

## ATH (Asymmetric Transfer Hydrogenation) Catalyst Kit

By using 2-propanol or formic acid as the hydrogen source, asymmetric transfer hydrogenation can avoid the use of high pressure hydrogen gas. In addition, experimental procedures are simple. Ruthenium complexes bearing chiral bidentate nitrogen ligand and arene are highly efficient for reduction of a broad range of ketones and imines to chiral alcohols and amines.

*This kit contains 250mg of each of the items listed below. All items are available for individual sale in 250mg, 1g & 5g unit sizes*

44-0148 RuCl[(R,R)-Tsdpen](p-cymene)	44-0154 RuCl[(R,R)-Tsdpen](mesitylene)	44-0156 RuCl[(R,R)-Fsdpen](p-cymene)	44-0185 (R,R)-Ts-DENEB®
44-0149 RuCl[(S,S)-Tsdpen](p-cymene)	44-0155 RuCl[(S,S)-Tsdpen](mesitylene)	44-0157 RuCl[(S,S)-Fsdpen](p-cymene)	44-0186 (S,S)-Ts-DENEB®
44-0217 (R)-RUCY®-XylBINAP	44-0218 (S)-RUCY®-XylBINAP	44-0255 Ru-(R,R)-Ms-DENEB®	44-0256 Ru-(S,S)-Ms-DENEB®

## 96-6955 Takasago ATH (Asymmetric Transfer Hydrogenation) Catalyst

Item#	Acronym	CAS#	Item#	Acronym	CAS#
44-0148	RuCl[(R,R)-Tsdpen](p-cymene)	192139-92-7	44-0149	RuCl[(S,S)-Tsdpen](p-cymene)	192139-90-5
44-0154	RuCl[(R,R)-Tsdpen](mesitylene)	174813-82-2	44-0155	RuCl[(S,S)-Tsdpen](mesitylene)	174813-81-1
44-0156	RuCl[(R,R)-Fsdpen](p-cymene)	1026995-71-0	44-0157	RuCl[(S,S)-Fsdpen](p-cymene)	1026995-72-1
44-0185	(R,R)-Ts-DENEB®	1333981-84-2	44-0186	(S,S)-Ts-DENEB®	1384974-37-1
44-0217	(R)-RUCY XylBINAP	1384974-38-2	44-0218	(S)-RUCY XylBINAP	1312713-89-5
44-0255	(R,R)-Ms-DENEB®	1333981-86-4	44-0256	(S,S)-Ms-DENEB®	1361318-83-3

*Sold in collaboration with Takasago*

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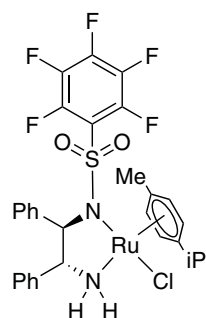
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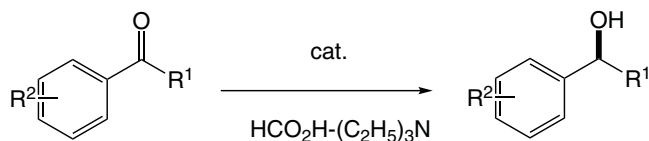
**44-0156** Chloro{[(1R,2R)-(-)-2-amino-1,2-diphenylethyl](pentafluorophenylsulfonyl)amido}(p-cymene)ruthenium(II), min. 90% RuCl[(R,R)-Fsdpen](p-cymene) (1026995-71-0)  
 C<sub>30</sub>H<sub>28</sub>ClF<sub>5</sub>N<sub>2</sub>O<sub>2</sub>RuS; FW: 712.14; orange to brown powdr.  
*air sensitive*  
 Note: Sold in collaboration with Takasago.

250mg  
1g  
5g



Technical Note:

- Catalyst used in the asymmetric transfer hydrogenation of ketones using formic acid-triethylamine mixture.



Tech. Note (1)  
Ref. (1)

References:

- J. Am. Chem. Soc.*, **1996**, *118*, 2521.

