

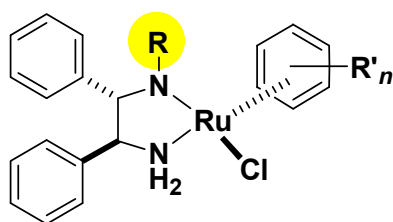
# Modified Asymmetric Transfer Hydrogenation Catalysts & Triflate Catalysts



## Product Outline

### Modified Asymmetric Transfer Hydrogenation Catalysts

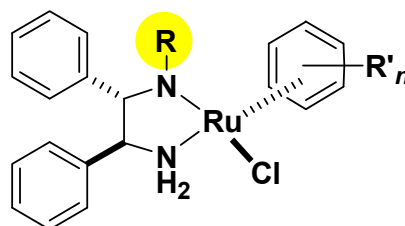
#### Prototype Catalysts (S,S)-form



R:  $\text{SO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$  (Ts)  
 $\text{SO}_2\text{CH}_3$  (Ms)

$\text{R}'_n$ : 1- $\text{CH}_3$ -4- $\text{CH}(\text{CH}_3)_2$   
 1,3,5- $(\text{CH}_3)_3$   
 1,2,3,4,5,6- $(\text{CH}_3)_6$

#### Modified Catalysts (S,S)-form



R:  $\text{BnSO}_2$   
 2',6'- $(\text{CH}_3)_2\text{BnSO}_2$   
 $i\text{-BuSO}_2$   
 Cs (camphor sulfonyl)

$\text{R}'_n$ : 1- $\text{CH}_3$ -4- $\text{CH}(\text{CH}_3)_2$   
 1,3,5- $(\text{CH}_3)_3$

KANTO CHEMICAL CO., INC. launched asymmetric transfer hydrogenation catalysts with Ts-diamine ligand, which were discovered by NOYORI Molecular Catalysis Project of Exploratory Research for Advanced Technology (ERATO) by Japan Science and Technology Corporation (JST). These catalysts are extremely effective ones for the asymmetric reduction of ketones and imines, and have established their reputation as conventional effective asymmetric reduction catalysts.

A research group of KANTO CHEMICAL CO., INC. examined the reaction conditions to achieve the maximum catalyst performance, and found out that a choice of the hydrogen source is the most important to achieve the higher reactivity and the enantioselectivity.

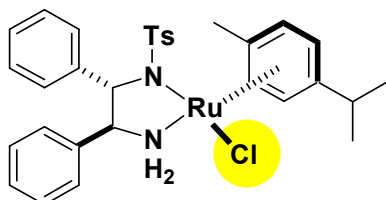
It was reported that the reaction in a mixture of formic acid and triethylamine is the irreversible reaction, leading to the high efficiency<sup>1</sup>. We revealed that a molar ratio of formic acid and triethylamine is important for the reaction of nitrogen-functionalized acetophenones<sup>2</sup>.

Then, it was reported that two phase reaction comprised of ketone and water (if necessary solvent is added) using sodium formate as a hydrogen source gives higher reactivity<sup>3</sup>. We developed this reaction system to the synthesis of some chiral compounds. In this two phase reaction, a drop of enantioselectivity is often observed for the reaction of a certain kind of ketones<sup>4</sup>. Based on the hypothesis that near the end of the reaction, the catalyst abstracts hydrogen from the product alcohol, leading to the drop of the optical purity of the product, the single phase reaction was developed by our group using formic acid salt as a hydrogen source. In the single phase reaction, the high reactivity is maintained with little drop of the optical purity of the product alcohol.

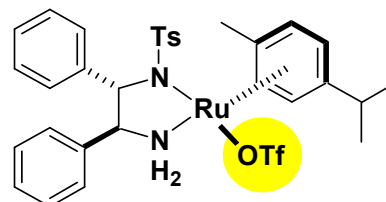
In terms of the modification of the catalysts, easily tunable sulfonyl group affects the enantioselectivity of the reaction, and we, launches modified Ru catalysts with higher catalyst performance.

## Triflate Catalysts

### Asymmetric Transfer Hydrogenation Catalysts (Chloro Complexes) (*S,S*)-form



### Asymmetric Hydrogenation Catalysts (Triflate Complexes) (*S,S*)-form



RuCl(Tsdpen)(arene) catalyst is an excellent asymmetric reduction catalyst using a kind of organic hydrogen source, but this catalyst can't use hydrogen gas. In the project in Chubu Technology Licensing Office of Nagoya Industrial Science Research Institute directed by Prof. Ryoji Noyori of Nagoya University and Prof. Takeshi Ohkuma of Hokkaido University, the asymmetric hydrogenation catalyst using hydrogen gas was developed, which has a similar structure to the above mentioned reduction catalyst<sup>5</sup>.

