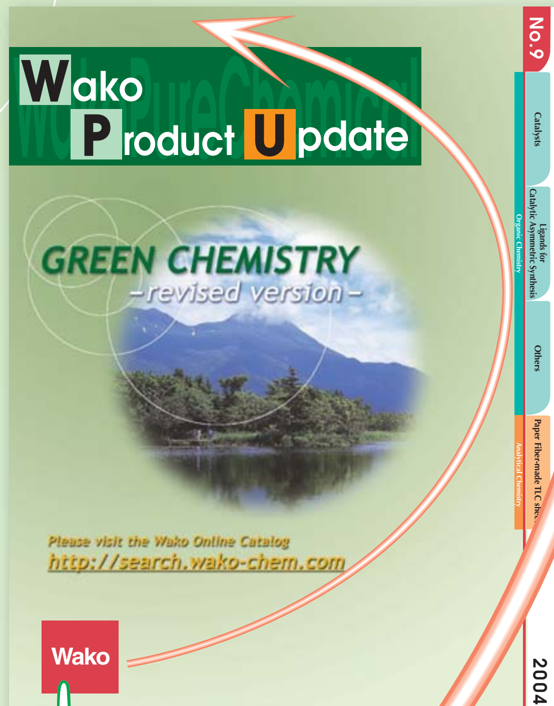
Wako Product Update

GREEN CHEMISTRY

– Supplement to Wako Product Update No. 9 –

Contents



http://www.wako-chem.co.jp/siyaku/journal/proup/pdf/proup9.pdf/

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Wako

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2006

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B. Metal Catalysts Index

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a. OsO_4, Immobilized Catalyst I [Os IC-I]

Osmium Oxide Adsorbed on Polymer Surfaces with High Solvent Resistance

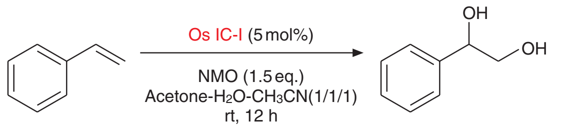
Osmium (VIII) Oxide is one of the best reagents for converting olefin into diol and is in demand for various purposes. However, there are almost no successful examples of it in terms of actual industrial processes. This is due to the fact that Osmium (VIII) Oxide is highly toxic, expensive and volatile; handling of the catalyst is difficult. This results in the need for special precautions in the workplace. There are also concerns for its impact and burden on the global environment. **Os IC-I** features an inexpensive fixed catalyst where the volatility and toxicity are reduced by having the Osmium (VIII) Oxide absorbed on polymer surfaces. In addition, using a polymer with high solvent resistance makes it usable with various reaction solvents, allowing for easier setting of reaction conditions.

[Features]

1. **Readily recoverable and reusable by filtration**
2. **Easy separation from reaction mixtures**
3. **Reduced toxicity and irritating odor by suppressing volatility**
4. **Various reaction solvents can be used due to high solvent resistance**

[Reaction 1]

Diol formation from styrene (reoxidant: NMO)



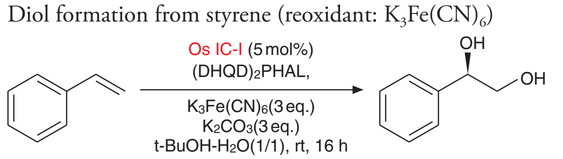
Run	1	2	3
Yield of Product (%)	84	83	83

<Reaction condition>

0.5 g (4.8 mmol) of styrene, 5 mL of CH_3CN, 5 mL of acetone, and 5 mL of water are combined, to which 0.97 g (7. 2mmol) of NMO and **Os IC-I** (OsO_4: equivalent of 0.24 mmol) are added. The mixture is stirred for 16 hours at room temperature. After completion of the reaction, while washing with ethyl acetate and water, **Os IC-I** is filtered off, the mother liquor is extracted twice with ethyl acetate, and with the organic layer the mixture is washed with 10 % sodium thiosulfate solution followed by saturated saline. In addition, after the organic layer is dried with anhydrous magnesium sulfate, filtered, and vacuum concentrated, the crude product is refined by silica gel column chromatography.

