

Chiral Catalysts

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- COP-CI Catalysts

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- Chiral Phosphines
- BINOLs
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- Ephedrines

Building Blocks

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- Chiral Diols
- Chiral Amines
- Chiral Pyrrolidines
- HKR Epoxides

Introduction

Sigma-Aldrich is proud to offer a new series of *ChemFiles*—called Synthetic Methods—to our Organic Chemistry and Drug Discovery customers. This edition will focus on asymmetric synthesis and present the latest product additions to our chiral product portfolio as well as some selected examples of notable chiral transformations.

Asymmetric synthesis remains a challenge to synthetic chemists as the demand for enantiomerically pure compounds continues to increase. Finding new methods of asymmetric synthesis has become a key activity for organic chemists. The number of scientific papers dedicated to asymmetric methodologies has tripled to approximately 4,500 per year since 1994.

Sigma-Aldrich is proud to carry over 5,000 chiral products for your research. We provide thousands of functionalized chiral building

blocks for applications in organic and medicinal chemistry, from simple chiral alcohols to protected amino acids to polysaccharides. Whether your research requires chiral transition metal catalysts, enzymes for organic transformations, chiral resolving agents, or a broad range of chiral auxiliaries, we offer the tools you need to synthesize your advanced chiral intermediates. For a complete listing of products related to asymmetric synthesis, please visit sigmaaldrich.com/asymmetric.

At Sigma-Aldrich, we are committed to being your preferred supplier for reagents and building blocks used in asymmetric synthesis. If you cannot find a product for your specific research in organic synthesis or drug discovery, we welcome your input. "Please Bother Us" with your suggestions and contact your local Sigma-Aldrich office (see back cover).

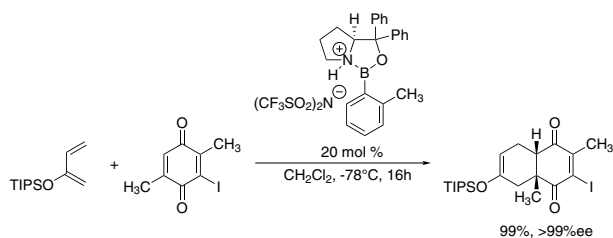
1. Chiral Catalysts

CBS Catalysts

2-Methyl-CBS-oxazaborolidine and *o*-tolyl-CBS-oxazaborolidine

Since 1987, the series of chiral oxazaborolidines known as CBS catalysts (after Corey, Bakshi, and Shibata) have been used for catalytic reduction of prochiral ketones,¹ imines,² and oximes³ to produce chiral alcohols, amines, and amino alcohols, respectively, in excellent yields and ee's. Sigma-Aldrich is pleased to offer both enantiomers of 2-methyl-CBS-oxazaborolidine as dry reagents, as well as 1 M solutions in toluene.

We are also pleased to offer *o*-tolyl-CBS-oxazaborolidine as a 0.5 M solution in toluene for your research needs. When protonated with trifluoromethanesulfonimide, these chiral oxazaborolidines generate chiral Lewis acids, which have demonstrated great utility in the enantioselective Diels-Alder reaction (Scheme 1).⁴

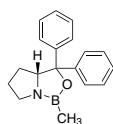


Scheme 1

(*R*)-(+)-2-Methyl-CBS-oxazaborolidine

NEW

C₁₈H₂₀BNO
MW: 277.17
[112022-83-0]

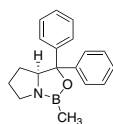


649317-1G	1 g	\$39.90
649317-10G	10 g	\$193.00

(*S*)-(-)-2-Methyl-CBS-oxazaborolidine

NEW

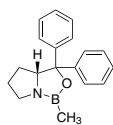
C₁₈H₂₀BNO
MW: 277.17
[112022-81-8]



649309-1G	1 g	\$35.00
649309-10G	10 g	\$175.00

(*R*)-(+)-2-Methyl-CBS-oxazaborolidine solution, 1 M in toluene

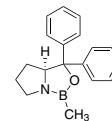
C₁₈H₂₀BNO
MW: 277.17
[112022-83-0]



457698-5ML	5 mL	\$58.30
457698-25ML	25 mL	\$187.00

(*S*)-(-)-2-Methyl-CBS-oxazaborolidine solution, 1 M in toluene

C₁₈H₂₀BNO
MW: 277.17
[112022-81-8]

