

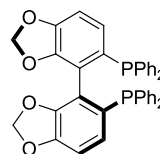
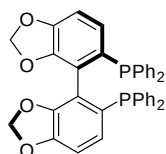
SEGPHOS®

SEGPHOS works particularly well in asymmetric hydrogenation of α -, β -, and γ -functionalized ketones. In most cases, catalytic activities and enantioselectivities achieved by SEGPHOS-ruthenium complexes are higher than those by BINAP counterparts.

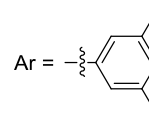
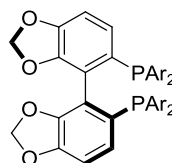
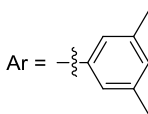
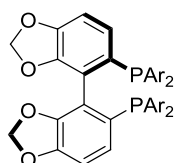
DM-SEGPHOS is great at producing high enantioselectivity in reductive amination of β -keto esters to β -amino acids. Replacing XylBINAP with DM-SEGPHOS as a ligand in Noyori's $[\text{RuX}_2(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]$ complex has been known to improve enantioselectivity in difficult reduction reactions.

"SEGPHOS" is a registered trademark of Takasago International Corporation in Japan and other countries.

(R)-(+)-SEGPHOS		(S)-(-)-SEGPHOS	
CAS No.	244261-66-3	CAS No.	210169-54-3
Formula	$\text{C}_{38}\text{H}_{28}\text{O}_4\text{P}_2$	Formula	$\text{C}_{38}\text{H}_{28}\text{O}_4\text{P}_2$
M.W.	610.59	M.W.	610.59



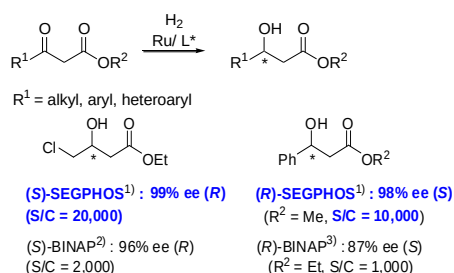
(R)-(+)-DM-SEGPHOS		(S)-(-)-DM-SEGPHOS	
CAS No.	850253-53-1	CAS No.	210169-57-6
Formula	$\text{C}_{46}\text{H}_{44}\text{O}_4\text{P}_2$	Formula	$\text{C}_{46}\text{H}_{44}\text{O}_4\text{P}_2$
M.W.	722.81	M.W.	722.81



Tech Note

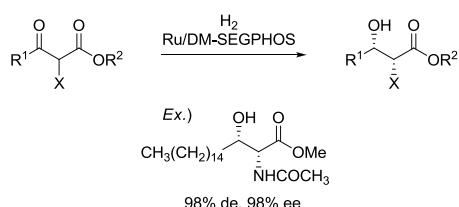
1 Ru Catalyzed Asymmetric Hydrogenation

1.1 β -Ketoesters



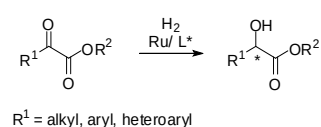
Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, 343, 264.
 doi:[10.1002/1615-4169\(20010330\)343:3<264::AID-ADSC264>3.0.CO;2-T](https://doi.org/10.1002/1615-4169(20010330)343:3<264::AID-ADSC264>3.0.CO;2-T)

1.2 Dynamic Kinetic Resolution



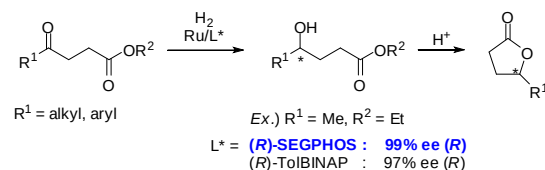
Sumi, K. *Topics Organomet. Chem.* **2004**, 6, 63.
 doi: [10.1007/b11768](https://doi.org/10.1007/b11768)

1.3 α -Ketoesters



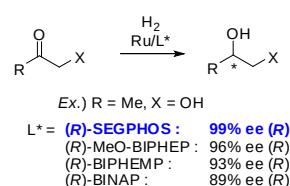
Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, 343, 264.
 doi:[10.1002/1615-4169\(20010330\)343:3<264::AID-ADSC264>3.0.CO;2-T](https://doi.org/10.1002/1615-4169(20010330)343:3<264::AID-ADSC264>3.0.CO;2-T)

1.4 γ -Ketoesters



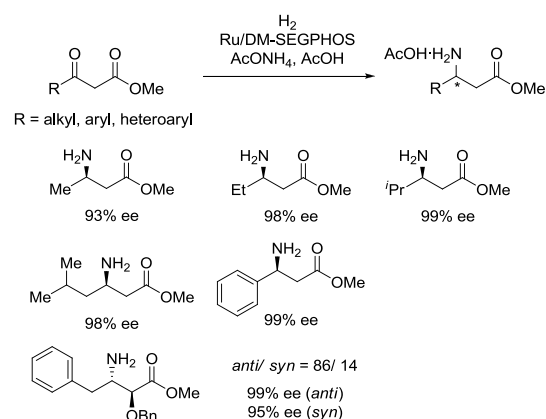
Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, 343, 264.
 doi:[10.1002/1615-4169\(20010330\)343:3<264::AID-ADSC264>3.0.CO;2-T](https://doi.org/10.1002/1615-4169(20010330)343:3<264::AID-ADSC264>3.0.CO;2-T)

