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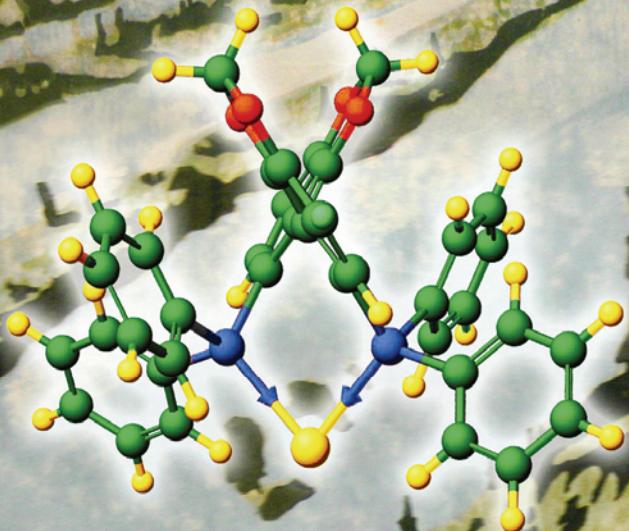
VOL. XXIII No. 1

May, 2007

Chiral Ligands & Their Complexes

Newly Available on a Commercial Scale

By Dr. Wataru Kuriyama,
Dr. Noboru Sayo and Dr. Takao Saito



A Publication of Strem Chemicals, Inc.

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Chiral Ligands & their Complexes, Newly Available on a Commercial Scale

Takasago Fine Chemicals Division



Dr. Takao Saito

Born in Ibaraki, Japan, in 1960. He joined Takasago International Corporation in 1985 and received his Ph.D. from Osaka University under the supervision of Professor Shunichi Murahashi in 1996. He is the inventor of SEGPHOS ligands and has also developed unique processes for pharmaceutical intermediates. He was promoted to be Vice President, General Manager and Sales Manager at the Fine Chemicals Division, Takasago International Corporation in 2006.

R&D Members

Takasago Fine Chemical Laboratory consists of 24 chemists. They are developing new chiral technologies and their applications to pharmaceutical intermediates and functional materials.

The head of the laboratory is Dr. Noboru Sayo (the center of the front row in the picture below), who joined Takasago in 1984 after obtaining his Ph. D. from Tokyo Institute of Technology under the supervision of Professor Takeshi Nakai and is now the executive director at the laboratory.



Catalysts Marketing Team

JAPAN: Shigeru Mitsuhashi (Director at Planning Department of Fine Chemicals Division)

Yuri Yoshimi (Planning Department of Fine Chemicals Division)

Motonobu Takenaka (Senior Account Executive at Sales Department of Fine Chemicals Division)

USA: Yutaka Okamura (Director at Fine Chemicals Division in Takasago International Co. USA)

About Takasago Fine Chemicals

Takasago was established in 1920 as a perfumery company. Our synthetic technology traces back to manufacture of Vanillin and Heliotropine in 1927. Ever since, many aroma chemicals have been produced. Our chiral technologies commenced with *l*-Menthol synthesis by catalytic asymmetric isomerization using BINAP ligand, which was developed in collaboration with Professor Ryoji Noyori, who was awarded the Nobel Prize for Chemistry in 2001, and who is a Takasago board member. The technology expanded to asymmetric hydrogenation to produce various kinds of chiral compounds, such as flavors, fragrances, and agrochemical and pharmaceutical ingredients. Our current chiral output from the technology is approximately 3,000 tons annually.

Takasago Fine Chemicals Division was established about 20 years ago when Takasago developed the catalytic asymmetric synthesis technology using BINAP ligands. In Takasago, we refer to BINAP as the first generation ligand. Over time Takasago Fine Chemicals has discovered several generations of novel chiral ligands, as well as many catalysts. Although we still think BINAP is the most famous chiral ligand in the world, Takasago is now focusing on the next generation ligand, SEGPHOS.

Though we had used the technology within Takasago only, now chiral ligands and their complexes have become commercially available through Strem Chemicals, Inc.

About the Cover of this *Strem Chemiker*

When you enter the main entrance of Strem Chemicals in Newburyport, you immediately see a large wood block print entitled "Sunset Snow" that presents a peaceful, tranquil influence. The artist is Eimei Machida, an artist/scientist who has a Ph.D. in Chemistry but is self-taught as an artist. His interest in art began in 1980 and in the past several years he has won several prizes at exhibits in Japan. He has also begun to exhibit in the USA and Europe.

Since this edition of *The Strem Chemiker* introduces Strem's cooperation with Takasago, we have added to the cover, the structure of Segphos, which Takasago relates to a seagull. We think the seagull fits well in the skies over Sunset Hill.

TAKASAGO's Ligands and Complexes, their Potential

By Dr. Wataru Kuriyama, Dr. Noboru Sayo, Dr. Takao Saito

1. SEGPHOS & BINAP Family of Ligands and their Complexes

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3. Conclusion

4. Future Aspects

1. SEGPHOS & BINAP Family of Ligands and their Complexes

1-1. Introduction

Both enantiomers of SEGPHOS (**1**), DM-SEGPHOS (**2**), DTBM-SEGPHOS (**3**)¹, BINAP (**4**)², TolBINAP (**5**)³, XylBINAP (**6**)⁴, H₈-BINAP (**7**)⁵ and their ruthenium complexes - [RuCl(*p*-cymene)(P^AP)]Cl (**I**)⁶, [NH₂Me₂][{RuCl(P^AP)}₂(μ-Cl)₃] (**II**)⁷, [Ru(OAc)₂(P^AP)] (**III**)⁸, [RuCl₂(P^AP)(N^AN)] (**IV**)⁹ - are Now Commercially Available.

Figure 1 SEGPHOS & BINAP Family of Ligands

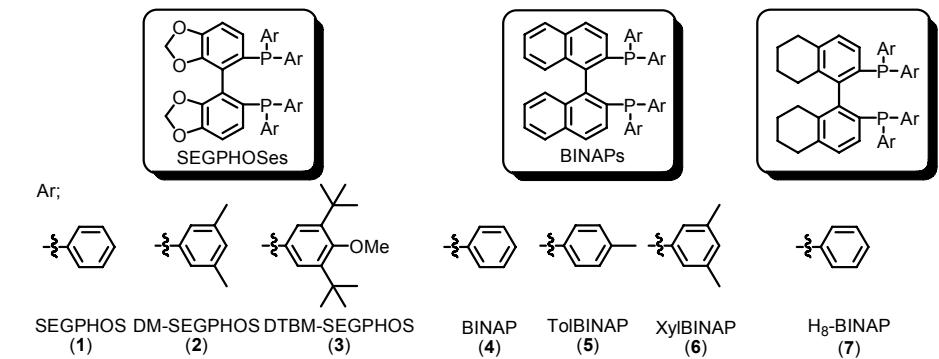
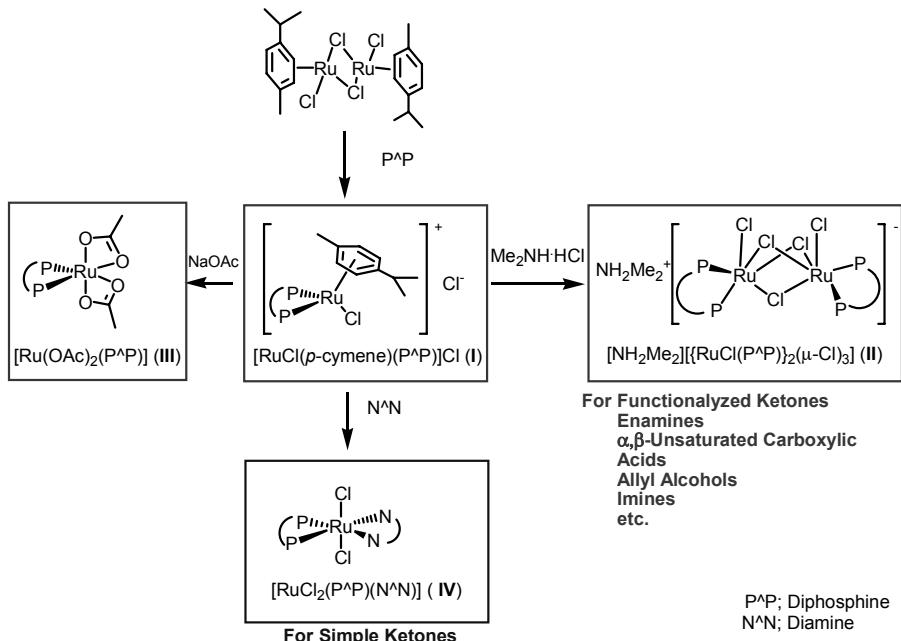


Figure 2 Various Types of Ruthenium Precatalysts for Asymmetric Hydrogenation



Takasago Int. Corp. produces these ligands and complexes based on our chiral technology.

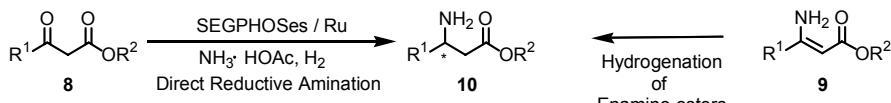
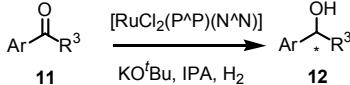
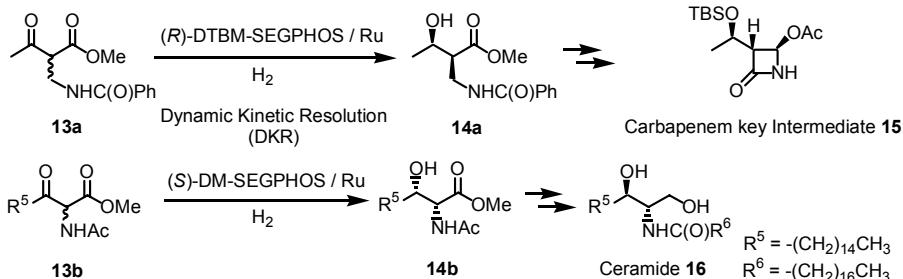
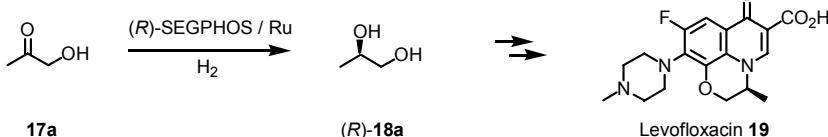
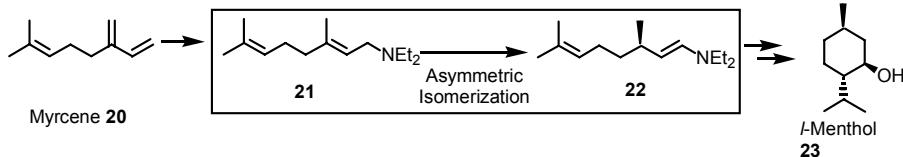
- Over 500 ligands and their complexes, and investigations about their applications.
- Over 20 years experience of industrial production, and laboratory research works.
- Over 2,000 Mt of annual production with cGMP & ISO certified facilities equipped with 1m³ to 10m³ Hastelloy & Stainless Autoclaves with 400 to 1,280 psi.

(<http://www.takasago.com>)

Now, everyone can access to Takasago's technologies by using these ligands and complexes.

Scheme 1

Examples of Takasago's Chiral Technologies: Efficient and Unique Catalysts

 β -Amino Acids**Chiral Alcohols** **α -Substituted- β -Hydroxy Esters****1,2-Propanediol****Menthol Since 1983**

Features of Ligands and Complexes are Outlined Below;

1-2. Ligands**SEGPHOS (1)**

shows its greatest competence in hydrogenation of α -, β - and γ -functionalized ketones. In most cases, higher catalytic activities and enantioselectivities are achieved by use of SEGPHOS / Ru complexes than by use of BINAP complexes.¹

DM-SEGPHOS (2)

has a slightly bulkier pendant group than SEGPHOS, which gives higher enantioselectivity in reductive amination of β -keto esters to β -amino acids.¹⁰ Replacing XylBINAP with **2** as ligand in Noyori's $[\text{RuX}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ complex also could increase the enantioselectivity in difficult hydrogenations.¹¹

DTBM-SEGPHOS (3)

produces an extremely sterically demanding environment around the metal center. In the asymmetric hydrogenation of **13a**, the DTBM-SEGPHOS Ru complex provides the highest enantioselectivity as well as dynamic kinetic resolution (DKR) to form a second chiral center. The former is enhanced by the SEGPHOS backbone and the latter is enhanced by the DTBM pendant group (Scheme 1).¹ Because of its unique structural features, many complexes of **3** with metals such as gold,¹² palladium,¹³ and especially copper¹⁴ show excellent activity and enantioselectivity in a variety of hydrogenation and C-C bond forming reactions.

BINAP (4)

is the parent compound of axially chiral biaryl ligands. BINAP is still a standard, much used ligand.

TolBINAP (5)

enjoys high solubility in organic solvents. This property solves the problems caused by low solubility intrinsic to BINAP and its complexes.¹⁵

XyIBINAP (6)

is usually used in the Noyori's Ru-Diphosphine-Diamine complexes for hydrogenation of simple ketones. In many cases this ligand gives higher ee values than those with BINAP or TolBINAP.¹⁶

H₈-BINAP (7)

hydrogenates unsaturated carboxylic acids in higher enantioselectivities than BINAP does.¹⁷

1-3. Complexes

[RuCl(*p*-cymene)(P[^]P)]Cl (I)

is easily prepared and can be applied to the asymmetric hydrogenation of various substrates. Slightly higher temperature is necessary to dissociate the arene ligand to activate this type of complex. This feature is advantageous when higher reaction temperature gives better results.

[NH₂Me₂] [RuCl(P[^]P)₂(μ-Cl)₃] (II)

shows catalytic activity even at relatively lower temperature, due to ease of generation of active species

[Ru(OAc)₂(P[^]P)] (III)

is frequently used for asymmetric hydrogenation of allyl alcohols,¹⁸ and unsaturated carboxylic acids,¹⁷ and for asymmetric reductive amination,¹⁰ etc.

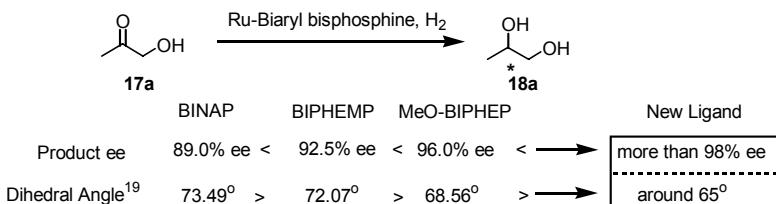
[RuCl₂(P[^]P)(N[^]N)] (VI)

is precatalyst, which gives excellent activity and enantioselectivity in the asymmetric hydrogenation of simple ketones.¹⁶

1-4. Design Concept of SEGPHOS

SEGPHOS resulted from an effort at Takasago to optimize the enantioselective hydrogenation of acetol (**17a**). First, a detailed survey was made of mechanistic studies of known ruthenium-catalyzed hydrogenation reactions of functionalized ketones, such as β-keto esters.¹ It was observed that in the asymmetric hydrogenation of acetol there was a tendency of ligands with narrower dihedral angles to give better ees (Scheme 2).¹ This became a driving force for us to design a ligand with a smaller dihedral angle.

Scheme 2 Asymmetric Hydrogenation of Acetol



It was predicted that a ligand with dihedral angle of around 65° would achieve more than 98% ee values of product. Finally, computational chemistry was used to predict that a ligand with the structure of SEGPHOS would have the desired smaller dihedral angle.

Figure 3 SEGPHOS Ligand: Named after the Figure of Top View



The SEGPHOS Ruthenium complex **A** has a narrow dihedral angle (64.99°).¹⁹ Hydrogenation of acetol resulted in 98.5% ee with S/C = 10,000 (Compare: 89% ee with S/C = 3,000 in the case of BINAP). The ligand remarkably increases not only enantioselectivity but also catalytic activity.¹

2. Applications to Catalytic Asymmetric Syntheses

2-1. Background

Molecular chirality is an important characteristic in the pharmaceutical, agrochemical, flavor and fragrance sphere, because it affects biological activities and functions of compounds.²⁰ In 1992 the FDA (Food and Drug Administration in the U.S.) introduced a guideline for drugs to be composed of single stereoisomers in consideration of effects on human health. As a result, the importance of chiral manufacturing technologies that produced single enantiomers (stereoisomers) for the pharmaceutical industry increased dramatically.²¹ Among such technologies, catalytic asymmetric synthesis has played a significant role because of its atom efficiency and wide application.²² Highly efficient asymmetric catalysis promotes green sustainable chemistry through waste reduction, rapid production and energy efficiency.

2-2. Asymmetric Hydrogenation

Asymmetric hydrogenation is one of the leading technologies for catalytic asymmetric synthesis.²³ Chiral ligands developed for such reactions have been critical to success.

2-2-1. Historical Overview

In 1966, Nozaki, Noyori, and Takaya reported the first transition metal complex catalyzed homogeneous asymmetric reaction.²⁴ At almost the same time, Knowles²⁵ and Horner²⁶ independently discovered that prochiral olefins were asymmetrically hydrogenated by using Wilkinson's catalyst modified by chiral mono-phosphine. In 1971 Kagan invented DIOP,²⁷ a ligand based on a new concept of *diphosphine* and *non-P-chiral* compound. The diphosphine concept has been used for most ligands after DIOP. Optically active L-DOPA had been manufactured by using P-chiral DIPAMP²⁸, developed by Knowles.

In 1980, Noyori and Takaya introduced atropisomeric chiral triarylphosphines to the ligand design concept by synthesizing enantiomerically pure BINAP.² As the BINAP complex, ruthenium has the ability to hydrogenate various kinds of multiple bonds, though rhodium complexes with various kinds of ligands have been applied mainly to asymmetric hydrogenation of C-C double bond. Finally in 1995, Noyori discovered the Ru-Diphosphine and diamine system that can hydrogenate even simple ketones.²⁹

In industrial applications, it is very fortunate that the metal which best achieves hydrogenation of various multiple bonds is not rhodium but ruthenium, because rhodium is one of the most expensive rare metals. Today, the less expensive ruthenium based technology is widely applied to industrial production.²² In 2001, Professor Ryoji Noyori won the Nobel Prize with Professor William S. Knowles for their excellent works on chirally catalyzed hydrogenation reactions.³⁰

Since the discovery, BINAP has been used for many types of asymmetric reactions. Success of the ligand has inspired many chemists to great efforts to attain higher activity and/or selectivity than those of BINAP by creating new ligands on the basis of various kinds of hypotheses and concepts.³¹ Today we can usually achieve optimum performance in every way by choosing from the large library of ligands and complexes available on a commercial scale.

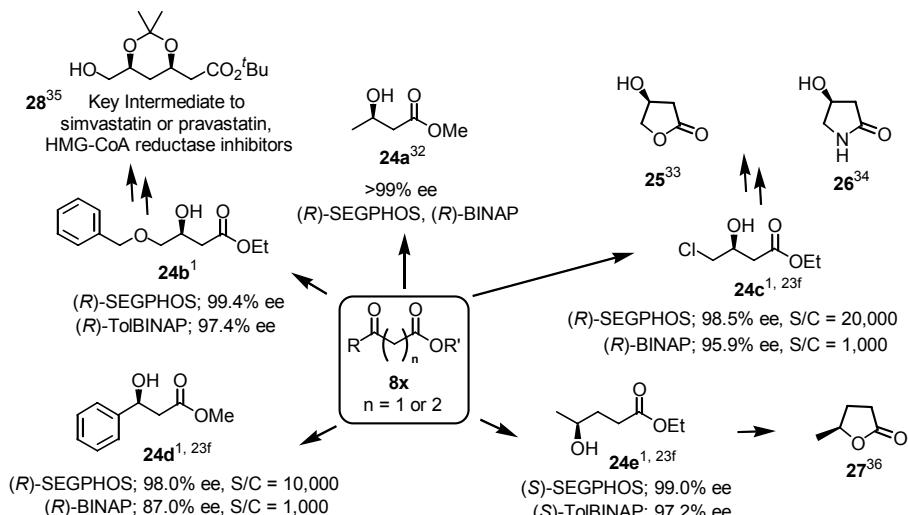
2-2-2. Functionalized Ketones

The term 'Functionalized ketone' means ketones having additional functional groups that help coordinate to the center metal, i.e. -C(O)OR, -OR, -NR₂ etc. Such functional groups play a role like an anchor to facilitate hydrogenation. Complexes of type of I or II, shown in figure 2, are usually used for this purpose.

β- & γ-Keto Esters

These materials are hydrogenated to hydroxy esters with promising high ee values and high catalytic activity.

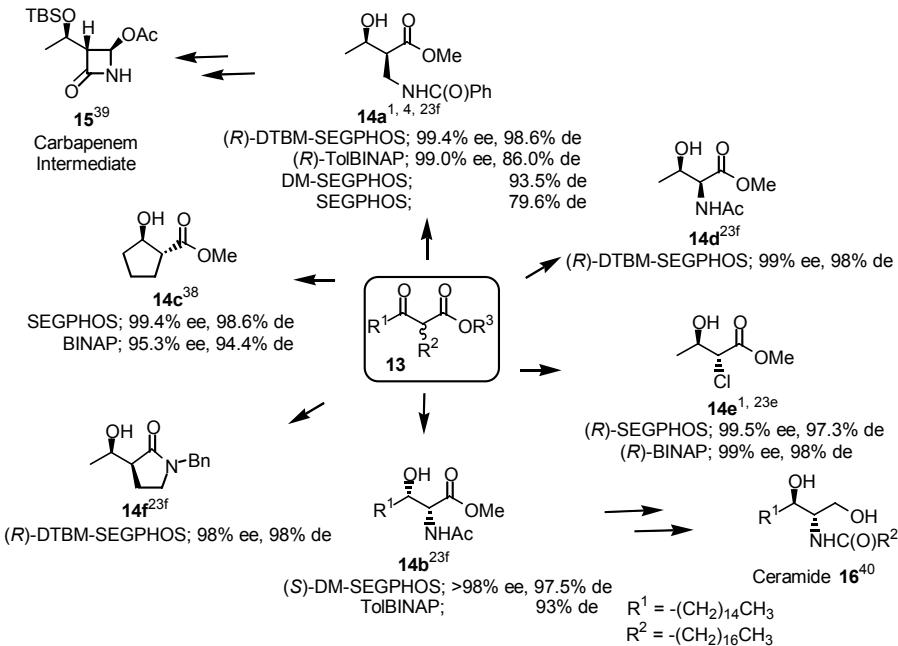
Scheme 3 Hydrogenation of β - & γ -Keto Esters



α -Substituted- β -Keto Esters

α -Substituted- β -hydroxy esters are obtained by asymmetric hydrogenation via *dynamic kinetic resolution*.³⁷ Asymmetric Hydrogenation via Dynamic Kinetic Resolution is a reaction where one enantiomer of racemic starting material is asymmetrically hydrogenated much faster than the other (kinetic resolution) with concurrent rapid racemization (dynamic). One of the four possible stereoisomers is obtained predominantly with 100% consumption of starting material. Thus two chiral centers can be constructed simultaneously. In the case of β -keto esters, strong acidity of the proton at 2-position leads to the required easy racemization. In general, high ee but low de values are obtained in Methanolic solvent. In dichloromethane de values improve, yet rate of reaction becomes too slow to apply the reaction industrially. Mixed dichloromethane and methanol solvent is usually used to obtain a reasonable balance of reaction rate and de selectivity. Furthermore DTBM-SEGPHOS or DM-SEGPHOS, ligands with narrow dihedral angles and bulky pendant groups, show superior ee and de values as observed in the hydrogenation of **13a** or **13b**. Tol-BINAP, used in industrial production of **15** in former times has now been replaced with DTBM-SEGPHOS.

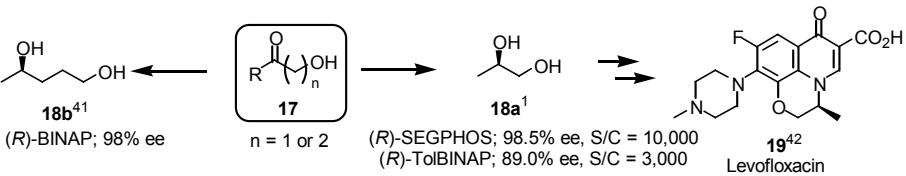
Scheme 4 Hydrogenation of α -substituted- β -Keto Esters



1,2- or 1,3-Diol; From Ketol

The Ru-SEGPHOS class of complexes are best for hydrogenation of α -hydroxy ketones. Thus, in the manufacture of 1,2-Propanediol, a chiral intermediate of Levofloxacin **19**, the ligand has been switched to SEGPHOS.