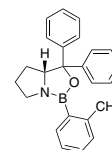


457701-5ML	5 mL	\$58.30
457701-25ML	25 mL	\$187.00

(*R*)-(+)-*o*-Tolyl-CBS-oxazaborolidine solution, 0.5 M in toluene

NEW

C₂₄H₂₄BNO
MW: 353.26
[α]_D²⁰: +18 ± 3°, c = 1 in toluene

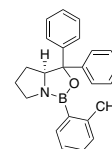


654299-5ML	5 mL	\$31.50
654299-25ML	25 mL	\$109.00

(*S*)-(-)-*o*-Tolyl-CBS-oxazaborolidine solution, 0.5 M in toluene

NEW

C₂₄H₂₄BNO
MW: 353.26
[α]_D²⁰: -18 ± 3°, c = 1 in toluene



654302-5ML	5 mL	\$31.50
654302-25ML	25 mL	\$109.00

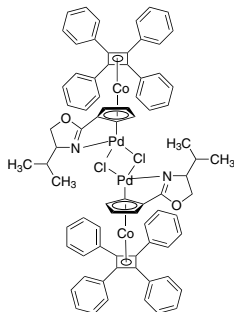
TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigmaaldrich.com.

COP-Cl Catalyst

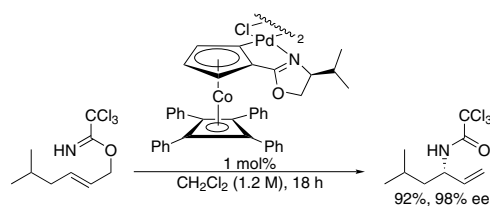
Allylic imidate rearrangements are the preferred method for converting readily available allylic alcohols to transposed allylic amines and their analogues. Overman recently employed a cationic palladium catalyst in an asymmetric version of this rearrangement. A set of (*E*)-allylic trichloroacetimidates provided transposed allylic trichloroacetamides in high yields and enantioselectivities (up to 98% ee), whereas the (*Z*)-allylic imidates showed slightly reduced selectivities (**Scheme 2**).⁵

COP-Cl Catalyst

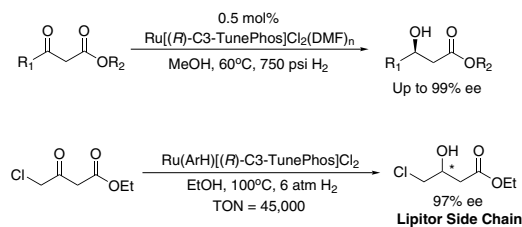
C₇₈H₆₆Cl₂Co₂N₂O₂Pd₂
MW: 1464.98
[612065-01-7]



646636-250MG	250 mg	\$44.10
646636-1G	1 g	\$123.00



Scheme 2



Scheme 3

2. Chiral Ligands

ChiralQuest Phosphines

Professor Xumu Zhang at Penn State has made remarkable advances by creating a toolbox of chiral phosphines which can be used on a variety of substrates, some of which have been historically resistant to facile hydrogenation. Furthermore, an additional benefit in some reductions is reduced catalyst loading, due to increased turnover numbers (TON). Sigma-Aldrich is pleased to announce an agreement with ChiralQuest to distribute research quantities of a series of Zhang's chiral phosphines for catalytic asymmetric hydrogenations.⁶

(S)-C3-TunePhos

C3-TunePhos, a member of the atropisomeric aryl bisphosphine ligand family with tunable dihedral angles, provides comparable or superior enantioselectivities and catalytic abilities to BINAP in Ru-catalyzed asymmetric hydrogenations of β -keto esters (**Scheme 3**),⁷ cyclic β -(acylamino)acrylates (**Scheme 4**),⁸ and α -phthalimide ketones (**Scheme 5**).⁹

(1S,1S',2R,2R')-TangPhos

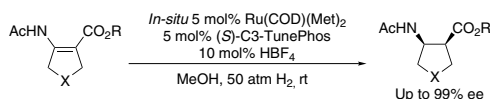
A highly electron-donating, low molecular weight, and rigid *P*-chiral bisphospholane ligand, TangPhos proves highly efficient in the rhodium-catalyzed hydrogenation of a variety of functionalized olefins such as α -dehydroamino acids (**Scheme 6**) and α -arylenamides (**Scheme 7**),¹⁰ β -(acylamino)acrylates (**Scheme 8**),¹¹ itaconic acids (**Scheme 9**), and enol acetates (**Scheme 10**).¹²

(S)-Binapine

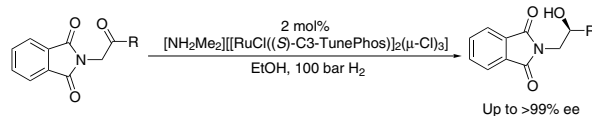
(*S*)-Binapine, a highly electron-donating rigid ligand, demonstrates excellent enantioselectivity and reactivity, with TON up to 10,000 for the asymmetric hydrogenation of *Z*- β -aryl(β -acylamino)acrylates (**Scheme 11**).¹³

