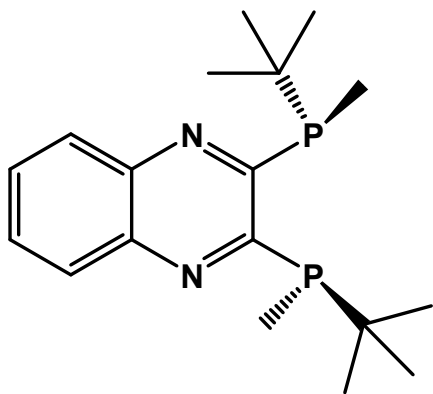


Chiral Ligand (*R, R*)-QuinoxP*

Date: 02/08/2011



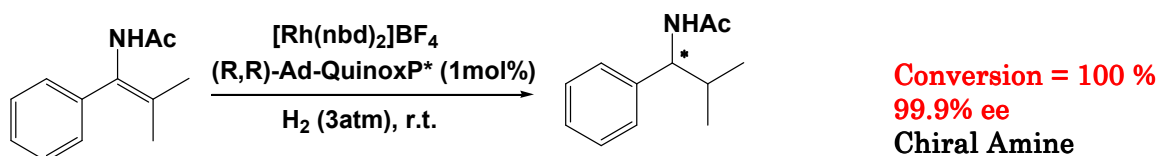
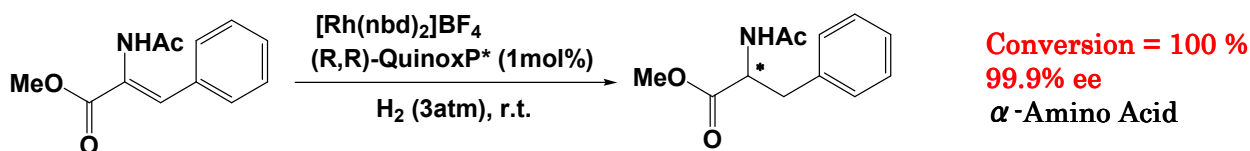
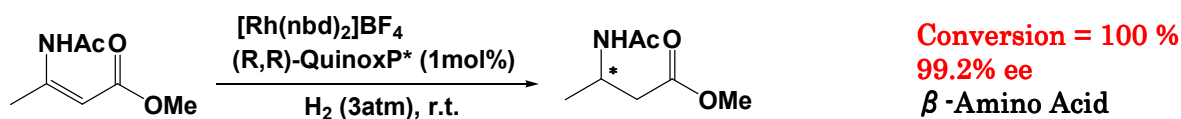
Appearance; Orange powder
 m.p.; 102-103 °C
 $[\alpha]^{22}_D$; -54.3 (c 1.00, CHCl₃)

(*R, R*)-QuinoxP* (*R, R*)-2,3-Bis(*tert*-butylmethylphosphino)quinoxaline

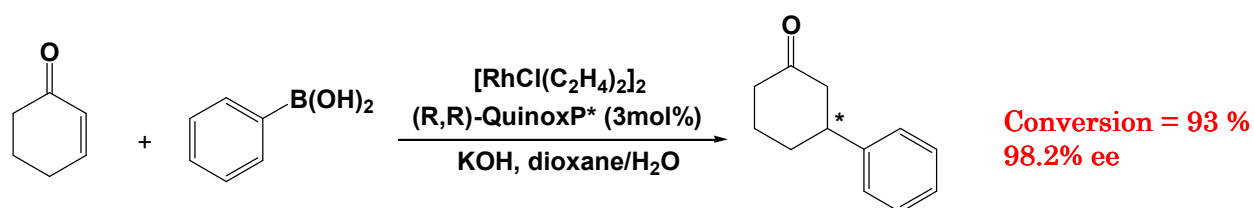
This P-chiral ligand developed by Prof. Imamoto (Chiba Univ.) is stable in air and moisture with excellent enantio-selectivities.

