New Pincer-type Rhodium Complex Catalyst

Advantages

• Convert Terminal Alkenes into Optically Active 1,2-Diols
• Catalyze Cross-coupling of Alkynes in the Formation of Stereoselective Ene-ynes etc.

Applications

Asymmetric Diboration of Terminal Alkenes and Their Conversion to the Optically Active 1,2-Diols

\[
\begin{align*}
\text{B4195} & \quad 1 \text{ mol}\% \\
\text{B}_2\text{pin}_2 & \quad [B1964] \quad 1.2 \text{ equiv.} \\
\text{NaO\text{Bu}} & \quad [S0450] \quad 5 \text{ mol}\% \\
\text{THF, 60 °C, 1 h}
\end{align*}
\]

\[
\begin{align*}
\text{NaBO}_3 \cdot 4\text{H}_2\text{O} & \quad [S0887] \quad (5 \text{ equiv.}) \\
\text{THF-H}_2\text{O}
\end{align*}
\]

Y 88%, 99% ee


Stereoselective Cross-coupling of Alkynes

\[
\begin{align*}
\text{Ph} & \quad [E0196] \\
+ \quad \text{MeO}_2\text{C} & \quad [A0090] \\
\text{B4195} & \quad 1 \text{ mol}\% \\
\text{H}_2 & \quad (1 \text{ atm}) \\
\text{toluene} & \quad 100 \degree\text{C, 4 h}
\end{align*}
\]

Y 85% (E:Z = 2:98)


B4195 Bis(acetato)\text{aqua}[(S,S)-4,6-bis(4-isopropyl-2-oxazolin-2-yl)-m-xylene]rhodium

10mg
Nishiyama and his coworkers have studied the design and synthesis of pincer type ligands and their use for preparation of organometallic catalysts. They also have researched the effective asymmetric reactions using them as pincer type organometallic catalysts. Pybox ligands, which having two oxazoline rings bound to a pyridine ring at the 2- and 6-positions, were first synthesized by his group. They have studied the chemistry of Pybox ligands and a number of attractive reactions have been developed. In addition, they also focus on Phebox ligands, the effective ligands which replace the pyridyl group of Pybox ligands with a phenyl group, and apply them to the asymmetric syntheses.

Pybox-Rh catalyzed highly enantioselective reduction of ketones

$$\text{B2218 (6 mol\%)}$$

$$\text{RhCl_3 (1 mol\%)}$$

$$\text{Ph_2SiH_2, AgBF_4}$$

$$\text{1) H^+}$$

$$\text{R=CH_2CH_2CO_2Et}$$

$$\text{CH_2CH_2Ph}$$

$$\beta\text{-Nap}$$

$$\text{Y (%) ee (%)}$$

91 95

92 66

93 93