(R)-Binaphane

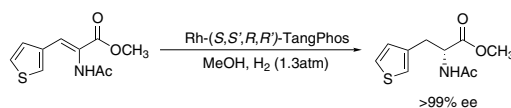
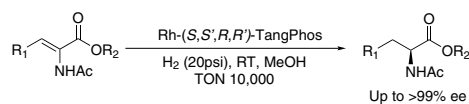
(*R*)-Binaphane shows excellent enantioselectivity (up to >99% ee) for hydrogenation of *E/Z*-isomeric mixtures of β -substituted arylenamides (**Scheme 12**).¹⁴



Scheme 4



Scheme 5



Scheme 6

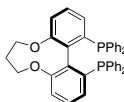


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(R)-C3-TunePhos

NEW

(R)-(6,6'-O-(1,3-Propylene)-oxylbiphenyl-2,2'-diyl)bis(diphenyl)phosphine
 $C_{39}H_{32}O_2P_2$
 MW: 594.62
 [301847-89-2]
 $[\alpha]_D^{20}$: -252 ± 5°, c = 1 in $CHCl_3$

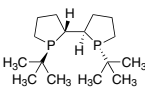


650862-100MG	100 mg	\$70.00
650862-500MG	500 mg	\$277.00

(S,S',R,R')-TangPhos

NEW

(1*S*,1'*S*',2*R*,2'*R*')-1,1'-Di-*tert*-butyl-(2,2')-diphospholane
 $C_{16}H_{32}P_2$
 MW: 286.37
 [470480-32-1]

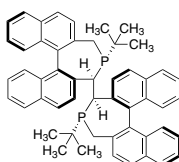


650889-100MG	100 mg	\$86.00
650889-500MG	500 mg	\$340.00

(S)-Binapine

NEW

(3*S*,3'*S*,4*S*,4'*S*,11*bS*,11'*bS*)-(+)-4,4'-Di-*t*-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepin
 $C_{52}H_{48}P_2$
 MW: 734.89
 [610304-81-9]

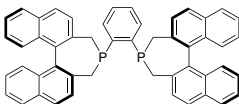


650870-100MG	100 mg	\$86.00
650870-500MG	500 mg	\$340.00

(R)-Binaphane

NEW

(*R,R*)-1,2-Bis[(*R*)-4,5-dihydro-3*H*-binaphtho(1,2-*c*:2',1'-*e*)phosphepino]-benzene
 $C_{50}H_{36}P_2$
 MW: 698.77
 [253311-88-5]



650854-100MG	100 mg	\$70.00
650854-500MG	500 mg	\$277.00

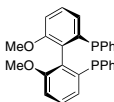
MeO-BIPHEP

With Ru-complexes of this atropisomeric diphosphine ligand, β-keto esters are reduced to their corresponding β-hydroxy esters in high enantioselectivities. Selected results are shown in **Scheme 13**.

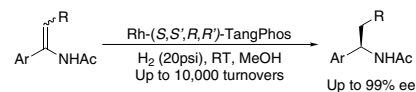
Further enantioselective transformations of the MeO-BIPHEP ligands include Rh(I)-catalyzed asymmetric isomerizations of allylamines to enamines¹⁵ and Pd(0) complexes for cyclizations of hydroxy allylic carbonates.¹⁶

(R)-(+)-2,2'-Bis-(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, puriss., ≥98.0% (sum of enantiomers, HPLC)

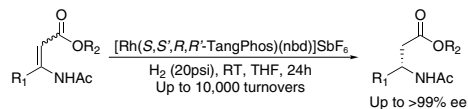
(*R*)-(+)-MeO-BIPHEP
 $C_{38}H_{32}O_2P_2$
 MW: 582.61
 [133545-16-1]
 $[\alpha]_D^{20}$: +102 ± 2°, c = 0.3 in toluene



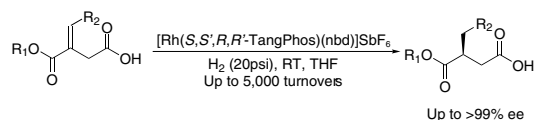
95536-250MG	250 mg	\$148.50
95536-1G	1 g	\$413.30