[Reaction 2]

Diol formation from styrene (reoxidant: $K_3Fe(CN)_6$)

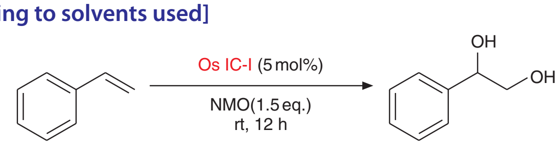


Run	1	2	3
Yield of Product (%)	85	85	83
ee (%)	xx	xx	xx

<Reaction condition>

0.5 g (4.8 mmol) of styrene, 8 mL of t-BuOH, and 8 mL of water are combined, to which 1.99 g (14.4 mmol) of K_2CO_3, 4.74 g (14.4 mmol) of $K_3Fe(CN)_6$, 187 mg (0.24 mmol) of $(DHQD)_2PHAL$, and **Os IC-I** (OsO_4: equivalent of 0.24 mmol) are added. The mixture is stirred for 16 hours at room temperature. After completion of the reaction, while washing with ethyl acetate and water, **Os IC-I** is filtered off, the mother liquor is extracted twice with ethyl acetate, and with the organic layer the mixture is washed with 10 % sodium thiosulfate solution followed by saturated saline. In addition, after the organic layer is dried with anhydrous magnesium sulfate, filtered, and vacuum concentrated, the crude product is refined by silica gel column chromatography.

[Comparison of recovery rates according to solvents used]



entry	Solv.	Yield (%)
1	water/THF(1/1)	85
2	water/$CHCl_3$(1/1)	73
3	water/AcOEt(1/1)	81
4	water/toluene/CH_3CN(1/1/1)	88

Note : Depending on the reaction substrates and reaction conditions, osmium may be dissolved out.

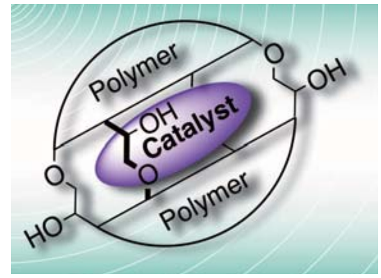
Description	abbreviation	Grade	Wako Cat No.	Package Size
Osmium Oxide, Immobilized Catalyst I	Os IC-I	for Organic Synthesis	153-02581	5 g
			151-02582	25 g

Os

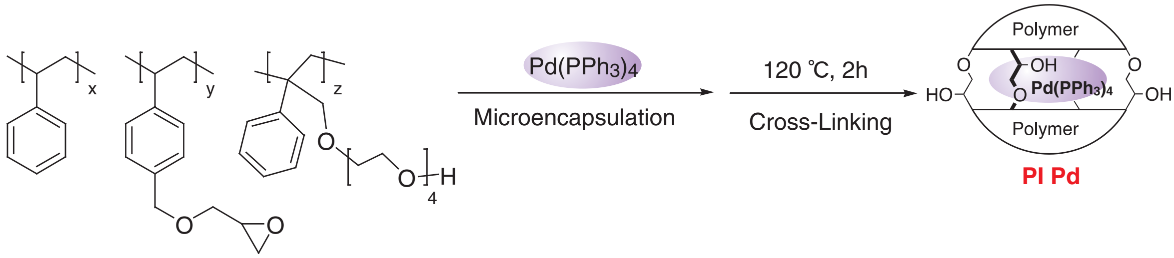
• Other services including industrial supply of osmium oxide, immobilized catalyst I, as custom synthesis of well as diol formation are available.

• Please free to contact us to inquire about other immobilized osmium oxides.

b. Polymer- Incarcerated Palladium [PI Pd]

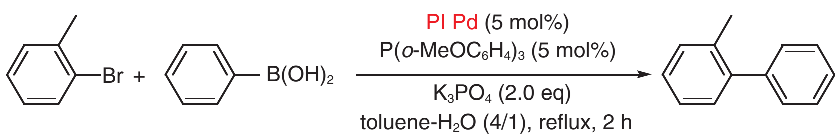


PI Pd is a new type of immobilized catalyst with the organic polymer physically supporting the palladium metal. The palladium catalyst features excellent resistance to solvents, high pressure and high temperature. Excellent activity of **PI Pd** has been demonstrated in hydrogenation of various olefins, benzyl ethers, and nitro and aromatic compounds. In addition, it can be recovered by simple filtration after the reaction and reused.