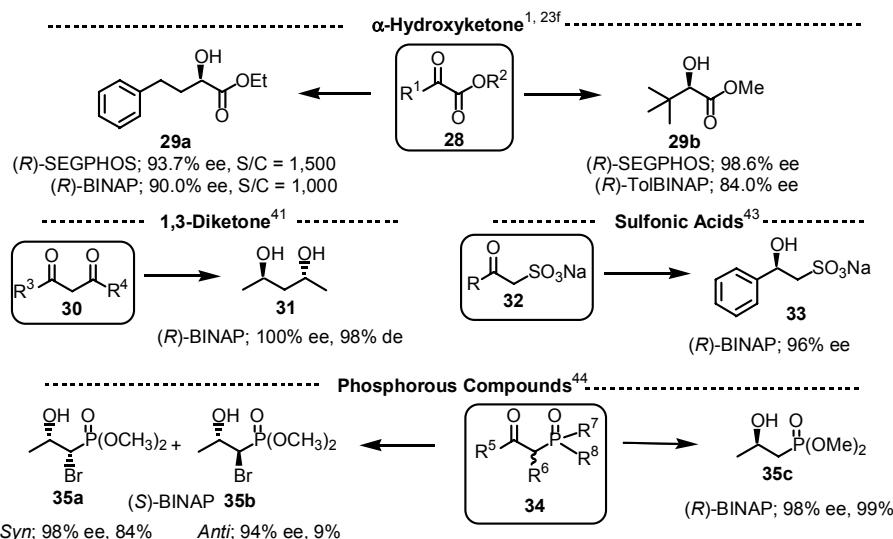
Scheme 5 Hydrogenation of α -, or β -Hydroxy Ketones



Other Functionalized Ketones

Asymmetric hydrogenations of all types of functionalized ketones are known.

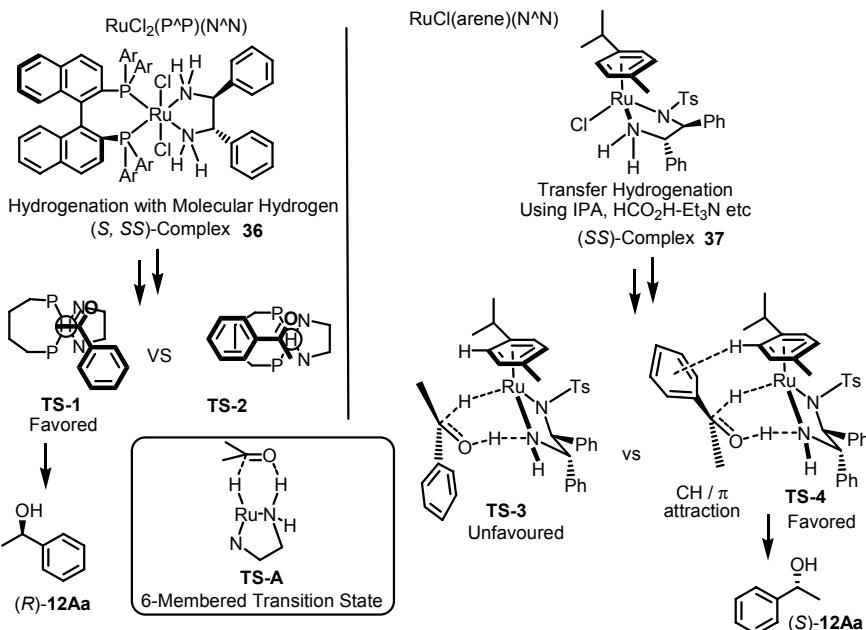
Scheme 6 Hydrogenation of Various Kinds of Functionalized Ketones



2-2-3. Simple Ketones

Asymmetric hydrogenation of simple ketones is practiced using either of two methods. One is Noyori's hydrogenation using $[\text{RuCl}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ complex and molecular hydrogen⁴⁵ and another is transfer hydrogenation with $[\text{RuCl}(\text{arene})(\text{N}^{\wedge}\text{N})]$ complex and a hydride source such as Isopropyl alcohol or $\text{HCO}_2\text{H}-\text{Et}_3\text{N}$.⁴⁶ Both reactions are proposed to proceed in the outer coordination sphere of the complex via a 6-membered transition state **TS-A**.⁴⁷ Catalytic activity of the hydrogenation reaction using $[\text{RuCl}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ complex is extremely high up to over 2,400,000 TON.

Scheme 7 Catalytic Asymmetric Reduction of Simple Ketones



In many cases the [RuCl₂(XylBINAP)(N^N)] complex gives excellent enantioselectivity. When results are not satisfactory, DM-SEGPHOS, used in place of XylBINAP, may solve the problem (Scheme-8).

Scheme 8 Hydrogenation of Quinuclidinone⁴⁸; DM-SEGPHOS Afforded Better Result.

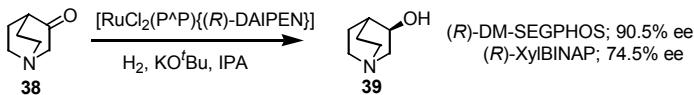
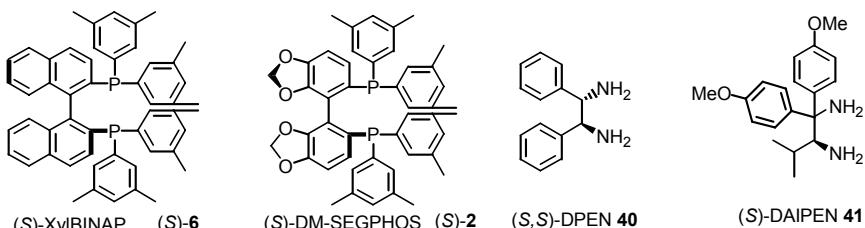


Figure 4 Phosphine and Diamine Ligands for Noyori's Complex

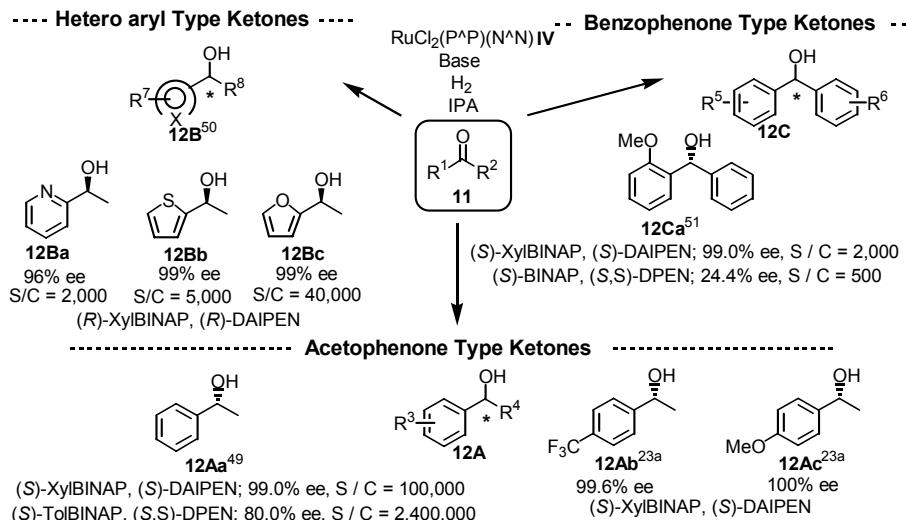


Various other combinations of diphosphines and diamines may improve enantioselectivities.

Simple Acetophenone, Benzophenone, and Heteroaryl Type Ketones

Application of the $[\text{RuCl}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ system to a large variety of ketones has been investigated.^{23a} In most cases, ee values of products exceed 95% ee with excellent catalytic activity. Over 99% ee values are often observed.

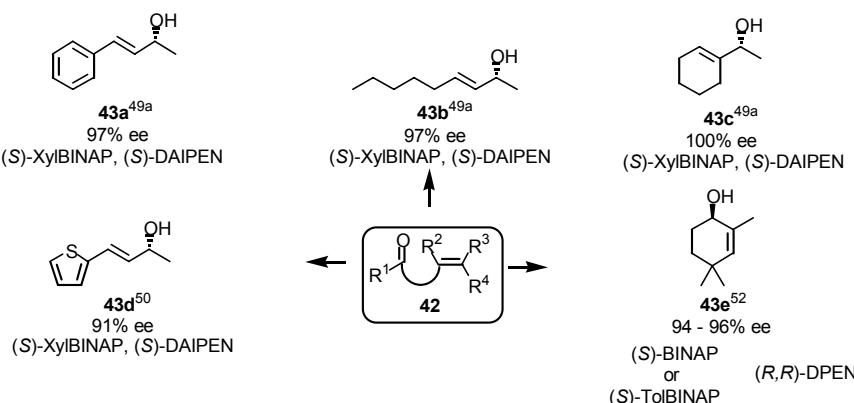
Scheme 9 Hydrogenation of Simple Ketones



Ketone Selective Reduction

Carbonyl groups are selectively reduced even when olefins exist in the same molecule, during the hydrogenation reaction when using Noyori's $[\text{RuCl}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ complex.

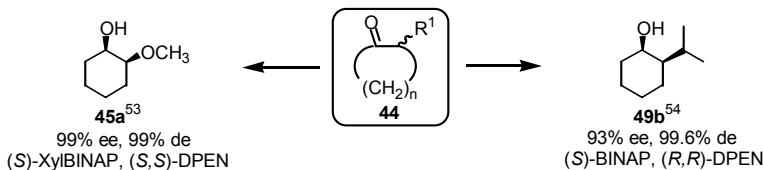
Scheme 10 Ketone Selective Hydrogenation



Hydrogenation of Simple Ketones via Dynamic Kinetic Resolution

Simple ketones, having substituents at α -position, are also hydrogenated to alcohols, producing two chiral carbon centers in high yield via dynamic kinetic resolution (DKR).

Scheme 11 Simple Ketones; Dynamic Kinetic Resolution



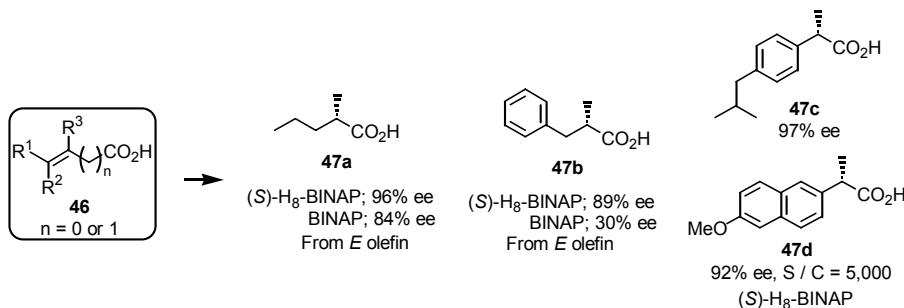
The DKR is caused by the basic KO'Bu used in Noyori's reduction. With alternative use of BH₄-Complex under neutral condition, no DKR is observed, and one enantiomer of the starting material remains unhydrogenated.⁵⁵

2-2-4. Olefins

Carboxylic acid

Among biaryl phosphine ligands, H₈-BINAP is promising for olefin hydrogenation, affording higher enantioselectivities than BINAP.

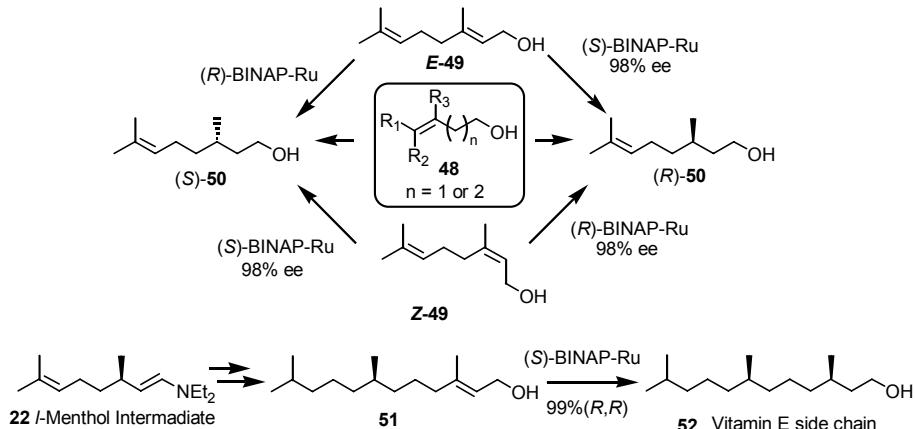
Scheme 12 Hydrogenation of Unsaturated Carboxylic Acids⁵⁶



Allyl Alcohol or Homo Allyl Alcohol

Olefins at the β,γ - or the γ,δ -position of the hydroxyl group are selectively hydrogenated.

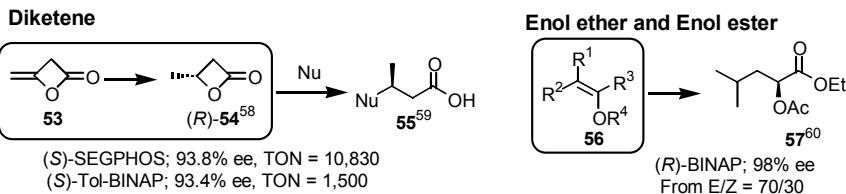
Scheme 13 Hydrogenation of Allylic Alcohols⁵⁷



Other Olefins

Diketene is hydrogenated to chiral β -lactone **54**, which can be transformed to various chiral 3-substituted carboxylic acids. Enol ethers and enol esters are also hydrogenated in high ees.

Scheme 14 Hydrogenation of Other Type of Olefins

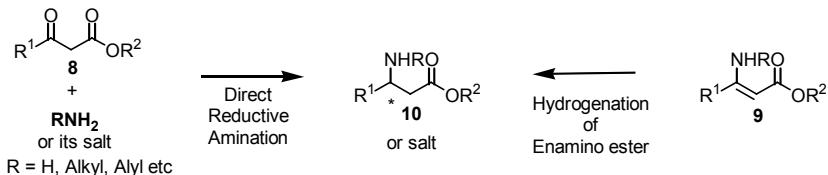


2-2-5. Enamino Esters and Reductive Amination to β -Amino Acid Derivatives

β -Amino Acids

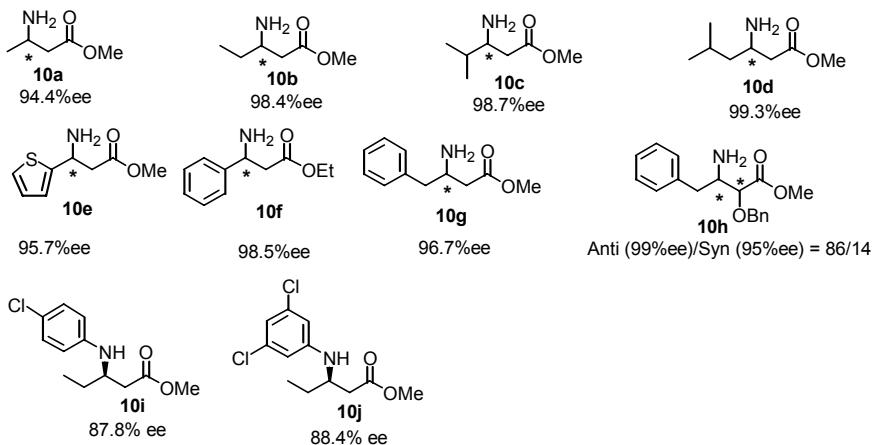
Chiral non-protected β -amino acids are obtained through Direct Reductive Amination (DRA) of β -ketoesters or through hydrogenation of enamino esters. Ruthenium catalysts give β -Amino acid derivatives in good yield via DRA as do Rhodium catalysts in low to modest yield. These methods are superior from both the economical and environmental point of view, because omission of two steps, protection and deprotection, decreases not only cost but also industrial waste.

Scheme 15 Synthesis of β -Amino Acids by Hydrogenation⁶¹



Various kinds of β -amino acid derivatives have already been synthesized using this method. In almost all cases, crude β -amino acid derivatives have high ee values of 94 to 99%.

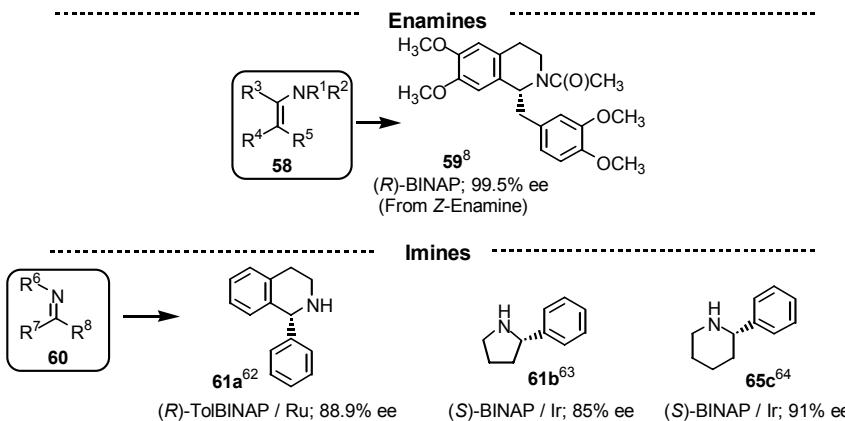
Figure 5 β -Amino Acid Library



Other N-Containing Compounds

Enamines and imines can be hydrogenated by using Ru-complexes or the related Ir-complexes.

Scheme 16 Synthesis of Amine



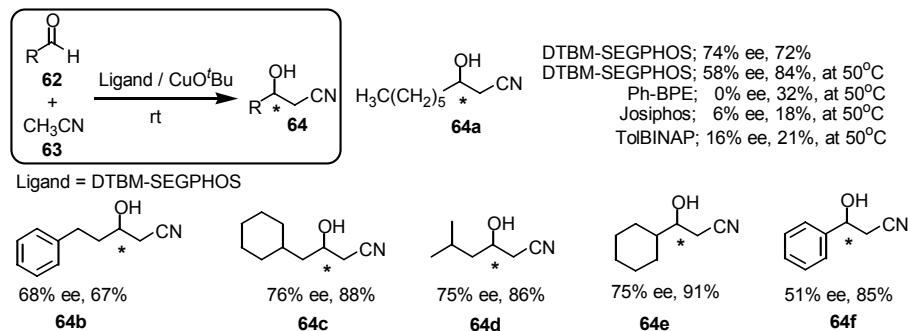
2-3. Other Reactions

There are numerous investigations of metal-biaryl phosphine complex catalyzed asymmetric reactions. Examples of SEGPHOS-related catalytic asymmetric reactions will be described below.

2-3-1. Aldol-Type Reaction⁶⁵

Cross Aldol type reactions of acetonitrile with aldehydes, including linear aldehydes, have been achieved. σ -Donating solvents improved chemical yield, preventing aldehydes from self-condensation but not inhibiting coordination of nitrile.

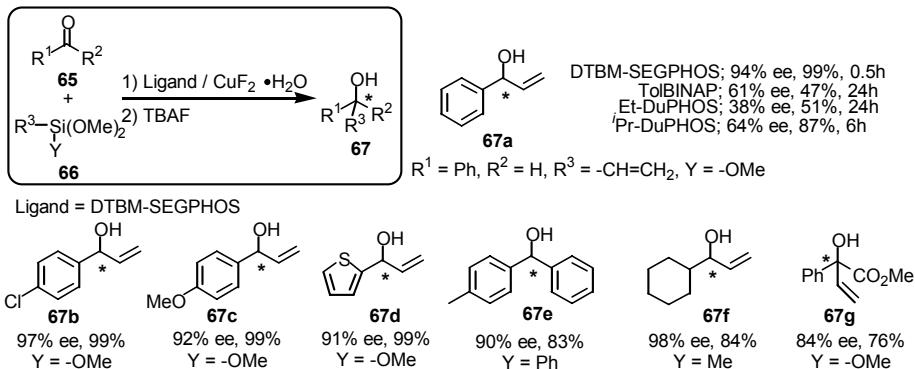
Scheme 17 Nitrile Aldol Reaction



2-3-2. Alkenylation and Arylation⁶⁶

Alkenylation and arylation of aldehydes by alkanyl or phenyl silanes were improved using the SEGPHOS class of ligands. Bulkiness is more important than electronic features for the ligand acceleration effect.

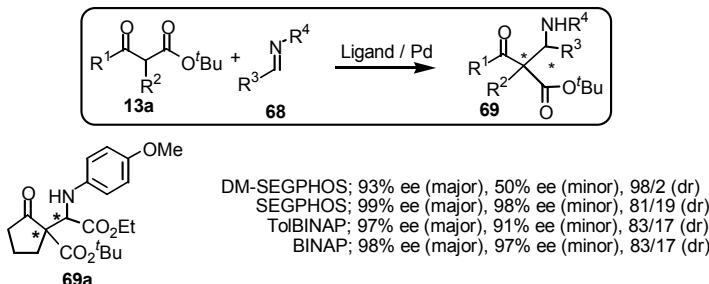
Scheme 18 Alkenylation and phenylation



2-3-3. Mannich reaction

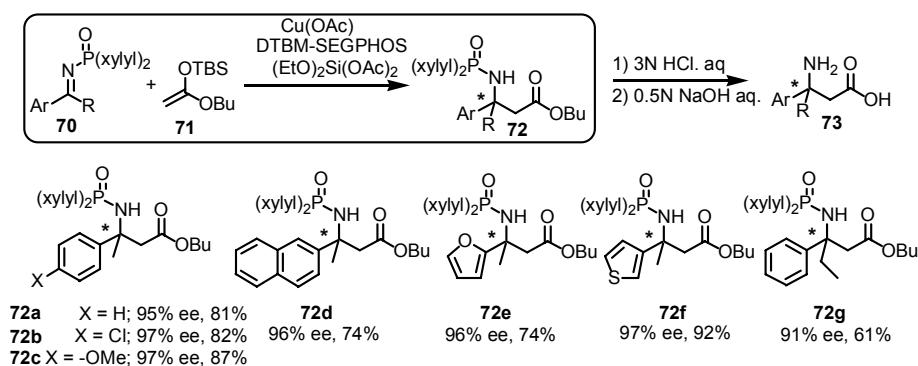
Palladium aqua complex $[Pd(P^{\wedge}P)(H_2O)_2][X]_2$ catalyzes the asymmetric Mannich reaction of β -keto esters. Palladium enolate derived from β -keto ester reacts with aldimines.

Scheme 19 Mannich Reaction of β -Keto esters⁶⁷



A DTBM-SEGPHOS / Cu complex also catalyzes a Mannich type reaction between Aryl-Alkyl ketimines and silyl enolate **71**.

Scheme 20 Mannich Reaction of Ketimines⁶⁸

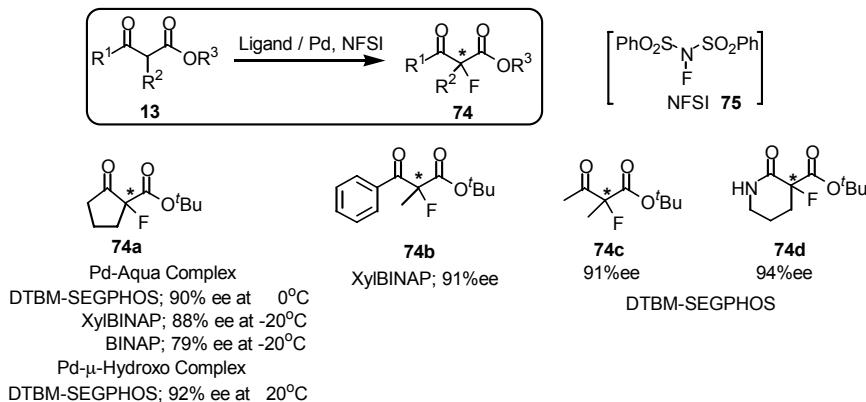


DuPHOS / Cu complex catalyzes a Mannich type reaction between aliphatic ketimines and silyl enolate **71** with moderate ee values.