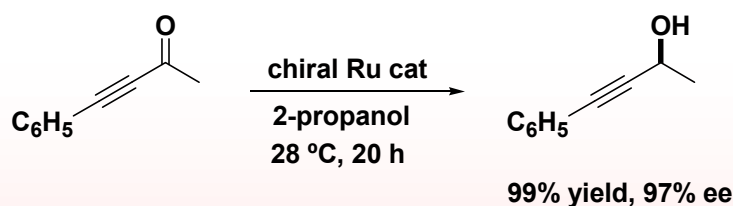
Because this asymmetric hydrogenation reaction proceeds without a base, this reaction system is applicable to the base sensitive ketones. For example, 4-chromanone is reduced in a mixture of formic acid and triethylamine with 97% ee, but in low yield 37% at S/C (substrate/catalyst molar ratio) of 500. In contrast, in this asymmetric hydrogenation reaction, 4-chromanone is reduced completely even at S/C = 3000<sup>5a</sup>, and the ton (turn over number) over 7000 can be obtained under a higher hydrogen pressure.

KANTO CHEMICAL CO., INC., launches chiral Ru Triflate asymmetric hydrogenation catalysts. Please refer to the section 2 (asymmetric hydrogenation of ketones).

## 1 Asymmetric Transfer Hydrogenation of Ketones

### 1-1 Choice of the Hydrogen Source

The choice of the hydrogen source is the first concerning point. The reaction in 2-propanol is a reversible reaction, and the limited efficiency (low concentration of the ketones and the moderate reactivity) is obtained. Although, in case of the reaction of the  $\alpha,\beta$ -acetylenic ketones, 2-propanol is reported to be the best choice<sup>1e</sup>.



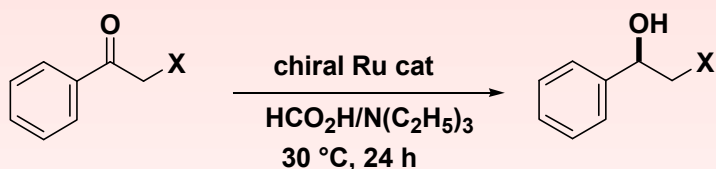
S/C = 200

[ketone] = 0.1 mol/L

chiral Ru cat:

Ru[(*S,S*)-Tsdpen](*p*-cymene)

The reaction efficiency is largely improved by the reaction in a mixture of formic acid and triethylamine than that in 2-propanol. Solvent can be added when the solubility of the ketone is not enough. The molar ratio of formic acid to triethylamine determines the result. For example, in case of the nitrogen-functionalized ketones,  $\alpha$ -cyano acetophenone is reduced in the presence of chiral Ru catalyst at the selected conditions (formic acid/triethylamine/ketone = 3.1:2.6:1.0) to give chiral cyano alcohol quantitatively with 98% ee<sup>2</sup>, but no reaction with the standard conditions (formic acid/triethylamine/ketone = 5.0:2.0:1.0).



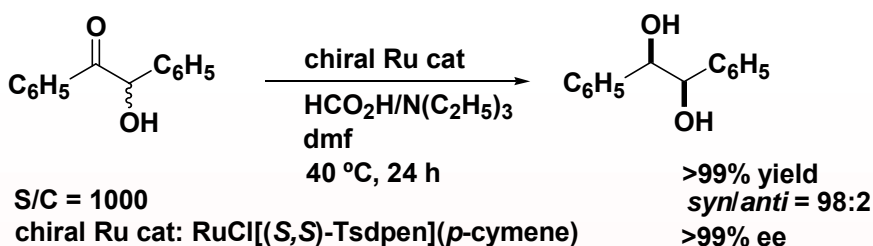
X = CN, N<sub>3</sub>, NO<sub>2</sub>

chiral Ru cat: RuCl[(S,S)-Tsdpen](*p*-cymene)

X	S/C	HCO <sub>2</sub> H/N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> /ketone	time, h	yield, %	ee, %	config
CN	1000	5/2/1	24	0	-	-
CN	1000	3.1/2.6/1	24	100	98	S
N <sub>3</sub>	100	3.1/2.6/1	24	65	92	R
NO <sub>2</sub> <sup>a</sup>	200	6.0/2.4/1	16	90	98	R

<sup>a</sup>[ketone]<sub>0</sub> = 1.0 mol/L in dmf.

The reaction of *racemic*-benzoin is useful for the production of chiral hydrobenzoin<sup>6</sup> indicates that the reaction in a mixture of formic acid and triethylamine is suitable for the asymmetric reaction with a dynamic kinetic resolution.