Technical notes

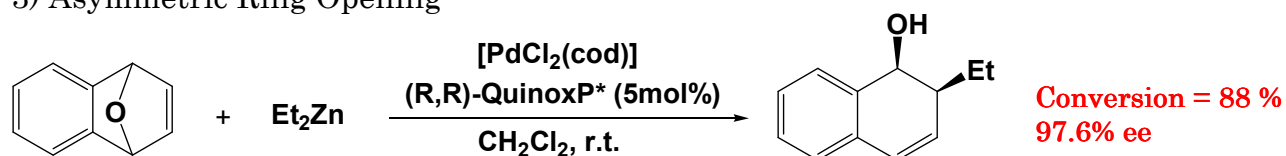
1) Enantio-selective Hydrogenation



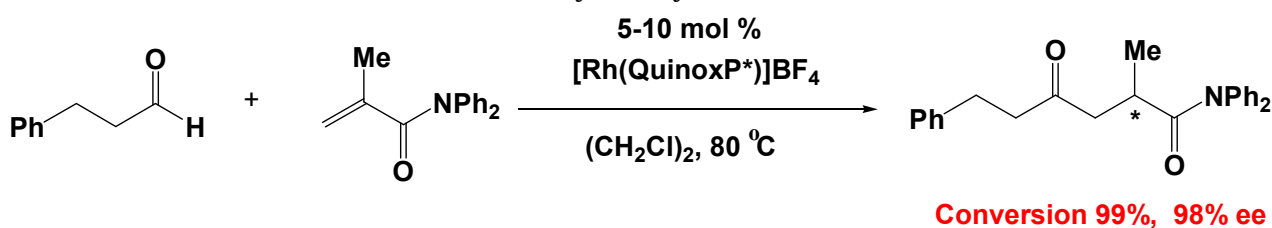
2) Asymmetric Addition of Boronic Acids to Cyclohexenone



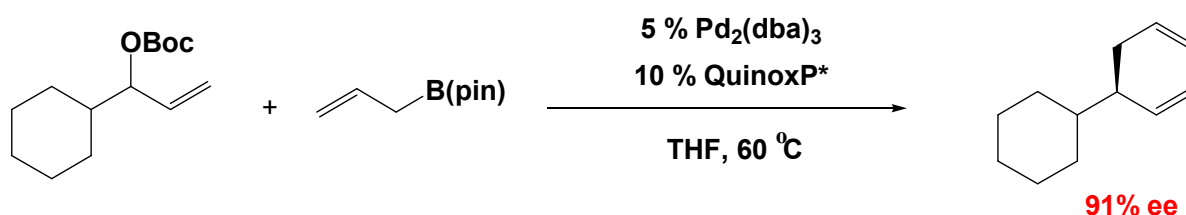
3) Asymmetric Ring Opening



4) Enantioselective Intermolecular Hydroacylation



5) Enantioselective Allyl-Allyl Cross-Coupling


Reference;

1. *J. Am. Chem. Soc.*, 2005, *127*, 11934-11935.
2. *J. Am. Chem. Soc.*, 2010, *132*, 5328-5329
3. *J. Am. Chem. Soc.*, 2009, *131*, 12552-12553
4. *J. Am. Chem. Soc.*, 2009, *131*, 11664-11665
5. *Angew. Chem. Int. Ed.* 2009, *48*, 1-5

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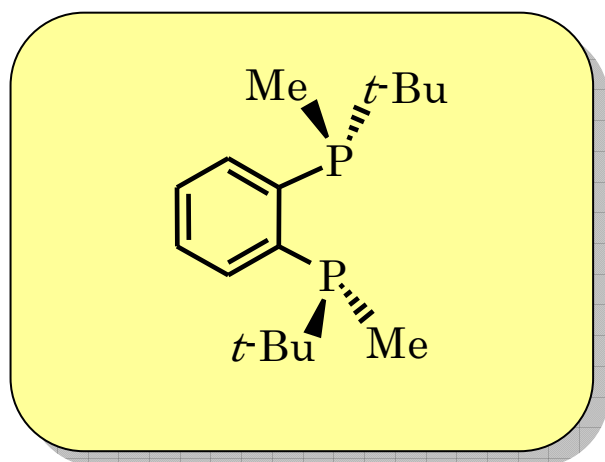
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P-Chiral Phosphine Ligand (*R,R*)-BenzP*