2-3-4. Fluorination

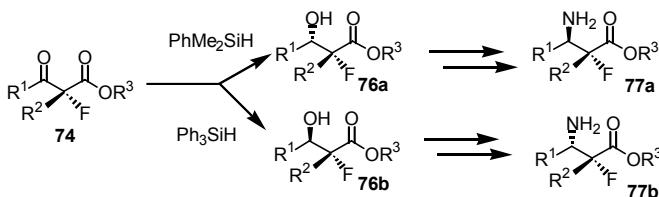
In contrast to the Mannich reaction (scheme 9) and the Michael addition (scheme 23), palladium μ -hydroxo complex $[Pd(P^{\wedge}P)(\mu-\text{OH})_2][X]_2$ also catalyzes the asymmetric fluorination of β -keto ester using *N*-Fluorobenzenesulfonimidate (NFSI) **75**. In many cases, reaction using DTBM-SEGPHOS as ligand gives the best result with high enantioselectivity.

Scheme 21 Fluorination of β -keto esters⁶⁹



Fluorinated β -Amino acids are obtained from the α -Fluorinated keto ester products. All four stereoisomers can be prepared individually by using proper reagents.

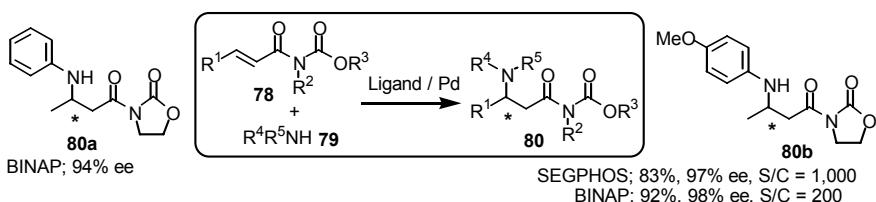
Scheme 22 Synthesis of α -fluorinated β -Amino Acids^{69a}



2-3-5. Michael Addition

Sodeoka's Pd-aqua complex also catalyzes hetero Michael reactions to afford β -amino acid derivatives.

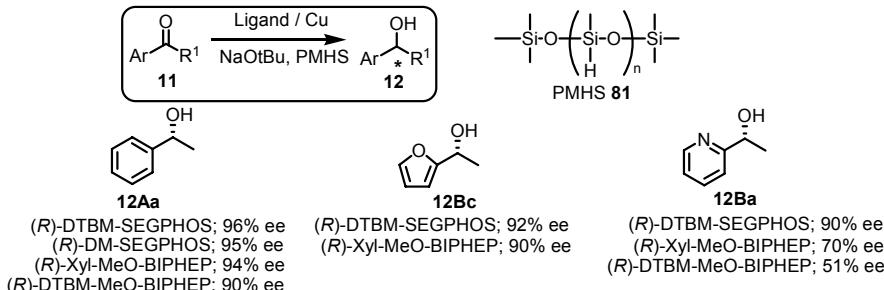
Scheme 23 Pd-Catalyzed Hetero Michael Addition⁷⁰



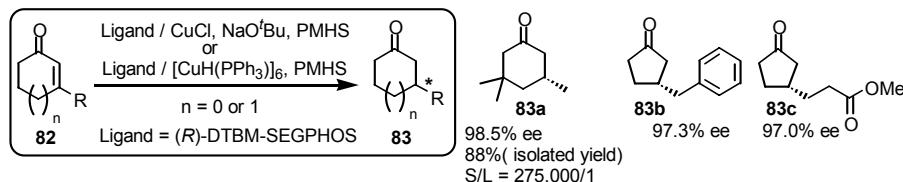
2-3-6. Hydrosilylation

B. Lipshutz's Group has reported hydrosilylation of aryl and heteroaryl ketones, α,β -unsaturated carbonyl compounds, and imines in many papers, where DTBM-SEGPHOS / Cu complexes give good results in terms of enantioselectivity and catalytic activity. Polymethylhydrosiloxane (PMHS), an inexpensive and air and moisture stable reagent, is commonly used as hydride source.

Scheme 24 Hydrosilylation of Aryl & Heteroaryl Ketones⁷¹

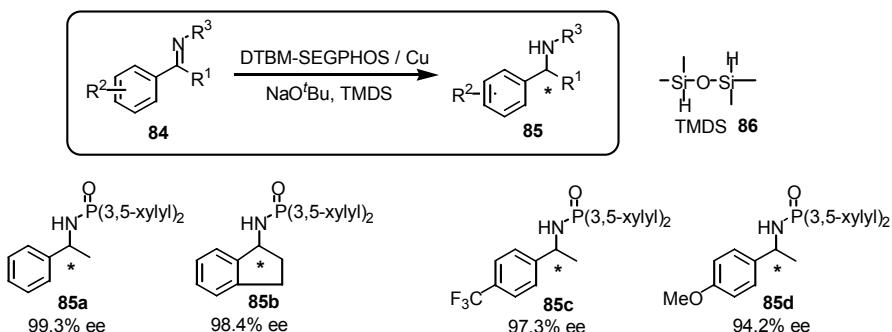


Scheme 25 1,4-Reduction of Cyclic α,β -Unsaturated ketones⁷²



In the case of acyclic α,β -unsaturated ketones, PPF-P(^tBu)₂ often works well.

Scheme 26 Hydrosilylation of Imines⁷³

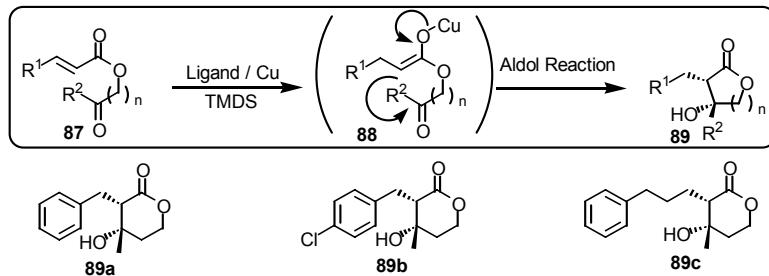


In this case, 1,1,3,3-tetramethyldisiloxane (TMDS) gives good result, though PMHS gives only modest results.

2-3-7. Reductive Aldol Reaction.

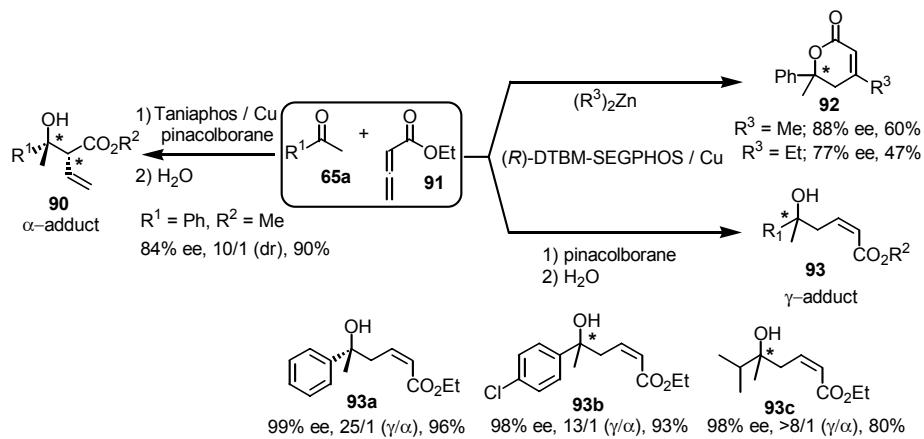
Copper enolates generated as a result of hydrosilylation of α,β -unsaturated esters react with ketones to form Aldol adducts. SEGPHOS and MeO-BIPHEP are efficient.

Scheme 27 Intramolecular Reaction⁷⁴



An intermolecular reductive aldol reaction is also reported. DTBM-SEGPHOS affords γ -adducts whereas Taniaphos gives α -adducts.

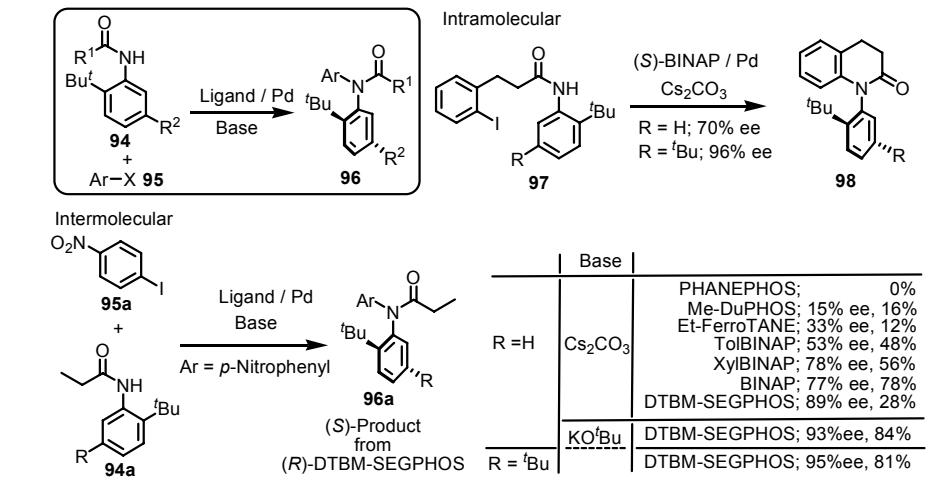
Scheme 28 Intermolecular Reaction⁷⁵



2-3-8. Aryl Amination

Palladium-catalyzed asymmetric *N*-Arylations of 2-substituted-*N*-acyl anilines afford optically active atropisomeric anilides.

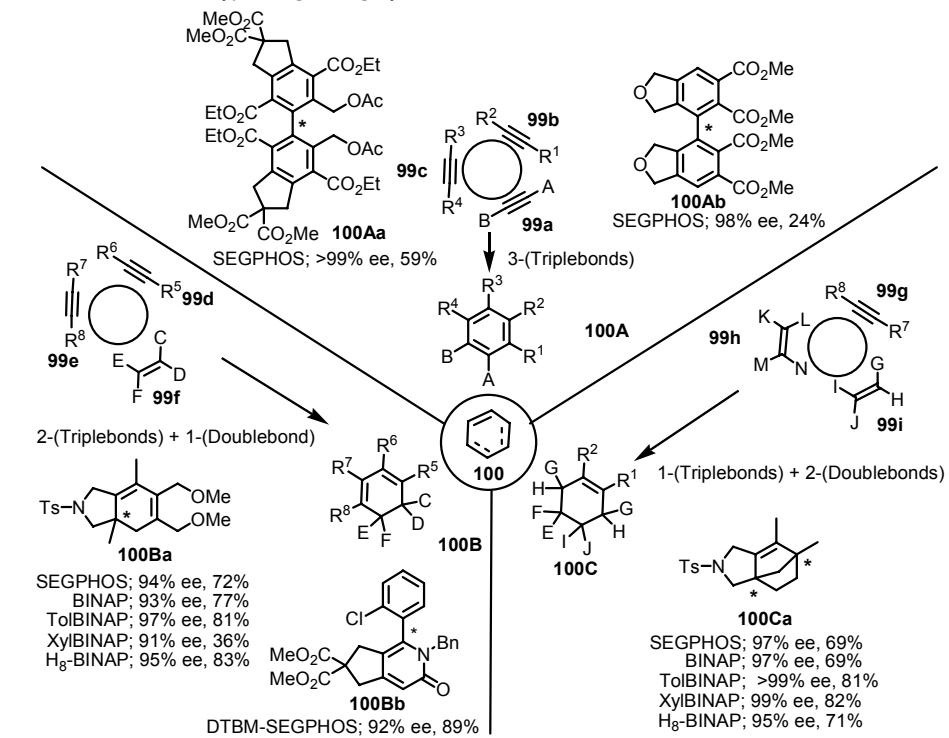
Scheme 29 Optically Active Atropisomeric Anilines⁷⁶



2-3-9. [2 + 2 + 2] Cycloaddition

Asymmetric [2+2+2] cycloaddition reactions between intermolecular or Intramolecular 3-triple bonds, 2-triple bonds and 1-double bond, and 1-triple bond and 2-double bonds proceed by rhodium catalysts.

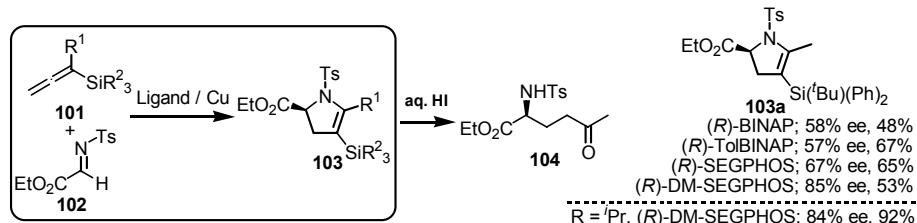
Scheme 30 Various Types of [2+2+2] Cycloaddition Reaction⁷⁷



2-3-10. [3 + 2] Cycloaddition

Copper-catalyzed asymmetric [3+2] cycloaddition reactions between allenylsilanes **101** and highly reactive aldimine **102** were achieved. When R¹ is H, the reaction did not proceed. Dehydroproline derivative **103** can be converted to keto amino acid **104**. DM-SEGPHOS gave the best result.

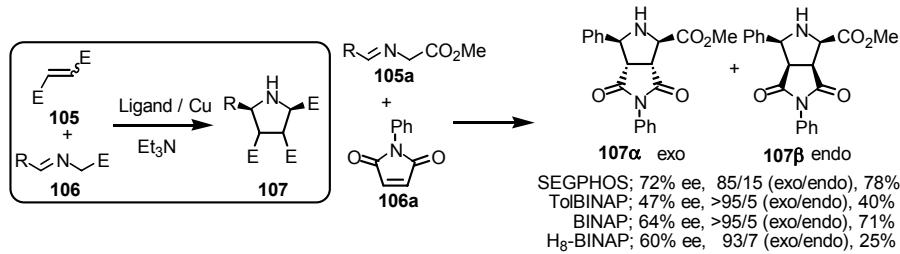
Scheme 31 [3+ 2] Cycloaddition Between Allenylsilane and Aldimine⁷⁸



2-3-11. 1,3-Dipolar Cycloaddition

Cu-phosphine complex catalyzed asymmetric 1,3-dipolar cycloaddition reactions showed *exo* selectivities, whereas most chiral metal complexes produced *endo* selectivities.

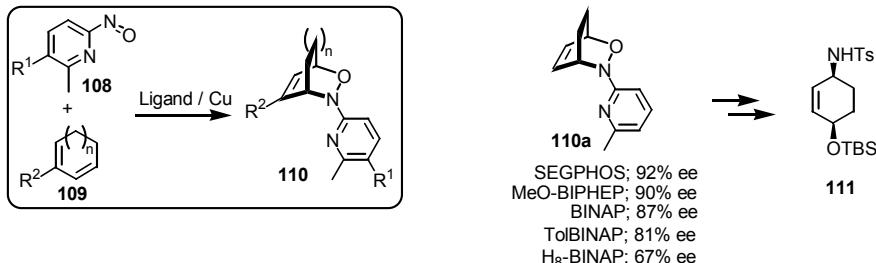
Scheme 32 Cu-Phosphine-Catalyzed *exo* Selective 1,3-Dipolar Cycloaddition Reactions⁷⁹



2-3-12. Diels-Alder Reaction

Nitroso Diels-Alder reactions between 6-Methyl-2-nitrosopyridine **108** and cyclic diene **109** were achieved with high enantioselectivities and complete regioselectivity catalyzed by Cu-SEGPHOS complex. Diels-Alder adducts can be transformed to protected amino alcohol **111**.

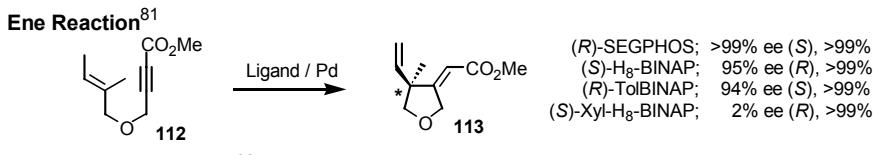
Scheme 33 Nitroso Diels-Alder Reaction⁸⁰



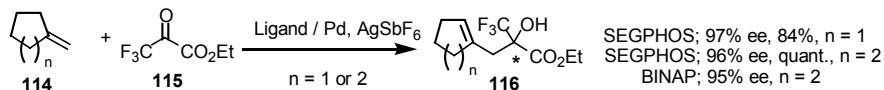
2-3-13. Ene-Type Reaction

Chiral quaternary carbon centers can be efficiently constructed.

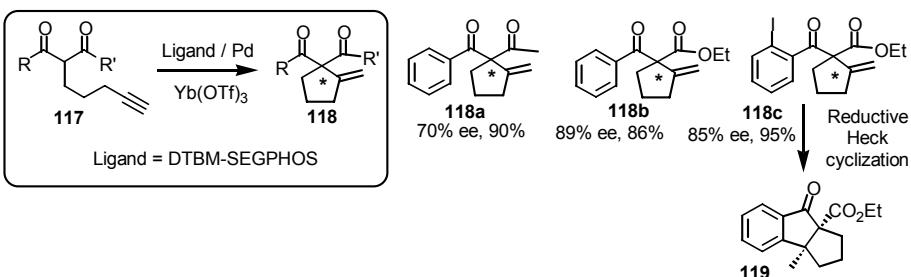
Scheme 34 Ene-Type Reactions



Carbonyl-Ene Reaction⁸²



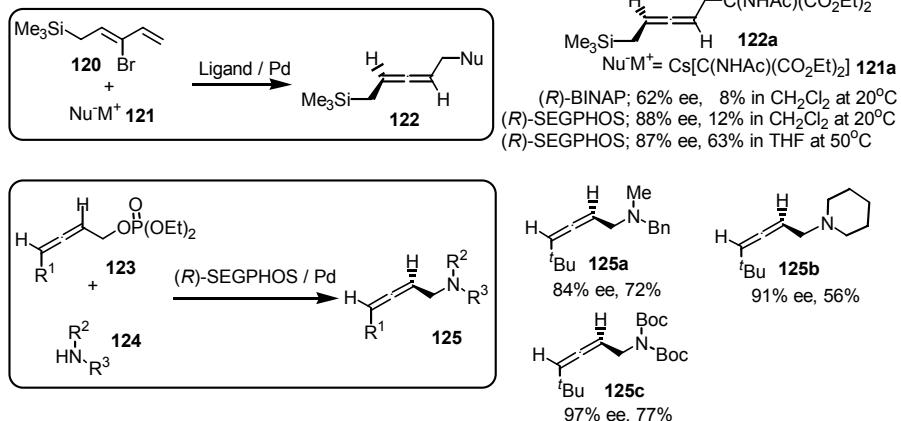
Conia-Ene Reaction⁸³



2-3-14. Nucleophilic Addition to π -Allylpalladium Complexes

Chiral Allenyl compounds were synthesized from bromodiene **120** or allenyl phosphate **123**. In the case of allenyl phosphate **123**, kinetic resolution was observed.

Scheme 35 Allene Compounds⁸⁴

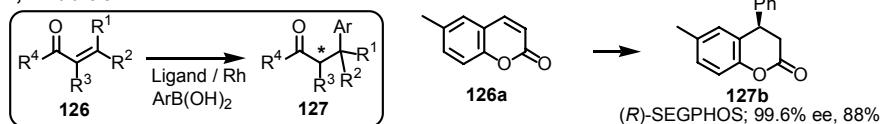


2-3-15. Aryl Addition Reaction

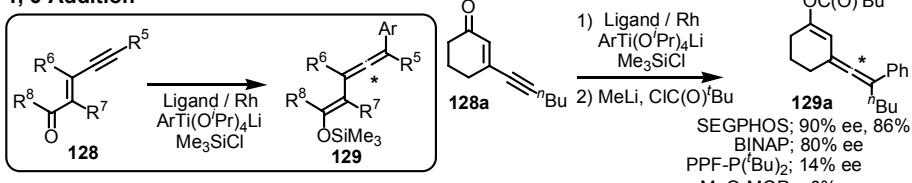
Asymmetric additions of aryl boronic acids and aryl titanium reagents were developed by means of rhodium catalysts.

Scheme 36 1,2-, 1,4-, 1,6-Aryl Addition Reactions

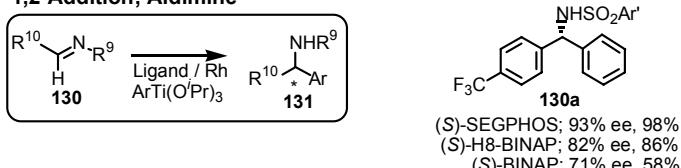
1,4-Addition⁸⁵



1, 6-Addition⁸⁶



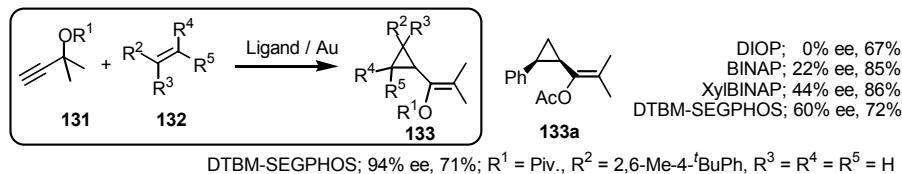
1,2-Addition; Aldimine⁸⁷



2-3-16. Cyclopropanation

High *cis* selective asymmetric cyclopropanation reaction proceeded by means of gold-phosphine catalysts.

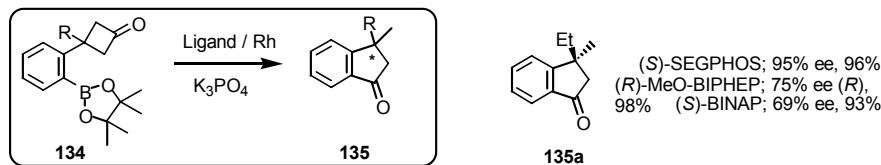
Scheme 37 Gold-catalyzed cyclopropanation reaction of olefins using propargyl esters⁸⁸



2-3-17. Enantioselective C-C Bond Cleavage

A chiral quaternary carbon center was produced by enantioselective C-C bond cleavage of rhodium cyclobutanolate, an intermediate in the following reaction.

Scheme 38 C-C Bond Cleavage⁸⁹



3. Conclusion

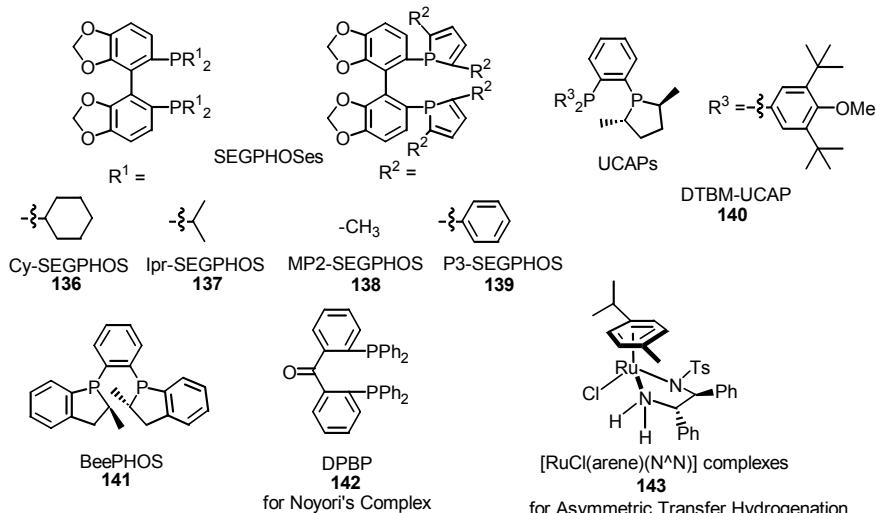
As seen above, reactions show diverse results depending on catalysts and/or ligands used, so chemists always desire to keep on hand a large variety of both catalysts and ligands to try.

There has been an enthusiastic acceptance of Takasago's new ligands and complexes which in addition to producing high activities and selectivities in catalysis, are now available in commercial quantities and in high quality via fully developed manufacturing processes.

4. Future Aspects

New catalysts, ligands and reactions are being developed at TAKASAGO. Some examples are shown in **Figure 5**.

Figure 5 Future Aspects.



