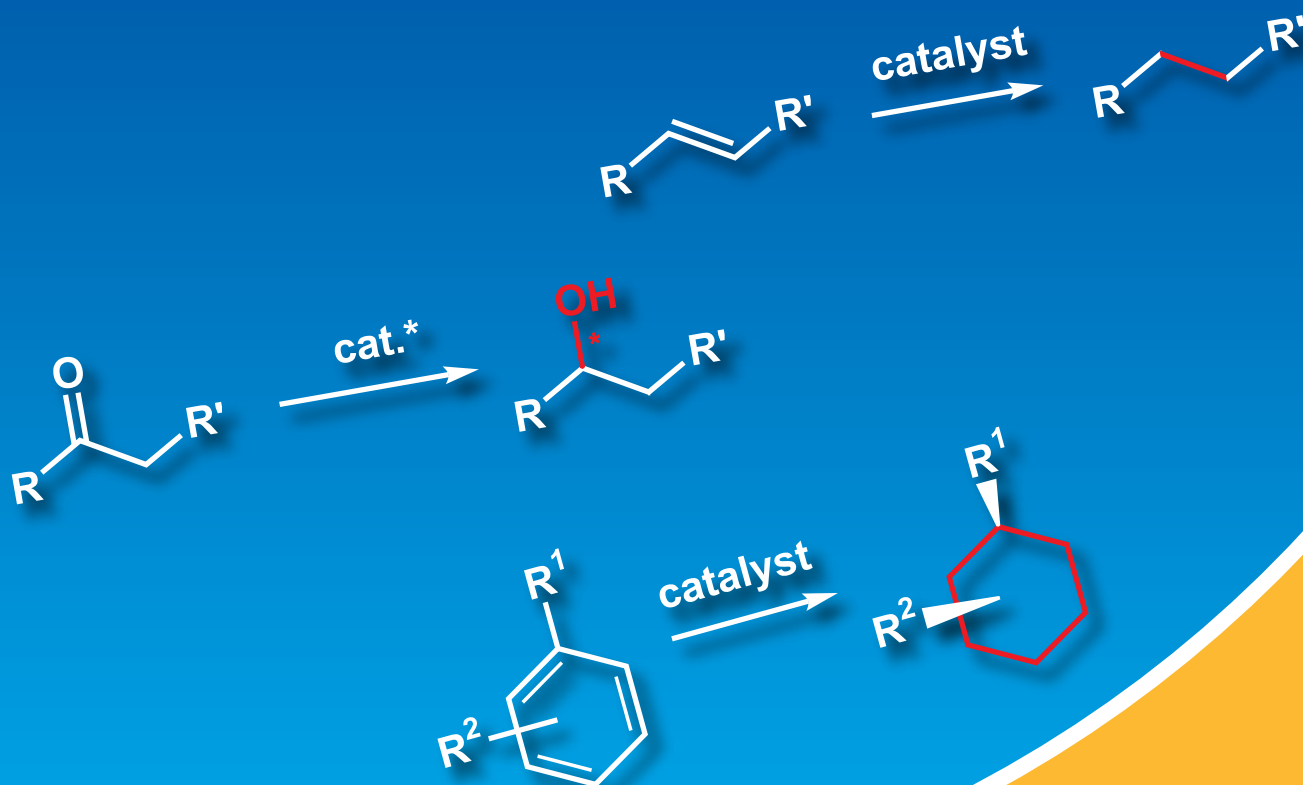


# Hydrogenation Catalysts



Catalysts for Hydrogenation

Catalysts for Asymmetric Hydrogenation

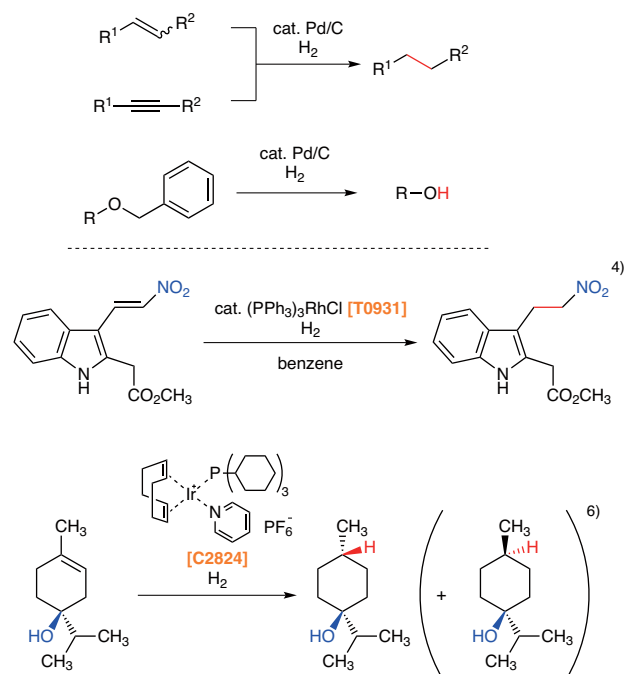
# Hydrogenation Catalysts

Hydrogenation is a common reaction wherein  $H_2$  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 hydrogenetic reduction.

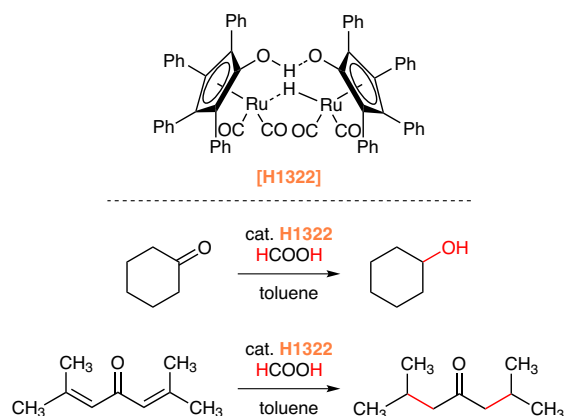
## Catalysts for Hydrogenation

Catalytic reduction is widely utilized in the hydrogenation of carbon-carbon bonds, nitro group reduction, and the removal of benzyl and benzyloxycarbonyl groups.<sup>1)</sup> Platinum metals are used in many forms such as Pd/C, and catalysts like Wilkinson's catalyst [T0931]<sup>2-4)</sup> and Crabtree's catalyst [C2824]<sup>5)</sup>. 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.<sup>6)</sup>