S/C = 1000

chiral Ru cat: RuCl[(S,S)-Tsdpen](*p*-cymene)

>99% yield  
syn/anti = 98:2  
>99% ee

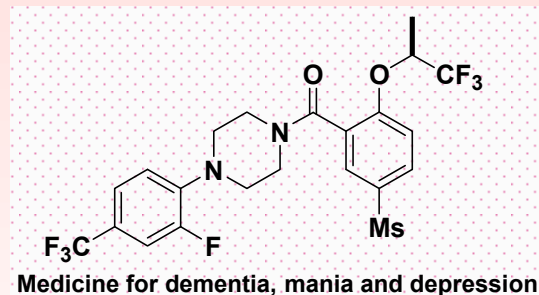
In 2004, it was reported that the two phase reaction comprised of acetophenone and water using sodium formate as a hydrogen source proceeds effectively<sup>3</sup>. In the reaction of acetophenone with a mixture of formic acid and triethylamine, only 1 % conversion is obtained at 0.5 h, but 76 % conversion is obtainable in two phase reaction using sodium formate at the same reaction time.



chiral Ru cat: RuCl[(S,S)-Tsdpen](*p*-cymene),  
S/C = 100.

hydrogen source	time, h	conv, %	ee, %
HCO <sub>2</sub> H/N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	0.5	1	>99
	12	98	97
HCO <sub>2</sub> Na	0.5	76	95

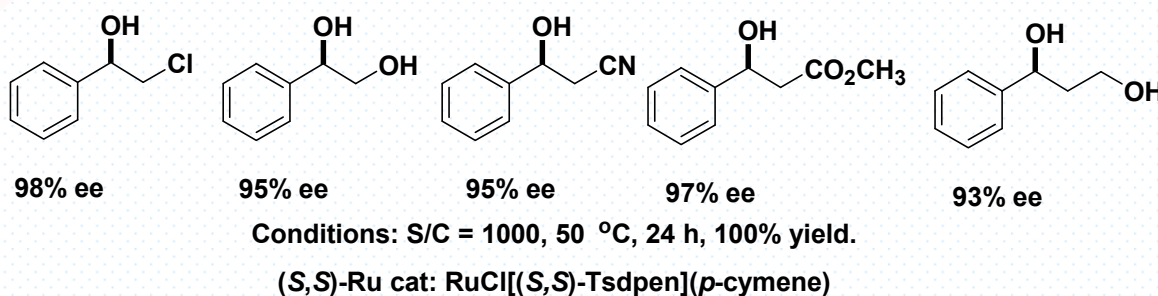
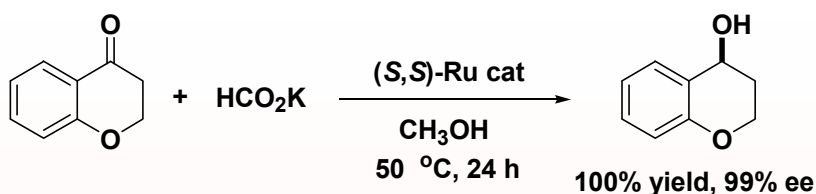
As mentioned above, the two phase reaction is a high speed reaction. Liquid ketones can be reducible without an added solvent and this reaction is successfully applied to the preparation of chiral 1,1,1-trifluoro-2-propanol, which has low boiling point (79 °C) and high solubility to the water. In fact, 1,1,1-trifluoroacetone is reduced in the presence of RuCl[(*S,S*)-Tsdpen](mesitylene) effectively to yield (*S*)-1,1,1-trifluoro-2-propanol in 97% ee quantitatively. The organic phase comprised of the crude alcohol without any solvents is easily purified by easy operations (drying, and simple distillation) to give the (*S*)-1,1,1-trifluoro-2-propanol, 97% ee in high isolated yield.



Two phase reaction has a high reactivity, but a small drop of enantioselectivity is observed in some cases. Time course study revealed that the optical purity of the product alcohol decreases to some extent. In case of a certain ketonic substrates, several % drop of optical purity is observed. Reaction with low speed stirring also enhances the racemization. The insufficient supply of the hydrogen source (present in water phase) to the catalyst (present in organic phase) is assumed to cause the racemization of alcohol<sup>4</sup>.

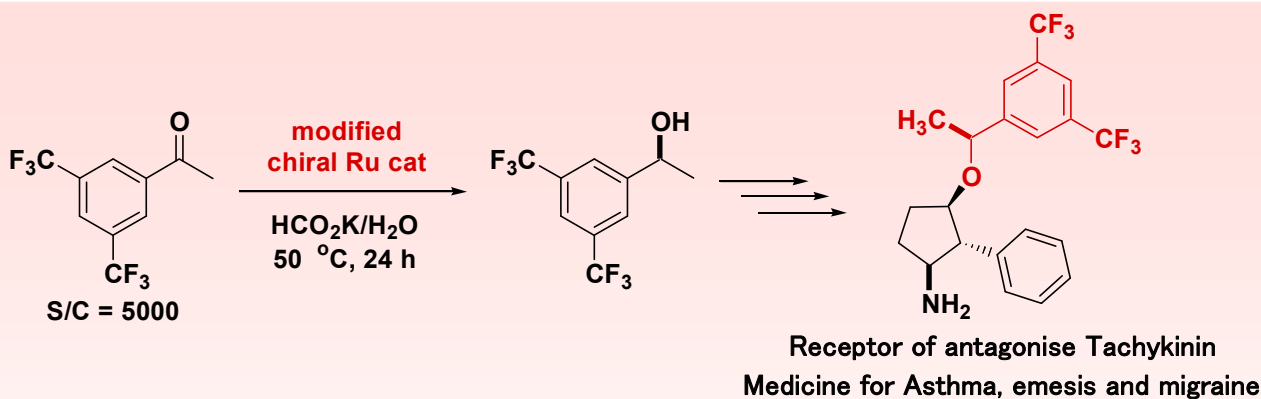
To solve the intrinsic nature of the two phase reaction, we developed the effective single phase reaction. High efficiency is maintained using formic acid salt as a hydrogen source, and suppresses the racemization of the product alcohol in this single phase reaction.