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- (10) See section 2-2-5.
- (11) See scheme-8.
- (12) See scheme-37.
- (13) (a) See scheme-19. (b) See scheme-21. (c) See scheme-23. (d) See scheme-29.
- (14) (a) See scheme-17. (b) See scheme-18. (c) See scheme-20. (d) See section 2-3-6.
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- (16) See section 2-2-3.
- (17) See scheme-12.
- (18) See scheme-13.
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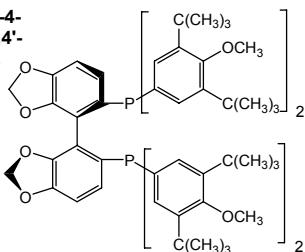
Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0066

NEW→

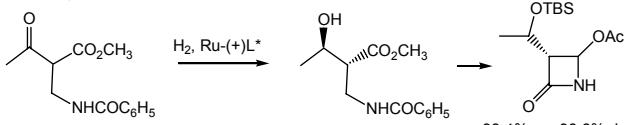
(R)-*5,5'*-Bis[di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole, min. 98%
(R)-DTBM-SEGPHOS
[566940-03-2]
 $C_{74}H_{100}O_2P_2$; FW: 1179.53;
 off-white pwdr.
 Note: Manufactured under
 license of Takasago patent.
 Takasago SEGPHOS Ligand
 Kit component see (page 52).



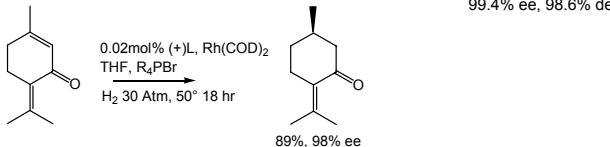
50mg
250mg

Technical Notes:

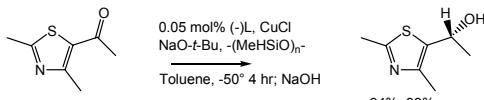
1. Biaryl bisphosphine ligand with a narrow dihedral angle. The DTBM SEGPHOS ligand, as the ruthenium complex, gives superior enantioselectivity and diastereoselectivity through dynamic kinetic resolution in the asymmetric hydrogenation of α -substituted- β -ketoesters useful in the synthesis of carbapenum antibiotics.
2. With rhodium, preferential enantioselective hydrogenation of more reactive olefin of extended enone structure.
3. With copper, enantioselective 1,2-reduction of heteraromatic ketones.
4. Rhodium-catalyzed chemo-, regio, and enantioselective [2 + 2 + 2] cycloaddition of alkynes with isocyanates.
5. With copper, enantioselective cross Aldol-type reaction of acetonitrile.
6. With copper, enantioselective vinylsilane alkenylation of aldehydes
7. Gold carbene mediated stereoselective cyclopropanation of propargyl esters.
8. With copper, enantioselective 1,4-reduction of α,β -unsaturated esters.
9. Enantioselective fluorination of β -keto esters with Sodeoka's Pd-aqua complex and a fluorinating reagent.



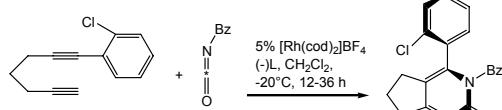
Tech. Note (1)
Ref. (1)



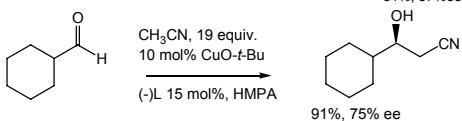
Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)



Tech. Note (4)
Ref. (4)



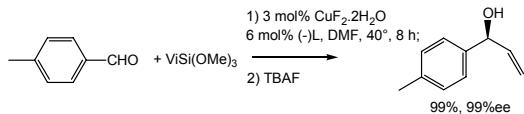
Tech. Note (5)
Ref. (5)

Products Referenced in the Article

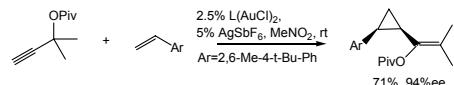
PHOSPHORUS (Compounds)

15-0066 (R)-(-)-5,5'-Bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole, min. 98% (R)-DTBM-SEGPHOS [566940-03-2]

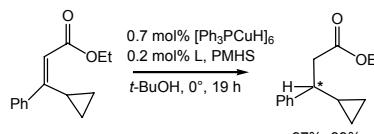
NEW→



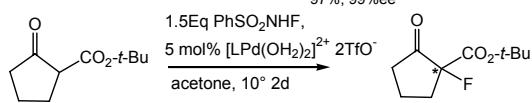
Tech. Note (6)
Ref. (6)



Tech. Note (7)
Ref. (7)



Tech. Note (8)
Ref. (8)



Tech. Note (9)
Ref. (9)

References:

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7. *J. Am. Chem. Soc.*, **2005**, 127, 18002.
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9. *J. Am. Chem. Soc.*, **2002**, 124, 14530.

15-0067 (S)-(+)-5,5'-Bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole, min. 98% (S)-DTBM-SEGPHOS [210169-40-7]

NEW→

50mg
250mg

C₇₂H₁₀₀O₈P₂; FW: 1179.53; off-white pwdr.

Note: Manufactured under license of Takasago patent.
Takasago SEGPHOS Ligand Kit component see (page 52).

Technical Note:

1. See 15-0066 (page 30).

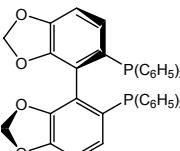
15-0136 (R)-(+)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole, min. 98% (R)-SEGPHOS [244261-66-3]

NEW→

50mg
250mg

C₃₈H₂₈O₄P₂; FW: 610.57; off-white pwdr.
Note: Manufactured under license of
Takasago patent. Takasago SEGPHOS

Ligand Kit component see (page 52).



Technical Notes:

1. Biaryl bisphosphine ligand with narrow dihedral angle. The SEGPHOS ligand has been applied to a variety of metal-catalyzed reactions. In many cases, yields and enantioselectivities, exceed results obtained earlier using BINAP. (Ref. 1, 2)
2. As the ruthenium complex, SEGPHOS generally gives higher levels of chiral induction in asymmetric hydrogens of α, β, and γ functionalized ketones. See ruthenium complexes 44-0096 (page 41), 44-0518 (page 48), 44-0168 (page 43).

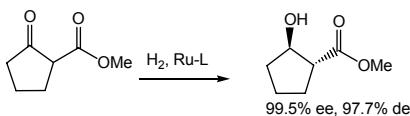
Products Referenced in the Article

PHOSPHORUS (Compounds)

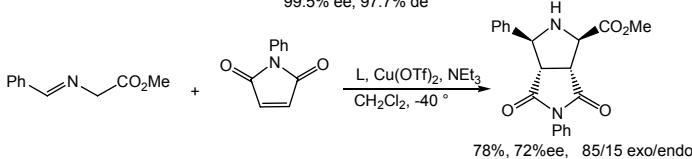
15-0136 (R)-(+)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole, min. 98% (R)-SEGPHOS (cont.) [244261-66-3]

NEW→

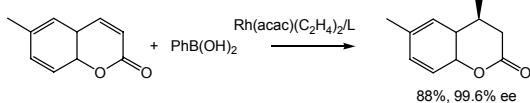
3. As ruthenium complex, asymmetric hydrogenation of α -substituted- β -ketoesters accompanied by dynamic kinetic resolution.
4. Copper-catalyzed asymmetric 1,3-dipolar cycloaddition of azomethine ylides.
5. Rhodium-catalyzed 1,4-addition of arylboronic acids to coumarins.
6. Palladium-catalyzed enantioselective cycloaddition of a 1,6-enyne.
7. Rhodium-catalyzed asymmetric addition of aryl titanium reagents to imines.
8. Copper-catalyzed nitroso Diels-Alder reaction.
9. Iridium-catalyzed asymmetric hydrogenation of quinolines activated by chloroformates.
10. Enantioselective copper-catalyzed reductive aldol condensation to produce β -hydroxylactones



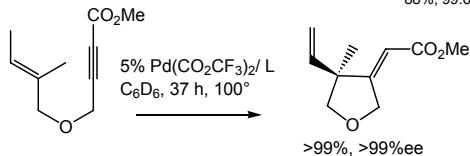
Tech. Note (3)
Ref. (1)



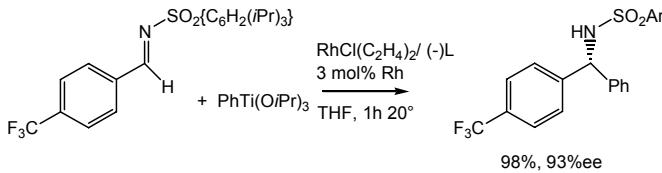
Tech. Note (4)
Ref. (3)



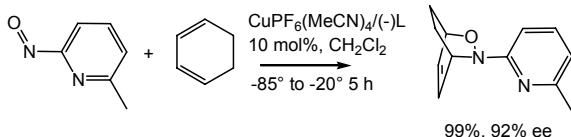
Tech. Note (5)
Ref. (4)



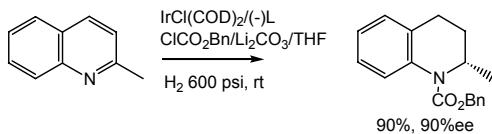
Tech. Note (6)
Ref. (5)



Tech. Note (7)
Ref. (6)



Tech. Note (8)
Ref. (7)



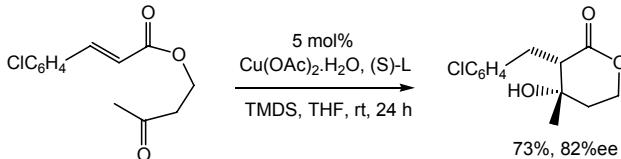
Tech. Note (9)
Ref. (8)

Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0136 (cont.) (R)-(+)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole, min. 98% (R)-SEGPHOS [244261-66-3]

NEW→



Tech Note (10)
Ref. (9)

References:

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5. *Angew. Chem. Int. Ed.*, **2001**, *40*, 249.
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9. *Org. Lett.*, **2005**, *7*, 4225.

15-0137 (S)-(-)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole, min. 98% (S)-SEGPHOS [210169-54-3]

NEW→

50mg
250mg

$\text{C}_{38}\text{H}_{28}\text{O}_4\text{P}_2$; FW: 610.57; off-white pwdr.

Note: Manufactured under license of Takasago patent.

Takasago SEGPHOS Ligand Kit component see (page 52).

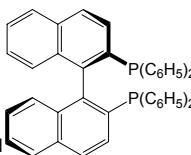
Technical Note:

1. See 15-0136 (page 31).

15-0150 (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl, 98% (R)-BINAP [76189-55-4]

$\text{C}_{44}\text{H}_{32}\text{P}_2$; FW: 622.70; white to light yellow xtl.; $[\alpha]_{D}^{20} +224.5^{\circ}$
(c 0.7, C_6H_6); m.p. 240.5–242°

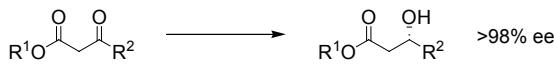
Note: Manufactured under license of Takasago patent. Takasago BINAP Ligand Kit component see (page 53).



250mg
1g
5g

Technical Notes:

1. (R)-BINAP or (R)-Tol-BINAP can be combined with dichloro(1,5-cyclooctadiene)ruthenium to form precursors to NOYORI CATALYST SYSTEMS. These systems exhibit very high catalytic activity and enantioselectivity in the hydrogenation of a wide range of substrates. NOYORI CATALYST SYSTEMS have been shown to effect highly enantioselective hydrogenation of functionalized ketones where the substituents are dialkylamino, hydroxy, siloxy, carbonyl, ester, amide or thioester.
2. Useful ligand in asymmetric Heck processes.
3. Useful as a ligand in Pd-catalyzed asymmetric arylation of ketones. (Ref. 7)
4. Useful as a ligand in Rh-catalyzed asymmetric 1,4-additions to enones. (Ref. 8)
5. Catalyst for the hydroamination of styrene derivatives.
6. Ligand employed in silver-catalyzed asymmetric Sakurai-Hosomi allylation and Mukaiyama Aldol reaction.
7. Ligand used in rhodium-catalyzed kinetic resolution of enynes.
8. Ligand used in asymmetric, rhodium-catalyzed hydroboration of cyclopropenes.
9. Ligand employed in the silver-catalyzed α -hydroxylation of stannyli enol ethers.
10. Ligand used in palladium-catalyzed synthesis of axially chiral allenes.
11. Ligand for Palladium-catalyzed enantioselective hetero Michael addition to form β -amino acid derivatives.



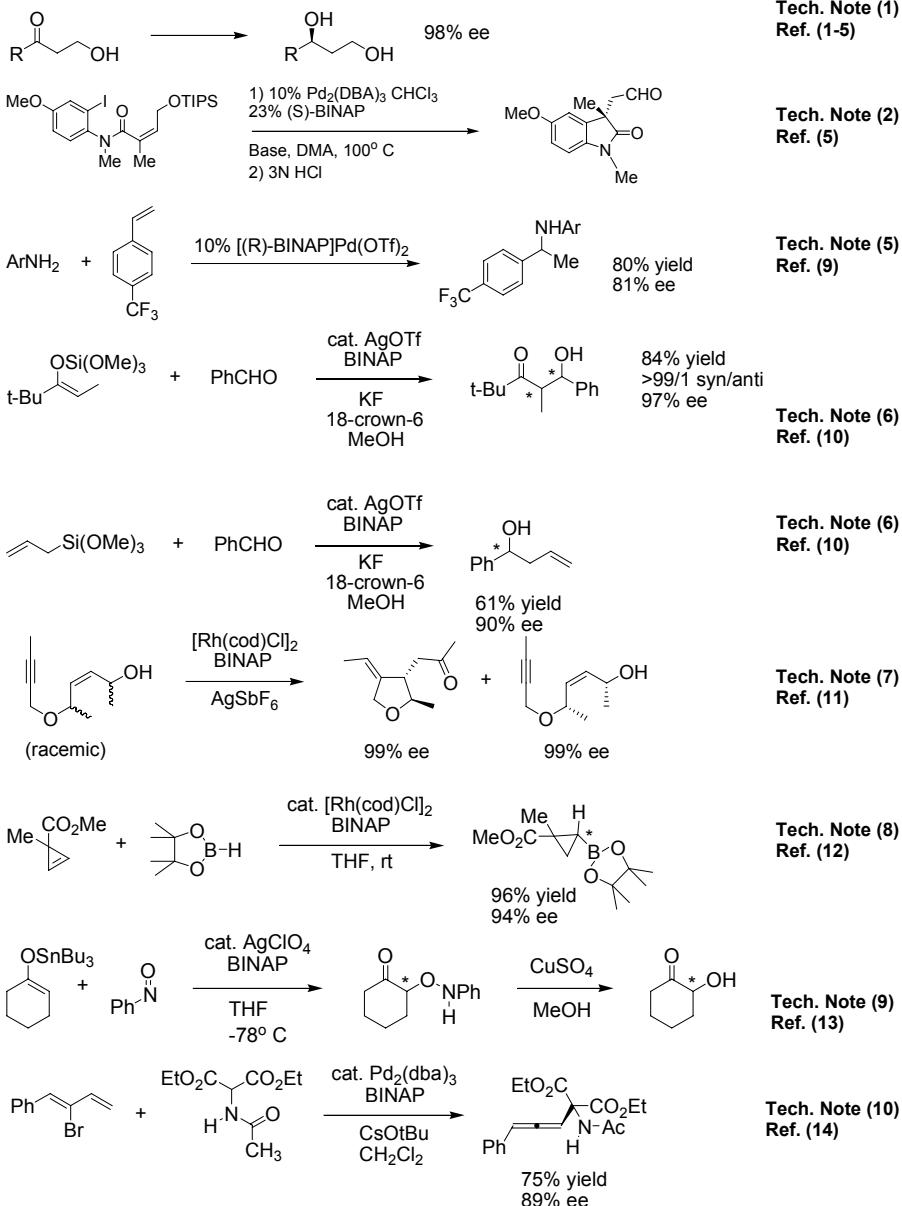
Tech. Note (1)
Ref. (1-5)



Products Referenced in the Article

PHOSPHORUS (Compounds)

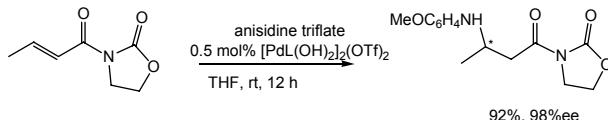
15-0150 (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl, 98% (R)-BINAP
(cont.) [76189-55-4]



Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0150 (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl, 98% (R)-BINAP
(cont.) [76189-55-4]



Tech. Note (11)
Ref. (15)

References:

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2. *Asymmetric Catalysis in Organic Synthesis*, **1993**, 61.
3. *J. Am. Chem. Soc.*, **1988**, 110, 629.
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13. *J. Am. Chem. Soc.*, **2003**, 125, 6038.
14. *J. Am. Chem. Soc.*, **2001**, 123, 2089.
15. US Patent Application US2006/0205968.

15-0151 (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl, 97%

250mg

(S)-BINAP [76189-56-5]

1g

$C_{44}H_{32}P_2$; FW: 622.70; white to light yellow xtl.; $[\alpha]_D$ -228°

5g

(c 0.68, C_6H_6); m.p. 241-242°

Note: Manufactured under license of Takasago patent.

Takasago BINAP Ligand Kit component see (page 53).

Technical Note:

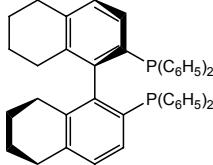
1. See 15-0150 (page 33).

15-2972 (R)-(+)-2,2'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (R)-H₈-BINAP
NEW →

50mg

250mg

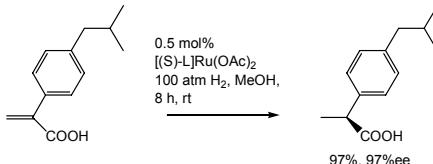
$f/139139-86-9$
 $C_{44}H_{40}P_2$; FW: 630.74; off-white pwdr.



Note: Manufactured under license of Takasago patent. Takasago BINAP Ligand Kit component see (page 53).

Technical Notes:

1. Biaryl bisphosphine ligand. The H8-BINAP ligand, as the ruthenium complex, catalyzes hydrogenation of unsaturated carboxylic acids to a higher ee than does BINAP. (Ref. 1,2)
2. The ruthenium-catalyzed hydrogenation of aryl propenoic acid to produce the drug Ibuprofen.
3. Rhodium-catalyzed asymmetric regioselective 1,4-addition of arylboronic acids to 3-substituted maleimides.



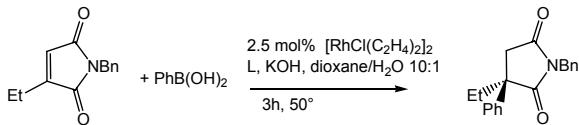
Tech. Note (1,2)
Ref. (1,2)

Products Referenced in the Article

PHOSPHORUS (Compounds)

15-2972
(cont.)
NEW→

(R)-(+)-2,2'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl
(R)-H₈-BINAP [139139-86-9]



Tech. Note (3)
Ref. (3)

References:
1. *J. Org. Chem.*, **1996**, *61*, 5510.
2. *Topics Organometal. Chem.* **2004**, *6*, 63 (review).
3. *J. Am. Chem. Soc.*, **2006**, *128*, 5628.

15-2973
NEW→

(S)-(-)-2,2'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (S)-H₈-BINAP [139139-93-8]

50mg
250mg

C₄₄H₄₀P₂; FW: 630.74; off-white pwdr.

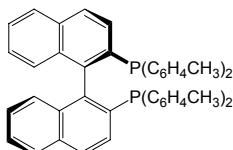
Note: Manufactured under license of Takasago patent.
Takasago BINAP Ligand Kit component see (page 53).

Technical Note:

- See 15-2972 (page 35).

15-0152

(R)-(+)-2,2'-Bis(di-p-tolyl-phosphino)-1,1'-binaphthyl, 98%
(R)-Tol-BINAP [99646-28-3]
C₄₈H₄₀P₂; FW: 678.79; white pwdr.;
[α]_D +156° (c 0.5, C₆H₆);
m.p. 255-257°

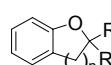
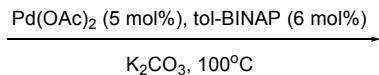
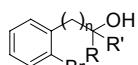


250mg
1g

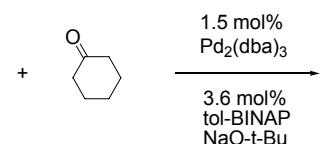
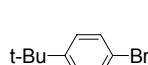
Note: Manufactured under license of
Takasago patent. Takasago BINAP
Ligand Kit component see (page 53).

Technical Notes:

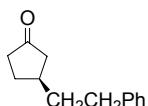
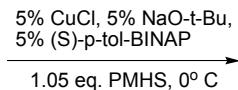
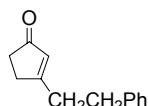
- See 15-0150 (page 33).
- Useful ligand for palladium-catalyzed carbon-oxygen bond formation.
- Ligand for palladium-catalyzed α-arylation of ketones.
- Ligand for Cu-catalyzed asymmetric conjugate reduction.
- Ligand for Cu-catalyzed asymmetric dienolate addition to aldehydes.
- Enantioselective conjugate reduction of lactones and lactams.
- Ligand used in the enantioselective cycloaddition of allenylsilanes with α-Imino esters.
- Catalytic Aldol reaction to ketones.
- Ligand with rhodium catalyses [2+2+2] cycloaddition reaction of alkenes and alkynes.



Tech. Note (2)
Ref. (1)



Tech. Note (3)
Ref. (2)



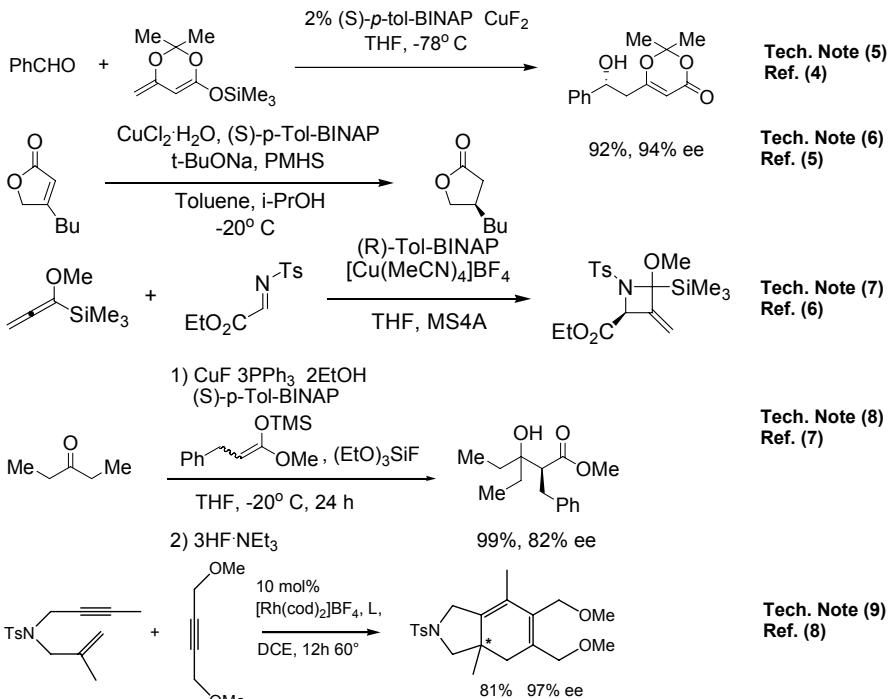
86%, 94% ee

Tech. Note (4)
Ref. (3)

Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0152 (R)-(+)-2,2'-Bis(di-p-tolyl-phosphino)-1,1'-binaphthyl, 98% (R)-Tol-BINAP [99646-28-3]
(cont.)



References:

1. J. Am. Chem. Soc., 1996, 118, 10333.
2. J. Am. Chem. Soc., 1997, 119, 11108.
3. J. Am. Chem. Soc., 2000, 122, 6797.
4. J. Am. Chem. Soc., 1998, 120, 837.
5. J. Am. Chem. Soc., 2003, 125, 11253.
6. Org. Lett., 2003, 5(20), 3691.
7. J. Am. Chem. Soc., 2003, 125, 5644.
8. Org. Lett., 2005, 7(22), 4955.

15-0153 (S)-(-)-2,2'-Bis(di-p-tolylphosphino)-1,1'-binaphthyl, 98% (S)-Tol-BINAP [100165-88-6]

C₄₈H₄₀P₂, FW: 678.79; white pwdr.; [α]_D -160° (c 0.5, C₆H₆); m.p. 255-257°

Note: Manufactured under license of Takasago patent.
Takasago BINAP Ligand Kit component see (page 53).

250mg

1g

Technical Notes:

1. See 15-0150 (page 33).
2. See 15-0152 (page 36).

Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0478

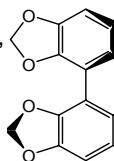
(R)-(+)-5,5'-Bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole, min. 98% (R)-DM-SEGPHOS

[850253-53-1]

C₄₆H₄₄O₄P₂; FW: 722.79; off-white to pale yellow pwdr.