**44-0157** Chloro{[(1S,2S)-(+)-2-amino-1,2-diphenylethyl](pentafluorophenylsulfonyl)amido}(p-cymene)ruthenium(II), min. 90% RuCl[(S,S)-Fsdpen](p-cymene) (1026995-72-1)  
 C<sub>30</sub>H<sub>28</sub>ClF<sub>5</sub>N<sub>2</sub>O<sub>2</sub>RuS; FW: 712.14; orange to brown powdr.  
*air sensitive*  
 Note: Sold in collaboration with Takasago. Takasago ATH Catalyst Kit component.

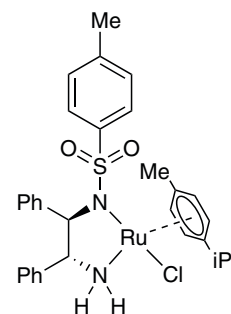
250mg  
1g  
5g

**44-0149** Chloro{[(1S,2S)-(+)-2-amino-1,2-diphenylethyl](4-toluenesulfonyl)amido}(p-cymene)ruthenium(II), min. 90% RuCl[(S,S)-Tsdpen](p-cymene) (192139-90-5)  
 C<sub>31</sub>H<sub>35</sub>ClN<sub>2</sub>O<sub>2</sub>RuS; FW: 636.21; yellow to dark brown solid  
*air sensitive*  
 Note: Sold in collaboration with Takasago. Takasago ATH Catalyst Kit component.

250mg  
1g  
5g

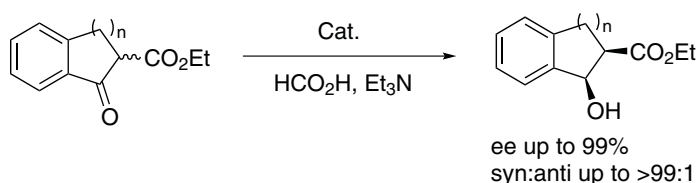
**44-0148** Chloro{[(1R,2R)-(-)-2-amino-1,2-diphenylethyl](4-toluenesulfonyl)amido}(p-cymene)ruthenium(II), min. 95% RuCl[(R,R)-Tsdpen](p-cymene) (192139-92-7)  
 C<sub>31</sub>H<sub>35</sub>ClN<sub>2</sub>O<sub>2</sub>RuS; FW: 636.21; yellow to dark brown solid  
*air sensitive*  
 Note: Sold in collaboration with Takasago. Takasago ATH Catalyst Kit component.

250mg  
1g  
5g

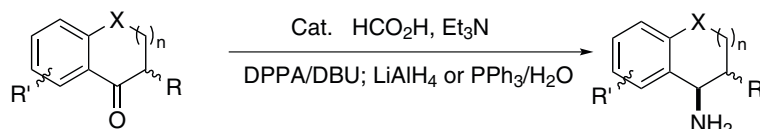


Technical Note:

- This catalyst has shown to effect highly enantioselective hydrogenation of functionalized ketones where the substituents are dialkylamino, hydroxy, siloxy, carbonyl, ester, amide or thioester.



Tech. Note (1)  
Ref. (1)



Tech. Note (1)  
Ref. (2)

n = 0, 1; R = alkyl, F, OAc; X = CH<sub>2</sub>, O

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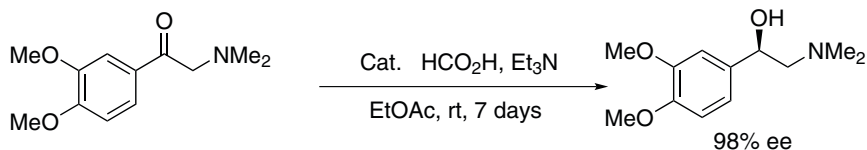
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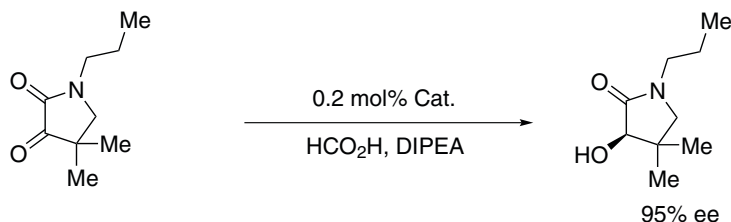
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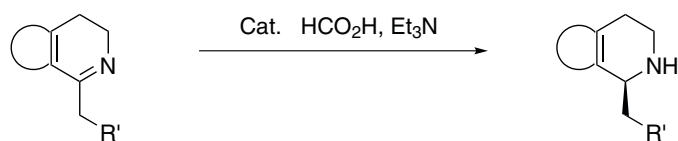
**44-0148** Chloro{[(1R,2R)-(-)-2-amino-1,2-diphenylethyl](4-toluenesulfonylamido)}(p-cymene)ruthenium(II), min. 95%  
(continued) RuCl[(R,R)-Tsdpen](p-cymene) (192139-92-7)



