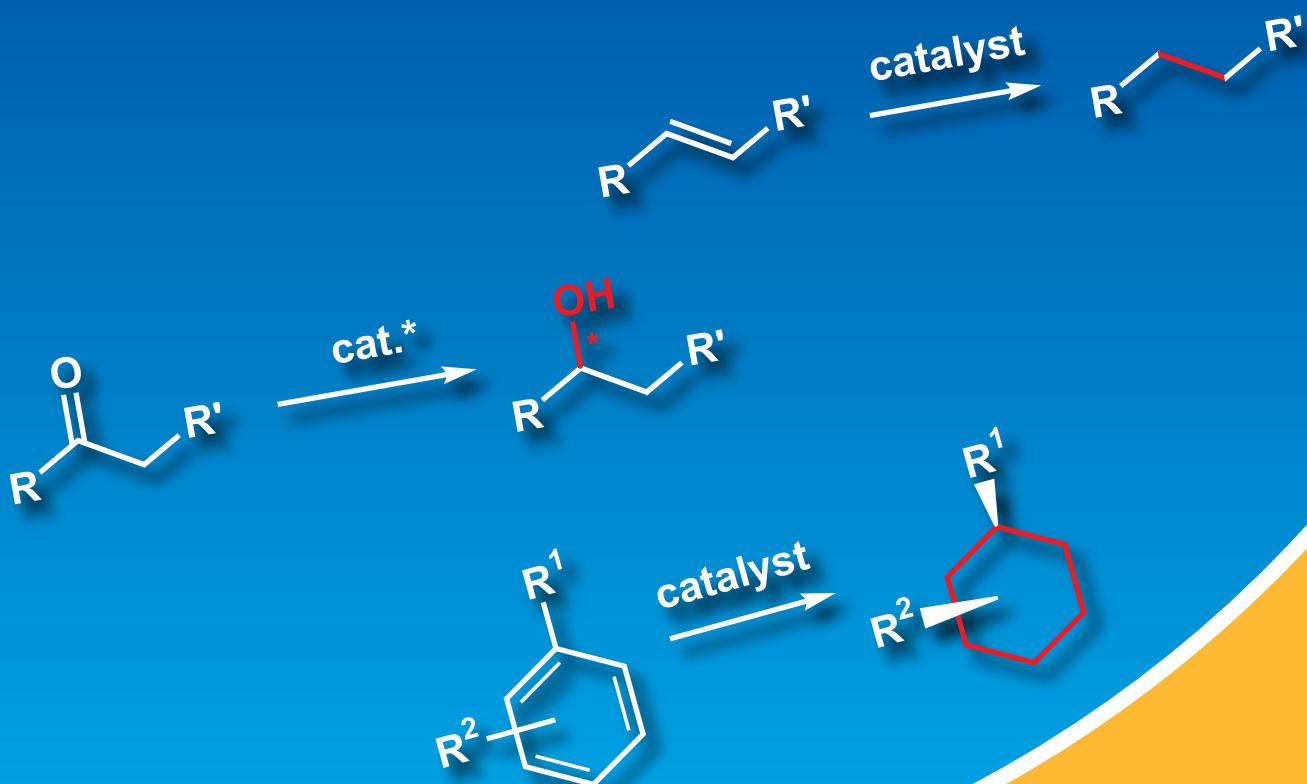


Hydrogenation Catalysts



Catalysts for Hydrogenation

Catalysts for Asymmetric Hydrogenation

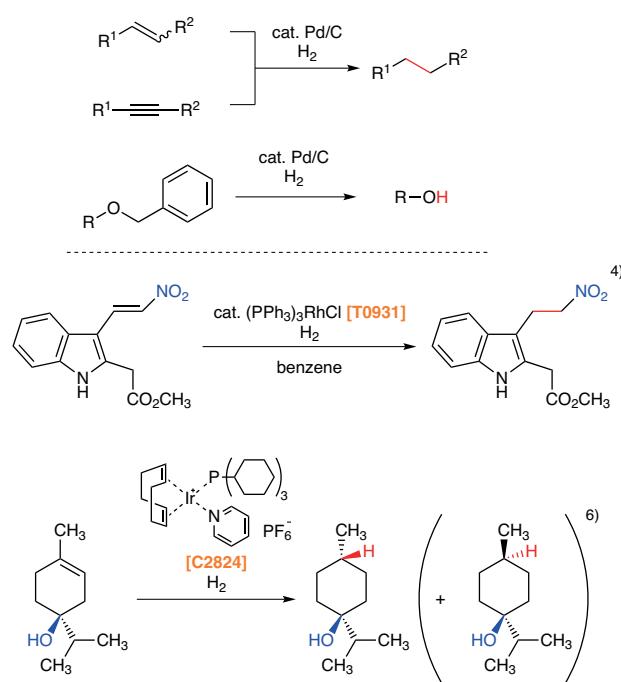
Hydrogenation Catalysts

Hydrogenation is a common reaction wherein H₂ is added across a double or triple bond, and is widely utilized in the laboratory and in industry applications. This reaction generally requires a metal catalyst to proceed, under which it is known as catalytic reduction or catalytic hydrogenation. These conditions are also used in the deprotection of benzyl and benzyloxycarbonyl groups.

Catalysts for hydrogenation also include heterogeneous catalysts such as palladium/charcoal (Pd/C), homogeneous catalysts such as Wilkinson's catalyst, and catalysts for asymmetric hydrogenation as well, and are used in numerous settings. This brochure introduces a variety of catalysts for hydrogenative reduction.