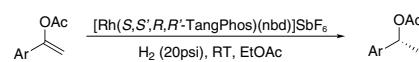
Scheme 7



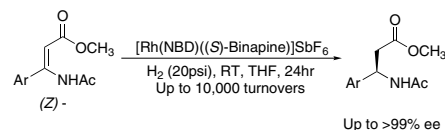
Scheme 8



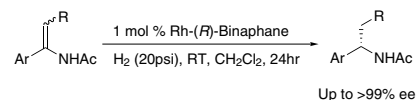
Scheme 9



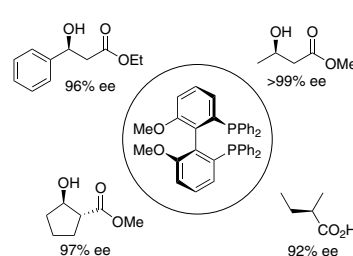
Scheme 10



Scheme 11



Scheme 12



Scheme 13

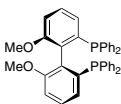
(S)-(-)-2,2'-Bis-(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, puriss., ≥98.0% (sum of enantiomers, HPLC)

(S)-(-)-MeO-BIPHEP

C₃₈H₃₂O₂P₂

MW: 582.61

[133545-17-2]

[α]_D²⁰: -102 ± 2°, c = 0.3 in toluene

76673-250MG	250 mg	\$148.50
76673-1G	1 g	\$413.30

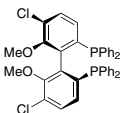
(S)-(+)-5,5'-Dichloro-2,2'-bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, purum, ≥95.0% (H NMR)

(S)-(+)-Cl-MeO-BIPHEP

C₃₈H₃₀Cl₂O₂P₂

MW: 651.5

[185913-97-7]

[α]_D²⁰: +59.0 ± 1°, c = 1 in CHCl₃

96738-250MG	250 mg	\$123.80
96738-1G	1 g	\$421.20

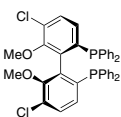
(R)-(-)-5,5'-Dichloro-2,2'-bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, purum, ≥97.0% (H NMR)

(R)-(-)-Cl-MeO-BIPHEP

C₃₈H₃₀Cl₂O₂P₂

MW: 651.5

[185913-98-8]

[α]_D²⁰: -59.0 ± 1°, c = 1 in CHCl₃

76854-250MG	250 mg	\$123.10
76854-1G	1 g	\$393.20

Other Chiral Phosphines**(R,R)-DIPAMP, ≥95%**

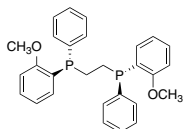
NEW

[(1R,2R)-(-)-Bis[(2-methoxyphenyl)phenylphosphino]ethane]

C₂₈H₂₈O₂P₂

MW: 458.47

[55739-58-7]

[α]_D²⁰: -88°, c = 1 in CHCl₃

461865-500MG	500 mg	\$222.50
461865-1G	1 g	\$370.50

(S,S)-DIPAMP, ≥95%

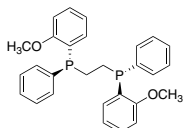
NEW

(1S,2S)-(+)-Bis[(2-methoxyphenyl)phenylphosphino]ethane

C₂₈H₂₈O₂P₂

MW: 458.47

[97858-62-3]



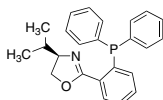
461873-1G	1 g	\$286.00
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(R)-(+)-2-[2-(Diphenylphosphino)phenyl]-4-isopropyl-2-oxazoline, purum, ≥97.0% (CHN)

(R)-(+)-2-[2-(Diphenylphosphino)phenyl]-4,5-dihydro-4-isopropylloxazole

C₂₄H₂₄NOP

MW: 373.43

[α]_D²⁰: +44 ± 3°, c = 1.4 in CHCl₃

72575-500MG	500 mg	\$485.20
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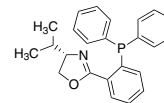
(S)-(-)-2-[2-(Diphenylphosphino)phenyl]-4-isopropyl-2-oxazoline, purum, ≥97.0% (CHN)

(S)-(-)-2-[2-(Diphenylphosphino)phenyl]-4,5-dihydro-4-isopropylloxazole

C₂₄H₂₄NOP

MW: 373.43

[148461-14-7]

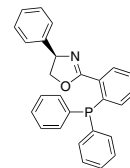
[α]_D²⁰: -48 ± 3°, c = 1 in CHCl₃

91716-500MG	500 mg	\$485.20
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(R)-(-)-2-[2-(Diphenylphosphino)phenyl]-4-phenyl-2-oxazoline, purum, ≥97.0% (P NMR)C₂₇H₂₂NOP