Tech. Note (1)  
Ref. (3)



Tech. Note (1)  
Ref. (4-6)



Tech. Note (1)  
Ref. (7,8)

References:

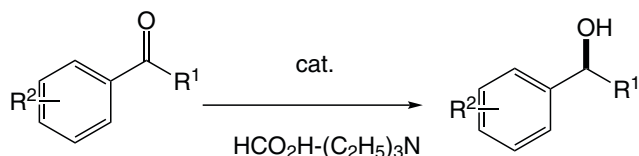
1. *Tetrahedron*, **2007**, 63, 7532
2. *Tetrahedron*, **2007**, 63, 6755
3. *Tetrahedron: Asymmetry*, **2009**, 20, 1138
4. *J. Org. Chem.*, **2009**, 74, 1411
5. *Org. Lett.*, **2007**, 9, 2461
6. *Org. Lett.*, **2009**, 11, 935
7. *Angew. Chem. Int. Ed.*, **2009**, 48, 7616
8. *Bioorg. Med. Chem. Lett.*, **2008**, 18, 4110

**44-0154** Chloro{[(1R,2R)-(-)-2-amino-1,2-diphenylethyl](4-toluenesulfonylamido)}  
(mesitylene)ruthenium(II), min. 90% RuCl[(R,R)-Tsdpen(mesitylene) (174813-82-2)  
C<sub>30</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>2</sub>RuS; FW: 622.18; orange powdr.  
*air sensitive*

Note: Sold in collaboration with Takasago. Takasago ATH Catalyst Kit component.

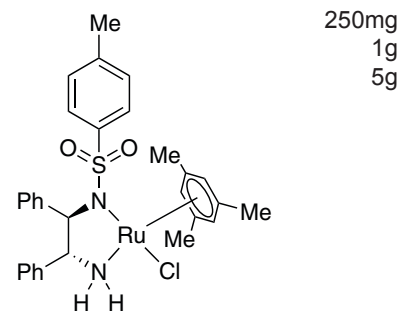
Technical Note:

1. Catalyst used in the asymmetric transfer hydrogenation of ketones using formic acid-triethylamine mixture.



References:

1. *J. Am. Chem. Soc.*, **1996**, 118, 2521.



Tech. Note (1)  
Ref. (1)

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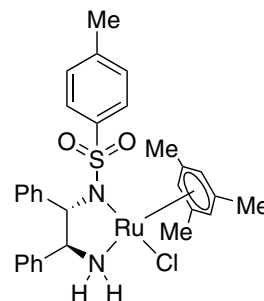
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**44-0155** Chloro{[(1S,2S)-(+)-2-amino-1,2-diphenylethyl](4-toluenesulfonylamido) (mesitylene)ruthenium(II), min. 90% RuCl[(S,S)-Tsdpen](mesitylene) (174813-81-1)  
 $C_{30}H_{33}ClN_2O_2RuS$ ; FW: 622.18; yellow to dark brown solid  
*air sensitive*  
 Note: Sold in collaboration with Takasago. US7129367B2. Takasago ATH Catalyst Kit component.

