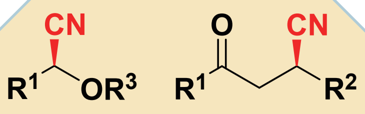
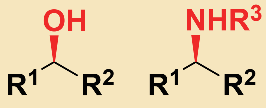
To contribute to society

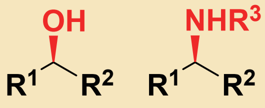
KANTO’S CATALYST TECHNOLOGIES



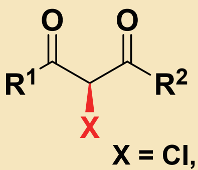
Asymmetric Cyanation of
Aldehydes or Ketones



Asymmetric Transfer
Hydrogenation of
Ketones, Imines



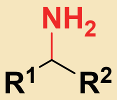
Asymmetric Hydrogenation
of Ketones,
Imines or Ketoesters



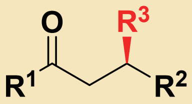
X = Cl, F

Asymmetric Halogenation
of β-Ketoesters

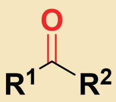
KANTO MOLECULAR CATALYST TECHNOLOGIES



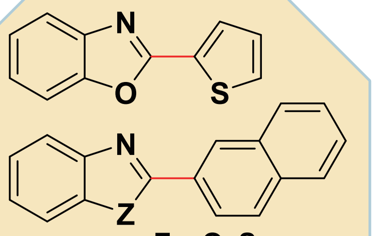
Reductive Amination of
Ketones or Ketoacids



Asymmetric 1,4-Additon of
α,β-Unsaturated Carbonyls



Oxidation of Alcohols



Z = O, S

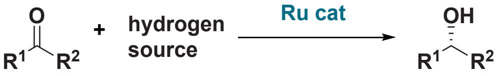
Cross-Coupling
Reaction of Azoles

Advanced Molecular Catalysts and Custom Synthesis

Kanto Chemical Co., Inc.

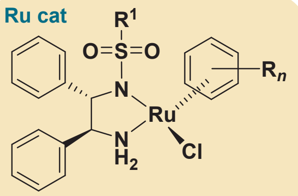
1. Asymmetric Transfer Hydrogenation

Modified chiral Ru catalysts on sulfonyl group have higher enantioselectivity for the reaction of a certain ketones. The choice of the hydrogen source is the first concerning point. The single phase reaction using formic acid salt in MeOH gives chiral alcohol with high enantioselectivity and high yield.



Selection of suitable system

hydrogen source	HCO_2H/NEt_3	HCO_2X in H_2O (X = Na, K)	HCO_2X in MeOH (X = Na, K)
efficiency	moderate to high	high	high
ee, %	high	a slight drop of ee	high

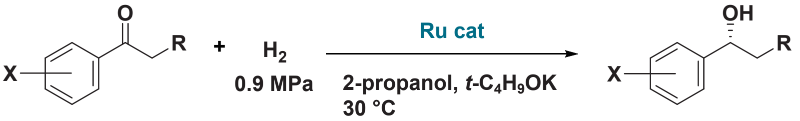


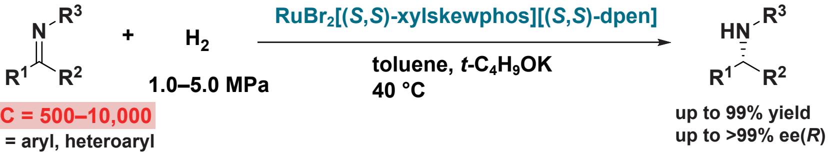
R^1 = Bn, CH_2-2’,6’-$(CH_3)_2C_6H_3$, *i*-Bu,Camphor

RuCl[(*S*,*S*)-R^1SO_2dpen](arene)

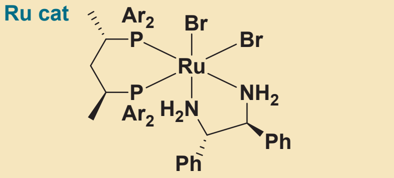
2. Asymmetric Hydrogenation

XylSkewphos catalysts hydrogenate aromatic ketones effectively with high enantioselectivity to yield optically active alcohols. To obtain high enatioselectivity, proper selection of the catalysts is necessary. RuBr$_2$(xylskewphos)(dpen) is an excellent catalyst for the asymmetric hydrogenation of imines. Various imines can be hydrogenated efficiently with this catalyst to afford the amine products in high ee’ s