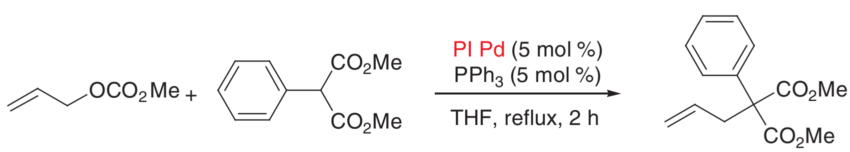
[Reactions]

1) Suzuki-Miyaura reaction[2]



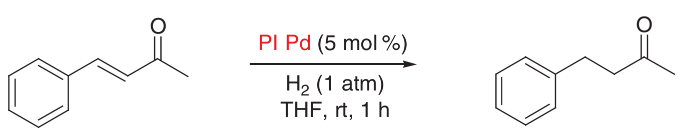
Run	1	2	3	4	5
Yield (%)	83	88	85	85	83

2) Allylic substitution reaction[1]



Yield
1st. 88 %
5th. 98 %

3) Hydrogenation of Benzalacetone[1), 3)]



Yield
1st. 85 %
5th. 90 %

Description	Purpose	Wako Cat No.	Package Size
Pd **PI Pd** (Pd: abt. 3 %)	for coupling reactions	168-21991	1 g
		164-21993	5 g

[References]

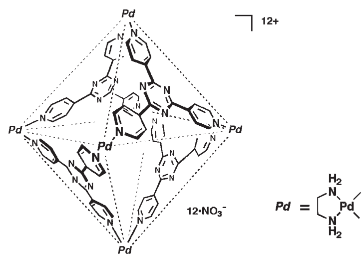
1) R. Akiyama, S. Kobayashi: *J. Am. Chem. Soc.*, **125**, 3412(2003).
2) K. Okamoto, R. Akiyama, S. Kobayashi: *Org. Lett.*, **6**, 1987(2004).
3) K. Okamoto, R. Akiyama, S. Kobayashi: J. *Org. Chem.*, **69**, 2871(2004).

c. 3D-Vacant Pd Complexes

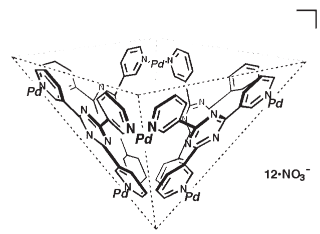
Water-soluble palladium complex with 3D pore

Certain three-dimensional chemical compounds have closed spaces, created by their skeletons, which are isolated from the outside. When a molecule is incorporated into such a space, it is expected to express new physical properties and reactivity. Pd-Nanocage and **Pd-Nanobowl** are types of 3D complexes with nanosized pores, which are instantaneously and quantitatively constructed by self-assembly driven by coordinate bonds with a transition metal. These 3D pores can provide a space for various reactions, including specific reactions using the shape and size of the isolated space, specific clathration of organic compounds, and organic synthesis in water. In addition to Pd-Nanocage, two new products have been added to this category; **Pd-Nanobowl** and **[(en)Pd](ONO$_2$)$_2$** , which aids in the assembly of 3D complexes.

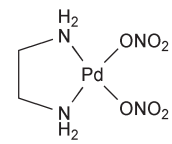
[Structural formula]



Pd-Nanocage



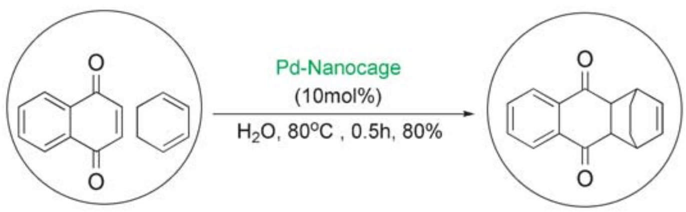
Pd-Nanobowl



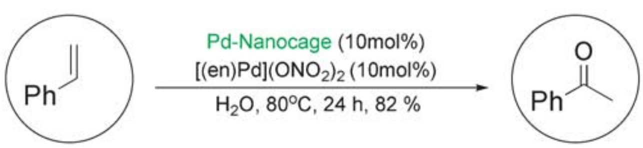
[(en)Pd] (ONO$_2$)$_2$

[Reactions]

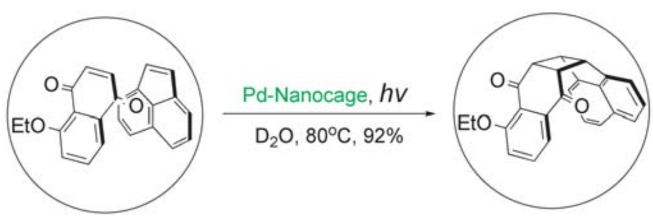
Diels-Alder reaction



Wacker reaction



[2+2] Photocyclization reaction between different molecules



Description	Purpose	Wako Cat No	Package Size
Palladium-Nanocage	For organic synthesis	160-20471	1 g
Palladium-Nanobowl	For organic synthesis	165-21761	200 mg
		161-21763	1 g
(Ethylenediamine)dinitratopalladium(II) Abbr. : **[(en)Pd] (ONO$_2$)$_2$**	For organic synthesis	052-07341	200 mg
		058-07343	1 g