250mg  
1g  
5g

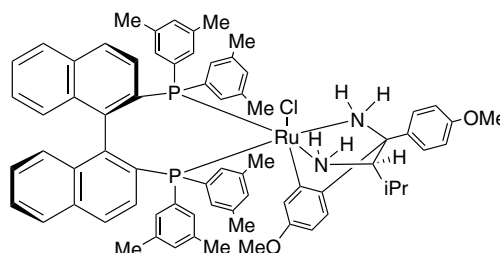


Technical Note:

1. See 44-0154 (page 3)

**44-0217** Chloro{(R)-(+)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl} [(2R)-(-)-1-(4-methoxyphenyl)-1'-(4-methoxyphenyl-kC)-3-methyl-1,2-butanediamine]ruthenium(II) (R)-RUCY®XylBINAP (1384974-38-2)  
 $C_{71}H_{73}ClN_2O_2P_2Ru$ ; FW: 1184.82;  
 yellow to dark brown/green solid  
*air sensitive*  
 Note: Sold in collaboration with Takasago. US Patent 9079931. Takasago BINAP Ru Diamine Catalyst Kit component. Takasago ATH Catalyst Kit component.

100mg  
250mg  
1g  
5g

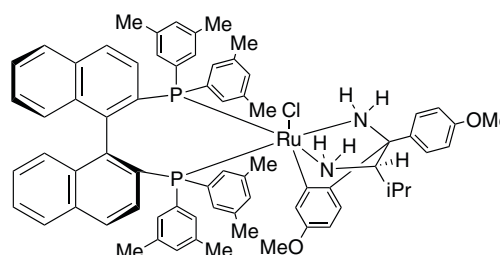


Technical Note:

1. See 44-0218 (page 4)

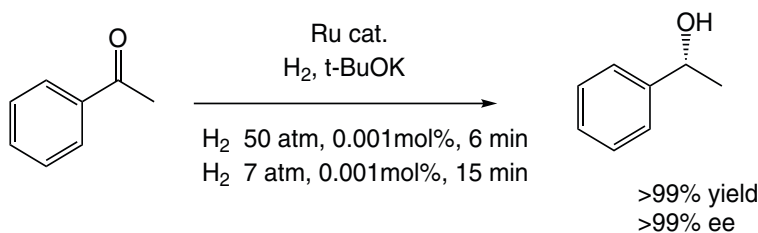
**44-0218** Chloro{(S)-(-)-2,2'-bis[di(3,5-xylyl) phosphino]-1,1'-binaphthyl}[(2S)- (+)-1-(4-methoxyphenyl)-1'-(4-methoxyphenyl-kC)-3-methyl-1,2-butanediamine]ruthenium(II) (S)-RUCY®XylBINAP (1312713-89-5)  
 $C_{71}H_{73}ClN_2O_2P_2Ru$ ; FW: 1184.82;  
 yellow to dark brown/green solid  
*air sensitive*  
 Note: Sold in collaboration with Takasago. US Patent 9079931. Takasago BINAP Ru Diamine Catalyst Kit component. Takasago ATH Catalyst Kit component.

250mg  
1g  
5g



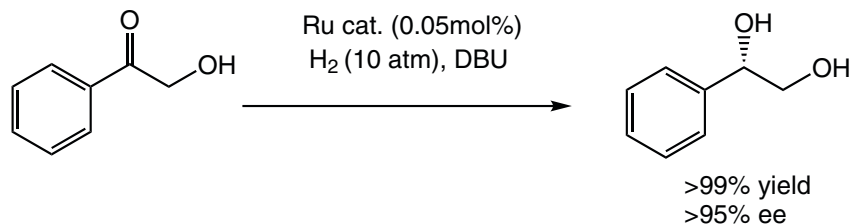
Technical Note:

1. Catalyst used for the rapid, and highly selective hydrogenation of ketones.



Tech. Note (1)  
Ref. (1)

"trans-RuCl<sub>2</sub>(xylbinap)(daipen) 0.001 mol%, 240 min"



Tech. Note (1)  
Ref. (1)