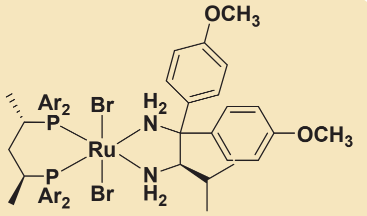


S/C = 500–10,000
R^1 = aryl, heteroaryl
R^2 = alkyl
R^3 = aryl, benzyl



Ar = 3,5-$(CH_3)_2C_6H_3$

RuBr$_2$[(*S*,*S*)-xylskewphos][(*S*,*S*)-dpen]

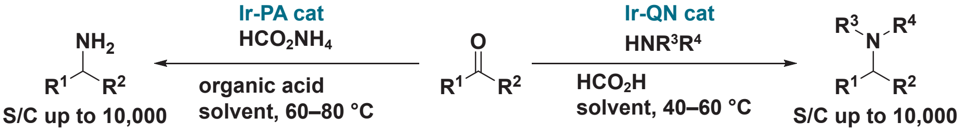


Ar = 3,5-$(CH_3)_2C_6H_3$

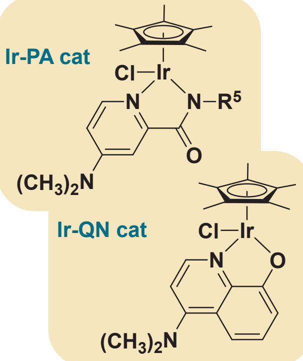
RuBr$_2$[(*S*,*S*)-xylskewphos][(*R*)-daipen]

3. Reductive Amination

Ir catalysts which have picolin amide ligands are suitable for primary amine synthesis. On the other hand, the synthesis of secondary amines and tertiary amines, the Ir catalysts with a quinolinol ligand are suitable. Reductive amination using these catalysts proceed under mild conditions.

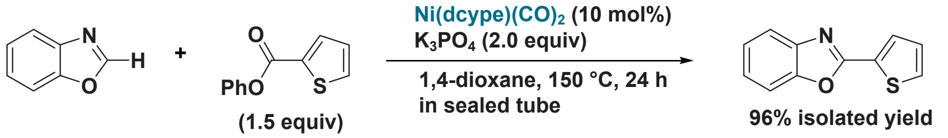


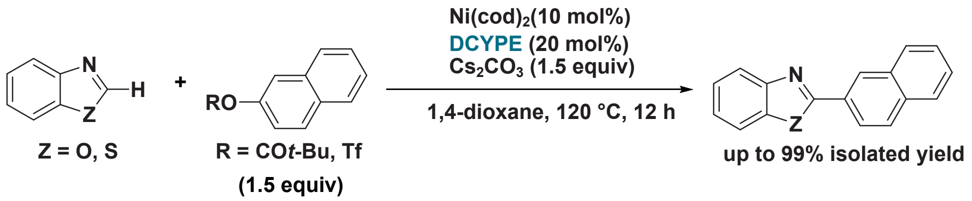
- ·air-stable
- ·safe and inexpensive formate
- ·lower temperture
- ·high activity and chemoselectivity
- ·clean and operationally simple
- ·diverse solvent selection

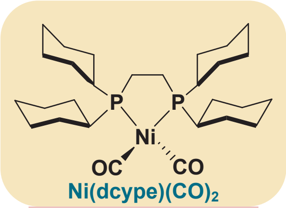


4. Cross-Coupling Reaction

Ni(dcype)(CO)$_2$ is applicable for the cross coupling reaction of 1,3-azoles and aromatic ester compounds via the elimination of ester group, leading to 2-arylazoles quantitatively. Ni-dcype is also effective for the cross coupling of azoles with phenol derivatives, leading to 2-arylazoles.

