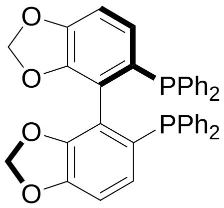
Tech Note

(*R*)-SEGPHOS
(*R*)-(+)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole

CAS Number	**244261-66-3**
CASName	**Phosphine, [(4*R*)-(4,4'-bi-1,3-benzodioxole)- 5,5'-diyl]bis [dipheny-**
Formula	$C_{38}H_{28}O_4P_2$
Molecular Weight	**610.59**



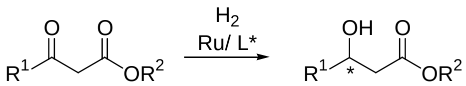
Representative references:

T. Saito, T. Yokozawa, T. Ishizaki, T. Moroi, N. Sayo, T. Miura, H. Kumobayashi, Adv. Synth. Catal., 2001, *343*, 264.

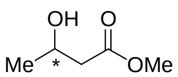
Performance Examples and References:

SEGPHOS shows its greatest competence in hydrogenation of α-, β- and γ-functionalized ketones. In most cases, higher catalytic activities and enantioselectivities are achieved by use of SEGPHOS / Ru complexes than by use of BINAP complexes.

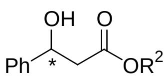
1. Ru catalyzed asymmetric hydrogenation
1.1 Functionalized ketone
a. β-ketoesters



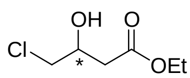
R^1 = alkyl, aryl, heteroaryl



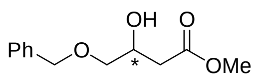
SEGPHOS : >99% ee
BINAP[1] : >99% ee



SEGPHOS[3] : 98% ee
(R^2 = Me, **S/C = 10,000**)
TolBINAP[3] : 87% ee
(R^2 = Et, S/C = 1,000)



SEGPHOS[2,3] : 98.5% ee
(S/C = 20,000)
TolBINAP[2,3] : 95.9% ee
(S/C = 1,000)

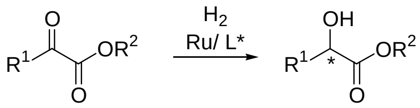


SEGPHOS[2,3] : 99.4% ee
TolBINAP[2,3] : 97.4% ee

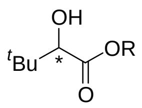
1) Noyori, R. *J. Am. Chem. Soc*. **1987**, *109*, 5856. 2) Saito, T. *Adv. Synth. Catal*. **2001**, *343*, 264. 3) Sumi, K. *Topics Organomet. Chem*. **2004**, *6*, 63. 4) JP H6-65226A, **1994**.

TAKASAGO
finechemicals@takasago.com

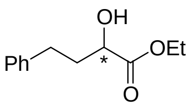
b. α-Ketoesters



R^1 = alkyl, aryl, heteroaryl

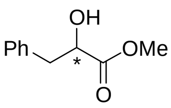


SEGPHOS[1,2] : 98.6% ee (R = Et)
TolBINAP[2) : 84.0% ee (R = Me)



SEGPHOS[1,2] : 93.7% ee
(S/ C = 1,500)

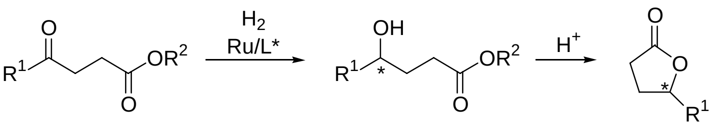
BINAP[1,2] : 90.0% ee
(S/ C = 1,000)



SEGPHOS[1) : 95.9% ee

1) Saito, T. *Adv. Synth. Catal*. **2001**, *343*, 264. 2) Sumi, K. *Topics Organomet. Chem*. **2004**, *6*, 63.

c. γ-Ketoesters



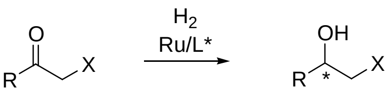
R^1 = alkyl, aryl

Ex.) R1 = Me, R2 = Et

L* = **SEGPHOS : 99% ee**
TolBINAP : 97.2% ee

Saito, T. *Adv. Synth. Catal*. **2001**, *343*, 264.

d. Hydroxyacetones, Amino ketones, and Keto phosphonates

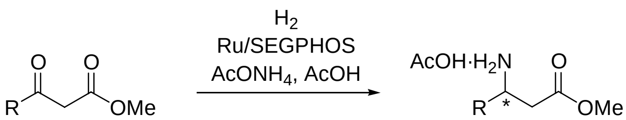


Ex.) R = Me, X = OH

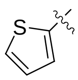
L* =		
	SEGPHOS :	**98.5% ee**
	MeO-BIPHEP :	96% ee
	BIPHEMP :	93% ee
	BINAP :	83% ee

Saito, T. *Adv. Synth. Catal*. **2001**, *343*, 264.

1.2. Direct reductive amination



R = alkyl, aryl, heteroaryl

Ex.) R = 

97.5% ee

WO 2005/028419 A3, **2004**.