Note: Manufactured under license of Takasago patent. Takasago

SEGPLOS Ligand Kit component see (page 52).



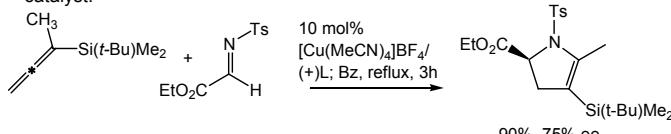
50mg

250mg

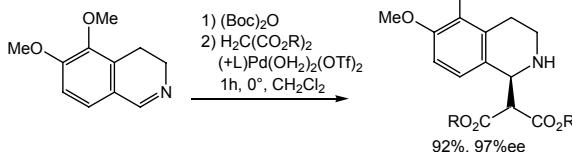
NEW→

Technical Notes:

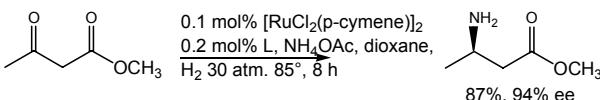
1. Biaryl bisphosphine ligand with narrow dihedral angle. The DM-SEGPHOS ligand, as the ruthenium complex, gives superior enantioselectivity and diastereoselectivity in the asymmetric hydrogenation of α -substituted- β -ketoesters. See 15-0066 (page 30).
2. Copper-catalyzed enantioselective [3 + 2] cycloaddition as a route to γ -amino ketones and 3-pyrrolidinones.
3. Palladium-catalyzed enantioselective addition of malonates to dihydroisoquinolines.
4. Ruthenium-catalyzed enantioselective synthesis of β amino acids by hydrogenation.
5. Ruthenium-catalyzed asymmetric hydrogenation of 3-quinuclidinone. See 44-0098 (page 42) for Ru catalyst.



Tech. Note (2)
Ref. (1)



Tech. Note (3)
Ref. (2)



Tech. Note (4)
Ref. (3)



Tech. Note (5)
Ref. (4)

References:

1. *Org. Lett.*, **2005**, 7, 1051.
2. *J. Am. Chem. Soc.*, **2006**, 128, 14010.
3. WIPO Pat. WO2005028419.
4. U.S. Pat. App. 2006047122.

15-0479

(S)-(-)-5,5'-Bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole, min. 98% (S)-DM-SEGPHOS [210169-57-6]

C₄₆H₄₄O₄P₂; FW: 722.79; off-white to pale yellow pwdr.

Note: Manufactured under license of Takasago patent.

Takasago SEGPLOS Ligand Kit component see (page 52).

50mg

250mg

Technical Note:

1. See 15-0478 (page 38).

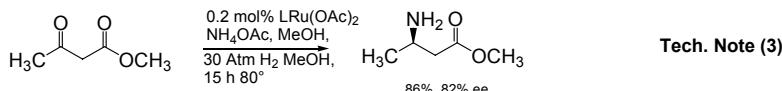
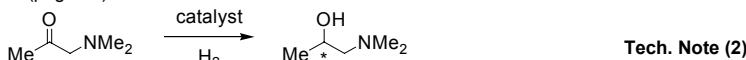
Products Referenced in the Article

PHOSPHORUS (Compounds)

15-0476	(R)-(+)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 98% (R)-3,5-xylyl-BINAP [137219-86-4] $C_{52}H_{48}P_2$; FW: 734.90; white to pale yellow xtl.; m.p. 203–206° Note: Manufactured under license of Takasago patent. Takasago BINAP Ligand Kit component see (page 53).	50mg 250mg

Technical Notes:

1. See 15-0150 (page 33).
2. Ligand used in the asymmetric hydrogenation of amino ketones.
3. Ligand used with ruthenium in the synthesis of β -amino acids by hydrogenation. See 44-0164 (page 45).



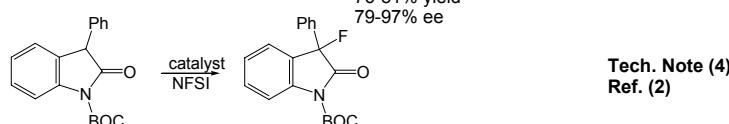
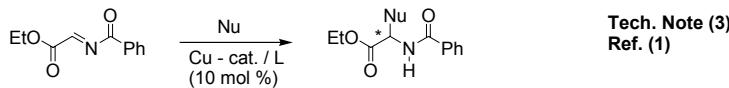
References:

1. *J. Am. Chem. Soc.*, **2000**, *122*, 6510.
2. World Patent WO2005/028419.

15-0477	(S)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 98% (S)-3,5-xylyl-BINAP [135139-00-3] $C_{52}H_{48}P_2$; FW: 734.90; white to pale yellow xtl.; m.p. 203–206° Note: Manufactured under license of Takasago patent. Takasago BINAP Ligand Kit component see (page 53).	50mg 250mg
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Technical Notes:

1. See 15-0150 (page 33).
2. See 15-0476 (page 39).
3. Ligand used in copper-catalyzed asymmetric Mannich-type reactions of N-acylimino esters.
4. Ligand used in the enantioselective fluorination of oxindoles.



References:

1. *J. Am. Chem. Soc.*, **2003**, *125*, 2507.
2. *J. Am. Chem. Soc.*, **2005**, *127*, 10164.

15-1005 NEW→	Di-t-butyl(2,2-diphenyl-1-methyl-1-cyclopropyl)phosphine Mo-Phos $C_{24}H_{33}P$; FW: 352.49; white pwdr. Note: Manufactured under license of Takasago patent.	250mg 1g

Products Referenced in the Article

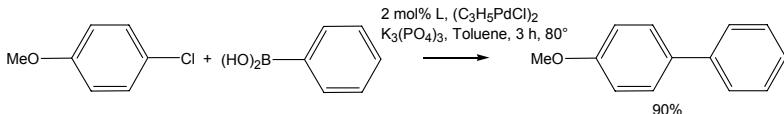
PHOSPHORUS (Compounds)

15-1005 Di-t-butyl(2,2-diphenyl-1-methyl-1-cyclopropyl)phosphine Mo-Phos
(cont.)

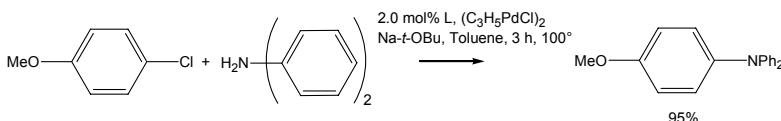
NEW→

Technical Notes:

1. Ligand effective for many classes of palladium-catalyzed coupling of aryl halides, including the Miyaura-Suzuki, Buchwald-Hartwig, Sonogashira, Heck, aryl etherification, and carbonylation reactions.
2. Ligand used in the palladium-catalyzed Suzuki-Miyaura coupling of aryl boronic acids.
3. Ligand employed in the palladium-catalyzed Buchwald-Hartwig aryl amination reaction.



Tech. Note (2)
Ref. (1)



Reference:

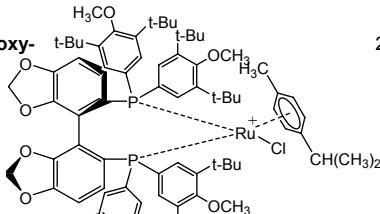
1. US Patent 7129367.

Tech. Note (2)
Ref. (1)

RUTHENIUM (Compounds)

44-0102 NEW→

Chloro{(*R*)-(-)-5,5'-bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole}(*p*-cymene)ruthenium(II) chloride
[$C_{84}H_{14}ClO_8P_2Ru$] $^+Cl^-$; FW: 1485.72; orange to brown pwdr. air sensitive
Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).



50mg
250mg

Technical Note:

1. See 15-0066 (page 30).

44-0103 NEW→

Chloro{(*S*)-(+)-5,5'-bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole}(*p*-cymene)ruthenium(II) chloride
[$C_{84}H_{14}ClO_8P_2Ru$] $^+Cl^-$; FW: 1485.72; orange to brown pwdr. air sensitive
Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).

50mg
250mg

Technical Note:

1. See 44-0102 (page 40).

Products Referenced in the Article

RUTHENIUM (Compounds)

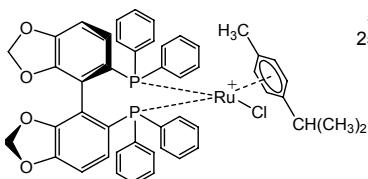
44-0096

NEW→

Chloro[(R)-(+)-5,5'-bis(di-phenylphosphino)-4,4'-bi-1,3-benzodioxole](p-cymene)ruthenium(II) chloride
[C₄₈H₄₂ClO₄P₂Ru]⁺Cl⁻; FW: 916.77; yellow pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.

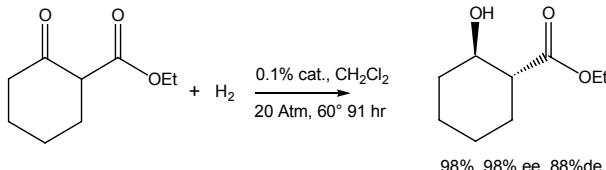
Takasago SEGPHOS Catalyst Kit component see (page 52).



50mg
250mg

Technical Notes:

- Highly active highly enantioselective catalyst for hydrogenation of functionalized ketones. Slightly higher temperature is necessary to activate the cymene complexes. See 15-0136 (page 32).
- Asymmetric hydrogenation of α -substituted- β -ketoesters accompanied by dynamic kinetic resolution.



**Tech. Note (1)
Ref. (1)**

Reference:

- U.S. Pat. 7038087.

44-0097

NEW→

Chloro[(S)-(-)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole](p-cymene)ruthenium(II) chloride
[C₄₈H₄₂ClO₄P₂Ru]⁺Cl⁻; FW: 916.77; yellow pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEGPHOS Catalyst Kit component see (page 52).

50mg
250mg

Technical Note:

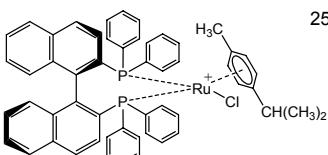
- See 44-0096 (page 41).

44-0084

NEW→

Chloro[(R)-(+)-2,2'-bis(di-phenylphosphino)-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride
[145926-28-9]
[C₅₄H₄₆ClP₂Ru]⁺Cl⁻; FW: 928.87; orange pwdr.
air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).



250mg
1g

Technical Note:

- See 15-0150 (page 33).

44-0086

NEW→

Chloro[(S)-(-)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride [130004-33-0]
[C₅₄H₄₆ClP₂Ru]⁺Cl⁻; FW: 928.87; orange pwdr.
air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).

250mg
1g

Technical Note:

- See 44-0084 (page 41).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0094 NEW→	Chloro[(R)-(-)2,2'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride [C ₅₄ H ₆₄ ClP ₂ Ru] ⁺ Cl ⁻ ; FW: 936.93; pale yellow pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).		50mg 250mg
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Technical Note:

- See 15-2972 (page 35).

44-0095 NEW→	Chloro[(S)-(-)2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride [C ₅₄ H ₆₄ ClP ₂ Ru] ⁺ Cl ⁻ ; FW: 936.93; pale yellow pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).		50mg 250mg
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Technical Note:

- See 44-0094 (page 42).

44-0088 NEW→	Chloro[(R)-(-)2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride [31614-43-2] [C ₅₈ H ₆₄ ClP ₂ Ru]; FW: 984.97; brown pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).		250mg 1g
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Technical Note:

- See 15-0152 (page 36).

44-0089 NEW→	Chloro[(S)-(-)2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl](p-cymene)ruthenium(II) chloride [228120-95-4] [C ₅₈ H ₆₄ ClP ₂ Ru] ⁺ Cl ⁻ ; FW: 984.97; brown pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).		250mg 1g
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Technical Note:

- See 44-0088 (page 42).

44-0098 NEW→	Chloro[(R)-(-)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole](p-cymene)ruthenium(II) chloride [C ₅₆ H ₅₈ ClO ₄ P ₂ Ru] ⁺ Cl ⁻ ; FW: 1028.98; orange to brown pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).		50mg 250mg
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Technical Note:

- See 15-0478 (page 38).

44-0099 NEW→	Chloro[(S)-(-)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole](p-cymene)ruthenium(II) chloride [C ₅₆ H ₅₈ ClO ₄ P ₂ Ru] ⁺ Cl ⁻ ; FW: 1028.98; orange to brown pwdr. <i>air sensitive</i> Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).		50mg 250mg
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Technical Note:

- See 44-0098 (page 42).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0092

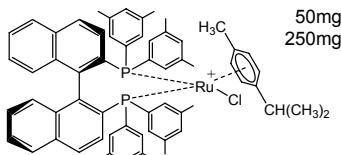
NEW→

Chloro{(*R*)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}(*p*-cymene)ruthenium(II) chloride

[C₆₂H₆₂ClP₂Ru]⁺Cl⁻; FW: 1041.08; orange to brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).



50mg

250mg

Technical Note:

- See 15-0476 (page 39).

44-0093

NEW→

Chloro{(*S*)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}(*p*-cymene)ruthenium(II) chloride

[C₆₂H₆₂ClP₂Ru]⁺Cl⁻; FW: 1041.08; orange to brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Cymene Catalyst Kit component see (page 53).

50mg

250mg

Technical Note:

- See 44-0092 (page 43).

44-0168

NEW→

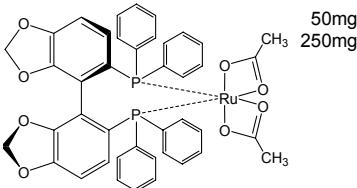
Diacetato{(*R*)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole}ruthenium(II)

C₄₉H₃₄O₈P₂Ru; FW: 829.73

dark yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).

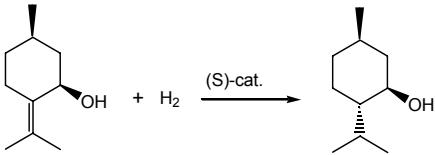


50mg

250mg

Technical Notes:

- Highly active highly enantioselective catalyst for hydrogenation of functionalized ketones. The acetate salts are frequently used for hydrogenation of allyl alcohols, unsaturated carboxylic acids and reductive amination. See 15-0136 (page 31).
- Asymmetric hydrogenation of substituted allyl alcohols.



33%, 81% ee

Reference:

- U.S. Pat. 6342644.

44-0169

NEW→

Diacetato{(*S*)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole}ruthenium(II) [373650-12-5]

C₄₉H₃₄O₈P₂Ru; FW: 829.73; dark yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).

50mg

250mg

Technical Note:

- See 44-0168 (page 43).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0152

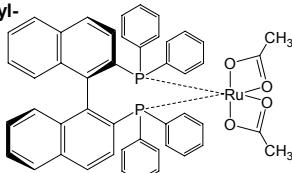
NEW→

Diacetato[(R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) [325146-81-4]

C₄₈H₃₈O₄P₂Ru; FW: 841.83; pale yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).



250mg

1g

Technical Note:

- See 15-0150 (page 33).

44-0153

NEW→

Diacetato[(S)-(--)2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) [261948-85-0]

C₄₈H₃₈O₄P₂Ru; FW: 841.83; pale yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).

250mg

1g

Technical Note:

- See 44-0152 (page 44).

44-0166

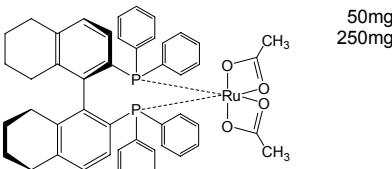
NEW→

Diacetato[(R)-(+)-2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]ruthenium(II) [374067-51-3]

C₄₈H₄₆O₄P₂Ru; FW: 849.89; pale orange pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).



50mg

250mg

Technical Note:

- See 15-2972 (page 35).

44-0167

NEW→

Diacetato[(S)-(--)2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]ruthenium(II) [142962-95-6]

C₄₈H₄₆O₄P₂Ru; FW: 849.89; pale orange pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).

50mg

250mg

Technical Note:

- See 44-0166 (page 44).

44-0162

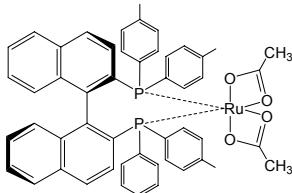
NEW→

Diacetato[(R)-(+)-2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl]ruthenium(II) [116128-29-1]

C₅₂H₄₆O₄P₂Ru; FW: 897.94; brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).



250mg

1g

Technical Note:

- See 15-0152 (page 36).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0163 NEW→	Diacetato[(S)-(-)2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl]ruthenium(II) [106681-15-6] $C_{52}H_{46}O_4P_2Ru$; FW: 897.94; brown pwdr. air sensitive	250mg 1g
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Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).

Technical Note:

- See 44-0162 (page 44).

44-0174 NEW→	Diacetato{(<i>R</i>)-(+)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole}ruthenium(II) $C_{50}H_{50}O_8P_2Ru$; FW: 941.95; orange pwdr. air sensitive		50mg 250mg
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Technical Note:

- See 15-0478 (page 38).

44-0176 NEW→	Diacetato{(S)-(-)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole}ruthenium(II) $C_{50}H_{50}O_8P_2Ru$; FW: 941.95; dark brown pwdr. air sensitive	50mg 250mg
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Note: Manufactured under license of Takasago patent. Takasago SEGPHOS Catalyst Kit component see (page 52).

Technical Note:

- See 44-0174 (page 45).

44-0164 NEW→	Diacetato{(<i>R</i>)-(+)2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}ruthenium(II) [374067-50-2] $C_{56}H_{54}O_4P_2Ru$; FW: 954.04; dark brown pwdr. air sensitive		50mg 250mg
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Technical Note:

- See 15-0476 (page 39).

44-0165 NEW→	Diacetato{(S)-(-)2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}ruthenium(II) [374067-49-9] $C_{56}H_{54}O_4P_2Ru$; FW: 954.04; dark brown pwdr. air sensitive	50mg 250mg
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Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Acetate Catalyst Kit component see (page 54).

Technical Note:

- See 44-0164 (page 45).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0214

NEW→

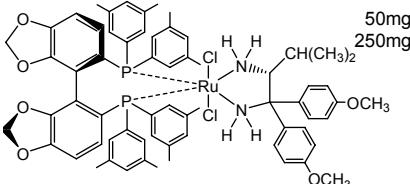
Dichloro[*(R*)-(+)-5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole][(2*R*)-(-)-1,1-bis(4-methoxyphenyl)-3-methyl-1,2-butanediamine]ruthenium(II)

C₆₅H₇₀Cl₂N₂O₂P₂Ru; FW: 1145.19; yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEPHOS Catalyst Kit component see (page 52).



50mg

250mg

44-0215

NEW→

Dichloro[*(S*)-(-)-5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole][(2*S*)-(+)-1,1-bis(4-methoxyphenyl)-3-methyl-1,2-butanediamine]ruthenium(II)

C₆₅H₇₀Cl₂N₂O₂P₂Ru; FW: 1145.19; yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEPHOS Catalyst Kit component see (page 52).

Technical Note:

- See 44-0214 (page 38).

44-0228

NEW→

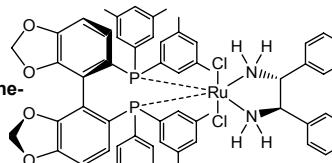
Dichloro[*(R*)-(+)-5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole][(1*R*,2*R*)-(+)-1,2-diphenylethylenediamine]ruthenium(II)

C₆₀H₅₈Cl₂N₂O₂P₂Ru; FW: 1073.04; yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEPHOS Catalyst Kit component see (page 52).



50mg

250mg

Technical Note:

- See 15-0478 (page 38).

44-0229

NEW→

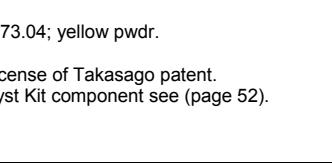
Dichloro[*(S*)-(-)-5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole][(1*S*,2*S*)-(-)-1,2-diphenylethylenediamine]ruthenium(II)

C₆₀H₅₈Cl₂N₂O₂P₂Ru; FW: 1073.04; yellow pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEPHOS Catalyst Kit component see (page 52).



50mg

250mg

Technical Note:

- See 44-0228 (page 46).

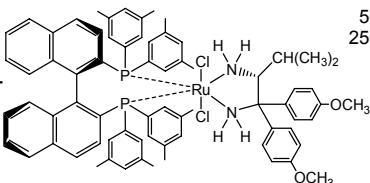
Products Referenced in the Article

RUTHENIUM (Compounds)

44-0212

NEW→

Dichloro{[(R)-(+)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl][(2R)-(-)-1,1-bis(4-methoxyphenyl)-3-methyl-1,2-butanediamine]ruthenium(II)} [220114-32-9]
 $C_{71}H_{74}Cl_2N_2O_2P_2Ru$; FW: 1221.28; orange pwdr.
air sensitive

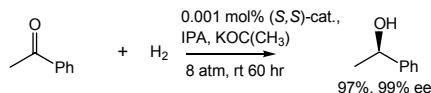


50mg
250mg

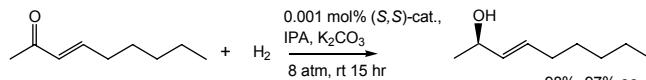
Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Diammine Catalyst Kit component see (page 54).

Technical Notes:

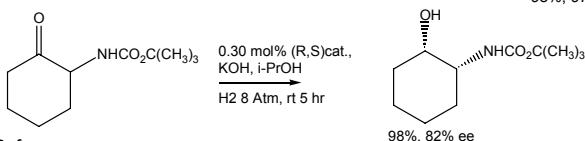
- Highly active catalyst for hydrogenation of simple ketones giving high enantioselectivity when sterically unsymmetrical ketones such as acetophenone, heteroaryl ketones, benzophenones, cyclopropyl ketones, and cyclohexyl ketones are substrates. Ee's are enhanced with XylBINAP relative to BINAP. The otherwise poorly bonded ketone is held in the transition state by hydrogen bonding to the protic bidentate amine.
- Carbonyl groups are selectively reduced even when olefins exist in the same molecule.
- In the presence of strong base, and catalyst, simple ketones, having substituents at the α -position, may be induced to undergo dynamic kinetic resolution during their hydrogenation to produce two chiral carbon centers in high yield.



Tech. Note (1)
Ref. (1-4)



Tech. Note (2)
Ref. (4)



Tech. Note (3)
Ref. (5)

References:

- Angew Chem. Int. Ed.*, **2001**, *40*, 40. (review article)
- Org. Lett.*, **2000**, *2*, 1749.
- Org. Lett.*, **2000**, *2*, 659.
- J. Am. Chem. Soc.*, **1998**, *120*, 13529.
- J. Am. Chem. Soc.*, **2000**, *122*, 6510.

44-0213

NEW→

Dichloro{[(S)-(-)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl][(2S)-(+)-1,1-bis(4-methoxyphenyl)-3-methyl-1,2-butanediamine]ruthenium(II)} [220114-01-2]
 $C_{71}H_{74}Cl_2N_2O_2P_2Ru$; FW: 1221.28; orange pwdr.
air sensitive

50mg
250mg

Note: Manufactured under license of Takasago patent.
Takasago BINAP Ru Diammine Catalyst Kit component see (page 54).

Technical Note:

- See 44-0212 (page 47).

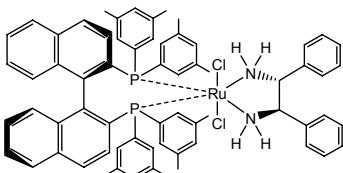
Products Referenced in the Article

RUTHENIUM (Compounds)

44-0226

NEW→

Dichloro{(*R*)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}{[(1*S*,2*R*)-1,2-diphenylethylenediamine]ruthenium(II)} [220114-38-5]
 $C_{66}H_{64}Cl_2N_2P_2Ru$; FW: 1119.15; yellow pwdr.
air sensitive



50mg

250mg

Technical Note:

- See 44-0220 (Visit www.strem.com for details).

44-0224

NEW→

Dichloro{(*S*)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}{[(1*S*,2*S*)-1,2-diphenylethylenediamine]ruthenium(II)} [220114-03-4]
 $C_{66}H_{64}Cl_2N_2P_2Ru$; FW: 1119.15; yellow pwdr.
air sensitive

50mg

250mg

Note: Manufactured under license of Takasago patent. Takasago BINAP Ru Diammine Catalyst Kit component see (page 54).

Technical Note:

- See 44-0226 (page 48).