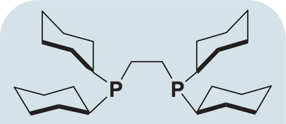






Ni(dcype)(CO)$_2$

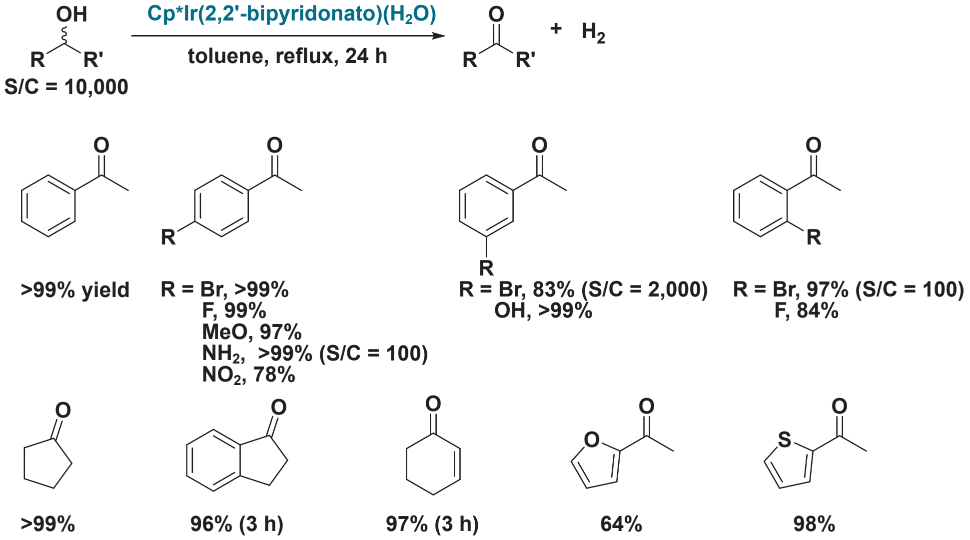
air-stable Ni complex

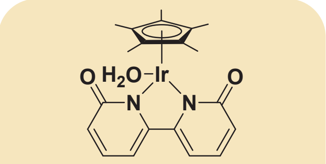


DCYPE

5. Oxidation of Alcohols

These Iridium catalysts oxidize alcohols to ketones without any oxidant. The reaction proceeds effectively with evolution of hydrogen gas. These oxidations can be carried out with some hydrogen acceptors without hydrogen gas production.

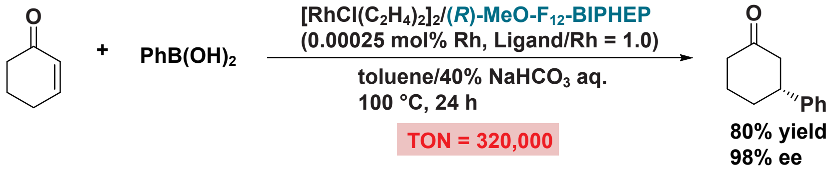


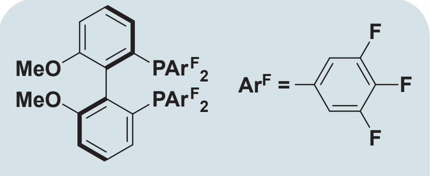


Cp*Ir(2,2'-bipyridonato)(H$_2$O)

6. Asymmetric 1,4-Addition

(*R*)-MeO-F$_{12}$-BIPHEP is a highly electron-deficient chiral diphosphine ligand. Using this ligand with Rhodium, the asymmetric 1,4-addition of phenyl boronic acid to α,β-unsaturated carbonyl compounds proceeds effectively.