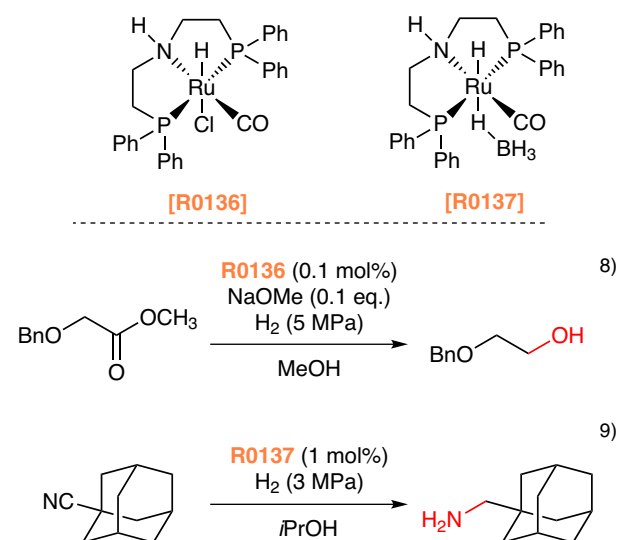
## 1. Shvo Catalyst

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



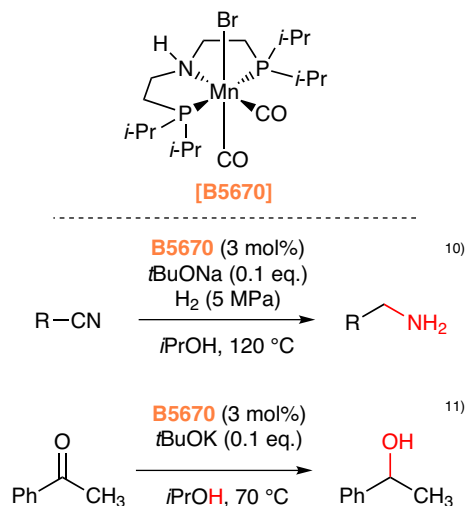
## 2. Ruthenium-complex Catalyst

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.<sup>8)</sup> However, benzyl and benzyloxycarbonyl groups, which are typically removed via conventional condition, are retained. Furthermore, **R0137** can also hydrogenate aldehydes, amides, and nitriles.<sup>9)</sup>



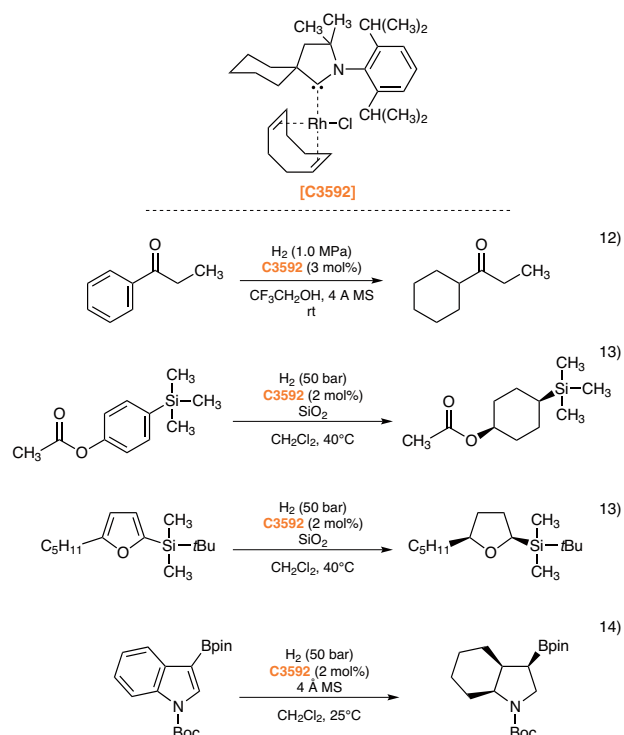
### 3. Manganese-complex Catalyst

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



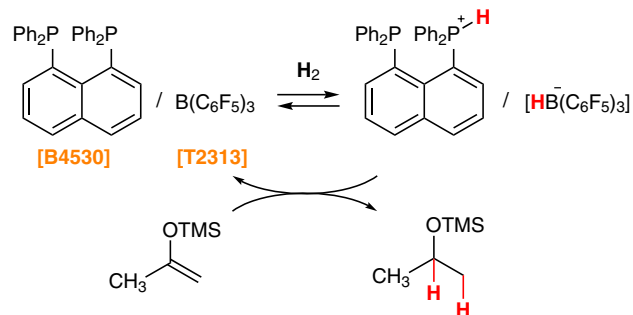
### 4. Rhodium Catalyst for *cis*-Selective Hydrogenation of Aromatic Rings

(Cyclohexyl-CAAC)Rh(COD)Cl **[C3592]** is used as an efficient and selective aromatic hydrogenation catalysts owing from the strongly  $\sigma$ -donating ligand. **C3592** can be used for the synthesis of cyclohexane moieties while still retaining various functional groups like carbonyls,<sup>12)</sup> silyls,<sup>13)</sup> and boryls<sup>14)</sup> in a single step. Under these conditions, the *cis*-configured saturated hydrocarbon is selectively provided.