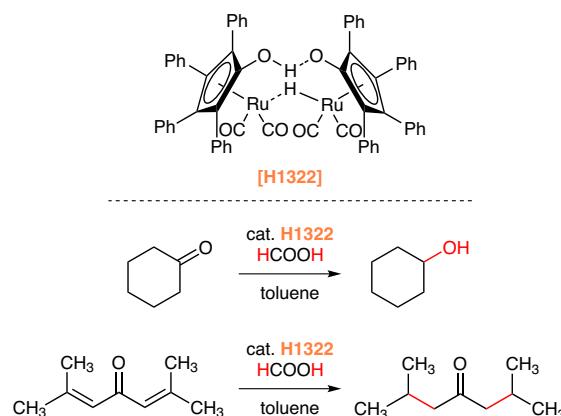
Catalysts for Hydrogenation

Catalytic reduction is widely utilized in the hydrogenation of carbon-carbon bonds, nitro group reduction, and the removal of benzyl and benzyloxycarbonyl groups.¹⁾ Platinum metals are used in many forms such as Pd/C, and catalysts like Wilkinson's catalyst [T0931]²⁻⁴⁾ and Crabtree's catalyst [C2824]⁵⁾. Both Wilkinson's catalyst and Crabtree's catalyst can hydrogenate alkenes and alkynes selectively. Furthermore, Crabtree's catalyst can hydrogenate stereoselectively due to its coordinating functional groups.⁶⁾



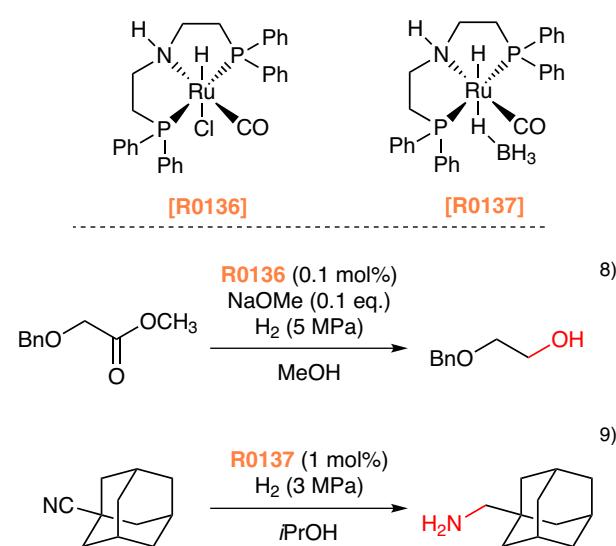
1. Shvo Catalyst

Shvo's group has reported a ruthenium binuclear complex [H1322] that catalyzes a hydrogenation of carbonyl groups and olefin moieties.⁷⁾ Formic acid is utilized as the hydrogen source. When α,β -unsaturated ketones are treated with Shvo catalyst, the olefin moiety is selectively hydrogenated.