For example, 4-chromanone is reduced in the presence of RuCl[(*S,S*)-Tsdpen](*p*-cymene) to give the (*S*)-4-chromanol with 99% ee quantitatively in single phase reaction. Phenacyl chloride is also reduced to give (*R*)-1-phenyl-2-chloroethanol with 98% ee, which is an important chiral building block. As shown above, single phase reaction using formic acid salt with chiral Ru catalyst gives chiral alcohol with high enantioselectivity and high yield.



## 1-2. Asymmetric Transfer Hydrogenation with Modified Chiral Ru Catalysts

Arene ligand, diamine ligand, and sulfonyl group are tunable parts in these chiral Ru catalysts. Modified chiral Ru catalysts on sulfonyl group have higher enantioselectivity for the reaction of a certain ketones. For example, the eantioselectivity of the reduction of 3',5'-bis(trifluoromethyl)acetophenone is influenced by the structure of the catalyst in two phase reaction with sodium formate as a hydrogen source. Chiral Ru catalyst with benzylsulfonyl group, or 2',6'-dimethylbenzylsulfonyl group has higher enantioselectivity for the reaction of 3',5'-bis(trifluoromethyl)acetophenone than prototype TsDPEN catalyst, leading to (*S*)-1-[3',5'-bis(trifluoromethyl)phenyl]ethanol with 95-97% ee's. As no racemization is observed in this two phase system (discussed above), the modified Ru catalyst improves the enantioselectivity.



	R	arene	yield, %	ee, %
modified chiral Ru cat 	Ts	<i>p</i> -CYMENE <sup>a</sup>	82	80.9
	BnSO <sub>2</sub>	<i>p</i> -CYMENE	94	90.7
		MESITYLENE <sup>b</sup>	89	94.9
	2',6'-(CH <sub>3</sub> ) <sub>2</sub> BnSO <sub>2</sub>	<i>p</i> -CYMENE	100	95.9
		MESITYLENE	83	96.8
	<i>i</i> -BuSO <sub>2</sub>	<i>p</i> -CYMENE	100	90.5
MESITYLENE <sup>c</sup>		100	83.1	
RuCl[( <i>S,S</i> )-Rdpn](arene)	( <i>S</i> )-Cs	<i>p</i> -CYMENE	92	75.5

<sup>a</sup>S/C = 3000, <sup>b</sup>S/C = 4000, <sup>c</sup>S/C = 2000.

Chiral Ru catalysts with Cs-sulfonyl group<sup>7</sup> have higher enantioselectivity for a kind of ketones as shown below.

R	yield, %, ee, % <sup>a</sup>	yield, %, ee, % <sup>b</sup>	yield, %, ee, % <sup>c</sup>
Ts	77, 91.3	85, 90.0	88, 81.5
BnSO <sub>2</sub>	60, 93.4	100, 94.3	99, 90.7
<i>i</i> -BuSO <sub>2</sub>	82, 93.3	94, 93.8	97, 91.4
( <i>S</i> )-Cs	83, 95.5	98, 95.8	97, 94.9

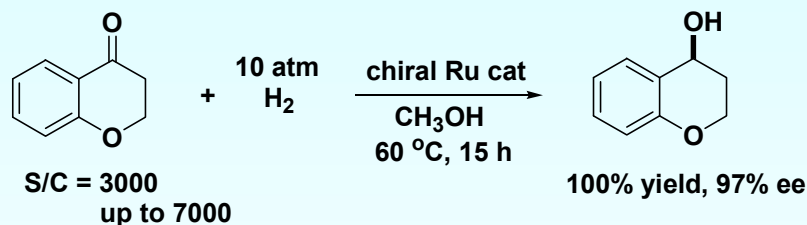
HCO<sub>2</sub>K in water, <sup>a</sup>S/C = 7000, <sup>b</sup>S/C = 5000, <sup>c</sup>S/C = 1000.