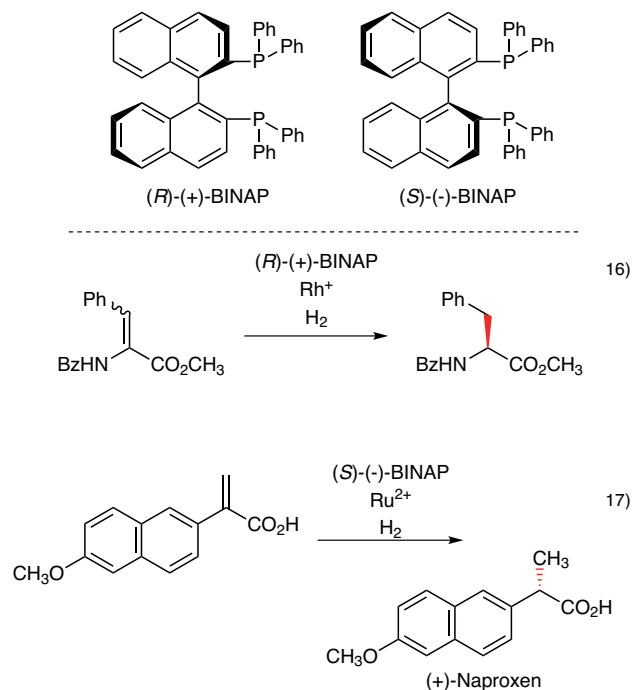
### 5. Organocatalysts for Metal-free Hydrogenations

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.<sup>15)</sup>

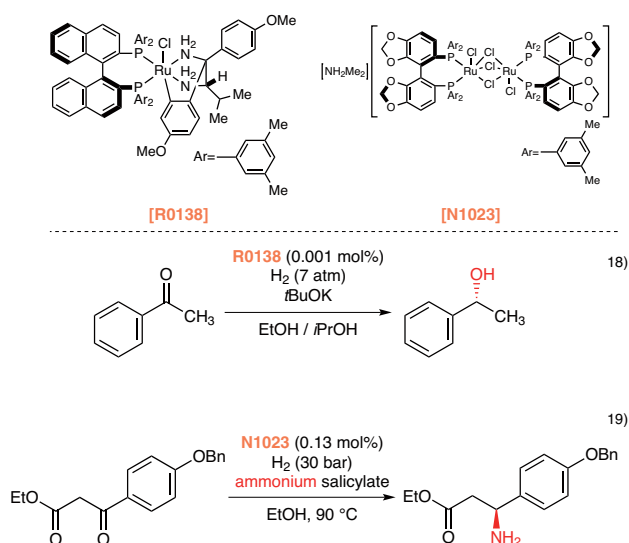


### ● Catalysts for Asymmetric Hydrogenation

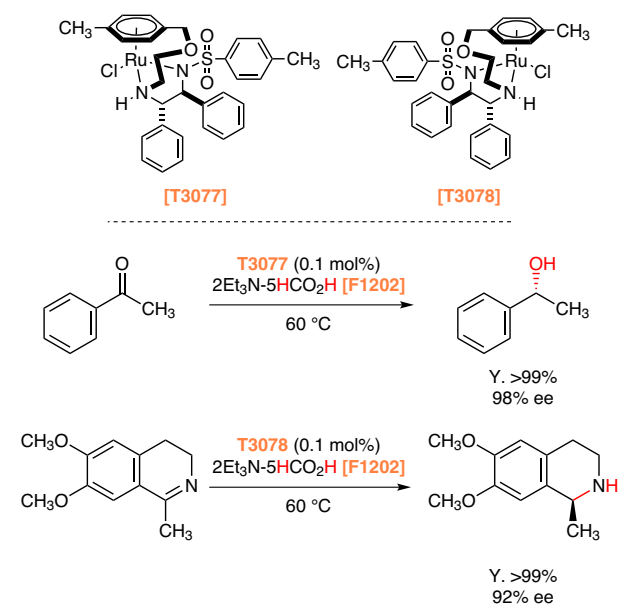
Noyori *et al.* have reported that the metal complex with a chiral 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) ligand can act as a catalyst for asymmetric hydrogenation of alkene moiety in high yields and enantioselectivity.<sup>16,17)</sup> This method has been utilized in the manufacturing 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.<sup>18)</sup> 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.<sup>19)</sup>