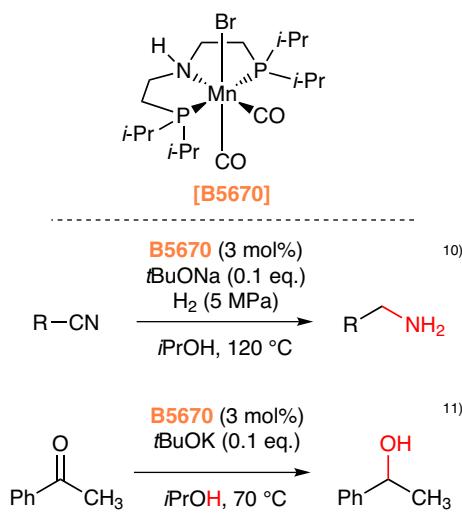
2. Ruthenium-complex Catalyst

The ruthenium catalyst [R0136] [R0137] can reduce esters to alcohols. In this condition, wide-ranged solvents can be chosen and the hydrogenation can proceed even under neat conditions.⁸⁾ However, benzyl and benzyloxycarbonyl groups, which are typically removed via conventional condition, are retained. Furthermore, R0137 can also hydrogenate aldehydes, amides, and nitriles.⁹⁾



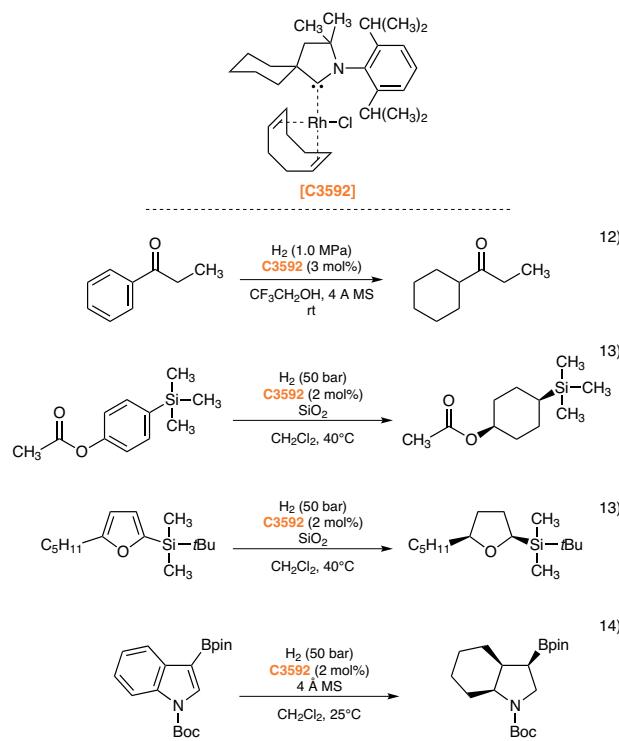
3. Manganese-complex Catalyst

Beller's group has reported that the manganese complex [B5670] is an excellent catalyst for the hydrogenation of nitriles.¹⁰⁾ This complex can also catalyze the reduction of ketones via a hydrogen atom transfer from isopropanol.¹¹⁾



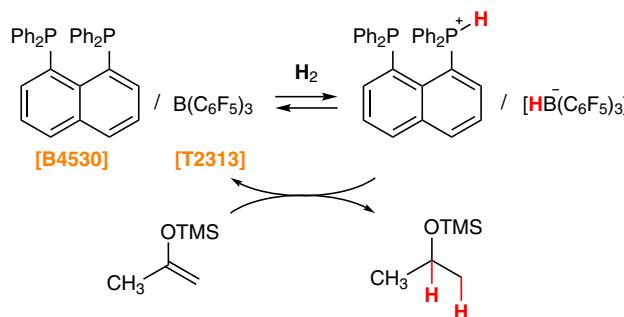
4. Rhodium Catalyst for *cis*-Selective Hydrogenation of Aromatic Rings

(Cyclohexyl-CAAC)Rh(COD)Cl [C3592] is used as an efficient and selective aromatic hydrogenation catalysts owning from the strongly σ-donating ligand. C3592 can be used for the synthesis of cyclohexane moieties while still retaining various functional groups like carbonyls,¹²⁾ silyls,¹³⁾ and boryls¹⁴⁾ in a single step. Under these conditions, the *cis*-configured saturated hydrocarbon is selectively provided.