MW: 407.44

[167171-03-1]

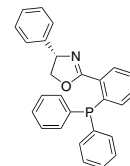
[α]_D²⁰: -29.5 ± 3°, c = 1 in CHCl₃

43158-500MG	500 mg	\$199.90
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(S)-(+)-2-[2-(Diphenylphosphino)phenyl]-4-phenyl-2-oxazoline, purum, ≥97.0% (P NMR)C₂₇H₂₂NOP

MW: 407.44

[148461-15-8]

[α]_D²⁰: +29.5 ± 3°, c = 1 in CHCl₃

43160-500MG	500 mg	\$247.60
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(R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene, 97%

(R)-(+)-BINAP

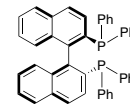
C₄₄H₃₂P₂

MW: 622.67

[76189-55-4]

[α]_D²⁰: +233°, c = 0.3 in C₆H₅CH₃

ee: 99% (HPLC)



295817-100MG	100 mg	\$10.50
295817-1G	1 g	\$69.30
295817-5G	5 g	\$277.00

(S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene, 97%

(S)-(-)-BINAP

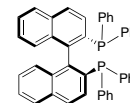
C₄₄H₃₂P₂

MW: 622.67

[76189-56-5]

[α]_D²⁰: -233°, c = 0.3 in C₆H₅CH₃

ee: 99% (GLC)



295825-100MG	100 mg	\$33.70
295825-1G	1 g	\$74.10
295825-5G	5 g	\$296.50



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BINOLs

The structural motif of 1,1'-binaphthyl is considered to be a privileged one for ligands in asymmetric synthesis. These kinds of ligands have shown broad applicability allowing high levels of enantiocontrol in many synthetic transformations.

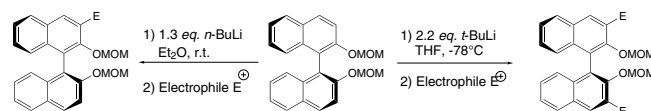
2,2'-Bis(methoxymethoxy)-1-1'-binaphthalene

By modifying the 1,1'-binaphthyl backbone, the electronic and steric properties around the metal center of a chiral catalyst can be influenced, thus allowing the catalyst system to be tuned for specific applications.¹⁷ Starting from (*R*)-2,2'-bis(methoxymethoxy)-1-1'-binaphthalene, both 3- or 3,3'-di-substituted products can be obtained easily via ortho-metallation and subsequent treatment with an electrophile to give the corresponding BINOL derivatives in good to excellent yields and without detectable racemization (Scheme 14).¹⁸

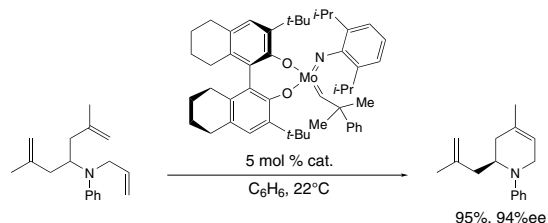
(*R*)-3,3'-Di-*tert*-butyl-5,5',6,6',7,7',8,8'-octahydro-1-1'-(bi-2-naphthol) dipotassium salt

Octahydro-BINOL was demonstrated to be an effective ligand in Mo-catalyzed desymmetrization of a triene by asymmetric ring closing metathesis (Scheme 15).¹⁹

Sigma-Aldrich now offers several new functionalized BINOLs for straightforward derivatization making modifications of your desired catalyst/ligand system more convenient.



Scheme 14

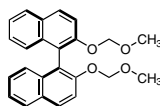


Scheme 15

(*R*)-(+)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthalene, 97%

NEW

C₂₄H₂₂O₄
MW: 374.43
[173831-50-0]
[α]_D²⁰: +92°, c = 1 in CHCl₃

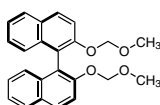


631582-250MG	250 mg	\$67.40
--------------	--------	---------

(*S*)-(-)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthalene, 97%

NEW

C₂₄H₂₂O₄
MW: 374.43
[142128-92-5]
[α]_D²⁰: -90°, c = 1 in CHCl₃

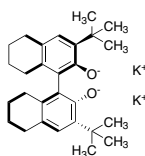


631574-250MG	250 mg	\$67.40
--------------	--------	---------

(*R*)-3,3'-Di-*tert*-butyl-5,5',6,6',7,7',8,8'-octahydro-1,1'-(bi-2-naphthol) dipotassium salt purum, ≥95.0% (dry substance, CHN)

NEW

C₂₈H₃₆K₂O₂
MW: 482.78
[350683-75-9]