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**.<sup>20)</sup> Conventional catalysts have often required high pressure conditions, but these catalysts can hydrogenate substances under atmospheric pressure requiring no special apparatuses.



## References

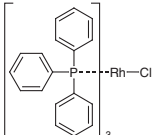
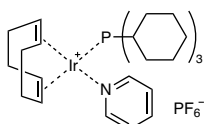
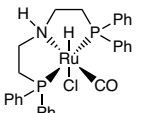
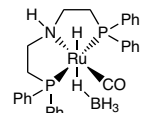
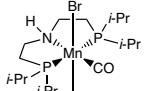
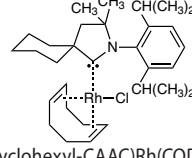
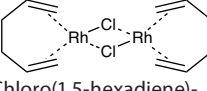
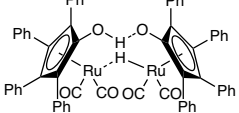
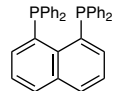
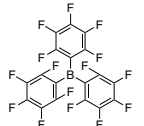
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## Catalysts for Hydrogenation

## Heterogeneous Catalysts

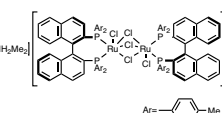
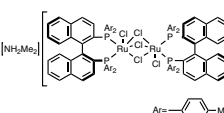
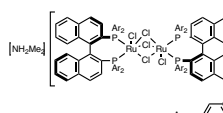
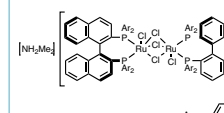
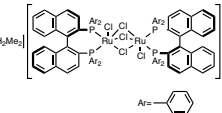
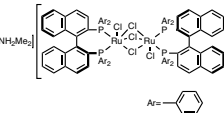
<b>P1785</b> 5g 25g	<b>P1701</b> 10g	<b>P1702</b> 5g 25g	<b>P1703</b> 5g 25g	<b>P1786</b> 1g
Pd Palladium 10% on Carbon (wetted with ca. 55% Water) [Useful catalyst for coupling reaction, etc.] CAS RN: 7440-05-3	Pd Palladium 5% on Barium Carbonate CAS RN: 7440-05-3	Pd Palladium 5% on Barium Sulfate CAS RN: 7440-05-3	Pd Palladium 5% on Calcium Carbonate (poisoned with Lead) CAS RN: 7440-05-3	Pd Palladium on SH Silica Gel (0.1mmol/g)
<b>P1528</b> 10g 50g	<b>P1720</b> 200mg	<b>S0487</b> 50g	<b>R0075</b> 1g	<b>R0076</b> 5g 25g
Pd(OH) <sub>2</sub> Pearlman's Catalyst (contains Pd, PdO) (wetted with ca. 50% Water) CAS RN: 12135-22-7	PtO <sub>2</sub> Platinum(IV) Oxide CAS RN: 1314-15-4	Ni Raney Nickel slurry in Water CAS RN: 7440-02-0	Rh Rhodium 5% on Carbon (wetted with ca. 55% Water) CAS RN: 7440-16-6	Ru Ruthenium 5% on Carbon (wetted with ca. 50% Water) CAS RN: 7440-18-8