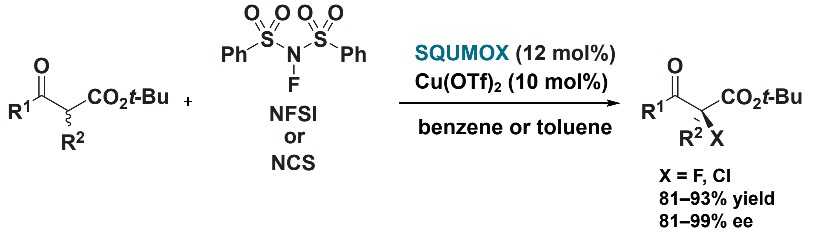


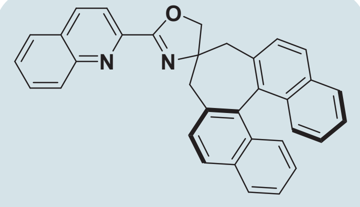


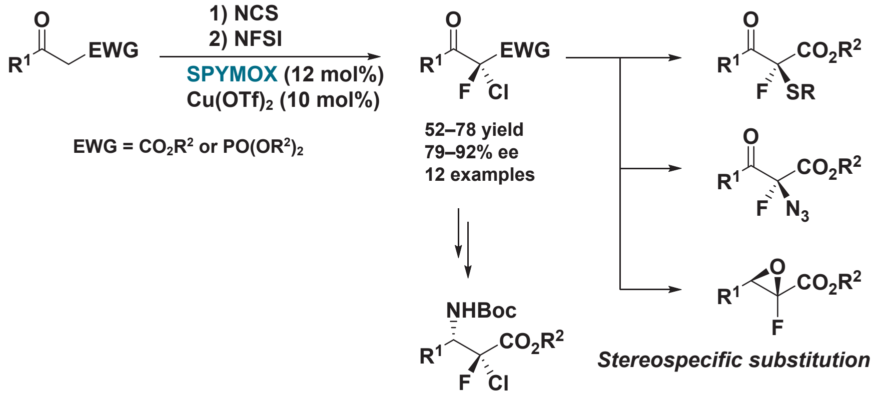
(*R*)-MeO-F$_{12}$-BIPHEP

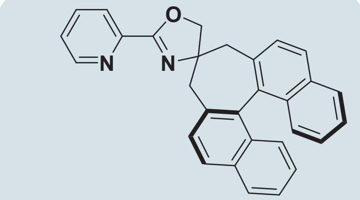
7. Asymmetric Halogenation of β-Ketoesters

Highly enantioselective fluorination and chlorination of β-ketoesters were performed using a chiral Lewis acid catalyst prepared from Cu(OTf)$_2$ and chiral spyro oxazoline ligands. Nucleophilic substitution of the resulting chlorides proceeded smoothly to afford various chiral molecules without less of enantiopurity. Also, These chiral spyro oxazoline ligands can be applied to bidentate ligand such as Box ligands.



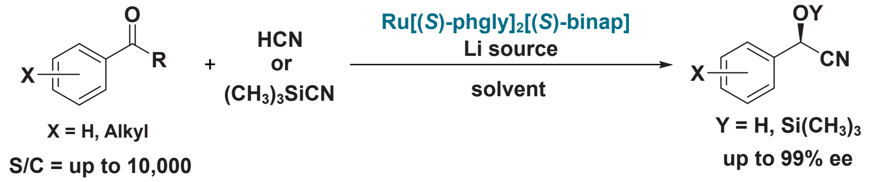

SQUMOX

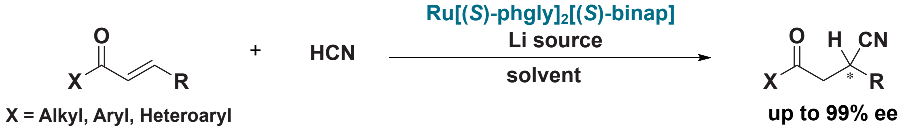


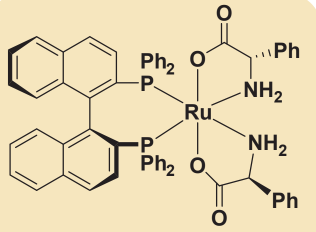

SPYMOX

8. Asymmetric Cyanation of Aldehydes or Ketones

The combined systems of phenylglycinate/BINAP/Ru(II) complex and Li compounds catalyze asymmetric cyanosilylation and hydrocyanation of aldehydes, ketones, α,β-unsaturated ketones, and N-protected aldimines. This complex is recyclable.







Ru[(*S*)-phgly]$_2$[(*S*)-binap]

Kanto Chemical Co., Inc.
REAGENT DIVISION

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

TEL : +81-3-6214-1092
FAX : +81-3-3241-1053
E-mail : kanto-61@gms.kanto.co.jp
HP : https://www.kanto.co.jp/english