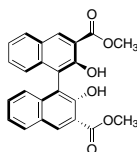


77939-100MG	100 mg	\$170.00
-------------	--------	----------

(*R*)-(+)-Dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate, 98%

NEW

C₂₄H₁₈O₆
MW: 402.4
[18531-91-4]
[α]_D²⁰: +135°, c = 1 in CHCl₃

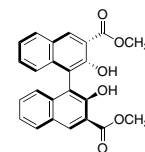


579343-2G	2 g	\$110.50
-----------	-----	----------

(*S*)-(-)-Dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate

NEW

C₂₄H₁₈O₆
MW: 402.4
[69678-00-8]
[α]_D²⁰: -135°, c = 1 in CHCl₃



98%

579971-2G	2 g	\$105.00
-----------	-----	----------

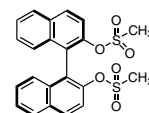
purum, 98%

652881-2G	2 g	\$105.00
-----------	-----	----------

(*R*)-(-)-1,1'-Bi-2-naphthyl dimethanesulfonate, 97%

NEW

C₂₂H₁₈O₆S₂
MW: 442.5
[α]_D²⁰: -73°, c = 1 in CHCl₃

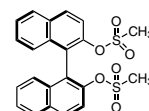


631795-250MG	250 mg	\$67.40
--------------	--------	---------

(*S*)-(+)-1,1'-Bi-2-naphthyl dimethanesulfonate, 97%

NEW

C₂₂H₁₈O₆S₂
MW: 442.5
[α]_D²⁰: +75°, c = 1 in CHCl₃

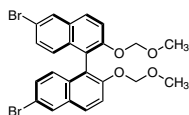


631787-250MG	250 mg	\$67.40
--------------	--------	---------

(R)-(+)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)binaphthalene, 97%

NEW

C₂₄H₂₀Br₂O₄
 MW: 346.01
 [179866-74-1]
 [α]_D²⁰: +19.5°, c = 1 in CHCl₃

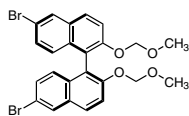


631604-250MG	250 mg	\$67.40
--------------	--------	---------

(S)-(-)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene, 97%

NEW

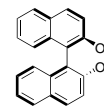
C₂₄H₂₀Br₂O₄
 MW: 346.01
 [211560-97-3]
 [α]_D²⁰: -18°, c = 1 in CHCl₃



631590-250MG	250 mg	\$67.40
--------------	--------	---------

(R)-(-)-1,1'-Bi(2-naphthol), 99%

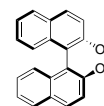
(R)-BINOL
 C₂₀H₁₄O₂
 MW: 286.32
 [18531-94-7]
 [α]_D²⁰: +34°, c = 1 in THF
 ee: 99% (HPLC)



246948-250MG	250 mg	\$23.70
246948-1G	1 g	\$51.70
246948-5G	5 g	\$204.00
246948-10G	10 g	\$367.50

(S)-(-)-1,1'-Bi(2-naphthol), 99%

(S)-BINOL
 C₂₀H₁₄O₂
 MW: 286.32
 [18531-99-2]
 [α]_D²⁰: -34°, c = 1 in THF
 ee: 99% (HPLC)



246956-250MG	250 mg	\$22.60
246956-1G	1 g	\$45.70
246956-5G	5 g	\$193.00
246956-10G	10 g	\$378.00

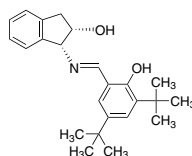
Indanols**1-[(3,5-Di-tert-butyl-2-hydroxybenzylidene)amino]-2-indanol**

These chiral imine-ligands have recently been used in the vanadium-catalyzed oxidation of sulfides in conjunction with hydrogen peroxide. Optically active sulfoxides are obtained in high yields and enantioselectivities (Scheme 16).²⁰

(1R,2S)-1-[(3,5-Di-tert-butyl-2-hydroxybenzylidene)amino]-2-indanol, 97%

NEW

C₂₄H₃₁NO₂
 MW: 365.51

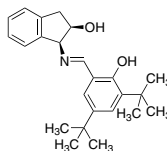


642959-1G	1 g	\$17.30
642959-5G	5 g	\$60.90

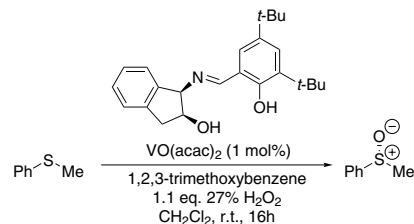
(1S,2R)-1-[(3,5-Di-tert-butyl-2-hydroxybenzylidene)amino]-2-indanol, 97%