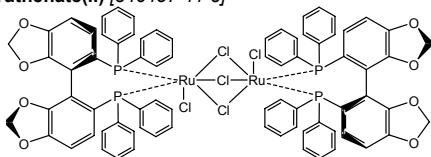
44-0518

NEW→

Dimethylammonium dichlorotri(μ -chloro)bis{[(*R*)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole]diruthenate(II)} [346457-41-8]

50mg

250mg



$(CH_3)_2NH_2^+[C_{76}H_{48}Cl_5O_8P_4Ru_2]$; FW: 1637.57;
 light brown pwdr.

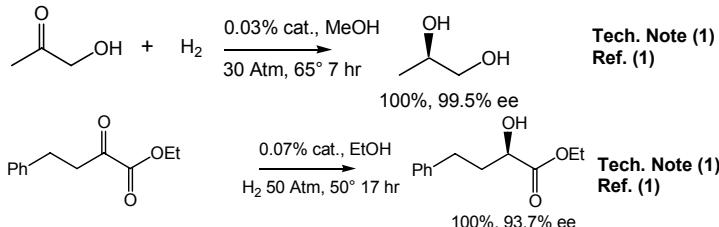
air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEGPHOS Catalyst Kit component see (page 52).

Technical Notes:

- Highly enantioselective, highly active catalyst for hydrogenation of functionalized ketones. The chlororuthenate salts show catalytic activity at relatively low temperature. See 15-0136 (page 31).
- Catalyst for enantioselective hydrogenation of enamines.

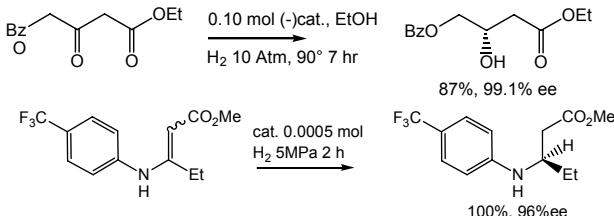


Products Referenced in the Article

RUTHENIUM (Compounds)

44-0518 Dimethylammonium dichlorotri(μ -chloro)bis[(R)-(+)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole]diruthenate(II)
 (cont.) [346457-41-8]

NEW →



Tech. Note (1)
 Ref. (2)

Tech. Note (2)
 Ref. (3)

References:

1. *Adv. Synth. Catal.*, **2001**, 343, 264.
2. U.S. Pat. 6608214.
3. U.S. Pat. App. 2006122225.

44-0519 Dimethylammonium dichlorotri(μ -chloro)bis[(S)-(−)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole]diruthenate(II) [488809-34-3]
 (CH₃)₂NH₂⁺[C₇₆H₆₄Cl₅O₈P₄Ru₂][−]; light brown pwdr.
air sensitive

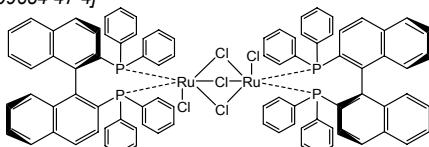
Note: Manufactured under license of Takasago patent.
 Takasago SEGPHTOS Catalyst Kit component see (page 52).

50mg
 250mg

Technical Note:

1. See 44-0518 (page 48).

44-0510 Dimethylammonium dichlorotri(μ -chloro)bis[(R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]diruthenate(II)
 [199684-47-4]



250mg
 1g

(CH₃)₂NH₂⁺[C₈₈H₆₄Cl₅P₄Ru₂][−]; FW: 1669.83; orange pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.
 Takasago BINAP Ru Dimer Catalyst Kit component see (page 53).

Technical Note:

1. See 15-0150 (page 33).

44-0511 Dimethylammonium dichlorotri(μ -chloro)bis[(S)-(−)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]diruthenate(II)
 [199541-17-8]

(CH₃)₂NH₂⁺[C₈₈H₆₄Cl₅P₄Ru₂][−]; FW: 1669.83; orange pwdr.
air sensitive

250mg
 1g

Note: Manufactured under license of Takasago patent.
 Takasago BINAP Ru Dimer Catalyst Kit component see (page 53).

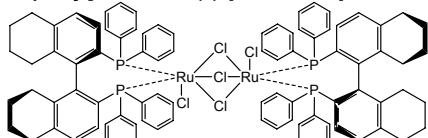
Technical Note:

1. See 44-0510 (page 49).

Products Referenced in the Article

RUTHENIUM (Compounds)

44-0516 NEW→	Dimethylammonium dichlorotri(μ -chloro)bis[(R)-(+)-2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]diruthenate(II) [204933-84-6]	50mg 250mg
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(CH₃)₂NH₂⁺[C₈₈H₈₀Cl₅P₄Ru₂]⁻; FW: 1685.96; red-brown pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.
Takasago BINAP Ru Dimer Catalyst Kit component
see (page 53).

Technical Note:

- See 15-2972 (page 35).

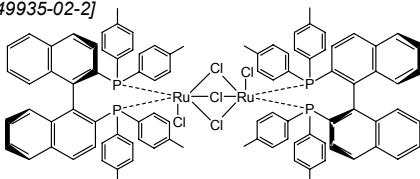
44-0517 NEW→	Dimethylammonium dichlorotri(μ -chloro)bis[(S)-(−)-2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]diruthenate(II) (CH ₃) ₂ NH ₂ ⁺ [C ₈₈ H ₈₀ Cl ₅ P ₄ Ru ₂] ⁻ ; FW: 1685.96; red-brown pwdr. air sensitive	50mg 250mg
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Note: Manufactured under license of Takasago patent.
Takasago BINAP Ru Dimer Catalyst Kit component
see (page 53).

Technical Note:

- See 44-0516 (page 50).

44-0512 NEW→	Dimethylammonium dichlorotri(μ -chloro)bis[(R)-(+)-2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl]diruthenate(II) [749935-02-2]	250mg 1g
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(CH₃)₂NH₂⁺[C₉₆H₈₀Cl₅P₄Ru₂]⁻; FW: 1782.05; brown pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.
Takasago BINAP Ru Dimer Catalyst Kit component
see (page 53).

Technical Note:

- See 15-0152 (page 36).

44-0513 NEW→	Dimethylammonium dichlorotri(μ -chloro)bis[(S)-(−)-2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl]diruthenate(II) [309735-86-2]	250mg 1g
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(CH₃)₂NH₂⁺[C₉₆H₈₀Cl₅P₄Ru₂]⁻; FW: 1782.05; brown pwdr.
air sensitive

Note: Manufactured under license of Takasago patent.
Takasago BINAP Ru Dimer Catalyst Kit component see
(page 53).

Technical Note:

- See 44-0512 (page 50).

Products Referenced in the Article

RUTHENIUM (Compounds)

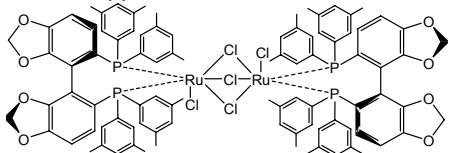
44-0520

NEW→

Dimethylammonium dichlorotri(μ -chloro)bis{(*R*)-(+)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole}diruthenate(II)

50mg

250mg



(CH₃)₂NH₂⁺[C₉₂H₈₈Cl₅O₈P₄Ru₂]⁻; FW: 1870.06;

light brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEGPHOS Catalyst Kit component see (page 52).

Technical Note:

- See 15-0478 (page 38).

44-0521

NEW→

Dimethylammonium dichlorotri(μ -chloro)bis{(*S*)-(--)5,5'-bis[di(3,5-xylyl)phosphino]-4,4'-bi-1,3-benzodioxole}diruthenate(II)

50mg

250mg

(CH₃)₂NH₂⁺[C₉₂H₈₈Cl₅O₈P₄Ru₂]⁻; FW: 1870.06; light brown

pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago SEGPHOS Catalyst Kit component see (page 52).

Technical Note:

- See 44-0520 (page 51).

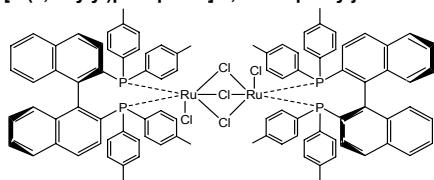
44-0514

NEW→

Dimethylammonium dichlorotri(μ -chloro)bis{(*R*)-(+)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}diruthenate(II)

50mg

250mg



(CH₃)₂NH₂⁺[C₁₀₄H₉₆Cl₅P₄Ru₂]⁻; FW: 1894.26; red-brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

Takasago BINAP Ru Dimer Catalyst Kit component see (page 53).

Technical Note:

- See 15-0476 (page 39).

44-0515

NEW→

Dimethylammonium dichlorotri(μ -chloro)bis{(*S*)-(--)2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl}diruthenate(II)

50mg

250mg

(CH₃)₂NH₂⁺[C₁₀₄H₉₆Cl₅P₄Ru₂]⁻; FW: 1894.26; red-brown pwdr.

air sensitive

Note: Manufactured under license of Takasago patent.

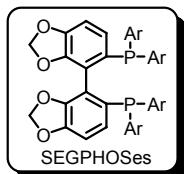
Takasago BINAP Ru Dimer Catalyst Kit component see (page 53).

Technical Note:

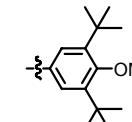
- See 44-0514 (page 51).

Kits Containing Products Referenced in the Article

SEPHOS CATALYST and LIGAND KITS manufactured under license of Takasago patent.



Ar;



SEPHOS DM-SEPHOS DTBM-SEPHOS

96-6900

Takasago SEPHOS Ligand Kit

kit contains 50mg unit of the 6 R- and S- items listed below

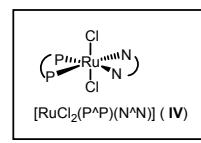
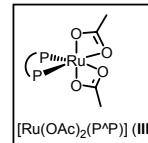
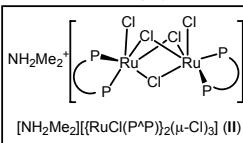
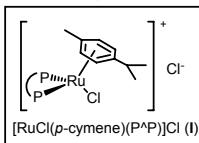
Individual items available for sale

	R-	CAS#	S-	CAS#	Size	Size
SEPHOS	15-0136	244261-66-3	15-0137	210169-54-3	50mg	250mg
DM-SEPHOS	15-0478	850253-53-1	15-0479	210169-57-6	50mg	250mg
DTBM-SEPHOS	15-0066	566940-03-2	15-0067	210169-40-7	50mg	250mg

96-6901

Takasago SEPHOS Ru Catalyst Kit

Metal Catalysts in the kit are the following type



kit contains 50mg unit of the 18 R- and S- items listed below

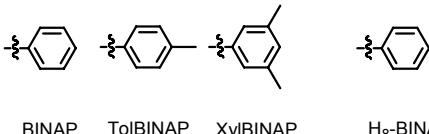
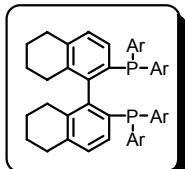
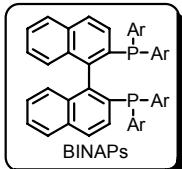
Individual items available for sale

Metal Catalyst = RuCl[(P-cymene)(L)]Cl

Ligand L=	R-	CAS#	S-	CAS#	Size	Size
SEPHOS	44-0096	None	44-0097	None	50mg	250mg
DM-SEPHOS	44-0098	None	44-0099	None	50mg	250mg
DTBM-SEPHOS	44-0102	None	44-0103	None	50mg	250mg
{[RuCl(L)}₂(u-Cl)₃][NH₂Me₂]						
SEPHOS	44-0518	346457-41-8	44-0519	488809-34-3	50mg	250mg
DM-SEPHOS	44-0520	None	44-0521	None	50mg	250mg
Ru(OAc)₂(L)						
SEPHOS	44-0168	None	44-0169	373650-12-5	50mg	250mg
DM-SEPHOS	44-0174	None	44-0176	None	50mg	250mg
Diamine System						
RuCl ₂ [(DM-SEPHOS) (DAIPEN)]	44-0214	None	44-0215	None	50mg	250mg
RuCl ₂ [(DM-SEPHOS) (DPEN)]	44-0228	None	44-0229	None	50mg	250mg

Kits Containing Products Referenced in the Article

BINAP CATALYST and LIGAND KITS manufactured under license of Takasago Patent.



96-6950 Takasago BINAP Ligand Kit

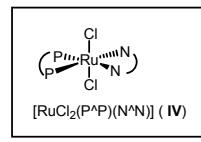
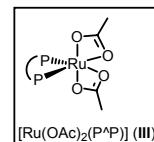
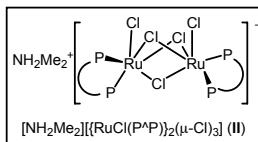
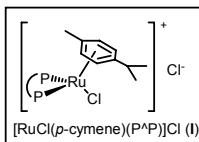
kit contains smallest unit of the 8 R- and S- items listed below

Individual items available for sale

R-	CAS#	S-	CAS#	Size	Size
BINAP*	15-0150	76189-55-4	15-0151	76189-56-5	250mg 1g
TolBINAP	15-0152	99646-28-3	15-0153	100165-88-6	250mg 1g
XylBINAP	15-0476	137219-86-4	15-0477	135139-00-3	50mg 250mg
H ₈ -BINAP	15-2972	139139-86-9	15-2973	139139-93-8	50mg 250mg

*5g size also available

BINAP - Metal Catalyst Kits are of the following type:



96-6951 Takasago BINAP Ru Cymene Catalyst Kit

kit contains smallest unit of the 8 R- and S- items listed below

Individual items available for sale

RuCl[(P-cymene)(L)]Cl

Ligand L=	R-	CAS#	S-	CAS#	Size	Size
BINAP	44-0084	145926-28-9	44-0086	130004-33-0	250mg	1g
TolBINAP	44-0088	131614-43-2	44-0089	228120-95-4	250mg	1g
XylBINAP	44-0092	None	44-0093	None	50mg	250mg
H ₈ -BINAP	44-0094	None	44-0095	None	50mg	250mg

96-6952 Takasago BINAP Ru Dimer Catalyst Kit

kit contains smallest unit of the 8 R- and S- items listed below

Individual items available for sale

[{RuCl(L)}₂(μ-Cl)₃][NH₂Me₂]

Ligand L=	R-	CAS#	S-	CAS#	Size	Size
BINAP	44-0510	199684-47-4	44-0511	199541-17-8	250mg	1g
TolBINAP	44-0512	749935-02-2	44-0513	309735-86-2	250mg	1g
XylBINAP	44-0514	None	44-0515	None	50mg	250mg
H ₈ -BINAP	44-0516	204933-84-6	44-0517	None	50mg	250mg

Kits Containing Products Referenced in the Article

96-6953 Takasago BINAP Ru Acetate Catalyst Kit

kit contains smallest unit of the 8 R- and S- items listed below

Individual items available for sale

Ru(OAc)₂(L)

Ligand L=	R-	CAS#	S-	CAS#	Size	Size
BINAP	44-0152	325146-81-4	44-0153	261948-85-0	250mg	1g
TolBINAP	44-0162	116128-29-1	44-0163	106681-15-6	250mg	1g
XylBINAP	44-0164	374067-50-2	44-0165	374067-49-9	50mg	250mg
H8-BINAP	44-0166	374067-51-3	44-0167	142962-95-6	50mg	250mg

96-6954 Takasago BINAP Ru Diammine Catalyst Kit

kit contains smallest unit of the 4 R- and S- items listed below

Individual items available for sale

Ru(P-P)(N-N)Cl₂

	R-	CAS#	S-	CAS#	Size	Size
RuCl ₂ [(XylBINAP)(DAIPEN)]	44-0212	220114-32-9	44-0213	220114-01-2	50mg	250mg
RuCl ₂ [(XylBINAP)(DPEN)]	44-0226	220114-38-5	44-0224	220114-03-4	50mg	250mg

KITS Introduced Since Catalog 21

96-5900

Chiral Quest Catalyst and Ligand Toolbox Kit for Asymmetric Hydrogenation

1kit



Contains 100mg unit of each of the following:

- 15-0103 (R,R)-(-)-1,2-Bis((R)-4,5-dihydro-3H-binaphtho[1,2-c:2',1'-e]phosphepino}benzene, 97% (R)-BINAPHANE
- 15-0106 (S,S)-(+)-1,2-Bis((S)-4,5-dihydro-3H-binaphtho[1,2-c:2',1'-e]phosphepino}benzene, 97% (S)-BINAPHANE
- 15-0175 R-(+)-1,13-Bis(diphenylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin, 97% (R)-C3-TUNEPHOS
- 15-0176 (S)-(+)-1,13-Bis(diphenylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin, 95% (S)-C3-TUNEPHOS
- 15-1015 (1S,1'S,2R,2'R)-(+)-1,1'-Di-t-butyl-[2,2']-diphospholane, 97% (S,S,R,R)-TANGPHOS
- 15-1053 (3S,3'S,4S,4'S,11B,11b'S)-(+)-4,4'-Di-t-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho[2,1-c:1',2'-e]phosphahepin, 97% (S)-BINAPINE
- 15-1060 (1R,1'R,2S,2'S)-(+)-2,2'-Di-t-butyl-2,3,2',3'-tetrahydro-1,1'-bi-1H-isophosphindole, min. 98% (R,R,S,S)-DUANPHOS
- 45-0653 (1S,1'S,2R,2'R)-(+)-1,1'-Di-t-butyl-[2,2']-diphospholane(1,5-cyclooctadiene)rhodium (I) tetrafluoroborate, min. 98% (S,S,R,R)-TANGPHOS-Rh
- 45-0663 (1R,1'R,2S,2'S)-(+)-2,2'-Di-t-butyl-2,3,2',3'-tetrahydro-1,1'-bi-1H-isophosphindole (1,5-cyclooctadiene)rhodium (I) tetrafluoroborate, min. 98% (R,R,S,S)-DUANPHOS-Rh
- 45-0795 (R,R)-(-)-1,2-Bis((R)-4,5-dihydro-3H-binaphtho[1,2-c:2',1'-e]phosphepino}benzene (1,5-cyclooctadiene)rhodium (I) tetrafluoroborate (R)-BINAPHANE-Rh
- 45-0657 (3S,3'S,4S,4'S,11B,11b'S)-(+)-4,4'-Di-t-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho[2,1-c:1',2'-e]phosphahepin(1,5-cyclooctadiene)rhodium (I) tetrafluoroborate (S)-BINAPINE-Rh
- 44-0109 Chloro{((R)-(-)-1,13-bis(diphenylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin} (p-cymene)ruthenium (II) chloride (R)-C3-TUNEPHOS-Ru

Note: For patent information visit www.strem.com.

Sold in collaboration with Chiral Quest for research purposes only.

Items available for individual sale. Visit our searchable catalog at www.strem.com for details.

KITS Introduced Since Catalog 21

96-1525 Long-Chain n-Alkylphosphonic Acid Kit

1 kit

NEW→

Contains 1g unit of each of the items listed below:

15-0958	n-Decylphosphonic acid, min. 97%	See page 68
15-1835	n-Dodecylphosphonic acid, min. 97%	See page 70
15-2400	n-Hexadecylphosphonic acid, min. 97%	See page 70
15-2410	n-Hexylphosphonic acid, min. 97%	See page 70
15-3510	n-Octadecylphosphonic acid, min. 97%	See page 70
15-3520	n-Octylphosphonic acid, min. 97%	See page 70
15-5145	n-Tetradecylphosphonic acid, min. 97%	See page 70

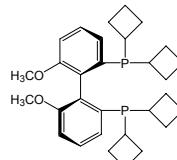
96-3655 Solvias (R)-MeO-BIPHEP Ligand Kit

NEW→

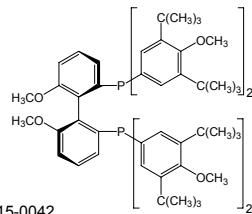
1 kit

Sold in collaboration with Solvias for research purposes only.

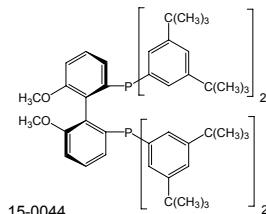
Contains 100mg unit of each of the items listed below:



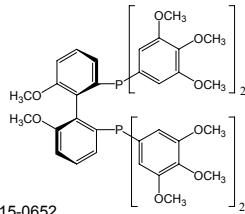
15-9570



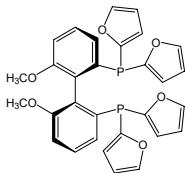
15-0042



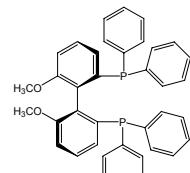
15-0044



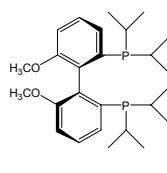
15-0652



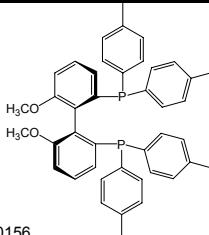
15-0112



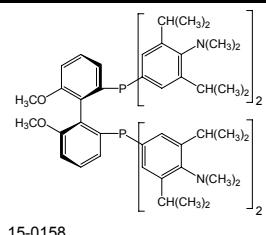
15-0178



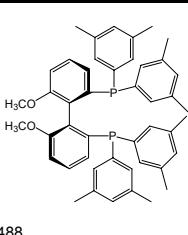
15-0654



15-0156



15-0158



15-0488

See next page for product description listing.

Kits Introduced Since Catalog 21

96-3655 (cont.)	Solvias (R)-MeO-BIPHEP Ligand Kit	1 kit
NEW→		
Sold in collaboration with Solvias for research purposes only.		
Contains 100mg unit of each of the items listed below:		
15-9570	(R)-(+)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 62
15-0042	(R)-(-)-2,2'-Bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-6,6'- dimethoxy-1,1'-biphenyl, min. 97%	See page 62
15-0044	(R)-(+)-2,2'-Bis[di(3,5-di-t-butylphenyl)phosphino]-6,6'-dimethoxy- 1,1'-biphenyl, min. 97%	See page 63
15-0652	(R)-(-)-2,2'-Bis[di(3,5-di-i-propyl-4-dimethylaminophenyl) phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 64
15-0112	(R)-(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 64
15-0178	(R)-(+)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% (R)-MeO-BIPHEP	See page 65
15-0654	(R)-(+)-2,2'-Bis(di-i-propylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 66
15-0156	(R)-(+)-2,2'-Bis(di-p-tolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 67
15-0158	(R)-(+)-2,2'-Bis[di(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy- 1,1'-biphenyl, min. 97%	See page 67
15-0488	(R)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 67

96-3656	Solvias (S)-MeO-BIPHEP Ligand Kit	1 kit
NEW→		
Sold in collaboration with Solvias for research purposes only.		
Contains 100mg unit of each of the items listed below:		
15-9571	(S)-(-)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 62
15-0043	(S)-(+)-2,2'-Bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-6,6'- dimethoxy-1,1'-biphenyl, min. 97%	See page 63
15-0045	S)-(-)-2,2'-Bis[di(3,5-di-t-butylphenyl)phosphino]-6,6'-dimethoxy-1,1'- biphenyl, min. 97%	See page 63
15-0653	(S)-(+)-2,2'-Bis[di(3,5-di-i-propyl-4-dimethylaminophenyl)phosphino]- 6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 64
15-0113	(S)-(-)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 64
15-0179	(S)-(-)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% (S)-MeO-BIPHEP	See page 66
15-0655	(S)-(-)-2,2'-Bis(di-i-propylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 66
15-0157	(S)-(-)-2,2'-Bis(di-p-tolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 67
15-0159	(S)-(-)-2,2'-Bis[di(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy- 1,1'-biphenyl, min. 97%	See page 67
15-0489	(S)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97%	See page 67

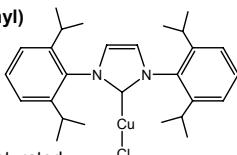
New Products Introduced Since Catalog 21

COPPER (Compounds)

29-4050

NEW→

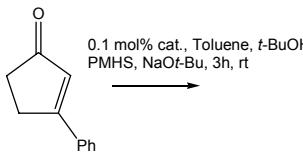
**Chloro[1,3-bis(2,6-di-i-propylphenyl)imidazol-2-ylidene]copper(I), 98% [578743-87-0]
C₂₇H₃₆ClCuN₂; FW: 487.59
air sensitive**



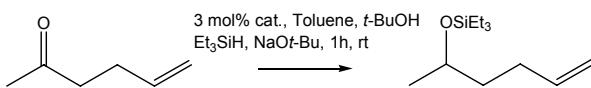
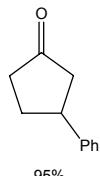
500mg
2g

Technical Notes:

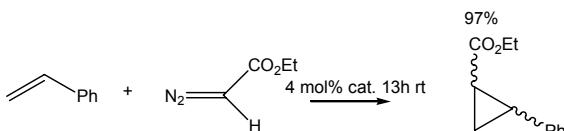
- Reduction of olefin in a conjugated α,β -unsaturated ketone.
- Reduction of carbonyl in an unconjugated unsaturated ketone.
- Catalysis of ethyldiazaoacetate carbene transfer reactions without diazo coupling side reactions.
- Catalyst for the aziridination of olefins.
- Mild catalyst, superior to CuCl, in the methylenetriphenylphosphorane methyleneation of aldehydes and ketones.