1.5 Hydroxyacetones

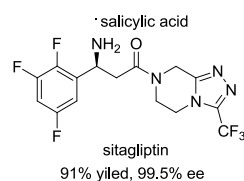
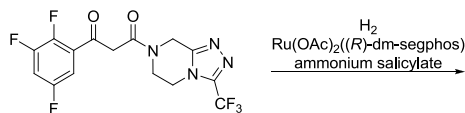


Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, 343, 264.
 doi:[10.1002/1615-4169\(20010330\)343:3<264::AID-ADSC264>3.0.CO;2-T](https://doi.org/10.1002/1615-4169(20010330)343:3<264::AID-ADSC264>3.0.CO;2-T)

1.6 Direct Reductive Amination of β -Keto Esters



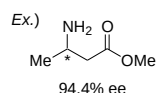
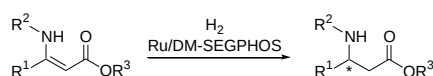
JP4705031B, EP1685092B, EP2100875B,
 US7626034B, [WO2005028419A](https://doi.org/10.1002/1615-4169(20050284)19A) (Takasago)



Matsumura, K. *J. Am. Chem. Soc.* **2009**, *131*, 11316.

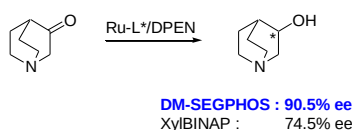
doi: [10.1021/ja905143m](https://doi.org/10.1021/ja905143m)

1.7 Hydrogenation of Enamino Esters



US7015348B, [EP1386901B](#) (Takasago)

1.8 Hydrogenation of Cycloalkanones



DM-SEGPHOS : 90.5% ee
XylBINAP : 74.5% ee

JP4490211B, US7462722B, [EP1650207B](#) (Takasago)

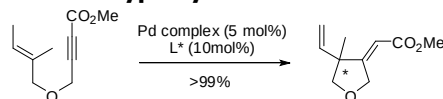
2 Pd Catalyzed Asymmetric Reaction

2.1 Ene-Reaction



Mikami, K.; Aikawa, K.; Kainuma, S.; Kawakami, Y.; Saito, T.; Sayo, N.; Kumobayashi, H. *Tetrahedron: Asymm.* **2004**, *15*, 3885.
doi: [10.1016/j.tetasy.2004.10.022](https://doi.org/10.1016/j.tetasy.2004.10.022)

2.2 Ene-Type Cyclization

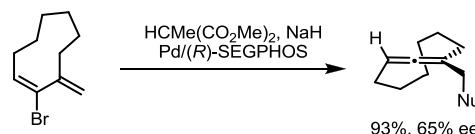


Pd complex	L*	% ee
$\text{Pd}(\text{OCOCF}_3)_2$	(R)-SEGPHOS	>99% (S)
$[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$	(S)-DM-SEGPHOS	96% (R)
$\text{Pd}(\text{OCOCF}_3)_2$	(S)-H ₈ -BINAP	95% (R)

Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 249.

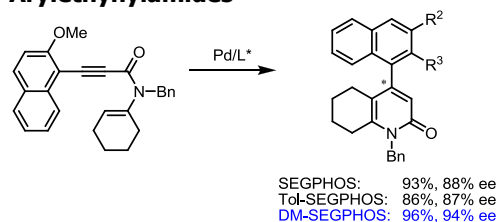
doi: [10.1002/1521-3773\(20010105\)40:1<249::AID-ANIE249>3.0.CO;2-0X](https://doi.org/10.1002/1521-3773(20010105)40:1<249::AID-ANIE249>3.0.CO;2-0X)

2.3 Stereoselective [2 + 2]Cycloaddition with Ketenes



Ogasawara, M.; Okada, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2009**, *11*, 177
doi: [10.1021/ol802280c](https://doi.org/10.1021/ol802280c)

2.4 Cycloisomerization of N-Alkenyl Arylethynylamides

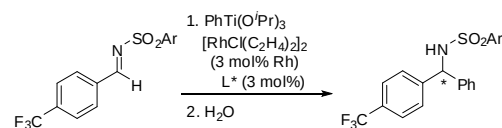


SEGPHOS: 93%, 88% ee
Tol-SEGPHOS: 86%, 87% ee
DM-SEGPHOS: 96%, 94% ee

Imase, H.; Suda, T.; Shibata, Y.; Noguchi, K.; Hirano, M.; Tanaka, K. *Org. Lett.* **2009**, *11*, 1805.
doi: [10.1021/ol900373z](https://doi.org/10.1021/ol900373z)