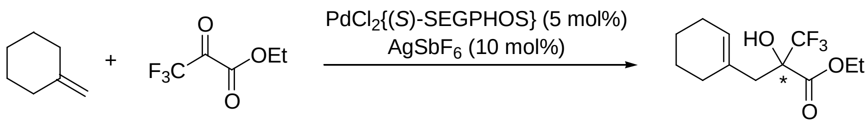
TAKASAGO

finechemicals@takasago.com

Tech Note

2. Pd catalyzed asymmetric reactions

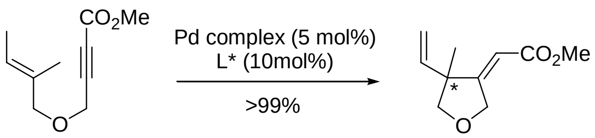
2.1 Ene-reaction



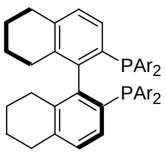
quant., 96% ee

Mikami, K. *Tetrahedron: Asymm.* **2004**, *15*, 3885.

2.2. Ene-type cyclization



Pd complex	L*	% ee
$Pd(OCOCF_3)_2$	**(*R*)-SEGPHOS**	**>99% (*S*)**
$[Pd(MeCN)_4](BF_4)_2$	(*S*)-DM-SEGPHOS	96% (*R*)
$Pd(OCOCF_3)_2$	(*S*)-H_8-BINAP	95% (*R*)
$[Pd(MeCN)_4](BF_4)_2$	(*S*)-Xyl-H_8-BINAP	94% (*R*)

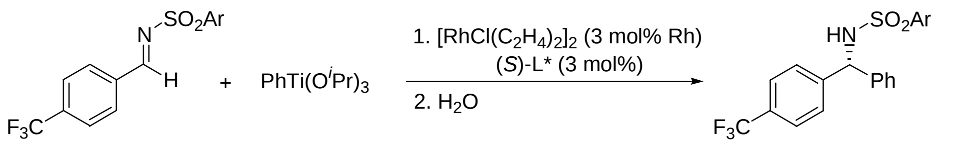


Ar = 3,5-xylyl
(*S*)-Xyl-H_8-BINAP

Mikami, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 249.

3. Rh catalyzed asymmetric reactions

3.1. 1,2-addition

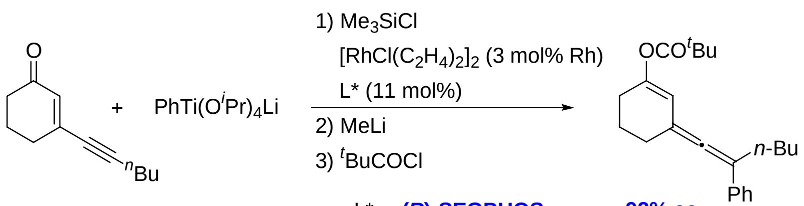


Ar = 2,4,6-(*i*-Pr)$_3$-C_6H_2

L* = **SEGPHOS** : **98%, 93% ee**
BINAP : 58%, 71% ee
H_8-BINAP : 86%, 82% ee

Hayashi, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 6125.

3.2. 1,6-Addition

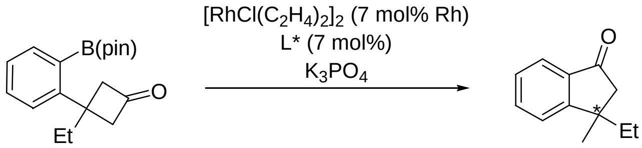


L* = **(*R*)-SEGPHOS :** **92% ee**
(*R*)-BINAP : 80% ee
(*S*)/(*R*)-PPPF-P(^{t}Bu)$_2$: 14% ee

Hayashi, T. *Org. Lett.* **2004**, *6*, 305.

Tech Note

3.3. C-C bond cleavage

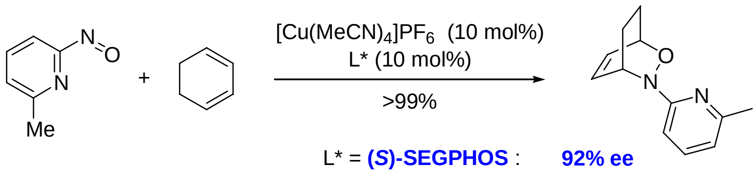


L* = **(*S*)-SEGPHOS : 95% ee (*S*)**
(*R*)-MeO-BIPHEP : 75% ee (*R*)
(*S*)-BINAP : 69% ee (*S*)

Murakami, M. *Org. Lett.* **2006**, *8,* 3379.

4. Cu catalyzed asymmetric reactions

Nitroso-Diels-Alder reaction



L* = **(*S*)-SEGPHOS** : **92% ee**
(*R*)-MeO-BIPHEP : 90% ee
(*R*)-BINAP : 87% ee
(*R*)-H_8-BINAP : 67% ee

Yamamoto, H. *J. Am. Chem. Soc.* **2004**, *126,* 4128.