## 2 Asymmetric Hydrogenation of Ketones

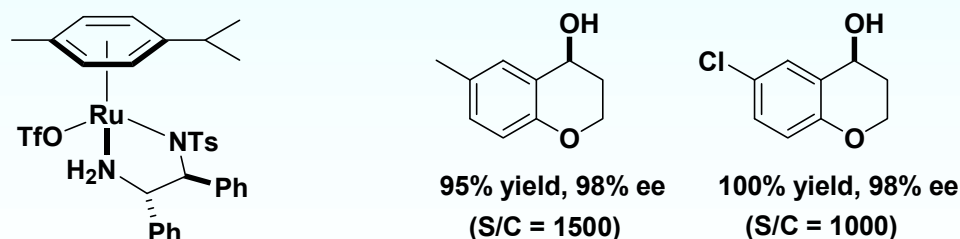
Chiral Ru complexes with diphosphine and diamine ligand, such as RuCl<sub>2</sub>(binap)(dpn)<sup>8</sup> have high reputation as asymmetric hydrogenation catalysts for ketones, and KANTO CHEMICAL CO., IMC. launched these complexes. Since the real catalyst is *in situ* prepared by mixing pre-formed Ru complex and a strong base such as KO-*t*Bu in this reaction, base sensitive ketones are not often applicable with this catalyst system.

In the point of the mechanism, RuCl(Tsdpn)(*p*-cymene) with Ts-diamine ligand, although they have structural similarity to RuCl<sub>2</sub>(binap)(dpn), have high catalytic activity for the reduction of ketones using organic hydrogen source such as 2-propanol and formic acid, can not activate hydrogen gas. Newly developed Ru(OTf)(Tsdpn)(*p*-cymene), which has a dissociative anionic OTf group, can hydrogenate ketones using hydrogen gas in methanol without a base<sup>5</sup>.

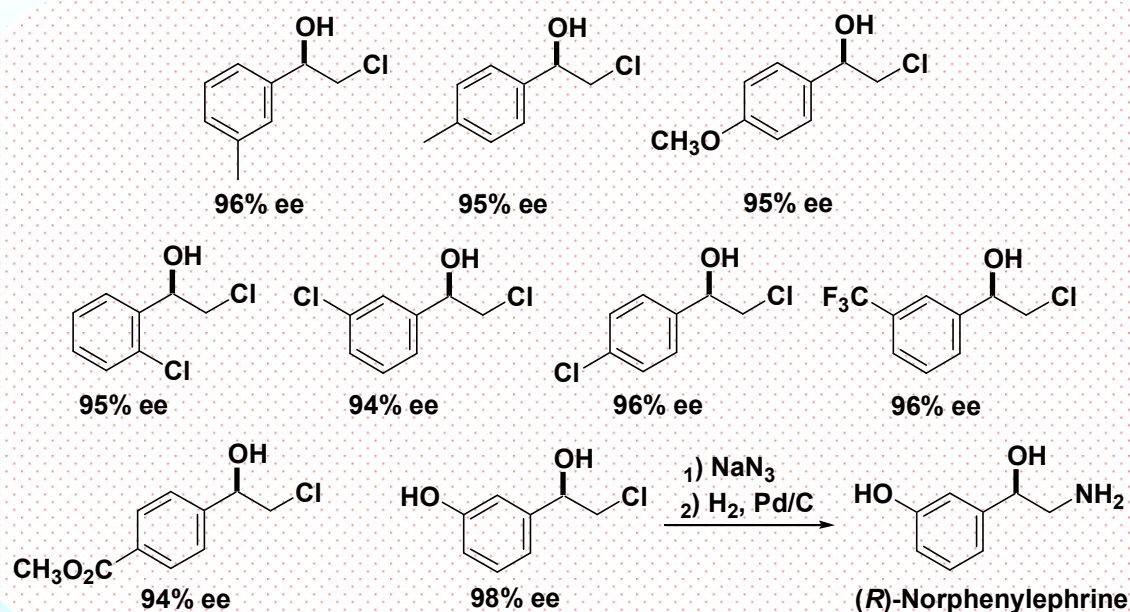
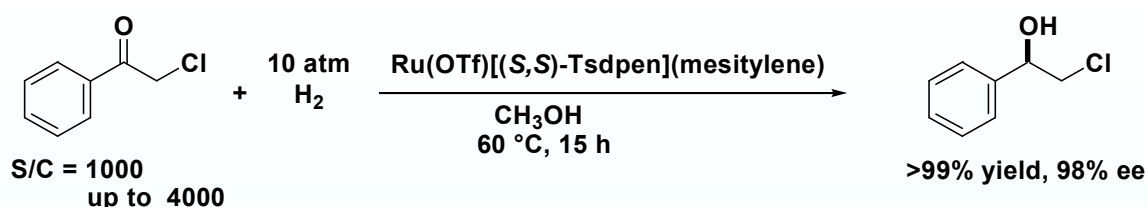
This catalyst is applicable to a kind of base sensitive ketones, which can not be hydrogenated with the previous hydrogenation catalysts effectively. For example, 4-chromanone is a base sensitive substrate, and a limited example was reported for the asymmetric hydrogenation of this compound<sup>9</sup>. 4-Chromanone is hydrogenated with Ru(OTf)[(S,S)-Tsdpen](*p*-cymene) catalyst even at S/C = 3000 (conditions: 60 °C, 15 h) to give (*S*)-4-chromanol with 97% ee quantitatively<sup>5a</sup>.



chiral Ru cat: Ru(OTf)[(S,S)-Tsdpen](*p*-cymene)



This catalyst is also applicable to a variety of base sensitive ketones. For example, phenacyl chloride is hydrogenated with Ru(OTf)[(S,S)-Tsdpen](*p*-cymene) to yield (*R*)-2-chloro-1-phenylethanol with 98% ee at S/C of 1000<sup>5b</sup>. Phenacyl chlorides with electron donating substituent such as methyl group and methoxy group, and those with electron withdrawing group such as chloro and trifluoromethyl group, are also hydrogenated effectively to give the chlorophenylethanols with high ee's. Phenacyl chloride with non protected phenolic hydroxyl group, can be hydrogenated to give chiral chlorophenylethanol, which is derived to (*R*)-norphenylephrine in two steps.