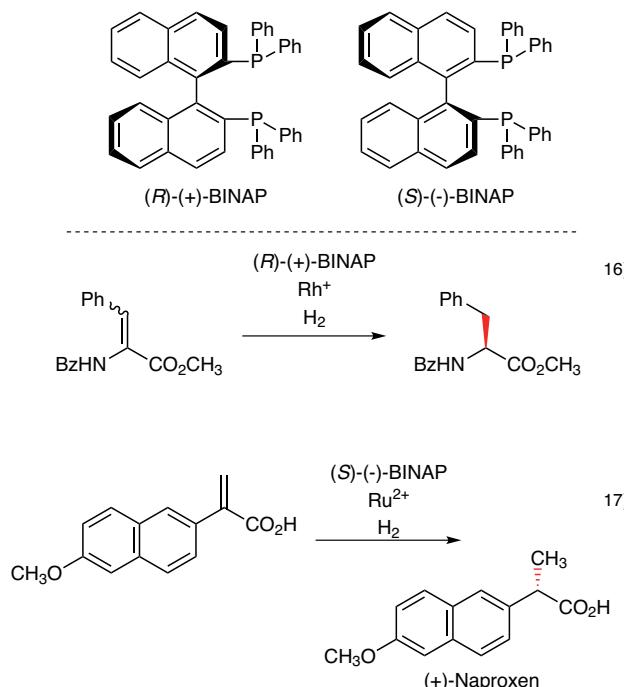
5. Organocatalysts for Metal-free Hydrogenations

1,8-Bis(diphenylphosphino)naphthalene [B4530] contains two diphenylphosphino groups and acts as a bulky Lewis base. The bulkiness of B4530 is also effective for forming unquenched Lewis acid-base pairs, "frustrated Lewis pairs (FLPs)", by treatment with a Lewis acid like tris(pentafluorophenyl)borane [T2313]. Erker *et al.* have applied them to activate a molecular hydrogen and the subsequent metal-free hydrogenations of silyl enol ethers. In this reaction, molecular hydrogens seem to be activated by the FLP-induced acid-base cooperation.¹⁵⁾