Pd

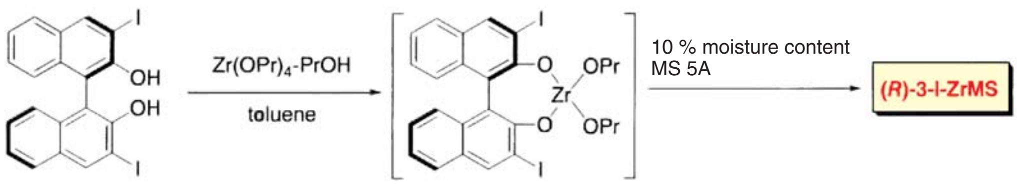
[References]

1) D. Oguro, M. Miyazawa, H. Oka, k. Yamaguchi, K. Ogura, M. Fujita : *Nature*, 378, 469 (1995).
2) T. Kusukawa, M. Fujita : *Angew. Chem., Int. Ed. Engl.*, 37, 3142 (1998).
3) H. Ito, T. Kusukawa, M. Fujita : *Chem. Lett.*, 598 (2000).
4) M. Yoshizawa, Y. Takeyama, T. Okano, M. Fujita : *J. Am. Chem. Soc.*, 125, 3243 (2003).
5) M. Fujita, S.-Y. Yu, T. Kusukawa, H. Fumaki, K. Ogura, K. Yamaguchi : *Angew. Chem., Int. Ed. Engl.*, 37, 2082 (1998).
6) S.-Y. Yu, T. Kusukawa, K. Biradha, M. Fujita : *J. Am. Chem. Soc.*, 122, 2665 (2000).

d. Chiral Zr Catalyst Combined with Molecular Sieves

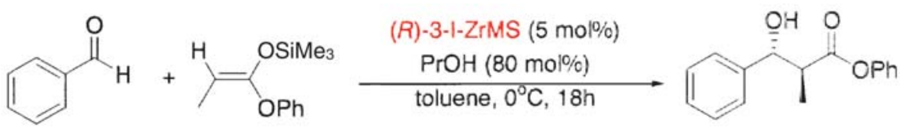
Air-stable optically active zirconium catalyst that can be stored for an extended period of time

Most catalysts easily degrade in the presence of oxygen and humidity, so must be used in inert gas systems and under strictly anhydrous conditions. These conditions have been a major obstacle to their industrialization. To solve these problems, asymmetrical Lewis acid catalysts with zirconium, as the central metal and molecular sieves (MS), a type of zeolite, were combined to develop high performance catalysts with significantly improved stability. These composite catalysts, which are air-stable and storable, are optically active Lewis acid catalysts that can be stored for an extended period of time and are easy to handle. Thus Industrialization of asymmetric catalytic reactions is highly anticipated.



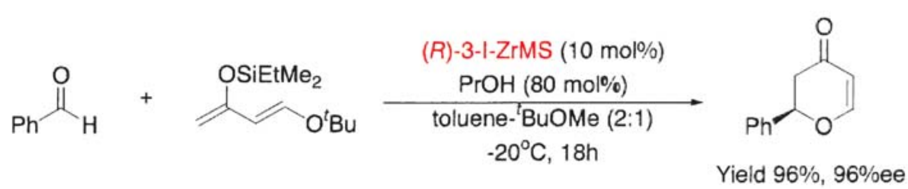
[Reactions]

Asymmetric Mukaiyama Aldol Reaction



Storage time (weeks)	0	2	6	13
Yield	quant.	quant.	quant.	quant.
syn / *anti*(%)	5 / 95	5 / 95	5 / 95	5 / 95
ee (%)(*anti*)	99	99	99	99

Asymmetric Hetero-Diels-Alder Reaction*



*The obtained product was treated with TFA.

