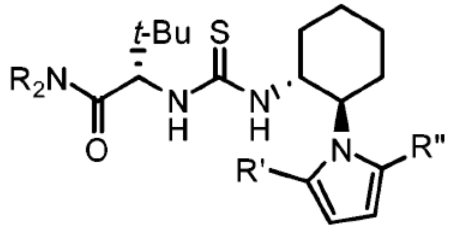
Akiyama's catalyst

Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566.

Bronsted Acid - Catalyzed Friedel Crafts - type Reactions
Pictet-Spengler Reaction

- Jacobsen's approach





1f: R = *i*-Bu, R' = CH_3, R" = Ph

product	R	R′	*T* (°C)	yield (%)^a	ee (%)^b
3a	H	$CH(CH_2CH_3)_2$	−30	65^c	93
3b	H	$CH(CH_3)_2$	−40	67^d	85
3c	H	n-C_5H_{11}	−60	65^d	95
3d	H	$CH_2CH(CH_3)_2$	−60	75^d	93
3e	H	CH_2CH_2OTBDPS	−60	77^d	90
3f	5-MeO	$CH(CH_2CH_3)_2$	−40	81^c	93
3g	6-MeO	$CH(CH_2CH_3)_2$	−50	76^d	86

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1) Taylor, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 10558.
2) Seayad, J.; Seayad, A. M.; List, B. *J. Am. Chem. Soc.* **2006**, ASAP.