## Homogeneous Catalysts

<b>T0931</b> 1g 5g	<b>C2824</b> 100mg	<b>R0136*</b> 200mg 1g	<b>R0137*</b> 200mg 1g
 Wilkinson Catalyst CAS RN: 14694-95-2	 Crabtree's Catalyst CAS RN: 64536-78-3	 Ru-MACHO® (contains 5% Toluene at maximum) CAS RN: 1295649-40-9	 Ru-MACHO®-BH CAS RN: 1295649-41-0
<b>B5670</b> 100mg	<b>C3592</b> 100mg 1g	<b>C3194</b> 100mg	<b>H1322</b> 100mg
 Bromodicarbonyl[bis[2-(diisopropylphosphino)ethyl]amine]manganese(I) CAS RN: 1919884-90-4	 (Cyclohexyl-CAAC)Rh(COD)Cl CAS RN: 1801869-83-9	 Chloro(1,5-hexadiene)-rhodium(I) dimer CAS RN: 32965-49-4	 Shvo's Catalyst CAS RN: 104439-77-2
<b>B4530</b> 1g 5g	<b>T2313</b> 1g 5g	<b>Others</b>	
 1,8-Bis(diphenylphosphino)-naphthalene CAS RN: 153725-04-3	 Tris(pentafluorophenyl)-borane CAS RN: 1109-15-5		

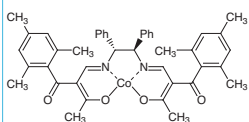
## Catalysts for Asymmetric Hydrogenation

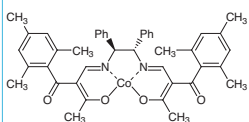
## Catalysts for Asymmetric Hydrogenation of Olefins and Functionalized Ketones

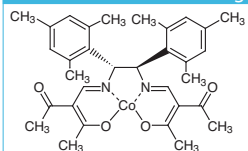
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 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((R)-tolbinap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 749935-02-2	 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((S)-tolbinap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 309735-86-2	 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((R)-xylbinap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 944451-08-5	 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((S)-xylbinap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 944451-10-9
<b>N1015*</b> 200mg 1g	<b>N1016*</b> 200mg 1g		
 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((R)-binap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 199684-47-4	 [NH <sub>2</sub> Me <sub>2</sub> ] [(RuCl((S)-binap)) <sub>2</sub> (μ-Cl) <sub>3</sub> ] CAS RN: 199541-17-8		