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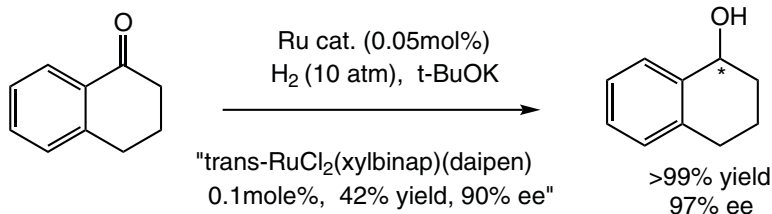
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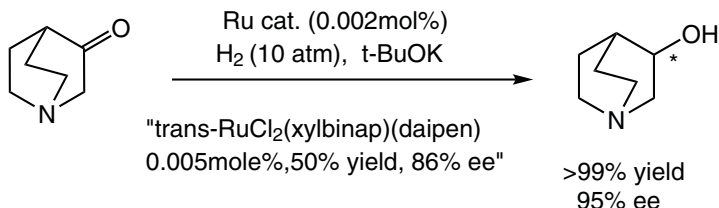
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**44-0218** Chloro{(S)-(-)-2,2'-bis[di(3,5-xylyl) phosphino]-1,1'-binaphthyl}[(2S)-(+)-1-(4-methoxyphenyl)-1'-(4-methoxyphenyl)-kC]-3-methyl-1,2-butanediamine]ruthenium(II) (S)-RUCY®XylBINAP (1312713-89-5)  
(continued)



Tech. Note (1)  
Ref. (1)

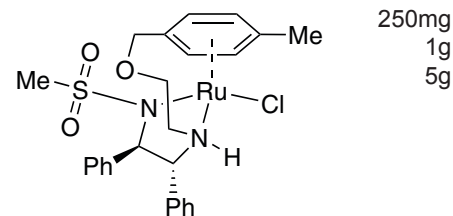


Tech. Note (1)  
Ref. (1)

References:

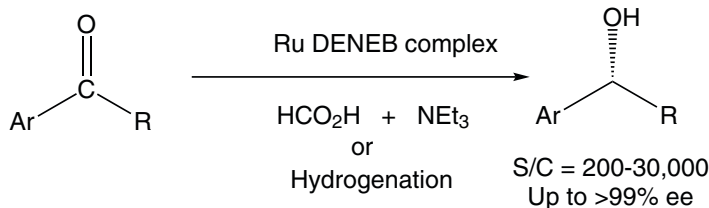
- (a) US. Pat. 9079931. (b) *J. Am. Chem. Soc.*, 2011, 133, 10696.

**44-0255** Chloro{N-[(1R,2R)-2-[(S)-[2-[[1,2,3,4,5,6-η]-4-methylphenyl]methoxy]ethyl]amino]-1,2-diphenylethylmethanesulfonamidato}ruthenium(II) (R,R)-Ms-DENE<sup>B</sup>® (1333981-86-4)  
C<sub>25</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>3</sub>RuS; FW: 574.10; light to dark brown powdr.  
Note: Sold in collaboration with Takasago. US. Patent 9217005.  
Takasago ATH Catalyst Kit component.

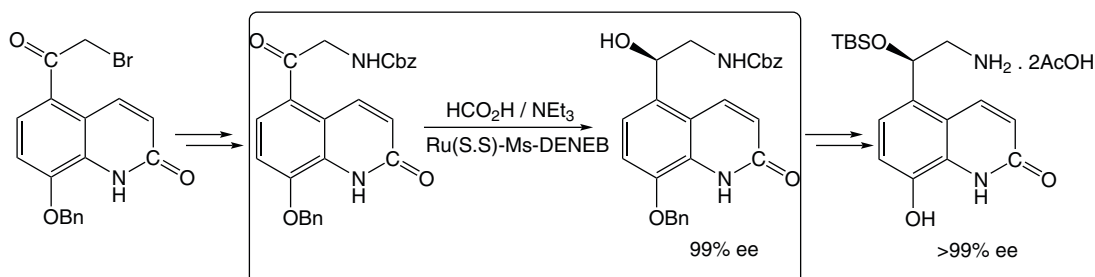


Technical Notes:

- Catalyst used for both hydrogenation and asymmetric transfer hydrogenation.
- Ruthenium catalyst used as a key intermediate in a synthesis of a receptor agonist.