Date: 2/4/2010



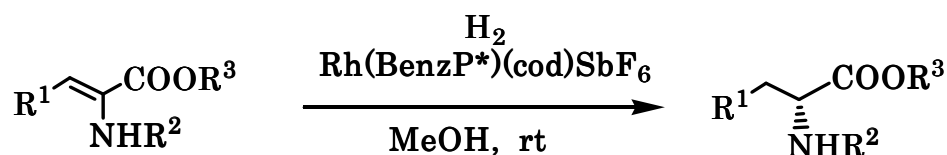
Appearance: White crystal
m.p.: 125-126 °C
[α]_{24D}: +223 (c 0.54, AcOEt)

(*R,R*)-BenzP* (*R,R*)-1,2-Bis(*tert*-butylmethylphosphino)benzene

BenzP* is an electron-rich P-stereogenic bisphosphine ligand. Its rhodium complex exhibited excellent enantioselectivities of up to 99.9% and high catalytic activity of up to 10 000 h⁻¹ TOF in asymmetric hydrogenations of various functionalized alkenes.

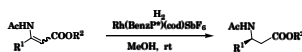
Technical notes

1) Asymmetric Hydrogenation of α -Dehydroamino Acids



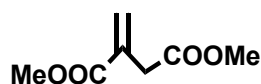
entry	R ¹	R ²	R ³	S/C	H ₂ (atm)	Time (h)	ee (%)
1	H	Ac	Me	10,000	5	1	99.9
2	Ph	Ac	Me	1,000	3	0.3	99.9
3	Ph	Ac	Me	10,000	5	5	99.8
4	Ph	Ac	H	1,000	3	0.5	99.5
5	<i>m</i> -FC ₆ H ₄	Ac	H	1,000	3	0.7	99.4
6	3-MeO-4-AcOC ₆ H ₃	Ac	Me	500	3	0.3	99.9
7	2-Furyl	Cbz	Me	200	3	3	99.1
8	2-pyrrolyl	Cbz	Me	200	3	3	94.1

2) Asymmetric Hydrogenation of β -Dehydroamino Acids

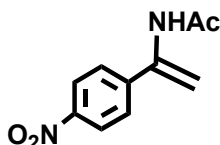


entry		R ¹	R ²	S/C	H ₂ (atm)	Time (h)	ee (%)
1	<i>E</i>	Me	Me	1,000	3	0.8	99.6
2	<i>Z</i>	Me	Me	1,000	3	0.8	97.6
3	<i>Z/E</i> 1:1	Me	Me	1,000	3	0.8	98.7
4	<i>Z/E</i> 1:1	Me	Me	5,000	5	21	97.9
5	<i>E</i>	<i>n</i> -Pr	Et	1,000	3	4	99.9
6	<i>Z</i>	<i>n</i> -Pr	Et	1,000	3	3	94.0
7	<i>Z</i>	<i>i</i> -Pr	Et	1,000	3	12	86.3
8	<i>Z</i>	Ph	Me	1,000	3	0.5	97.2
9	<i>Z</i>	<i>p</i> -MeOC ₆ H ₄	Et	1,000	3	2	98.5

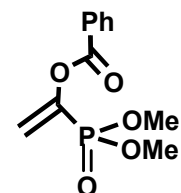
3) Asymmetric Hydrogenation of Other Functionalized Alkenes



S/C 500 3 atm 97.2% ee



S/C 1,000 3 atm 99.2% ee



S/C 1,000 3 atm 97.6% ee

(*S,S*)-BenzP* is also commercially available.

Reference: *Org. Lett.* 2010, 12, 4400-4403.