**A. References**

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**B. Patents**

1. Preparation of optically active alcohols 2962668 (Japan)
2. Ruthenium complexes with diamine ligands and preparation of optically active alcohols with these catalysts 3040353 (Japan)
3. Preparation of optically active 1,2-diols 3630002 (Japan)
4. Chiral catalysts and preparation of optically active alcohols with these catalysts 2010-248091 (Japan)
5. Preparation of optically active alcohols 2010-111120 (Japan)
6. Preparation of optically active aliphatic fluoro-alcohols 2010-1462190 (Japan)
7. Sulfonate catalysts and preparation of optically active alcohols with these catalysts WO2006-137195

**KANTO CHEMICAL CO., INC.** supplies suitable catalyst for your substrates, and has know-how such as the choice of the hydrogen source and the reaction conditions. Please consult us about the usage of these chiral reduction catalysts and the optimization of the reaction conditions. We also develop the asymmetric reduction process with these catalysts and apply to custom synthesis.

# Product List

## Modified Asymmetric Transfer Hydrogenation Catalysts

Product Name	Product Number	Package Size
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(isobutanesulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07710-95	200mg
<b>RuCl[(<i>R,R</i>)-<i>i</i>-BuSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>28</sub> H <sub>36</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 601.29	07710-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(isobutanesulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07711-95	200mg
<b>RuCl[(<i>S,S</i>)-<i>i</i>-BuSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>28</sub> H <sub>36</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 601.29	07711-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(isobutanesulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium(II)	07721-95	200mg
<b>RuCl[(<i>R,R</i>)-<i>i</i>-BuSO<sub>2</sub>dpen](mesitylene)</b> C <sub>27</sub> H <sub>34</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 587.16	07721-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(isobutanesulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium(II)	07722-95	200mg
<b>RuCl[(<i>S,S</i>)-<i>i</i>-BuSO<sub>2</sub>dpen](mesitylene)</b> C <sub>27</sub> H <sub>34</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 587.16	07722-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-[(1 <i>R</i> )-camphorsulfonyl]-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07715-95	200mg
<b>RuCl[(<i>R</i>)-Cs-(<i>R,R</i>)dpen](<i>p</i>-cymene)</b> C <sub>34</sub> H <sub>42</sub> ClN <sub>2</sub> O <sub>3</sub> RuS F.W : 695.30	07715-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-[(1 <i>S</i> )-camphorsulfonyl]-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07716-95	200mg
<b>RuCl[(<i>S</i>)-Cs-(<i>S,S</i>)dpen](<i>p</i>-cymene)</b> C <sub>34</sub> H <sub>42</sub> ClN <sub>2</sub> O <sub>3</sub> RuS F.W : 695.30	07716-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(benzylsulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07717-95	200mg
<b>RuCl[(<i>R,R</i>)-BnSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>30</sub> H <sub>32</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 621.18	07717-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(benzylsulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07718-95	200mg
<b>RuCl[(<i>S,S</i>)-BnSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>30</sub> H <sub>32</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 621.18	07718-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(benzylsulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium( II )	07719-95	200mg
<b>RuCl[(<i>R,R</i>)-BnSO<sub>2</sub>dpen](mesitylene)</b> C <sub>29</sub> H <sub>30</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 607.15	07719-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(benzylsulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium( II )	07720-95	200mg
<b>RuCl[(<i>S,S</i>)-BnSO<sub>2</sub>dpen](mesitylene)</b> C <sub>29</sub> H <sub>30</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 607.15	07720-65	1g



Product Name	Product Number	Package Size
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(2',6'-dimethylbenzylsulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07734-95	200mg
<b>RuCl[(<i>R,R</i>)-2',6'-(CH<sub>3</sub>)<sub>2</sub>BnSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>32</sub> H <sub>36</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 649.23	07734-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(2',6'-dimethylbenzylsulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II )	07735-95	200mg
<b>RuCl[(<i>S,S</i>)-2',6'-(CH<sub>3</sub>)<sub>2</sub>BnSO<sub>2</sub>dpen](<i>p</i>-cymene)</b> C <sub>32</sub> H <sub>36</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 649.23	07735-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )-N-(2',6'-dimethylbenzylsulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium( II )	07736-95	200mg
<b>RuCl[(<i>R,R</i>)-2',6'-(CH<sub>3</sub>)<sub>2</sub>BnSO<sub>2</sub>dpen](mesitylene)</b> C <sub>31</sub> H <sub>34</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 635.20	07736-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )-N-(2',6'-dimethylbenzylsulfonyl)-1,2-diphenylethanediamine](mesitylene)ruthenium( II )	07737-95	200mg
<b>RuCl[(<i>S,S</i>)-2',6'-(CH<sub>3</sub>)<sub>2</sub>BnSO<sub>2</sub>dpen](mesitylene)</b> C <sub>31</sub> H <sub>34</sub> ClN <sub>2</sub> O <sub>2</sub> RuS F.W : 635.20	07737-65	1g