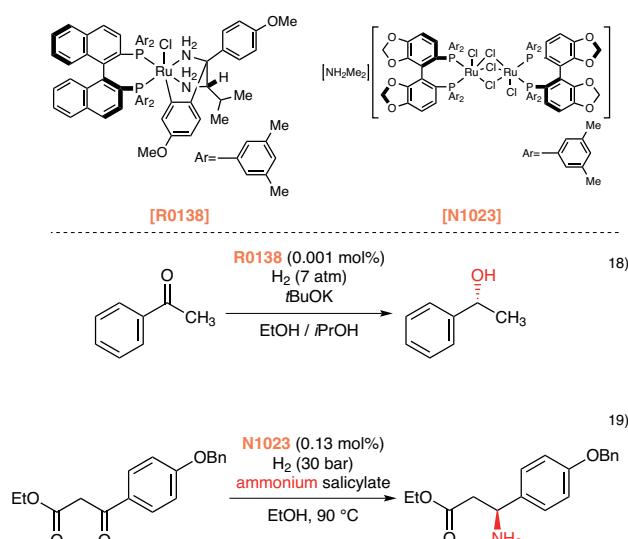


● Catalysts for Asymmetric Hydrogenation

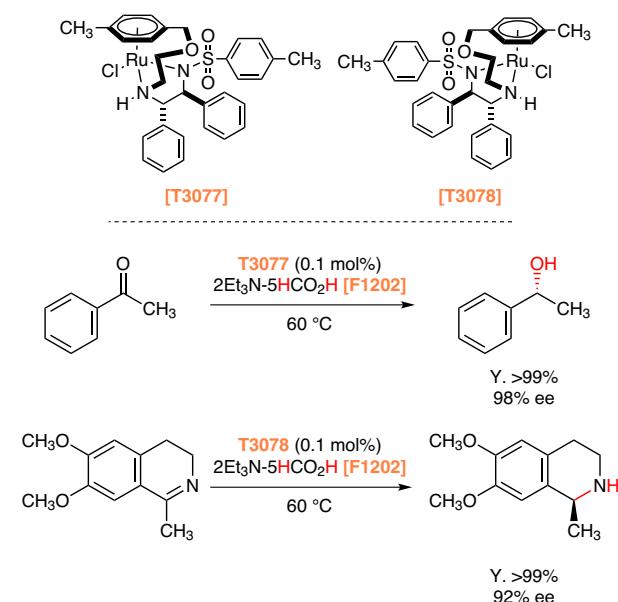
Noyori *et al.* have reported that the metal complex with a chiral 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) ligand can act as a catalyst for asymmetric hydrogenation of alkene moiety in high yields and enantioselectivity.^{16,17)} This method has been utilized in the manufacturing of aroma chemicals and medicines.



Catalysts with a BINAP moiety have high turnover number (TON) and some catalysts such as **R0138** are able to reach a TON of 100 000.¹⁸⁾ So far, many types of BINAP analogues have been developed. The catalyst **N1023** is utilized in asymmetric amination like as well as reduction of ketones and olefins.¹⁹⁾



Ikariya *et al.* have reported an asymmetric hydrogenation using formic acid salt **[F1022]** as a proton source and ruthenium catalysts with a chiral diamine ligand **[T3077]** **[T3078]**.²⁰⁾ Conventional catalysts have often required high pressure conditions, but these catalysts can hydrogenate substances under atmospheric pressure requiring no special apparatuses.



References

- 1) review:
 - a) R. E. Harmon, S. K. Gupta, D. J. Brown, *Chem. Rev.* **1973**, *73*, 21.
 - b) B. R. James, *Adv. Organomet. Chem.* **1979**, *17*, 319.
 - c) H.-U. Blaser, Christophe, M. B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *1*-2, 103.
- 2) J. F. Young, J. A. Osborn, F. H. Jardine, G. Wilkinson, *Chem. Commun.* **1965**, *131*.
- 3) J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, *1711*.
- 4) S. Mahboobi, K. Bernauer, *Helv. Chim. Acta* **1988**, *71*, 2034.
- 5) R. H. Crabtree, M. W. Davis, *J. Org. Chem.* **1986**, *51*, 2655.
- 6) R. H. Crabtree, M. W. Davis, *Organometallics* **1983**, *2*, 681.
- 7) N. Menashe, E. Salant, Y. Shvo, *J. Organomet. Chem.* **1996**, *514*, 97.
- 8) W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo, T. Saito, *Org. Process Res. Dev.* **2012**, *16*, 166.
- 9) J. Neumann, C. Bornschein, H. Jiao, K. Junge, M. Beller, *Eur. J. Org. Chem.* **2015**, *27*, 5944.
- 10) S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2016**, *138*, 8809.
- 11) M. Perez, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, *ChemSusChem* **2017**, *10*, 83.
- 12) Y. Wei, B. Rao, X. Cong, X. Zeng, *J. Am. Chem. Soc.* **2015**, *137*, 9250.
- 13) M. P. Wiesenfeldt, T. Knecht, C. Schlepphorst, F. Glorius, *Angew. Chem. Int. Ed.* **2018**, *57*, 8297.
- 14) M. Wollenburg, D. Moock, F. Glorius, *Angew. Chem. Int. Ed.* **2018**, *57*, 1.
- 15) H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966.
- 16) A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932.
- 17) T. Ohta, H. Takaya, M. Kitamura, K. Nagai, R. Noyori, *J. Org. Chem.* **1987**, *52*, 3174.
- 18) K. Matsumura, N. Arai, K. Hori, T. Saito, N. Sayo, T. Ohkuma, *J. Am. Chem. Soc.* **2011**, *133*, 10696.
- 19) G. F. Busscher, L. Lefort, J. G. O. Cremers, M. Mottinelli, R. W. Wiertz, B. de Lange, Y. Okamura, Y. Yusa, K. Matsumura, H. Shimizu, J. G. de Vries, A. H. M. de Vries, *Tetrahedron: Asymm.* **2010**, *21*, 1709.
- 20) T. Touge, T. Hakamata, H. Nara, T. Kobayashi, N. Sayo, T. Saito, Y. Kayaki, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 14960.