Description	Grade	Wako Cat No.	Package Size
Zr (*R*)-3-I-ZrMS	for organic synthesis	097-05271	1g
		093-05273	5 g

[References]

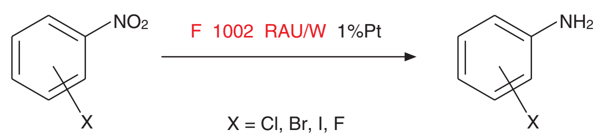
1) S. Kobayashi, S. Saito, M. Ueno, Y. Yamashita: *Chem. Commun.*, **2016** (2003).
2) S. Kobayashi, M. Ueno, S. Saito, Y. Mizuki, H. Ishitani, Y. Yamashita: *Proc. Natl. Acad. Sci. USA*, **101**, 5476 (2004).

e. Precious Metal Powder Catalysts

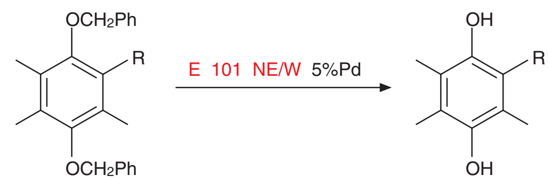
The demand for high performance, high activity catalysts in the fields of specialty chemicals (fine chemicals, electronic materials, etc.) and life science (drugs, agrichemicals, and intermediates) is increasing along with tighter environmental standards and increasing requests for reduced manufacturing costs. The following 7 precious powder metal catalysts are widely suitable for reactions where these are frequently used in the above fields.

[Reactions]

Selectively hydrogenated reaction



Debenzylation reaction



Description	Purpose	Wako Cat No	Package Size
5% Palladium on Activated Carbon, Degussa type E 101 O/W (wetted with ca.55% water)	Disproportionation, reductive amination reaction, etc.	327-81641	5 g
		325-81642	25 g
5% Palladium on Activated Carbon, Degussa type E 101 NE/W (wetted with ca.55% water)	Deprotection, Debenzylation, etc.	324-81651	5 g
		322-81652	25 g
5% Palladium on Activated Carbon, Degussa type E 1533 R/W (wetted with ca.55% water)	Reduction of nitro group, nitrile group, etc.	321-81661	5 g
		329-81662	25 g
5% Palladium on Activated Carbon, Degussa type E 1002 NN/W (wetted with ca.55% water)	Hydrogenation of C=C bonds, dehalogenation reaction, etc.	328-81671	5 g
		326-81672	25 g
3% Platinum on Activated Carbon, Degussa type F 1002 RCA/W (wetted with ca.55% water)	Reduction of imine, hydrogenation of heterocycles, etc.	325-81681	5 g
		323-81682	25 g
1% Platinum on Activated Carbon, Degussa type F 1002 RAU/W (wetted with ca.55% water)	Selective hydrogenation (inhibits halogen desorption)	322-81691	5 g
		320-81692	25 g
5% Rhodium on Activated Carbon, Degussa type G 106 NB/W (wetted with ca.55% water)	Hydrogenation of aromatic rings, reduction of nitrile, etc.	325-81701	5 g
		323-81702	25 g

Pd

Pt

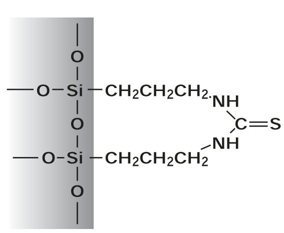
Rh

f. Metal Scavengers *(Organofunctional polysiloxanes)*

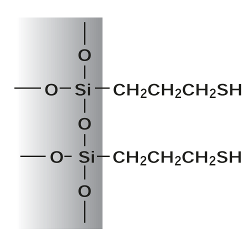
Deloxan®

Precious metals dissolved in reaction liquids used in the medical industry cause serious problems such as the loss of valuable precious metals and product contamination. Deloxan® effectively solves such problems by quantitatively and efficiently adsorbing precious metals (Rh, Pd, Pt, Ir, Ru, Ag, Au) and non-precious metals (e.g. Ni, Cu, Bi, Ga, Fe) (1 ppm or less of the residual metals in the solution) as well as by allowing for the recovery of precious metals.

Deloxan® THP II
Functional group: thiourea

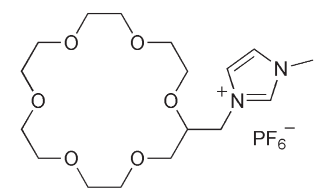


Deloxan® MP
Functional group: mercapto



Description	Purpose	Wako Cat No	Package Size
Metal Scavenger, Degussa type Deloxan® MP	Removal of precious metals	325-83521	5 g
		323-83522	25 g
Metal Scavenger, Degussa type Deloxan® THP II	Removal of precious metals	328-83511	5 g
		326-83512	25 g