NEW

C₂₄H₃₁NO₂
 MW: 365.51



644145-1G	1 g	\$16.50
644145-5G	5 g	\$58.00



Scheme 16



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3. Chiral Auxiliaries

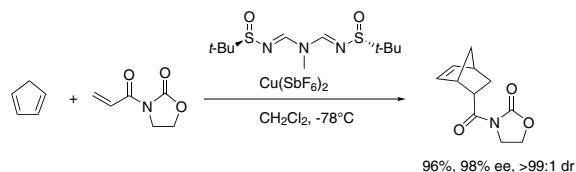
S-Chirogenic Auxiliaries

2-Methyl-2-propanesulfinamide (Ellman Sulfinamide)

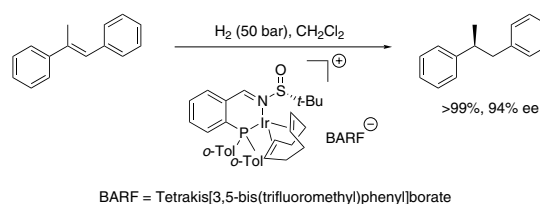
Developed by Ellman, these chiral sulfinamides have found widespread use in diastereoselective alkylations, the synthesis of protected chiral amines, the Strecker synthesis of α -alkyl α -amino acids, and the preparation of novel ligands for asymmetric Lewis acid catalysis. In 2001, Ellman et al. reported on an example of a Lewis acid catalyzed Diels–Alder reaction using a chiral bis(sulfinyl)imidoamidate copper complex, readily synthesized in a straightforward and modular synthesis starting from (*R*)-(+)-2-methyl-2-propanesulfinamide. Extremely high enantio- and diastereoselectivities were achieved with a range of substrates (**Scheme 17**).²¹

The application of chiral *P,N*-sulfinyl imine ligands in Ir-catalyzed hydrogenation of olefins using (*R*)-(+)-2-methyl-2-propanesulfinamide as starting material was demonstrated by the same author. Enantioselectivities of up to 94% were observed (**Scheme 18**).²²

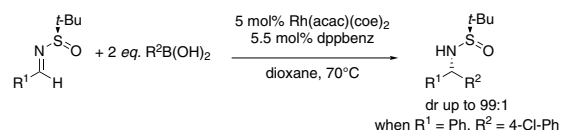
Very recently, Weix et al. reported on the diastereoselective Rh(I)-catalyzed addition of arylboronic acids to *N-tert*-butanesulfinyl aldimines readily prepared from (*R*)-(+)-2-methyl-2-propanesulfinamide (**Scheme 19**).²³ The chiral sulfinyl group is easily cleaved from the addition products under mildly acidic conditions. Thus, this method provides access to highly enantiomerically enriched α -branched secondary amines.



Scheme 17



Scheme 18



Scheme 19

(*R*)-(+)-2-Methyl-2-propanesulfinamide, 98%

C₄H₁₁NO₅

MW: 121.2

[196929-78-9]

[α]_D²⁰: +4°, c = 1.0242 in CHCl₃ + amylenes

497401-1G	1 g	\$60.90
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(*S*)-(-)-2-Methyl-2-propanesulfinamide, 97%

C₄H₁₁NO₅

MW: 121.2

[343338-28-3]

[α]_D²⁰: -4.5°, c = 1 in CHCl₃

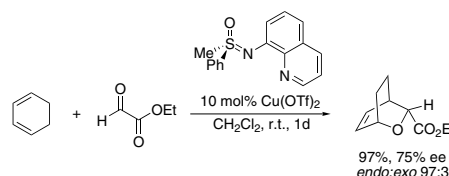
513210-1G	1 g	\$73.00
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S-Methyl-S-phenylsulfoximine

Chiral sulfoximines have shown to be versatile compounds for asymmetric synthesis.²⁴ Most of today's chemistry involving chiral sulfoximines can be reduced to a small number of key intermediates. Sigma-Aldrich is pleased to announce one of these "key" sulfoximines, available in both enantiomeric forms as precursor materials for the modular preparation of *S*-chirogenic ligands for asymmetric synthesis.