Catalysts for Hydrogenation

Heterogeneous Catalysts

P1785 5g 25g

Pd
Palladium 10% on Carbon
(wetted with ca. 55% Water) [Useful catalyst for coupling reaction, etc.]
CAS RN: 7440-05-3

P1701 10g

Pd
Palladium 5% on Barium Carbonate
CAS RN: 7440-05-3

P1702 5g 25g

Pd
Palladium 5% on Barium Sulfate
CAS RN: 7440-05-3

P1490 5g 25g

Pd
Palladium 5% on Carbon
(wetted with ca. 55% Water)
CAS RN: 7440-05-3

P1491 5g 25g

Pd
Palladium 10% on Carbon
(wetted with ca. 55% Water)
CAS RN: 7440-05-3

P1528 10g 50g

Pd(OH)₂
Pearlman's Catalyst
(contains Pd, PdO)
(wetted with ca. 50% Water)
CAS RN: 12135-22-7

P1720 200mg

PtO₂
Platinum(IV) Oxide
CAS RN: 1314-15-4

S0487 50g

Ni
Raney Nickel slurry in Water
CAS RN: 7440-02-0

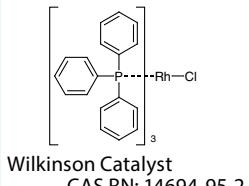
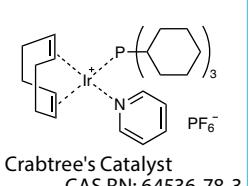
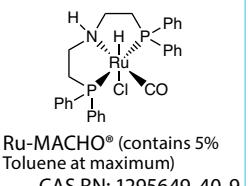
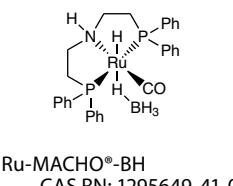
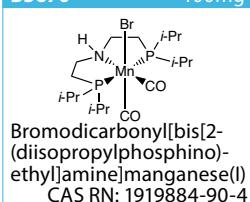
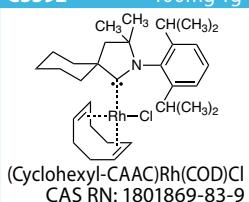
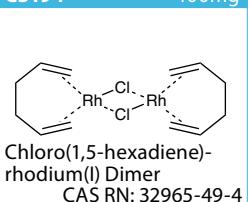
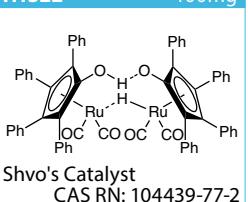
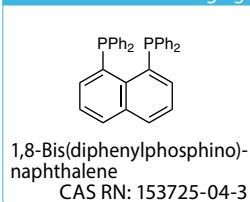
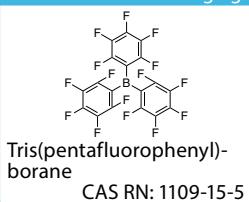
P0075 1g

Rh
Rhodium 5% on Carbon
(wetted with ca. 55% Water)
CAS RN: 7440-16-6

P1786 1g

Pd
Palladium on SH Silica Gel
(0.1mmol/g)

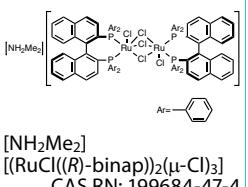
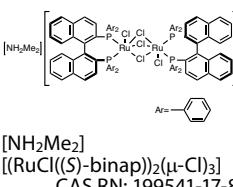
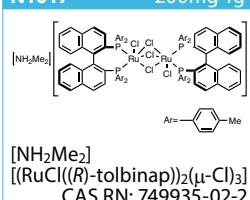
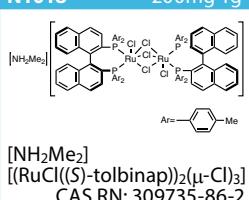
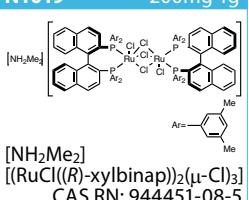
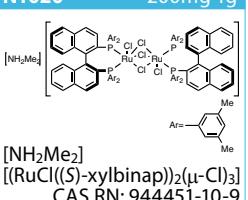
Homogeneous Catalysts