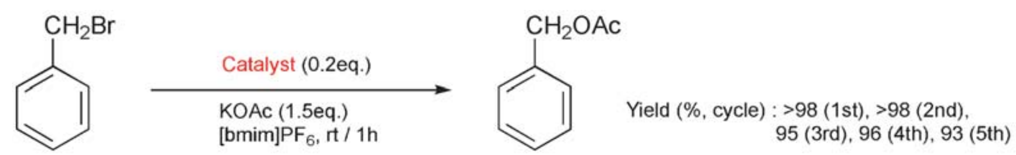
Crown ether has the property to catalyze organic reactions by forming a stable complex with metallic cation and generating a chemically stable anion. In addition, the ionic liquid can be recovered and reused because it is an organic liquid that is composed only of ions that are nonvolatile, highly conductive, and catalytically active, and thus does not blend with organic solvents. The 18-crown-6-supported ionic liquid shows the catalytic activity of the crown ether and the immiscibility with the organic solvents of ionic liquids. The use of this catalyst allows for a high yield of the objective substance in nucleophilic substitution of potassium acetate in ionic liquid solvents by benzyl bromide. To reuse the ionic liquid, the reaction liquid is extracted using liquids such as ether, and the residual ionic liquid is dried.



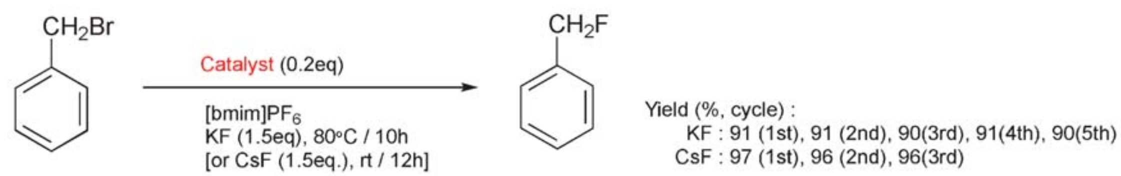
1-(2-Methyl-18-crown-6)-3-methylimidazolium Hexafluorophosphate

[Reactions]

Acylation reaction



Fluorination reaction



<Reaction condition>

1-(2-methyl-18-crown-6)-3-methylimidazolium Hexafluorophosphate (50 mg, 0.1 mmol, 0.2 eq) and 1-butyl-3-methylimidazolium Hexafluorophosphate (6 mL) (dried by vacuum pump for 5 hours at 80 ℃) are combined, to which a reaction substrate (0.5 mmol) and a reaction reagent (0.75 mmol) are added. The mixture is stirred at each temperature and time. After the reaction, the liquid is extracted using ether, then condensed to obtain the objective substance.

<Recovery and Reuse of the Catalyst>

After the reaction, dichloromethane (10 mL) and water (1 mL) are poured in the mixture (about 5 mL) of the residual 1-(2-methyl-18-crown-6)-3-methylimidazolium Hexafluorophosphate and 1-butyl-3-methylimidazolium Hexafluorophosphate obtained by ether extraction, and stirred for 4 hours at room temperature. The organic layer is left to dry for 5 hours at 80℃ under reduced pressure, and is reused during for a subsequent reaction.

Description	Purpose	Wako Cat No	Package Size
1-(2-Methyl-18-crown-6)-3-methylimidazolium Hexafluorophosphate	for organic synthesis	134-14981 130-14983	100 mg 500 mg

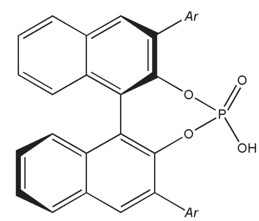
(*R*)-(−)-3,3′-Bis(4-nitrophenyl)-1,1′-binaphthyl-2,2′-diyl Hydrogen Phosphate (First paragraph is okay)

Brønsted acid-assisted chiral Lewis acid (BLA) catalyst

Enantioselective asymmetric synthesis reactions using chiral catalysts are an excellent coupling method of optically-active compounds and are thus frequently used in research. They are normally achieved using metal Lewis acid catalysts. However, some of the downfalls involve the stability of metallic complexes and the existence of residual transition metals in the compounds.

Meanwhile, asymmetric synthesis using chiral organic catalysts constitutes a research area that is gaining increased attention. In particular, chiral Bronsted acid is stable, allowing for reactions under mild conditions, as well as easy recovery of catalysts.

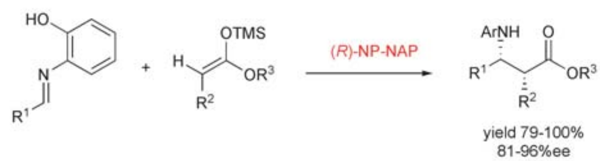
Asymmetric catalysts have been the exclusive organic metal catalysts until now. Chiral catalysts have rapidly become an issue of growing interest, and thus further development is anticipated in these areas.