Tech. Note (1)  
Ref. (1)



Tech. Note (2)  
Ref. (2)

References:

- J. Am. Chem. Soc.*, 2011, 133, 14960
- Org. Process Res. Dev.*, 2015, 19, 315

**44-0256** Chloro{N-[(1S,2S)-2-[(R)-[2-[[1,2,3,4,5,6-η]-4-methylphenyl]methoxy]ethyl]amino]-1,2-diphenylethylmethanesulfonamidato}ruthenium(II) (S,S)-Ms-DENE<sup>B</sup>® (1361318-83-3)  
C<sub>25</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>3</sub>RuS; FW: 574.10; light to dark brown powdr.  
Note: Sold in collaboration with Takasago. US. Patent 9217005. Takasago ATH Catalyst Kit component.

250mg  
1g  
5g

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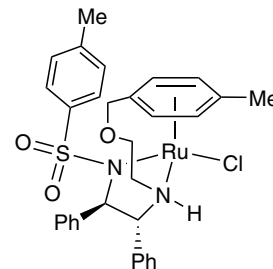
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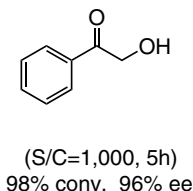
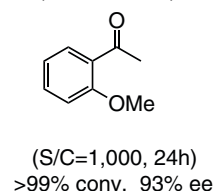
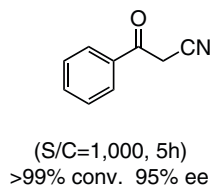
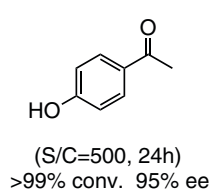
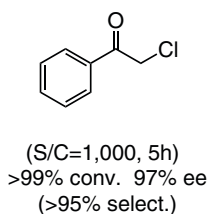
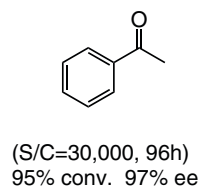
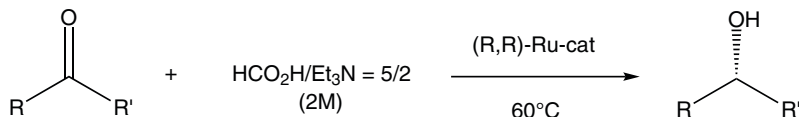
**44-0185 N-[(1R,2R)-1,2-Diphenyl-2-(2-(4-methylbenzyloxy)ethylamino)-ethyl]-4-methylbenzene sulfonamide(chloro)ruthenium(II) (R,R)-Ts-DENE<sup>B</sup>**  
 (1333981-84-2)  
 C<sub>31</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>3</sub>RuS; FW: 650.19; gray to brown solid  
 Note: Sold in collaboration with Takasago. US. Patent 9079931.

250mg  
 1g  
 5g

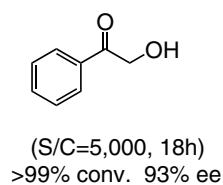
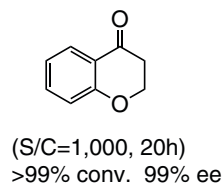
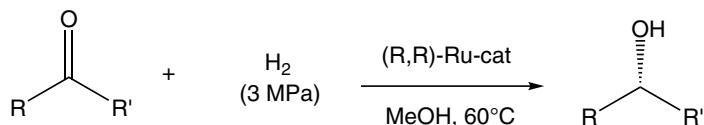


Technical Notes:

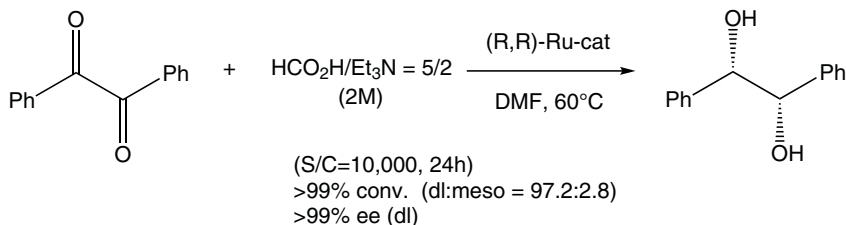
1. Catalyst used for asymmetric  $\alpha$ -transfer hydrogenation.
2. Catalyst used for asymmetric H<sub>2</sub> – hydrogenation.
3. Catalyst used for dynamic kinetic resolution.
4. Catalyst used for asymmetric transfer hydrogenation of unsymmetrical benzophenones.
5. Catalyst used for asymmetric transfer hydrogenation of Aryl N-Heteroaryl Ketones.
6. Catalyst used for asymmetric transfer hydrogenation of  $\alpha$ -Substituted Ketone.