3 Rh Catalyzed Asymmetric Reaction

3.1 1,2-Addition

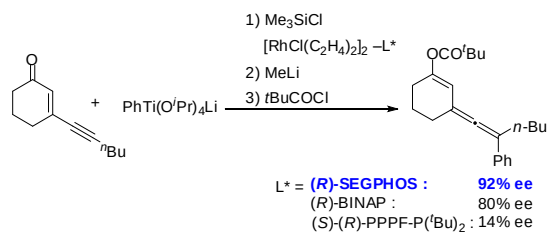


Ar = 2,4,6-(i-Pr)₃-C₆H₂

L* = (S)-SEGPHOS : 98%, 93% ee (R)
(S)-BINAP : 58%, 71% ee (R)
(S)-H₈-BINAP : 86%, 82% ee (R)

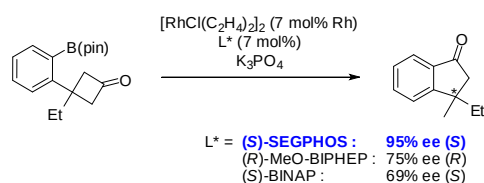
Hayashi, T.; Kawai, M.; Tokunaga, N. *Angew. Chem. Int. Ed.* **2004**, *43*, 6125.
doi: [10.1002/anie.200461338](https://doi.org/10.1002/anie.200461338)

3.2 1,6-Addition



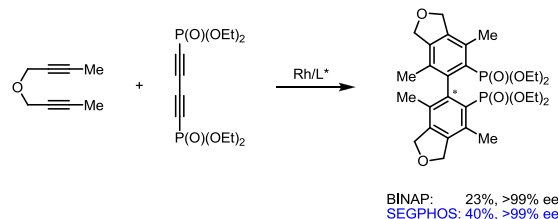
Hayashi, T.; Tokunaga, N.; Inoue, K. *Org. Lett.* **2004**, 6, 305.
 doi: [10.1021/ol036309f](https://doi.org/10.1021/ol036309f)

3.3 C-C Bond Cleavage



Matsuda, T.; Shigeno, M.; Makino, M.; Murakami, M. *Org. Lett.* **2006**, 8, 3379.
 doi: [10.1021/ol061359g](https://doi.org/10.1021/ol061359g)

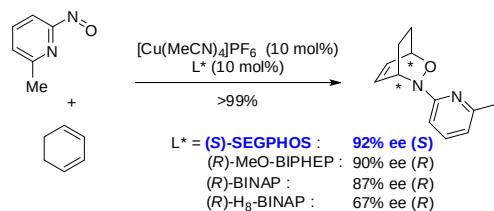
3.4 Double [2 + 2 + 2] Cycloaddition



Nishida, G; Ogaki, S; Yusa, Y; Yokozawa, T; Noguchi, K; Tanaka, K. *Org. Lett.* **2008**, 10, 2849.
 doi: [10.1021/ol801013v](https://doi.org/10.1021/ol801013v)

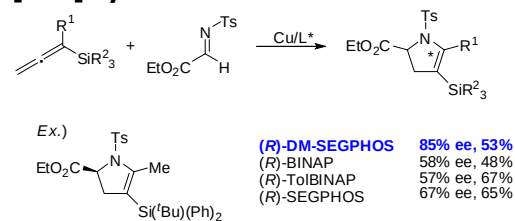
4 Cu Catalyzed Asymmetric Reaction

4.1 Nitroso-Diels-Alder Reaction



Yamamoto, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2004**, 126, 4128.
 doi: [10.1021/ja049849w](https://doi.org/10.1021/ja049849w)

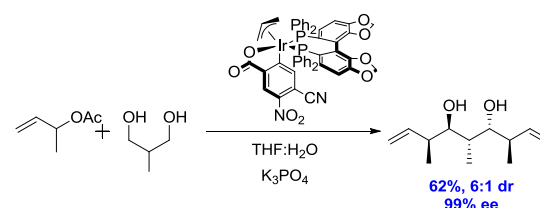
4.2 Cu Catalyzed Asymmetric Reaction: [3+2] Cycloaddition



Daidouji, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2005**, 7, 1051.
 doi: [10.1021/ol047343c](https://doi.org/10.1021/ol047343c)

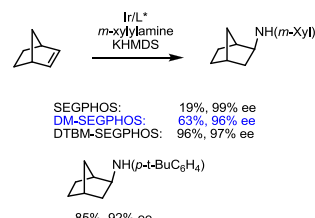
5 Ir Catalyzed Asymmetric Reaction

5.1 Crotylation of 1,3-Diols



Krische, M. J. et al, *J. Am. Chem. Soc.*, **2011**, 133, 12795.
 doi: [10.1021/ja204570w](https://doi.org/10.1021/ja204570w)

5.2 Asymmetric Hydroamination



Zhou, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, 130, 12220.
 doi: [10.1021/ja803523z](https://doi.org/10.1021/ja803523z)