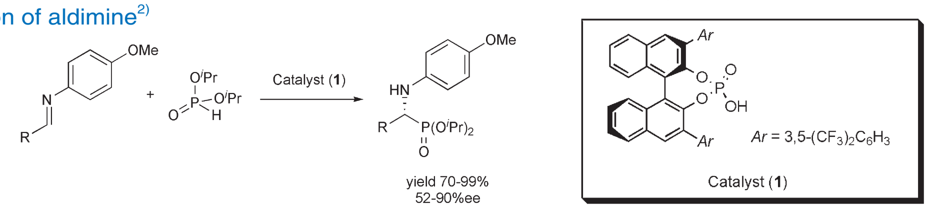
Ar=4-$NO_2C_6H_4$
(*R*)-NP-NAP

[Reactions]

Mannich-type reaction[1)]



Hydrophosphonylation of aldimine[2)]



Description	Purpose	Wako Cat No	Package Size
(*R*)-NP-NAP	for organic synthesis	145-07861	200 mg

[References]

1) T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe : *Angew. Chem. Int. Ed.*, 43, 1566-1568 (2004).
2) T. Akiyama, H. Morita, J. Itoh, K. Fuchibe : *Org. Lett.*, 7, 2583-2585 (2005).
3) T. Akiyama, Y. Saitoh, H. Morita, K. Fuchibe : *Adv. Synth. Catal.*, 347, in press (2005).

4. Rare Earth Triflate

Green chemistry aims to eliminate the use of auxiliary substances during organic reactions, or if unavoidable to choose substances that have little impact on the environment.

The auxiliary substances most commonly used in organic reactions are solvents.

The use of water for reactions conducted in organic solvents significantly reduces the burden on the environment. Rare earth triflate is used in various reactions as a Lewis acid catalyst that can be used in water solution.

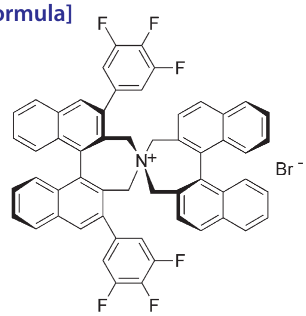
Description	Molecular formula/CAS No.	Wako Cat No	Package Size	
Lanthanum(III) Trifluoromethanesulfonate [References] 1) S. Kobayashi : *Synlett*, 689 (1994). 2) J. Inanaga, Y. Yokoyama, T. Hanamoto : *Tetrahedron Lett.*, **34**. 2791 (1993). 3) J. H. Forsberg, V. T. Spaziano, T. M. Balasubramanian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown, J. L. Miller : *J. Org. Chem.*, **52**. 1017 (1987).	$(CF_3SO_3)3La$=586.11 [52093-26-2]	126-05231 124-05232	5 g 25 g	La
Neodymium Trifluoromethanesulfonate	$(CF_3SO_3)_3Nd$=591.45 [34622-08-7]	147-08301 145-08302	5 g 25 g	Nd
Scandium(III) Trifluoromethanesulfonate [References] 1) S. Kobayashi, I. Hachiya, M. Araki, and H. Ishitani : *Tetrahedron Lett.*, **34**. 3755 (1993). 2) S. Kobayashi : *Synlett*, 689 (1994).	$(CF_3SO_3)_3Sc$=492.16 [144026-79-9]	195-11391 191-11393	1 g 5 g	Sc
Thulium Trifluoromethanesulfonate	$(CF_3SO_3)_3Tm$=616.14 [141478-68-4]	205-16421 203-16422	5 g 25 g	Tm
Ytterbium(III) Trifluoromethanesulfonate n-Hydrate [References] 1) S. Kobayashi, I. Hachiya, T. Takahori : *Synthesis*, 371 (1993). 2) S. Kobayashi, I. Hachiya : *J. Org. Chem.*, **59**. 3590 (1994). 3) S. Kobayashi : *Synlett*, **689** (1994).	$(CF_3SO_3)_3Yb \cdot xH_2O$=620.25(As an anhydride) [54761-04-5]	254-00521 252-00522	5 g 25 g	Yb

Chiral Phase-Transfer Catalysts (PTC)

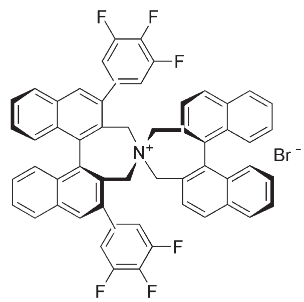
Chiral phase-transfer catalysts, which are optically active spiro ammonium salts with 2 binaphthyl rings that allow for easy molecule designing, were invented by Professor Maruoka of the Kyoto University.