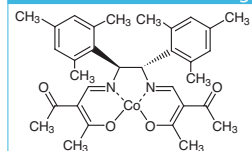
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<p><b>R0154*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((R)-segphos*)]Cl CAS RN: 944451-28-9</p>	<p><b>R0155*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((S)-segphos*)]Cl CAS RN: 944451-29-0</p>	<p><b>R0156*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((R)-dm-segphos*)]Cl CAS RN: 944451-30-3</p>	<p><b>R0157*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((S)-dm-segphos*)]Cl CAS RN: 944451-31-4</p>	<p><b>R0158*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((R)-dtbm-segphos*)]Cl CAS RN: 944451-32-5</p>
<p><b>R0159*</b> 200mg 1g</p> <p>[RuCl(p-cymene)((S)-dtbm-segphos*)]Cl CAS RN: 944451-33-6</p>	<p><b>R0166*</b> 200mg 1g</p> <p>Ru(OAc)<sub>2</sub>((R)-binap) CAS RN: 325146-81-4</p>	<p><b>R0167*</b> 200mg 1g</p> <p>Ru(OAc)<sub>2</sub>((S)-binap) CAS RN: 261948-85-0</p>	<p><b>R0168*</b> 200mg 1g</p> <p>Ru(OAc)<sub>2</sub>((R)-tolbinap) CAS RN: 116128-29-1</p>	<p><b>R0169*</b> 200mg 1g</p> <p>Ru(OAc)<sub>2</sub>((S)-tolbinap) CAS RN: 106681-15-6</p>
<p><b>Catalysts for Asymmetric Hydrogenation of Ketones</b></p>				
	<p><b>R0122*</b> 200mg 1g</p> <p>RuCl((S,S)-Fsdpen)(p-cymene) CAS RN: 1026995-72-1</p>	<p><b>R0123*</b> 200mg 1g</p> <p>RuCl((R,R)-Fsdpen)(p-cymene) CAS RN: 1026995-71-0</p>	<p><b>R0124*</b> 200mg 1g</p> <p>RuCl((S,S)-Tsdpen)(p-cymene) CAS RN: 192139-90-5</p>	<p><b>R0125*</b> 200mg 1g</p> <p>RuCl((R,R)-Tsdpen)(p-cymene) CAS RN: 192139-92-7</p>
<p><b>R0126*</b> 200mg 1g</p> <p>RuCl((S,S)-Tsdpen)(mesitylene) CAS RN: 174813-81-1</p>	<p><b>R0127*</b> 200mg 1g</p> <p>RuCl((R,R)-Tsdpen)(mesitylene) CAS RN: 174813-82-2</p>	<p><b>T3077*</b> 200mg 1g</p> <p>(S,S)-Ts-DENEB® CAS RN: 1384974-37-1</p>	<p><b>T3078*</b> 200mg 1g</p> <p>(R,R)-Ts-DENEB® CAS RN: 1333981-84-2</p>	<p><b>R0128*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((S)-dm-segphos*)((S)-daipen) CAS RN: 944450-44-6</p>
<p><b>R0129*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((R)-dm-segphos*)((R)-daipen) CAS RN: 944450-43-5</p>	<p><b>R0130*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((S)-dm-segphos*)((S,S)-dpen) CAS RN: 944450-46-8</p>	<p><b>R0131*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((R)-dm-segphos*)((R,R)-dpen) CAS RN: 944450-45-7</p>	<p><b>R0132*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((S)-xylbinap)((S)-daipen) CAS RN: 220114-01-2</p>	<p><b>R0133*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((R)-xylbinap)((R)-daipen) CAS RN: 220114-32-9</p>
<p><b>R0134*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((S)-xylbinap)((S,S)-dpen) CAS RN: 220114-03-4</p>	<p><b>R0135*</b> 200mg 1g</p> <p>RuCl<sub>2</sub>((R)-xylbinap)((R,R)-dpen) CAS RN: 220114-38-5</p>	<p><b>R0138*</b> 200mg 1g</p> <p>(S)-RUCY®-XylBINAP CAS RN: 1312713-89-5</p>	<p><b>R0139*</b> 200mg 1g</p> <p>(R)-RUCY®-XylBINAP CAS RN: 1384974-38-2</p>	

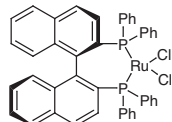
## Others

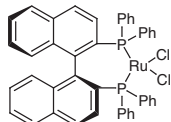
**B1844** 100mg

**(R)-MPAC**  
 CAS RN: 212250-92-5

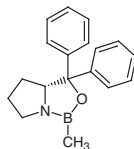
**B1845** 100mg

**(S)-MPAC**  
 CAS RN: 171200-71-8

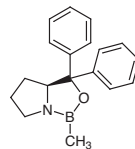
**B2314** 100mg

**(R)-AMAC**  
 CAS RN: 361346-80-7

**B2315** 100mg

**(S)-AMAC**  
 CAS RN: 259259-80-8

**B3067** 250mg

**[(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) Dichloride**  
 CAS RN: 132071-87-5

**B3068** 250mg

**[(S)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium(II) Dichloride**  
 CAS RN: 134524-84-8

**D2130** 1g 5g

**(R)-Me-CBS Catalyst**  
 CAS RN: 112022-83-0

**D2131** 1g 5g

**(S)-Me-CBS Catalyst**  
 CAS RN: 112022-81-8

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