T0931 1g 5g**C2824** 100mg**R0136*** 200mg 1g**R0137*** 200mg 1g**B5670** 100mg**C3592** 100mg 1g**C3194** 100mg**H1322** 100mg**B4530** 1g 5g**T2313** 1g 5g

Others

Catalysts for Asymmetric Hydrogenation

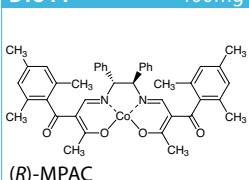
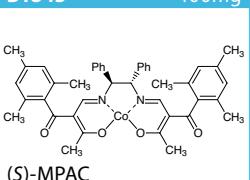
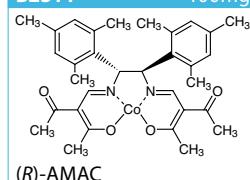
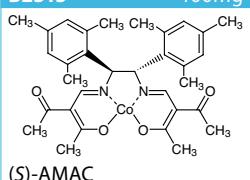
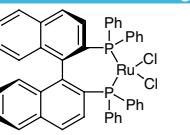
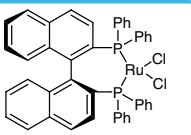
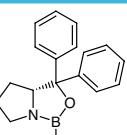
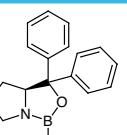
Catalysts for Asymmetric Hydrogenation of Olefins and Functionalized Ketones

N1015* 200mg 1g**N1016*** 200mg 1g**N1017*** 200mg 1g**N1018*** 200mg 1g**N1019*** 200mg 1g**N1020*** 200mg 1g

Hydrogenation Catalysts

N1021* [NH ₂ Me ₂][RuCl((R)-segphos®)(μ-Cl)] CAS RN: 346457-41-8	N1022* [NH ₂ Me ₂][RuCl((S)-segphos®)(μ-Cl)] CAS RN: 488809-34-3	N1023* [NH ₂ Me ₂][(RuCl((R)-dm-segphos®)) ₂ (μ-Cl)] CAS RN: 935449-46-0	N1024* [NH ₂ Me ₂][(RuCl((S)-dm-segphos®)) ₂ (μ-Cl)] CAS RN: 944451-14-3	R0146* [RuCl(<i>p</i> -cymene)((R)-binap)]Cl CAS RN: 145926-28-9
R0147* [RuCl(<i>p</i> -cymene)((S)-binap)]Cl CAS RN: 130004-33-0	R0148* [RuCl(<i>p</i> -cymene)((R)-tolbinap)]Cl CAS RN: 1034001-51-8	R0149* [RuCl(<i>p</i> -cymene)((S)-tolbinap)]Cl CAS RN: 228120-95-4	R0150* [RuCl(<i>p</i> -cymene)((R)-xylbinap)]Cl CAS RN: 944451-24-5	R0151* [RuCl(<i>p</i> -cymene)((S)-xylbinap)]Cl CAS RN: 944451-25-6
R0154* [RuCl(<i>p</i> -cymene)((R)-segphos®)Cl] CAS RN: 944451-28-9	R0155* [RuCl(<i>p</i> -cymene)((S)-segphos®)Cl] CAS RN: 944451-29-0	R0156* [RuCl(<i>p</i> -cymene)((R)-dm-segphos®)Cl] CAS RN: 944451-30-3	R0157* [RuCl(<i>p</i> -cymene)((S)-dm-segphos®)Cl] CAS RN: 944451-31-4	R0158* [RuCl(<i>p</i> -cymene)((R)-dtbm-segphos®)Cl] CAS RN: 944451-32-5
R0159* [RuCl(<i>p</i> -cymene)((S)-dtbm-segphos®)Cl] CAS RN: 944451-33-6	R0160* Ru(OAc) ₂ ((R)-binap) CAS RN: 325146-81-4	R0161* Ru(OAc) ₂ ((S)-binap) CAS RN: 261948-85-0	R0162* Ru(OAc) ₂ ((R)-tolbinap) CAS RN: 116128-29-1	R0163* Ru(OAc) ₂ ((S)-tolbinap) CAS RN: 106681-15-6
Catalysts for Asymmetric Hydrogenation of Ketones				
R0126* RuCl[(S,S)-Tsdpen](mesitylene) CAS RN: 174813-81-1	R0127* RuCl[(R,R)-Tsdpen](mesitylene) CAS RN: 174813-82-2	T3077* (S,S)-Ts-DENE ^B CAS RN: 1384974-37-1	T3078* (R,R)-Ts-DENE ^B CAS RN: 1333981-84-2	R0128* RuCl ₂ (S-dm-segphos®)[(S)-daipen] CAS RN: 944450-44-6
R0129* RuCl ₂ ((R)-dm-segphos®)[(R)-daipen] CAS RN: 944450-43-5	R0130* RuCl ₂ ((S)-dm-segphos®)[(S,S)-dpen] CAS RN: 944450-46-8	R0131* RuCl ₂ ((R)-dm-segphos®)[(R,R)-dpen] CAS RN: 944450-45-7	R0132* RuCl ₂ ((S)-xylbinap)[(S)-daipen] CAS RN: 220114-01-2	R0133* RuCl ₂ ((R)-xylbinap)[(R)-daipen] CAS RN: 220114-32-9
R0134* RuCl ₂ ((S)-xylbinap)[(S,S)-dpen] CAS RN: 220114-03-4	R0135* RuCl ₂ ((R)-xylbinap)[(R,R)-dpen] CAS RN: 220114-38-5	R0138* (S)-RUCY®-XyIBINAP CAS RN: 1312713-89-5	R0139* (R)-RUCY®-XyIBINAP CAS RN: 1384974-38-2	