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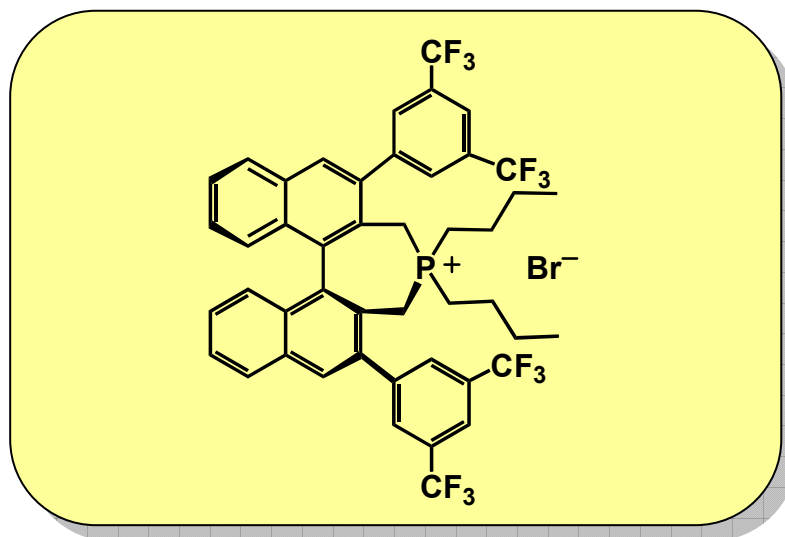
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(S)-MARUOKA CAT **P-NB**

Date: 2/4/2010



(S)-MARUOKA CAT P-NB

(S)-4,4-Dibutyl-2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium Bromide

Specification

Purity :	98.9 % (31P-NMR (202MHz, CDCl ₃))
Appearance:	White powder
m.p.:	262 °C ~ 263 °C
F.W.:	C ₄₆ H ₃₈ BrF ₁₂ P=929.65
Optical purity:	[α] _D ²⁷ ; -29.0 (c 0.50, CHCl ₃) (lit. [α] _D ²⁷ ; -26.8 (c 0.50, CHCl ₃))

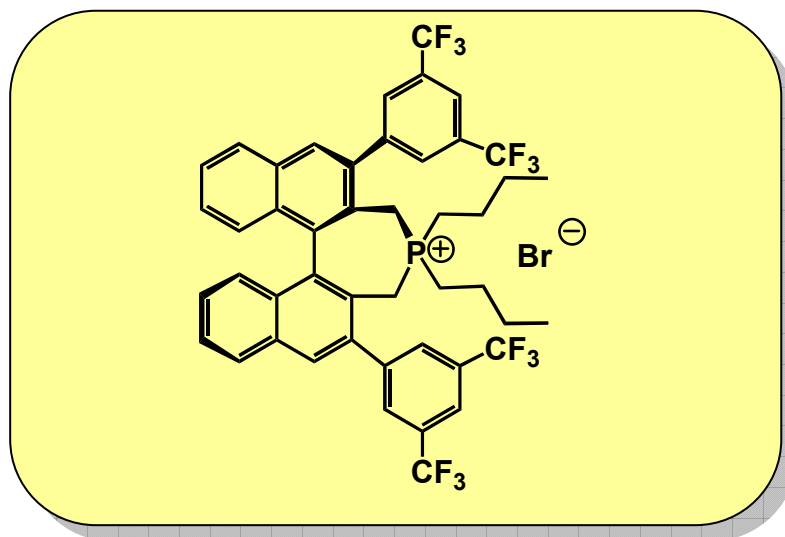
CAS# : 1110711-01-7

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(R)-MARUOKA CAT **P-NB**

Date: 2/4/2010



(R)-MARUOKA CAT P-NB

(R)-4,4-Dibutyl-2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium Bromide

Specification

Purity : >99 % (31P-NMR (202MHz, CDCl₃))
Appearance: White powder
m.p.: 262 °C ~ 263 °C
F.W.: C₄₆H₃₈BrF₁₂P=929.65
Optical purity: [α]_{27D}; +29.8 (c 0.50, CHCl₃)