### Triflate Catalysts

Product Name	Product Number	Package Size
[(1 <i>R</i> ,2 <i>R</i> )-N-( <i>p</i> -toluenesulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II ) triflate	41068-95	200mg
<b>Ru(OTf)[(<i>R,R</i>)-Tsdpen](<i>p</i>-cymene)</b> C <sub>32</sub> H <sub>35</sub> F <sub>3</sub> N <sub>2</sub> O <sub>5</sub> RuS <sub>2</sub> F.W : 749.83	41068-65	1g
[(1 <i>S</i> ,2 <i>S</i> )-N-( <i>p</i> -toluenesulfonyl)-1,2-diphenylethanediamine]( <i>p</i> -cymene)ruthenium( II ) triflate	41069-95	200mg
<b>Ru(OTf)[(<i>S,S</i>)-Tsdpen](<i>p</i>-cymene)</b> C <sub>32</sub> H <sub>35</sub> F <sub>3</sub> N <sub>2</sub> O <sub>5</sub> RuS <sub>2</sub> F.W : 749.83	41069-65	1g

## Related Product

### Prototype Asymmetric Transfer Hydrogenation Catalysts

Product Name	Product Number	Package Size
Chloro[(1 <i>R</i> ,2 <i>R</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>RuCl[(<i>R,R</i>)-Tsdpen](<i>p</i>-cymene)</b>	08154-95	200mg
	08154-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>RuCl[(<i>S,S</i>)-Tsdpen](<i>p</i>-cymene)</b>	08153-95	200mg
	08153-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>mesitylene</i> )ruthenium(II) <b>RuCl[(<i>R,R</i>)-Tsdpen](<i>mesitylene</i>)</b>	08173-95	200mg
	08173-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>mesitylene</i> )ruthenium(II) <b>RuCl[(<i>S,S</i>)-Tsdpen](<i>mesitylene</i>)</b>	08174-95	200mg
	08174-65	1g
Chloro[(1 <i>R</i> ,2 <i>R</i> )- <i>N</i> -(methanesulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>RuCl[(<i>R,R</i>)-Msdpen](<i>p</i>-cymene)</b>	08175-95	200mg
	08175-65	1g
Chloro[(1 <i>S</i> ,2 <i>S</i> )- <i>N</i> -(methanesulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>RuCl[(<i>S,S</i>)-Msdpen](<i>p</i>-cymene)</b>	08176-95	200mg
	08176-65	1g
[(1 <i>R</i> ,2 <i>R</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>Ru[(<i>R,R</i>)-Tsdpen](<i>p</i>-cymene)</b>	41066-95	200mg
	41066-65	1g
[(1 <i>S</i> ,2 <i>S</i> )- <i>N</i> -( <i>p</i> -toluensulfonyl)-1,2-diphenylethanediamine]-( <i>p</i> -cymene)ruthenium(II) <b>Ru[(<i>S,S</i>)-Tsdpen](<i>p</i>-cymene)</b>	41067-95	200mg
	41067-65	1g

### Prototype Asymmetric Hydrogenation Catalysts

Product Name	Product Number	Package Size
Dichloro[( <i>R</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]-[( <i>R,R</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuCl<sub>2</sub>[(<i>R</i>)-binap][(<i>R,R</i>)-dpen]</b>	11404-95	200mg
	11404-65	1g
Dichloro[( <i>R</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]-[( <i>S,S</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuCl<sub>2</sub>[(<i>R</i>)-binap][(<i>S,S</i>)-dpen]</b>	11405-95	200mg
	11405-65	1g
Dichloro[( <i>S</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]-[( <i>R,R</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuCl<sub>2</sub>[(<i>S</i>)-binap][(<i>R,R</i>)-dpen]</b>	11402-95	200mg
	11402-65	1g
Dichloro[( <i>S</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]-[( <i>S,S</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuCl<sub>2</sub>[(<i>S</i>)-binap][(<i>S,S</i>)-dpen]</b>	11403-95	200mg
	11403-65	1g