(*R*, *R*)-3,4,5-Trifluorophenyl-NAS Bromide shows high catalytic activity and high enantioselectivity in asymmetric alkylation of a-amino acid derivatives[1]. By using (*R*, *R*)-3,5-Bistrifluoromethylpehnyl-NAS Bromide, *β*-hydroxy *α*-amino acid derivatives, which are important chiral units of biologically active proteins, are obtained in good yield by the aldol reaction of glycine derivatives with aldehydes. It was found that erythro isomers, which are major products, were obtained with high enantioselectivity[2].

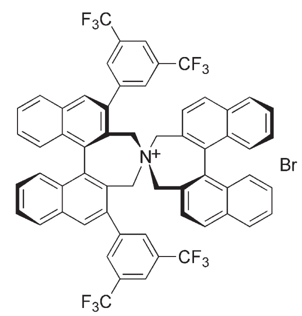
[Structural formula]



(*R*,*R*)-3,4,5-Trifluorophenyl-NAS Bromide
Maruoka catalyst *RR*-Trifluorophenyl Br Form



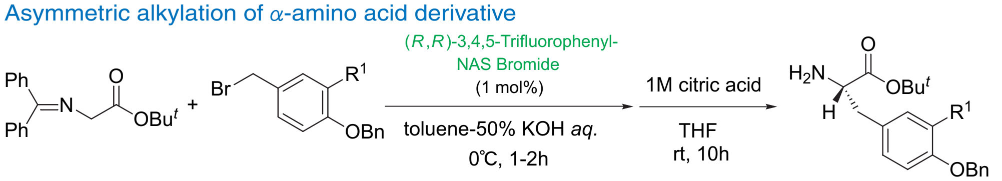
(*S*,*S*)-3,4,5-Trifluorophenyl-NAS Bromide
Maruoka catalyst *SS*-Trifluorophenyl Br Form



(*R*,*R*)-3,5-Bistrifluoromethylphenyl-NAS Bromide
Maruoka catalyst *RR*-Bistrifluoromethylphenyl Br Form

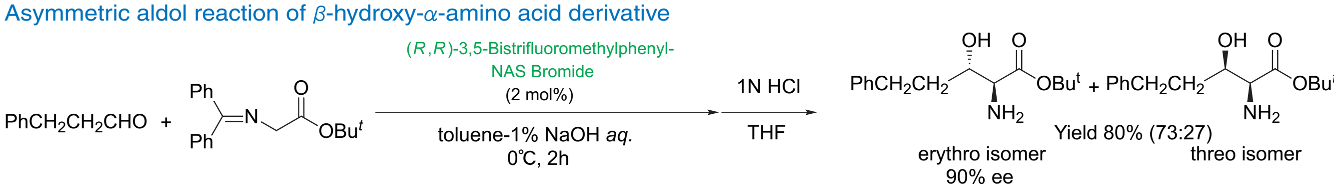
[Reactions]

Asymmetric alkylation of *α*-amino acid derivative



R^1=OBn : Yield 81%, 98% ee
R^1=H : Yield 83%, 98% ee

Asymmetric aldol reaction of *β*-hydroxy-*α*-amino acid derivative



Description	Purpose	Wako Cat No	Package Size
(*R*, *R*)-3, 4, 5-Trifluorophenyl-NAS Bromide [Maruoka catalyst *RR*-Trifluorophenyl Br Form]	For organic synthesis	1201-15921	100 mg
		207-15923	500 mg
(*S*, *S*)-3, 4, 5-Trifluorophenyl-NAS Bromide [Maruoka catalyst *SS*-Trifluorophenyl Br Form]	For organic synthesis	201-16401	100 mg
		207-16403	500 mg
(*R*, *R*)-3, 5-Bistrifluoromethylphenyl-NAS Bromide [Maruoka catalyst *RR*-Bistrifluoromethylphenyl Br Form]	For organic synthesis	029-14921	100 mg
		025-14923	500 mg

[References]

1) T. Ooi, M. Kameda, H. Tannai, K. Maruoka : *Tetrahedron Lett.*, 41, 8339 (2000).
2) T. Ooi, M. Taniguchi, M. Kameda, K. Maruoka : *Angew. Chem. Int. Ed.*, 41, 4542 (2002).

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