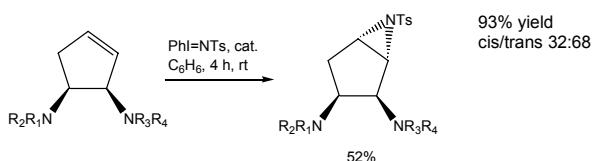
Tech. Note (1)
Ref. (1)



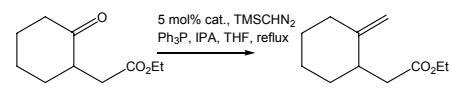
Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)



Tech. Note (4)
Ref. (4)



Tech. Note (5)
Ref. (5)

References:

- Org. Lett., 2003, 5, 2417.
- Organometallics, 2004, 23, 1157.
- J. Am. Chem. Soc., 2004, 126, 10846.
- J. Am. Chem. Soc., 2006, 128, 6054.
- J. Org. Chem., 2007, 72, 144.

GOLD (Compounds)

79-0740

NEW→

**Chlorotri-*t*-butylphosphinegold(I), 99% [69550-28-3]
AuClP(C₄H₉)₃; FW: 434.74; white microcryst.**

250mg
1g

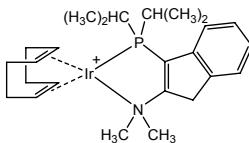
New Products Introduced Since Catalog 21

IRIDIUM (Compounds)

77-1115

NEW → 3-Di-i-propylphosphino-2-(N,N-dimethylamino)-1H-indene(1,5-cyclooctadiene) iridium(I) hexafluorophosphate, min. 98% [870077-94-4] $[\text{IrC}_{25}\text{H}_{38}\text{NP}]^+\text{PF}_6^-$; FW: 720.73; orange pwdr.

Note: Sold under license from Dalhousie for research purposes only. Provisional US patents 60/778,368 and 60/778,358.



250mg
1g

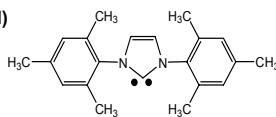
Technical Note:

- See 45-0197 (page 72).

NITROGEN (Compounds)

07-0600

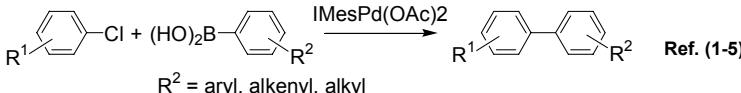
NEW → HAZ 1,3-Bis(2,4,6-trimethyl-phenyl)imidazol-2-ylidene, min. 98% [141556-42-5] $\text{C}_{21}\text{H}_{24}\text{N}_2$; FW: 304.43; white to off-white pwdr. air sensitive, moisture sensitive



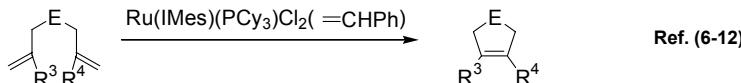
500mg
2g

Technical Notes:

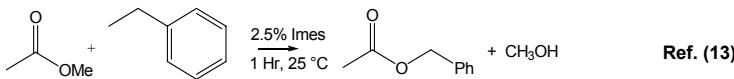
- Nucleophilic carbene that serves as a bulky, electron-rich "phosphine mimic" for metal-catalyzed reactions.
 - Palladium-catalyzed Suzuki-Miyaura cross-coupling of aryl chlorides.



- Ruthenium-carbene complexes serve as more reactive catalysts for ring-closing metathesis.



- Nucleophilic carbene that serves as a bulky, electron-rich organocatalyst.
 - Efficient Transesterification catalyst.



References:

- J. Org. Chem., **1999**, *64*, 3804.
- Org. Lett., **2005**, *7*, 1829.
- Ann. Rptis. Prog. Chem. B. **2006**, *102*, 168.
- Organometallics, **2002**, *21*, 5470.
- J. Organometal. Chem., **2002**, *653*, 69.
- See 44-7775 (Visit www.strem.com for details).
- Organometallics **1999**, *121*, 2674.
- Org. Lett., **2000**, *2*, 1517.
- J. Org. Chem., **2000**, *65*, 2204.
- Organometallics, **1999**, *18*, 3760.
- Angew. Chem. Int. Ed., **2002**, *41*, 1290.
- J. Am. Chem. Soc., **1999**, *121*, 2674.
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New Products Introduced Since Catalog 21

NITROGEN (Compounds)

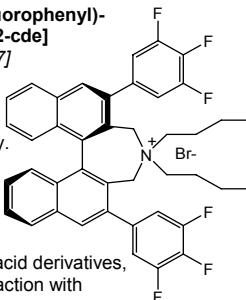
07-0380

NEW → (R)-4,4-Dibutyl-2,6-bis(3,4,5-trifluorophenyl)-4,5-dihydro-3H-dinaphtho[7,6,1,2-cde]azepinium bromide [887938-70-7]

[C₄₂H₃₆F₆N]⁺Br⁻; FW: 748.64;

brown pwdr.

Note: Sold in collaboration with Nagase for research purposes only. US Patent 6,340,753.

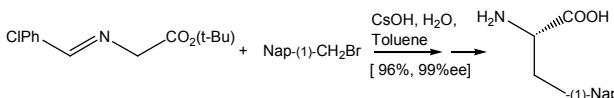


50mg

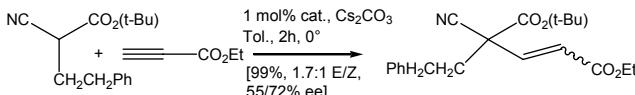
250mg

Technical Notes:

1. Second Generation Maruoka chiral phase transfer catalyst, for enantioselective alkylation of α -amino acid derivatives, that is easily recovered for recycle by extraction with fluorous solvent.
2. Catalyst for asymmetric conjugate addition of α -substituted- α -cyanoacetates to α,β -unsaturated acetylenic esters.



**Tech. Note (2)
Ref. (2)**



**Tech. Note (2)
Ref. (2)**

References:

1. *Tetrahedron Asymm.*, **2006**, *17*, 603.
2. *J. Am. Chem. Soc.*, **2007**, *129*, 1038.

07-0381

NEW → (S)-4,4-Dibutyl-2,6-bis(3,4,5-trifluorophenyl)-4,5-dihydro-3H-dinaphtho[7,6,1,2-cde]azepinium bromide [851942-89-7]

[C₄₂H₃₆F₆N]⁺Br⁻; FW: 748.64; brown pwdr.

Note: Sold in collaboration with Nagase for research purposes only. US Patent 6,340,753.

50mg

250mg

Technical Note:

1. See 07-0380 (page 59).

PALLADIUM (Compounds)

46-0045

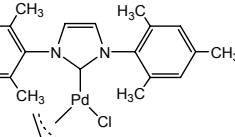
NEW → Allylchloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium(II),

98% [478980-04-0]

C₂₄H₂₆ClN₂Pd; FW: 487.37; white pwdr.

Note: Sold in collaboration with

Umicore for research purposes only. Patent WO 2004014550, US 6,316,380 and EP 721 953 A1.



250mg

1g

Technical Note:

1. See 46-0040 (Visit www.strem.com for details).

New Products Introduced Since Catalog 21

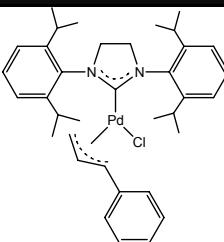
PALLADIUM (Compounds)

46-0274

NEW→

Chloro[(1,2,3-η)-3-phenyl-2-propenyl][1,3-bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazol-2-ylidene]palladium(II), min. 97% [884879-24-7]

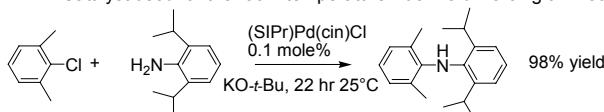
C₃₆H₄₄ClN₂Pd; yellow microcrts.
Note: Sold in collaboration with Umicore.
WO 2004014550, US 6,316,380,
EP 721 953 A1.



250mg
1g

Technical Note:

1. Catalyst used for the room temperature Buchwald-Hartwig amination of hindered aryl chlorides.



References:

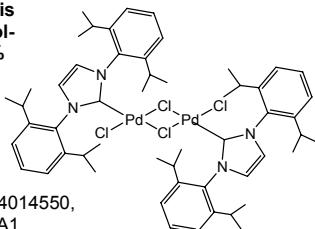
1. *J. Am. Chem. Soc.*, **2006**, *128*, 4101.
2. *Chem. Eur. J.*, **2006**, *12*, 5142.

46-0860

NEW→

Dichloro(di-μ-chloro)bis[1,3-bis(2,6-di-i-propylphenyl)imidazol-2-ylidene]dipalladium (II), 97% [444910-17-2]

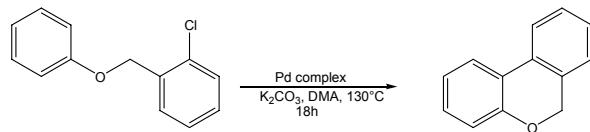
C₅₆H₇₂Cl₄N₄Pd₂; FW: 1131.83; orange to tan pwdr.
Note: Sold in collaboration with Umicore for research purposes only. Patent WO 2004014550, US 6,316,380 and EP 721 953 A1.



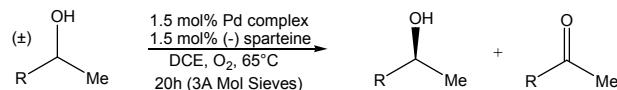
250mg
1g

Technical Notes:

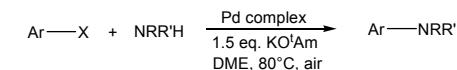
1. Catalyst used for the intramolecular direct arylation reaction with aryl chlorides.
2. Catalyst used for aerobic oxidative kinetic resolution of secondary alcohols.
3. Catalyst used for aryl amination.



Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)

References:

1. *Org. Lett.*, **2005**, *7*, 1857.
2. *Org. Lett.*, **2003**, *5*, 63.
3. *Org. Lett.*, **2002**, *4*, 2229.

46-0900

NEW→

Dichloro(norbornadiene)palladium (II), 99% [12317-46-3]

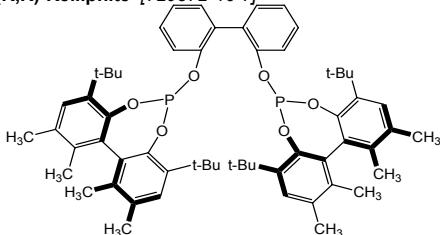
C₇H₈PdCl₂; FW: 269.46; yellow to orange pwdr.

250mg
1g

New Products Introduced Since Catalog 21

PHOSPHORUS (Compounds)

15-0057 NEW→	(R,R)-(-)-6,6'-(1,1'-Biphenyl-2,2'-diyl)bis(oxy)]bis[4,8-di-t-butyl-1,2,10,11-tetramethyl]dibenzo[d,f][1,3,2]dioxaphosphepin bisacetonitrile adduct, min. 95%	[729572-46-7]	100mg 500mg
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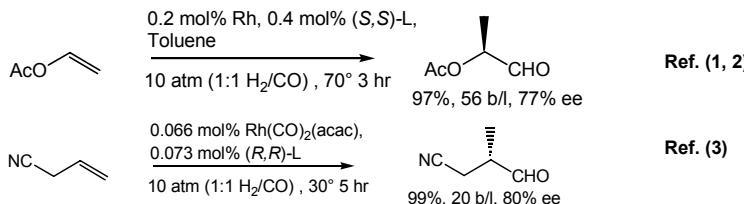
C₆₀H₇₂O₆P₂ 2CH₃CN; FW: 951.16 (1033.26); white to off-white pwdr.; [α]_D -365° (c 1.0, CH₂Cl₂); m.p. 149-155°

air sensitive, moisture sensitive

Note: Sold in collaboration with Chirotech for research purposes only. US Patent 7015360B2.

Technical Note:

1. Ligand used with rhodium to catalyze asymmetric hydroformylation of prochiral functional olefins under mild conditions. High substrate concentrations and a wide variety of functional groups are tolerated. High enantioselectivities and regioselectivities have been demonstrated.



References:

1. *Org. Lett.*, **2004**, *6*, 3277.
2. *J. Am. Chem. Soc.*, **2005**, *127*, 5040.
3. *J. Org. Chem.*, **2004**, *69*, 4031.

15-0058 NEW→	(S,S)-(+)-6,6'-(1,1'-Biphenyl-2,2'-diyl)bis(oxy)]bis[4,8-di-t-butyl-1,2,10,11-tetramethyl]dibenzo[d,f][1,3,2]dioxaphosphepin bisacetonitrile adduct, min. 95%	[729572-33-2]	100mg 500mg
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C₆₀H₇₂O₆P₂∙2CH₃CN; FW: 951.16 (1033.26); white to off-white pwdr.; [α]_D +365° (c 1.0, CH₂Cl₂); m.p. 149-155°

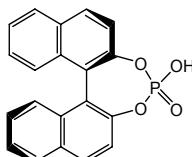
air sensitive, moisture sensitive

Note: Sold in collaboration with Chirotech for research purposes only. US Patent 7015360B2.

Technical Note:

1. See 15-0057 (page 61).

15-0052 NEW→	(R)-(-)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate, min. 98% [39648-67-4]	C ₂₀ H ₁₃ O ₄ P; FW: 348.30; white pwdr.; [α] _D -605° (c 1.35, CH ₃ OH)	1g 5g
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New Products Introduced Since Catalog 21

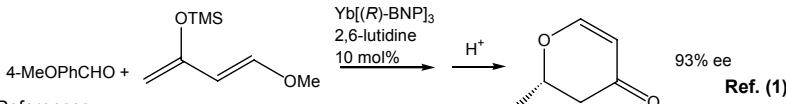
PHOSPHORUS (Compounds)

15-0052 (*R*)-(-)-1,1'-Binaphthyl-2,2'-diylhydrogenphosphate, min. 98%
 (cont.) [39648-67-4]

NEW→

Technical Notes:

- Asymmetric hetero Diels-Alder reaction catalyzed by chiral lanthanide(III) complex.
- Acidic Resolving agent for certain amine racemic mixtures. (Ref. 2,3)



References:

- Org. Lett., **2000**, *2*, 49.
- J. Org. Chem., **1991**, *56*, 485.
- US 6,162,919.

15-0053 (*S*)-(+)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate,

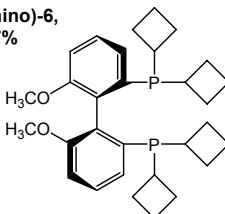
NEW→ min. 98% [35193-64-7] $\text{C}_{20}\text{H}_{13}\text{O}_4\text{P}$; FW: 348.30; white pwdr.; $[\alpha]_D +595^\circ$ (c 1.35, CH_3OH)

Technical Note:

- See 15-0052 (page 61).

15-9570 (*R*)-(+)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [150971-49-6]

$\text{C}_{30}\text{H}_{46}\text{O}_2\text{P}_2$; FW: 494.60; white pwdr.
 Note: Sold in collaboration with Solvias for research purposes only.
 Solvias (*R*)-MeO-BIPHEP Ligand Kit component see (page 55).



100mg
500mg

Technical Note:

- See 15-0178 (page 65).

15-9571 (*S*)-(-)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [150971-51-0]

$\text{C}_{30}\text{H}_{46}\text{O}_2\text{P}_2$; FW: 494.60; white pwdr.
 Note: Sold in collaboration with Solvias for research purposes only. Solvias (*S*)-MeO-BIPHEP Ligand Kit component see (page 56).

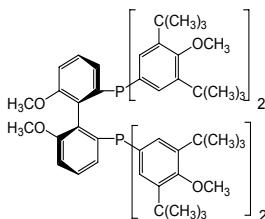
100mg
500mg

Technical Note:

- See 15-0178 (page 65).

15-0042 (*R*)-(-)-2,2'-Bis[di(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [352655-61-9]

$\text{C}_{74}\text{H}_{104}\text{O}_6\text{P}_2$; FW: 1151.60; white xtl.
 Note: Sold in collaboration with Solvias for research purposes only.
 Solvias (*R*)-MeO-BIPHEP Ligand Kit Component see (page 55).



100mg
500mg

New Products Introduced Since Catalog 21

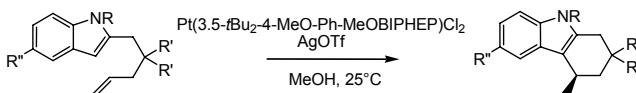
PHOSPHORUS (Compounds)

15-0042 (R)-*(*-2,2'-Bis[di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [352655-61-9]

NEW→

Technical Note:

- Various asymmetric C-C coupling reactions such as Rh-catalyzed reductive coupling of acetylene to aldehydes and α -ketoesters, Pt-catalyzed intramolecular hydroarylation of unactivated alkenes with indoles and glyoxalate-ene reaction or the Pd-catalyzed enantioselective Heck reaction of p-XC₆H₄OTf (X = OMe, H, CO₂Me) with dihydrofuran.
- See 15-0178 (page 63).



Reference:

- Org. Lett. **2006**, 8, 3801.

56-96%, ee up to 90%

15-0043 (S)-(+)-2,2'-Bis[di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [910134-30-4]

C₇₄H₁₀₄O₂P₂; FW: 1151.60; white xtl.

Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

100mg

500mg

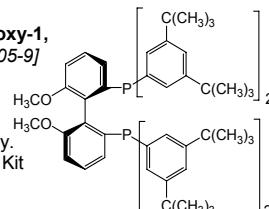
Technical Note:

- See 15-0042 (page 62).

15-0044 (R)-(+)-2,2'-Bis[di(3,5-di-*t*-butyl-phenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [192138-05-9]

C₇₀H₉₆O₂P₂; FW: 1031.49; white pwdr.

Note: Sold in collaboration with Solvias for research purposes only. Solvias (R)-MeO-BIPHEP Ligand Kit component see (page 55).

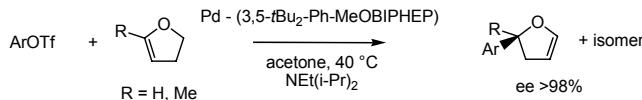


100mg

500mg

Technical Notes:

- Various asymmetric C-C coupling reactions such as Rh-catalyzed reductive coupling of acetylene to aldehydes and α -ketoesters, Pt-catalyzed intramolecular hydroarylation of unactivated alkenes with indoles and glyoxalate-ene reaction or the Pd-catalyzed enantioselective Heck reaction of p-XC₆H₄OTf (X = OMe, H, CO₂Me) with dihydrofuran.
- See 15-0178 (page 65).



Reference:

- Organometallics **1999**, 18, 670.

15-0045 (S)-(-)-2,2'-Bis[di(3,5-di-*t*-butylphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [167709-31-1]

C₇₀H₉₆O₂P₂; FW: 1031.49; white pwdr.

Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

100mg

500mg

Technical Note:

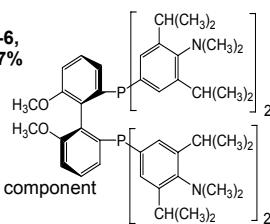
- See 15-0044 (page 63).

New Products Introduced Since Catalog 21

PHOSPHORUS (Compounds)

15-0652

NEW→ (*R*)-*2,2'-Bis[di(3,5-di*i*-propyl-4-dimethylaminophenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [352655-40-4] C₇₀H₁₀₀N₄O₂P₂; FW: 1091.55; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (*S*)-MeO-BIPHEP Ligand Kit component See (page 55).*



100mg

500mg

Technical Note:

- See 15-0178 (page 65).

15-0653

NEW→ (*S*)-*(+)-2,2'-Bis[di(3,5-di*i*-propyl-4-dimethylaminophenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [919338-66-2] C₇₀H₁₀₀N₄O₂P₂; FW: 1091.55; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (*S*)-MeO-BIPHEP Ligand Kit component see (page 56).*

100mg

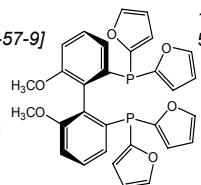
500mg

Technical Note:

- See 15-0178 (page 65).

15-0112

NEW→ (*R*)-*(+)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [145214-57-9] C₃₀H₂₄O₆P₂; FW: 542.47; off-white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (*R*)-MeO-BIPHEP Ligand Kit Component see (page 55).*



100mg

500mg

Technical Note:

- See 15-0178 (page 65).

15-0113

NEW→ (*S*)-*(-)-2,2'-Bis(di-2-furanylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [145214-59-1] C₃₀H₂₄O₆P₂; FW: 542.47; off-white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (*S*)-MeO-BIPHEP Ligand Kit component see (page 56).*

100mg

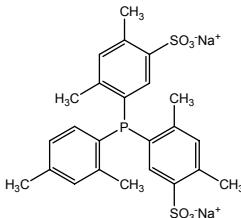
500mg

Technical Note:

- See 15-0178 (page 65).

15-0099

NEW→ Bis(4,6-dimethyl-3-sulfonatophenyl)(2,4-dimethylphenyl)phosphine, disodium salt hydrate, min. 95% TXPDS C₂₄H₂₅Na₂O₆PS₂; FW: 550.54; white pwdr.



250mg

1g

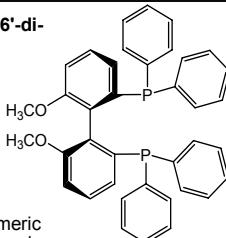
New Products Introduced Since Catalog 21

PHOSPHORUS (Compounds)

15-0178
NEW →

(R)-(+)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97%
(R)-MeO-BIPHEP [133545-16-1]

C₃₆H₃₂O₂P₂; FW: 582.53; off-white xtl.
Note: Sold in collaboration with
Solvias for research purposes only.
Solvias (R)-MeO-BIPHEP Ligand
Kit component see (page 55).

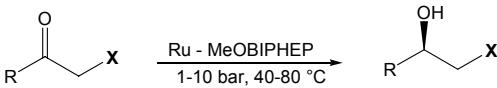


100mg
500mg

Technical Notes:

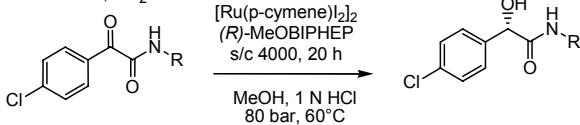
In many respects the catalytic profile of the MeOBIPHEP ligands is similar to that of other atropisomeric diphosphines such as binap and its many analogs. The nature of the PR₂ group strongly influences the catalytic performance of the metal complexes. The rhodium and ruthenium MeOBIPHEP catalysts are highly effective for the hydrogenation of various C=O, C=C and C=N bonds and several synthetically useful CC coupling reactions.

1. Ru-catalyzed asymmetric hydrogenation of β-keto esters, β-keto sulfones and α-keto amides.
2. Ru and Ir-catalyzed dynamic kinetic resolution for the synthesis of β-hydroxy-α-amino acid derivatives.
3. Ru-catalyzed hydrogenation of C=C bonds, especially α,β-unsaturated acids, allylic alcohols and with other activated groups.
4. Ir-catalyzed enantioselective hydrogenation of heteroaromatic compounds.
5. Various asymmetric C-C coupling reactions such as Rh-catalyzed reductive coupling of acetylene to aldehydes and α-ketoesters, Pt-catalyzed intramolecular hydroarylation of unactivated alkenes with indoles and glyoxylate-ene reaction or the Pd-catalyzed enantioselective Heck reaction of p-XC₆H₄OTf (X = OMe, H, CO₂Me) with dihydrofuran.