Tech. Note (1)  
 Ref. (1)



Tech. Note (2)  
 Ref. (1)



Tech. Note (3)  
 Ref. (1)

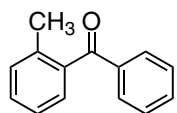
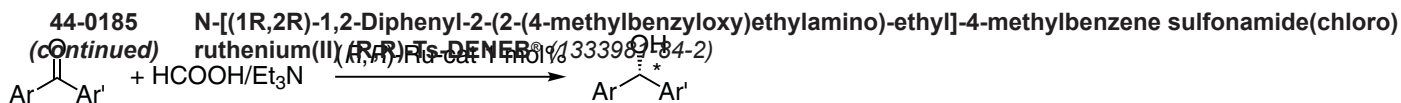
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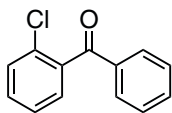
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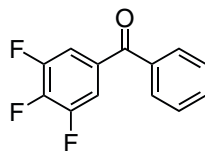
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(60 °C, 18 h)  
98% yield. 98% ee

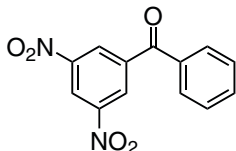


(40 °C, 17 h)  
>99% yield. 98% ee

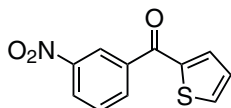


(30 °C, 16 h)  
>99% yield. 95% ee

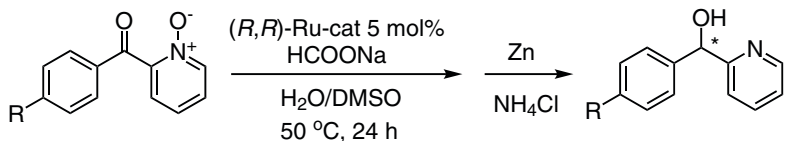
Tech. Note (4)  
Ref. (2)



(30 °C, 26 h)  
90% yield. >99% ee

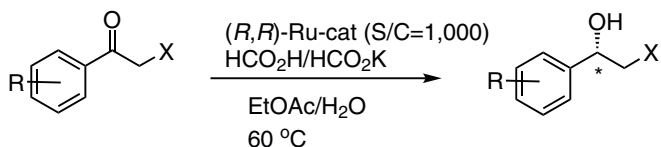


(10 °C, 8 h)  
96% yield. 98% ee

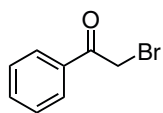


R=H : 86% yield. 97.8% ee  
R=Cl : 92% yield. 99.8% ee

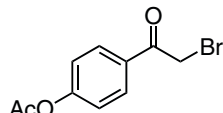
Tech. Note (5)  
Ref. (3)



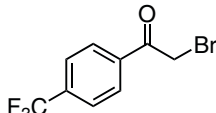
Tech. Note (6)  
Ref. (4)



(4 h)  
93% yield. 96% ee



(6 h)  
93% yield. 95% ee



(4 h)  
94% yield. 94% ee

#### References:

1. *J. Am. Chem. Soc.*, **2011**, *133*, 14960
2. *J. Am. Chem. Soc.* **2016**, *138*, 10084.
3. *Org. Lett.* **2017**, *19*, 2094.
4. *Adv. Synth. Catal.* **2017**, *360*, 568

**44-0186** N-[(1*S*,2*S*)-1,2-Diphenyl-2-(2-(4-methylbenzyloxy)ethylamino)-ethyl]-4-methylbenzene sulfonamide(chloro) ruthenium(II) (*S,S*)-Ts-DENEB® (1384974-37-1) 250mg  
 C<sub>31</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>3</sub>RuS; FW: 650.19; gray to brown solid 1g  
 Note: Sold in collaboration with Takasago. US Pat. 9217005, US Pat. 9073827. 5g

#### Technical Note:

1. See 44-0185 (page 6)

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