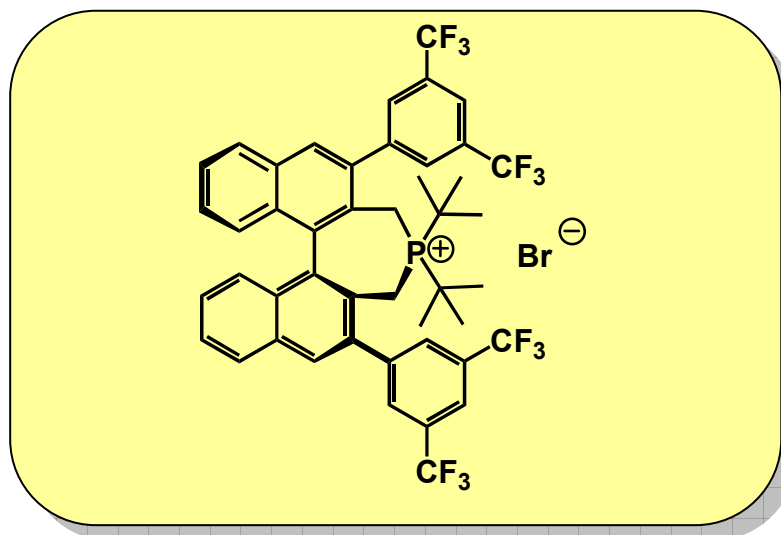
CAS# : Not available yet

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(S)-MARUOKA CAT **P-TB**

Date: 2/4/2010



(S)-MARUOKA CAT P-TB

(S)-4,4-Di-*t*-butyl-2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepinium Bromide

Specification

Purity : >99 % (31P-NMR (202MHz, CDCl₃))
 Appearance: White powder
 m.p.: **202 °C ~ 203 °C**
 F.W.: C₄₆H₃₈BrF₁₂P=929.65
 Optical purity: [α]_D²⁵; +14.3 (c 0.50, CHCl₃)

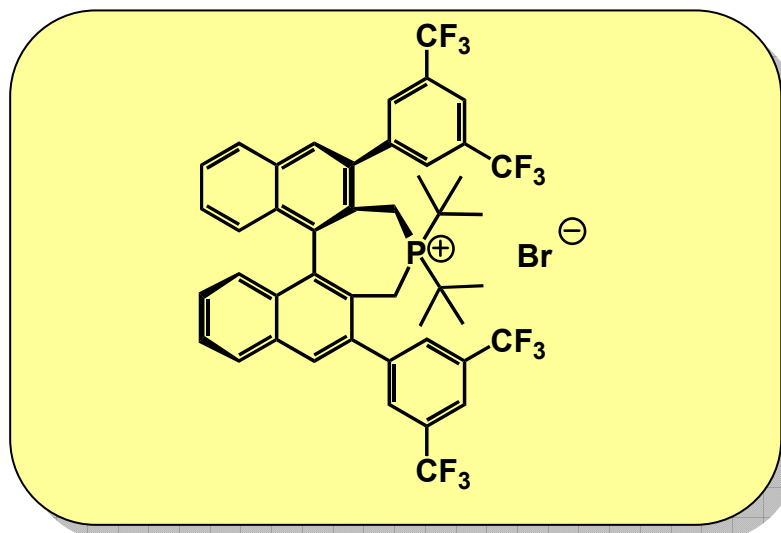
CAS# : Not available yet

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(R)-MARUOKA CAT **P-TB**

Date: 2/4/2010



(R)-MARUOKA CAT P-TB

(R)-4,4-Di-*t*-butyl-2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepinium Bromide

Specification

Purity : >99 % (31P-NMR (202MHz, CDCl₃))
Appearance: White powder
m.p.: **202 °C ~ 204 °C**
F.W.: C₄₆H₃₈BrF₁₂P=929.65
Optical purity: [α]_D²⁵; -13.8 (c 0.50, CHCl₃)

CAS# : Not available yet

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