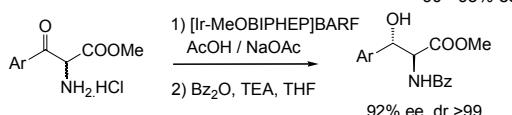


Tech. Note (1)
Ref. (1-3)

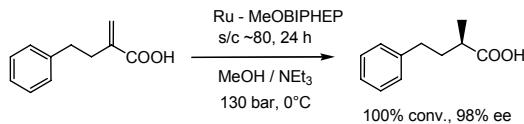
R = alkyl, (subst) Ph, Np
X = COOR', SO₂Ph



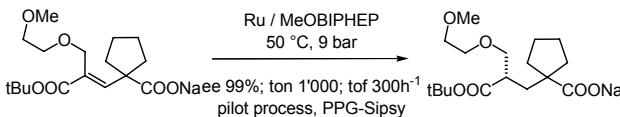
Tech. Note (1)
Ref. (4)



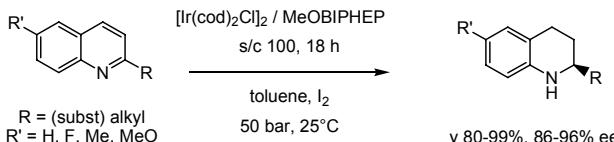
Tech. Note (2)
Ref. (5)



Tech. Note (3)
Ref. (6-9)



Tech. Note (3)
Ref. (10)



Tech. Note 4)
Ref. (11)

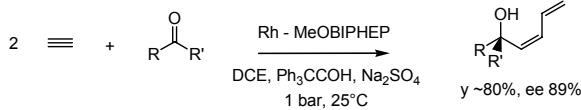
R = (subst) alkyl
R' = H, F, Me, MeO

New Products Introduced Since Catalog 21

PHOSPHORUS (Compounds)

15-0178 (R)-(+)-2,2'-Bis(diphenylphosphino)-6,6'-di-methoxy-1,1'-biphenyl, min. 97%
 (cont.) (R)-MeO-BIPHEP [133545-16-1]

NEW→



Tech. Note (5)
 Ref. (12)

References:

1. *Adv. Synth. Catal.* **2003**, 345, 261.
2. *J. Organomet. Chem.* **2000**, 603, 128.
3. *Tetrahedron: Asymmetry* **1999**, 10, 1369.
4. *Adv. Synth. Catal.* **2004**, 346, 842.
5. *Org. Lett.* **2006**, 8, 4573.
6. *Tetrahedron Lett.* **2006**, 47, 9261.
7. *Comprehensive Asymmetric Catalysis*, **1999**, 1439.
8. *Chimia* **1997**, 51, 303.
9. *J. Am. Chem. Soc.* **2003**, 125, 8779.
10. *Org. Process Res. Devel.* **2001**, 5, 438.
11. *J. Am. Chem. Soc.* **2003**, 125, 10536.
12. *J. Am. Chem. Soc.* **2006**, 128, 16040.

15-0179 (S)-(-)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% (S)-MeO-BIPHEP [133545-17-2]

NEW→

100mg
 500mg

$C_{38}H_{32}O_2P_2$; FW: 582.53; white xtl.
 Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

Technical Note:

1. See 15-0178 (page 65).

15-0430 Bis(1,5-diphenylphosphino)pentane, min. 98% [27721-02-4]
 (NEW→)

1g
 5g

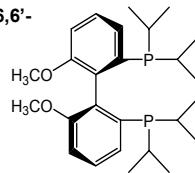
$(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$; FW: 440.51; white to off-white solid; m.p. 46-49°

15-0654 (R)-(+)-2,2'-Bis(di-i-propylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [150971-45-2]

NEW→

100mg
 500mg

$C_{26}H_{40}O_2P_2$; FW: 446.56; white pwdr.
 Note: Sold in collaboration with Solvias for research purposes only. Solvias (R)-MeO-BIPHEP Ligand Kit component see (page 55).



Technical Note:

1. See 15-0178 (page 65).

15-0655 (S)-(-)-2,2'-Bis(di-i-propylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [150971-43-0]

NEW→

100mg
 500mg

$C_{26}H_{40}O_2P_2$; FW: 446.56; white pwdr.
 Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

Technical Note:

1. See 15-0178 (page 65).

New Products Introduced Since Catalog 21

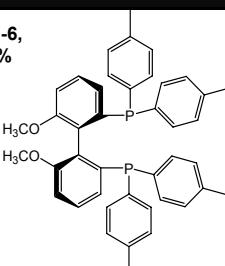
PHOSPHORUS (Compounds)

15-0156

(R)-(+)-2,2'-Bis(di-p-tolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [133545-24-1]

NEW→

C₄₂H₄₆O₂P₂; FW: 638.73; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only.
Solvias (R)-MeO-BIPHEP Ligand Kit component see (page 55).



100mg
500mg

Technical Note:

- See 15-0178 (page 65).

15-0157

(S)(-)-2,2'-Bis(di-p-tolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [133545-25-2]

NEW→

C₄₂H₄₆O₂P₂; FW: 638.73; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

100mg
500mg

Technical Note:

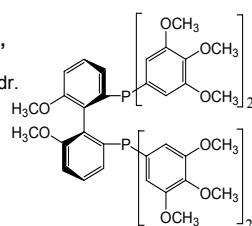
- See 15-0178 (page 65).

15-0158

(R)-(+)-2,2'-Bis[di(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [256390-47-3]

NEW→

C₅₀H₅₆O₁₄P₂; FW: 942.94; off-white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (R)-MeO-BIPHEP Ligand Kit component see (page 55).



100mg
500mg

Technical Note:

- See 15-0178 (page 65).

15-0159

(S)(-)-2,2'-Bis[di(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [256235-61-7]

NEW→

C₅₀H₅₆O₁₄P₂; FW: 942.94; off-white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component see (page 56).

100mg
500mg

Technical Note:

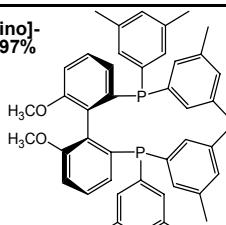
- See 15-0178 (page 65).

15-0488

(R)-(+)-2,2'-Bis[di(3,5-xylyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [394248-45-4]

NEW→

C₄₆H₄₈O₂P₂; FW: 694.84; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (R)-MeO-BIPHEP Ligand Kit component see (page 55).



100mg
500mg

Technical Note:

- See 15-0178 (page 65).

15-0489

(S)(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl, min. 97% [362634-22-8]

NEW→

C₄₆H₄₈O₂P₂; FW: 694.84; white pwdr.
Note: Sold in collaboration with Solvias for research purposes only. Solvias (S)-MeO-BIPHEP Ligand Kit component See (page 56).

100mg
500mg

Technical Note:

- See 15-0178 (page 65).

New Products Introduced Since Catalog 21

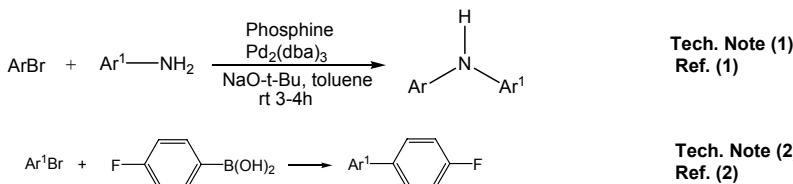
PHOSPHORUS (Compounds)

15-0958	n-Decylphosphonic acid, min. 97% [6874-60-8] CH ₃ (CH ₂) ₉ P(O)(OH) ₂ ; FW: 222.26; white to off-white pwdr.; m.p. 103-104° Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).	1g 5g
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15-1017	Di-t-butylneopentylphosphine, min. 95% [60633-21-8] (C ₄ H ₉) ₂ (C ₅ H ₁₁)P; FW: 216.35; colorless to yellow liq. <i>pyrophoric</i>	1g 5g
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Technical Notes:

1. The phosphine, used in combination with a palladium source, produces a highly effective catalyst for the Buchwald-Hartwig amination of aryl bromides at room temperature.
2. Phosphine used in the palladium-catalyzed, Suzuki cross-coupling reaction.



References:

1. *J. Org. Chem.*, **2006**, *71*, 5117.
2. *Organometallics*, **2006**, *25*, 2978.

15-1018	Di-t-butylneopentylphosphine, min. 95% (10 wt% in hexane) [60633-21-8] (C ₄ H ₉) ₂ (C ₅ H ₁₁)P; FW: 216.35; colorless to pale yellow liq. <i>air sensitive</i>	10g 50g
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Technical Note:

1. See 15-1017 (page 68).

15-1019	Di-t-butylneopentylphosphonium tetrafluoroborate, min. 95% [886059-84-3] [(C ₄ H ₉) ₂ (C ₅ H ₁₁)PH] ⁺ BF ₄ ⁻ ; FW: 304.17; white solid	1g 5g
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Technical Note:

1. See 15-1017 (page 68).

15-1748	1-Diphenylphosphino-2-(N,N-dimethylamino)-1H-indene, 99% [628323-64-8] C ₂₂ H ₂₂ NP; FW: 343.40; off-white xtl. Note: Sold under license from Dalhousie for research purposes only. Provisional US patents 60/778,368 and 60/778,358.	1g 5g
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Technical Note:

1. See 45-0197 (page 72).

15-1765	2-[2-(Diphenylphosphino)ethyl]pyridine, min. 97% [10150-27-3] C ₁₉ H ₁₈ NP; FW: 291.33; white pwdr. <i>air sensitive</i>	250mg 1g
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New Products Introduced Since Catalog 21

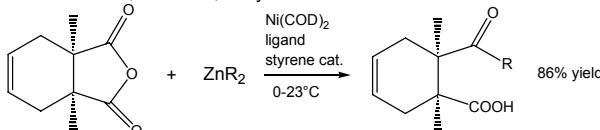
PHOSPHORUS (Compounds)

15-1765 2-[2-(Diphenylphosphino)ethyl]pyridine, min. 97% [10150-27-3]
(cont.)

NEW →

Technical Note:

1. Catalyst used for the room temperature cross-coupling of organozinc reagents with carboxylic fluorides, chlorides, anhydrides and thioesters.



References:

1. *Org. Lett.*, **2006**, *8*, 4307.
2. *J. Am. Chem. Soc.*, **2004**, *126*, 15964.

15-1784

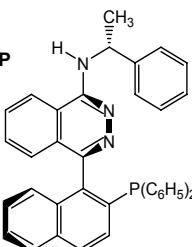
NEW → (R) - $(+)$ -4-[2-(Diphenylphosphino)-1-naphthalenyl]-N-[(R)-1-phenylethyl]-1-
phthalazinamine, min. 97% (R) -N-PINAP
[828927-97-5]

$C_{38}H_{30}N_3P$; FW: 559.64; colorless xtl.;
 $[\alpha]_D +127.3^\circ$ (*c* 0.39, $CHCl_3$);
m.p. 185–188°

air sensitive

Note: Sold under license from
Sumitomo for research purposes.

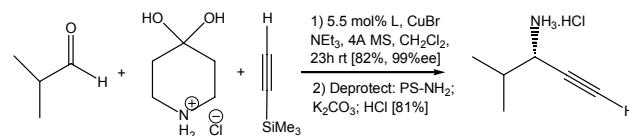
US application 11/149,643, PCT
application PCT/JP2005/010746.



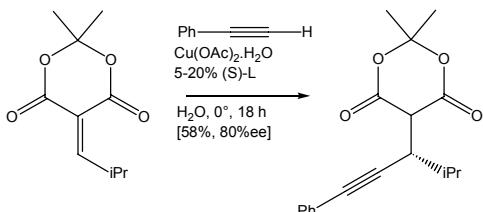
50mg
250mg

Technical Notes:

1. The PINAP family of P,N ligands is a synthetically more accessible but a similarly performing analog of the QUINAP (15-1777, 15-1778) ligand in enantioselective hydroboration, alkyne addition, and azomethine cycloaddition reactions. (Ref. 1)
2. With copper, enantioselective addition of alkynes to aldehydes to synthesize propargylamines.
3. With copper, catalytic, enantioselective, conjugate alkyne addition in aqueous media.



**Tech. Note (2)
Ref. (1,2)**



**Tech. Note (3)
Ref. (3)**

References:

1. *Angew. Chem. Int. Ed.*, **2004**, *43*, 5971.
2. *Org. Lett.*, **2006**, *8*, 2437.
3. *J. Am. Chem. Soc.*, **2005**, *127*, 9682.

New Products Introduced Since Catalog 21

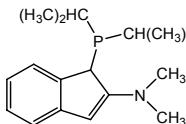
PHOSPHORUS (Compounds)

15-1786	(S)-(-)-4-[2-(Diphenylphosphino)-1-naphthalenyl]-N-[(R)-1-phenylethyl]-1-phthalazinamine, min. 97% (S)-N-PINAP	50mg
NEW→		250mg
	[828927-96-4] C ₃₈ H ₃₀ N ₃ P; FW: 559.64; colorless xtl.; [α] _D -162° (C 0.54, CHCl ₃); m.p. >210° air sensitive	
	Note: Sold under license from Sumitomo for research purposes. US application 11/149,643, PCT application PCT/JP2005/010746.	

Technical Note:

- See 15-1784 (page 69).

15-1802	1-Di-i-propylphosphino-2-(N,N-dimethyl-amino)-1H-indene, 99% [540492-51-5]	250mg
NEW→		1g
	C ₁₇ H ₂₆ NP; FW: 275.37; off-white xtl. air sensitive	
	Note: Sold under license from Dalhousie for research purposes only. Provisional US patents 60/778,368 and 60/778,358.	



Technical Note:

- See 45-0197 (page 72).

15-1835	n-Dodecylphosphonic acid, min. 97% [5137-70-2]	1g
NEW→	CH ₃ (CH ₂) ₁₁ P(O)(OH) ₂ ; FW: 250.31; white to off-white pwdr.; m.p. 96-98°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

15-2400	n-Hexadecylphosphonic acid, min. 97% [4721-17-9]	1g
NEW→	CH ₃ (CH ₂) ₁₅ P(O)(OH) ₂ ; FW: 306.42; white to off-white pwdr.; m.p. 96-99°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

15-2410	n-Hexylphosphonic acid, min. 97% [4721-24-8]	1g
NEW→	CH ₃ (CH ₂) ₅ P(O)(OH) ₂ ; FW: 166.16; white to off-white pwdr.; m.p. 105-106°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

15-3510	n-Octadecylphosphonic acid, min. 97% [4724-47-4]	1g
NEW→	CH ₃ (CH ₂) ₁₇ P(O)(OH) ₂ ; FW: 334.47; white to off-white pwdr.; m.p. 100-101°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

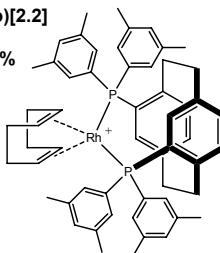
15-3520	n-Octylphosphonic acid, min. 97% [4724-48-5]	1g
NEW→	CH ₃ (CH ₂) ₇ P(O)(OH) ₂ ; FW: 194.21; white to off-white pwdr.; m.p. 102-103°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

15-5145	n-Tetradecylphosphonic acid, min. 97% [4671-75-4]	1g
NEW→	CH ₃ (CH ₂) ₁₃ P(O)(OH) ₂ ; FW: 278.37; white to off-white pwdr.; m.p. 96-98°	5g
Note: Long-Chain n-Alkylphosphonic Acid Kit component see (page 55).		

15-7830	Tris(2,4-dimethylphenyl)phosphine, 98% [49676-42-8]	500mg
NEW→	[(CH ₃) ₂ C ₆ H ₃] ₃ P; FW: 346.45; white pwdr.; m.p. 157-158°	2g

RHODIUM (Compounds)

45-0213	(R)-(-)-4,12-Bis(di-3,5-xylylphosphino)[2.2]paracyclophane(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, min. 97% [f19334-93-9] [C₅₆H₆₂P₂Rh]⁺BF₄⁻	100mg
NEW→		500mg
FW: 986.75; yellow-orange xtl. air sensitive Note: Sold in collaboration with JM for research purposes only. Patent WO 2006/067412, US5874629.		



Technical Note:

- See 45-0214 (page 71).

New Products Introduced Since Catalog 21

RHODIUM (Compounds)

45-0214

(S)-(+)-4,12-Bis(di-3,5-xylylphosphino)[2.2]paracyclophane (1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, min. 97% [619334-93-9]

100mg

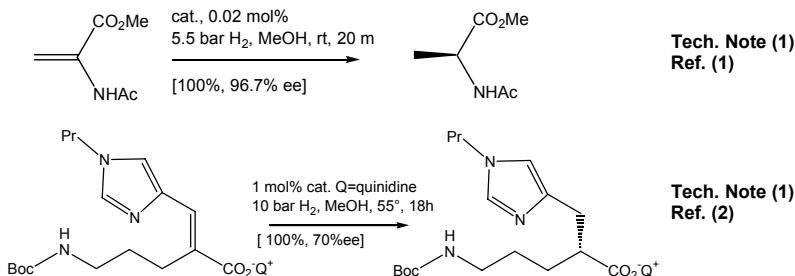
500mg

[$C_{56}H_{62}P_2Rh]^+BF_4^-$; FW: 986.75; yellow-orange xtl.
air sensitive

Note: Sold in collaboration with JM for research purposes only.
Patent WO 2006/067412, US5874629.

Technical Note:

1. Catalyst for the enantioselective hydrogenation of unsaturated amino acid derivatives.



References:

1. *Org. Lett.*, 2004, 6, 1927.
2. *Org. Lett.*, 2005, 7, 1931.

45-0652

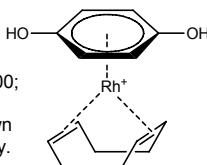
Cyclooctadiene(hydroquinone) rhodium(I) tetrafluoroborate [120967-70-6]

250mg

1g

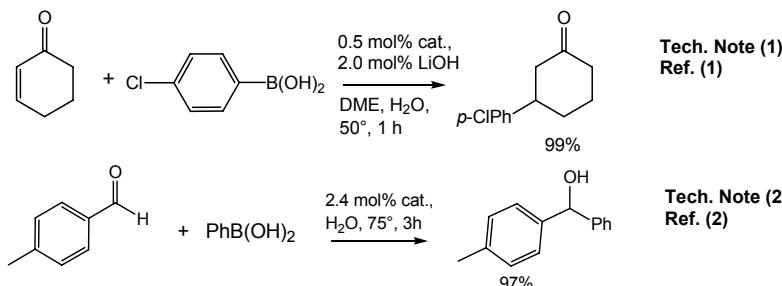
[$Rh(C_8H_{12})(C_6H_4O_2)^+BF_4^-$; FW: 408.00; yellow pwdr.

Note: Sold in collaboration with Brown University for research purposes only. Commercial use requires a license. US Patent Application 11/454,760.



Technical Notes:

1. A phosphorous free pre-catalyst for the efficient 1,4-conjugate addition of arylboronic acids to enones.
2. A pre-catalyst for addition of arylboronic acids to aryl aldehydes.
3. With aluminum isopropoxide forms a self-supported heterogeneous catalyst for the stereoselective polymerization of phenylacetylene to *cis*-poly(phenylacetylene). (Ref. 3)



References:

1. *Organometallics*, 2006, 25, 3548.
2. *J. Am. Chem. Soc.*, 2005, 127, 12238.
3. *J. Am. Chem. Soc.*, 2006, 128, 8740.

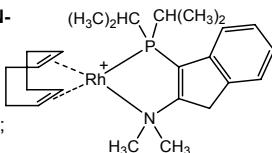
New Products Introduced Since Catalog 21

RHODIUM (Compounds)

45-0198

NEW→ 3-Di-i-propylphosphino-2-(N,N-dimethylamino)-1H-indene (1,5-cyclooctadiene)rhodium(I) hexafluorophosphate, min. 98% $[\text{RhC}_{25}\text{H}_{33}\text{NP}]^+\text{PF}_6^-$; FW: 631.42; orange pwdr.

Note: Sold under license from Dalhousie for research purposes only. Provisional US patents 60/778,368 and 60/778,358.



250mg
1g

Technical Note:

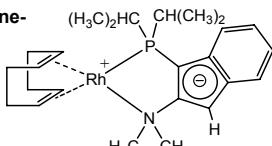
- See 45-0197 (page 72).

45-0197

NEW→ 3-Di-i-propylphosphoranylidene-2-(N,N-dimethylamino)-1H-indene(1,5-cyclooctadiene)rhodium(I), min. 95% [540492-55-5]

$\text{C}_{25}\text{H}_{37}\text{NPRh}$; FW: 485.45; orange-red xtl.

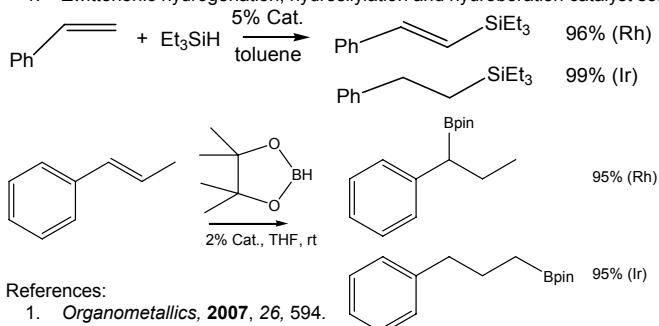
Note: Sold under license from Dalhousie for research purposes only. Provisional US patents 60/778,368 and 60/778,358.



250mg
1g

Technical Note:

- Zwitterionic hydrogenation, hydrosilylation and hydroboration catalyst soluble in non-polar solvents



References:

- Organometallics*, 2007, 26, 594.
- Organometallics*, 2006, 25, 5965.

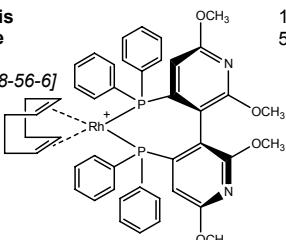
45-2110

NEW→ (R)-(+)2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine (1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, min. 97% [573718-56-6]

$[\text{C}_{46}\text{H}_{46}\text{N}_2\text{O}_4\text{P}_2\text{Rh}]^+\text{BF}_4^-$; FW: 942.53; yellow-orange xtl.

air sensitive

Note: Sold in collaboration with JM for research purposes only. Patent US5886182.



100mg
500mg

Technical Note:

- See 15-5210, technical note 4 (Visit www.strem.com for details).

New Products Introduced Since Catalog 21

RHODIUM (Compounds)

45-2111	(S)-(-)-2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, min. 97% [573718-56-6] [C ₄₆ H ₄₆ N ₂ O ₄ P ₂ Rh] ⁺ BF ₄ ⁻ ; FW: 942.53; yellow-orange xtl. air sensitive Note: Sold in collaboration with JM for research purposes only. Patent US5886182.	100mg 500mg
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Technical Note:

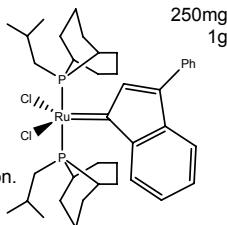
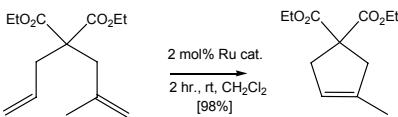
1. See 15-5210, technical note 4 (Visit www.strem.com for details).

RUTHENIUM (Compounds)

44-7778	3-Phenyl-1H-inden-1-ylidene[bis(i-butylphoban)] ruthenium(II) dichloride Neolyst™ M3 C ₃₀ H ₄₆ Cl ₂ P ₂ Ru; FW: 758.78; red pwdr. Note: Sold in collaboration with Umicore for research purposes only.	250mg 1g
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Technical Note:

1. This catalyst exhibits high selectivity as a general purpose metathesis catalyst for applications other than polymerization. It has improved air, moisture and heat resistance.



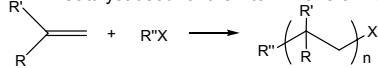
Reference:

1. *Umicore studies to be published, 2007.*

44-7777	Tricyclohexylphosphine[3-phenyl-1H-inden-1-ylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium (II) dichloride, min. 95% Neolyst™ M2 [536724-67-1] C ₅₄ H ₆₈ Cl ₂ N ₂ PRu; FW: 949.09; dark red pwdr. Note: Sold in collaboration with Umicore for research purposes only. For use in lifescience applications and research purposes only.	100mg 500mg
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Technical Note:

1. Catalyst used for the Atom Transfer Radical Polymerization (ATRP) of vinyl monomers.



Reference:

1. *New J. Chem., 2003, 27, 257.*

TUNGSTEN (Compounds)

74-2201	Tungsten carbonyl, 99% (<0.1%-Mo) [14040-11-0] W(CO) ₆ ; FW: 351.92; white to off-white pwdr.; m.p. 169-170° dec.	5g 25g
74-2202	Tungsten carbonyl, 99% (99.9+-W) sublimed [14040-11-0] W(CO) ₆ ; FW: 351.92; white xtl.; m.p. 169-170° dec.	5g 25g

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