Others

B1844  (R)-MPAC CAS RN: 212250-92-5	B1845  (S)-MPAC CAS RN: 171200-71-8	B2314  (R)-AMAC CAS RN: 361346-80-7	B2315  (S)-AMAC CAS RN: 259259-80-8
B3067  [(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) Dichloride CAS RN: 132071-87-5	B3068  [(S)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) Dichloride CAS RN: 134524-84-8	D2130  (R)-Me-CBS Catalyst CAS RN: 112022-83-0	D2131  (S)-Me-CBS Catalyst CAS RN: 112022-81-8
100mg	100mg	100mg	100mg

Products with a “*” are merchandised under a technical agreement with TAKASAGO INTERNATIONAL CORPORATION. Ru-MACHO®, RUCY®, DENEBO® and sephos® are registered trademarks of TAKASAGO INTERNATIONAL CORPORATION.

We offer this product only in quantities for laboratory use.

Ordering and Customer Service

TCI AMERICA

Tel : 800-423-8616 / 503-283-1681
Fax : 888-520-1075 / 503-283-1987
E-mail : Sales-US@TCIchemicals.com

TCI EUROPE N.V.

Tel : +32 (0)3 735 07 00
Fax : +32 (0)3 735 07 01
E-mail : Sales-EU@TCIchemicals.com

TCI Deutschland GmbH

Tel : +49 (0)6196 64053-00
Fax : +49 (0)6196 64053-01
E-mail : Sales-DE@TCIchemicals.com

Tokyo Chemical Industry UK Ltd.

Tel : +44 (0)1865 784560
Fax : +44 (0)1865 784561
E-mail : Sales-UK@TCIchemicals.com

TCI Chemicals (India) Pvt. Ltd.

Tel : 1800 425 7889 / 044-2262 0909
Fax : 044-2262 8902
E-mail : Sales-IN@TCIchemicals.com

梯希爱(上海)化成工业发展有限公司

Tel : 800-988-0390 / 021-67121386
Fax : 021-6712-1385
E-mail : Sales-CN@TCIchemicals.com

TOKYO CHEMICAL INDUSTRY CO., LTD.

Tel : +81 (0)3-5640-8878
Fax : +81 (0)3-5640-8902
E-mail : globalbusiness@TCIchemicals.com

Availability, price or specification of the listed products are subject to change without prior notice. Reproduction forbidden without the prior written consent of Tokyo Chemical Industry Co., Ltd.