Product Name	Product Number	Package Size
Dichloro[( <i>R,R</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]- [( <i>R,R</i> )-1,1-bis( <i>p</i> -methoxyphenyl)-2-isopropylethane-1,2-diamine]- ruthenium(II) <b>RuCl<sub>2</sub>[(<i>R,R</i>)-binap][(R,R)-daipen]</b>	11408-95	200mg
	11408-65	1g
Dichloro[( <i>S,S</i> )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]- [( <i>S,S</i> )-1,1-bis( <i>p</i> -methoxyphenyl)-2-isopropylethane-1,2-diamine]- ruthenium(II) <b>RuCl<sub>2</sub>[(<i>S,S</i>)-binap][(S,S)-daipen]</b>	11409-95	200mg
	11409-65	1g

## Highly Selective Hydrogenation Catalysts XyLSKEWPHOS Catalysts

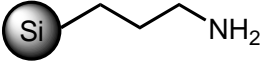
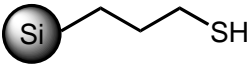
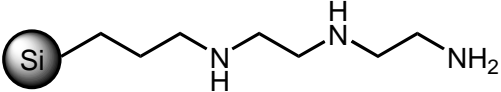
Product Name	Product Number	Package Size
Dibromo[( <i>R,R</i> )-2,4-bis(di-3',5'-xylylphosphino)pentane]- [( <i>R,R</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuBr<sub>2</sub>[(<i>R,R</i>)-xylskewphos][(R,R)-dpen]</b>	10535-68	100mg
	10535-95	500mg
Dibromo[( <i>R,R</i> )-2,4-bis(di-3',5'-xylylphosphino)pentane]- [( <i>S,S</i> )-1,1-bis( <i>p</i> -methoxyphenyl)-2-isopropyl-1,2-ethanediamine]- ruthenium(II) <b>RuBr<sub>2</sub>[(<i>R,R</i>)-xylskewphos][(S)-daipen]</b>	10537-68	100mg
	10537-95	500mg
Dibromo[( <i>S,S</i> )-2,4-bis(di-3',5'-xylylphosphino)pentane]- [( <i>S,S</i> )-1,2-diphenylethanediamine]ruthenium(II) <b>RuBr<sub>2</sub>[(<i>S,S</i>)-xylskewphos][(S,S)-dpen]</b>	10536-68	100mg
	10536-95	500mg
Dibromo[( <i>S,S</i> )-2,4-bis(di-3',5'-xylylphosphino)pentane]- [( <i>R</i> )-1,1-bis( <i>p</i> -methoxyphenyl)-2-isopropyl-1,2-ethanediamine]- ruthenium(II) <b>RuBr<sub>2</sub>[(<i>S,S</i>)-xylskewphos][(R)-daipen]</b>	10538-68	100mg
	10538-95	500mg

## Chiral Alcohols

Product Name	Product Number	Package Size
<i>(R)</i> -4-Chromanol	08288-55	5g
	08288-35	25g
<i>(S)</i> -4-Chromanol	08347-55	5g
	08347-35	25g
<i>(R,R)</i> -(+)-Hydrobenzoin	18617-55	5g
	18617-35	25g
<i>(S,S)</i> -(-)-Hydrobenzoin	18618-55	5g
	18618-35	25g
<i>(R)</i> -(-)-1-Indanol	20318-65	1g
	20318-35	25g
<i>(S)</i> -(+)-1-Indanol	20342-65	1g
	20342-35	25g
<i>(R)</i> -(+)-Phenylethanol	32123-35	25g
<i>(S)</i> -(+)-Phenylethanol	32124-35	25g

Product Name	Product Number	Package Size
( <i>R</i> )-1,1,1-Trifluoro-2-propanol	41181-35	25g
( <i>S</i> )-1,1,1-Trifluoro-2-propanol	41182-35	25g
( <i>R</i> )-1-[3,5-Bis(trifluoromethyl)phenyl]ethanol	☆	☆
( <i>S</i> )-1-[3,5-Bis(trifluoromethyl)phenyl]ethanol	☆	☆

### Metal Scavenger (*R-Cat-Sil*)

Product Name	Product Number	Package Size
<b><i>R-Cat-Sil AP</i></b> Loading : 2.0mmol/g <Metals removed> Pd, Ru, Rh, Co, Cu, Fe, Ni		36044-55
		36044-35
		36044-25
<b><i>R-Cat-Sil MP</i></b> Loading : 1.2mmol/g <Metals removed> Pd, Ru, Rh, Cu, Pt, Pb, Ag, Hg		36045-55
		36045-35
		36045-25
<b><i>R-Cat-Sil TA</i></b> Loading : 1.0mmol/g <Metals removed> Pd, Rh, Co, Cu, Fe, Zn, Pt		36046-55
		36046-35
		36046-25

<Reference Data> Particle size : 50 $\mu$ m, Specific surface : 730m<sup>2</sup>/g



 **KANTO CHEMICAL CO., INC.**

REAGENT DIVISION

East Muromachi Mitsui BLDG, 2-1, Nihonbashi Muromachi 2-chome,  
Chuo-ku, Tokyo, 103-0022 JAPAN

Telephone +813-6214-1092

Telefax +813-3241-1053

<http://www.kanto.co.jp> E-mail:kanto-61@gms.kanto.co.jp