In 2003, Bolm et al. introduced a new class of C₁-symmetric monosulfoximine ligands derived from (*R*)-(-)-*S*-methyl-*S*-phenylsulfoximine for enantioselective hetero-Diels–Alder reactions. Under optimized conditions, cycloadducts could be obtained in excellent diastereo- and enantioselectivities (**Scheme 20**).²⁵



Scheme 20

(*R*)-(-)-*S*-Methyl-*S*-phenylsulfoximine, puriss., ≥99.0% (GC)

C₇H₉NOS

MW: 155.22

[33903-50-3]

[α]_D²⁰: -28.0 ± 2.0, c = 1 in acetonitrile

68916-250MG	250 mg	\$45.30
68916-1G	1 g	\$147.10



(*S*)-(+)-*S*-Methyl-*S*-phenylsulfoximine, puriss., ≥99.0% (GC)

C₇H₉NOS

MW: 155.22

[60933-65-5]

[α]_D²⁰: +28.0 ± 2.0, c = 1 in acetonitrile

08708-250MG	250 mg	\$45.30
08708-1G	1 g	\$147.10



Ephedrine

Both enantiomers of ephedrine, pseudoephedrine, norephedrine, and their derivatives are used as practical chiral auxiliaries for asymmetric synthesis. Enolates of readily available (1*R*,2*R*)-(-) and (1*S*,2*S*)-(+)-pseudoephedrinepropionamide are substrates for diastereoselective alkylation reactions (**Scheme 21**), which after cleavage of the auxiliary, give rise to highly enantiomerically enriched carboxylic acids, alcohols, aldehydes, and ketones.²⁶

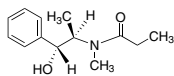
(1*R*,2*R*)-(-)-Pseudoephedrinepropionamide, 98%

C₁₃H₁₉NO₂

MW: 221.30

[α]_D²⁰: -102.5°, c = 1 in CH₃OH

ee: 99% (HPLC)



540552-5G	5 g	\$78.00
-----------	-----	---------

(1*S*,2*S*)-(+)-Pseudoephedrinepropionamide, 98%

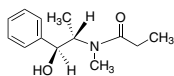
C₁₃H₁₉NO₂

MW: 221.3

[159213-03-3]

[α]_D²⁰: +102.5°, c = 1 in CH₃OH

ee: 99% (HPLC)



540544-5G	5 g	\$78.00
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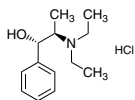
(+)-*N,N*-Diethylnorephedrine hydrochloride, purum, ≥95.0% (AT)

NEW

(1*S*,2*R*)-2-Diethylamino-1-phenyl-1-propanol hydrochloride

C₁₃H₂₁NO · HCl

MW: 243.77



92494-1G	1 g	\$22.00
92494-5G	5 g	\$85.70

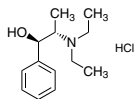
(-)-*N,N*-Diethylnorephedrine hydrochloride, purum, ≥95.0% (AT)

NEW

(1*R*,2*S*)-2-Diethylamino-1-phenyl-1-propanol hydrochloride

C₁₃H₂₁NO · HCl

MW: 243.77



73072-1G	1 g	\$21.40
73072-5G	5 g	\$85.70

(1*R*,2*S*)-(-)-Ephedrine, 99%

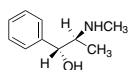
(1*R*,2*S*)-(-)-2-Methylamino-1-phenyl-1-propanol

C₁₀H₁₅NO

MW: 165.23

[299-42-3]

[α]_D²⁰: -41°, c = 5 in 1 N HCl



134910-5G	5 g	\$32.70
134910-25G	25 g	\$52.40
134910-100G	100 g	\$107.00

(1*R*,2*S*)-(-)-Ephedrine hydrochloride, 99%

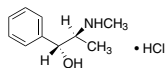
(1*R*,2*S*)-(-)-2-Methylamino-1-phenyl-1-propanol hydrochloride

C₁₀H₁₅NO · HCl

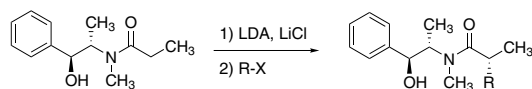
MW: 201.69

[50-98-6]

[α]_D²⁰: -34°, c = 4 in water



862231-25G	25 g	\$35.30
862231-100G	100 g	\$64.70



R-X	Yield (%)	de (%)
BnBr	90	>99
BuI	80	>99
BOMBr	80	98
Ph(CH ₂) ₂ I	86	95
<i>t</i> -BuO ₂ CCH ₂ Br	78	96
CH ₂ =CHCH ₂ I	93	99
TBSO(CH ₂) ₂ I	91	97
TIPSO(CH ₂) ₂ I	89	97

Scheme 21

(1*S*,2*R*)-(+)-Ephedrine hydrochloride, 99%

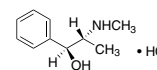
(1*S*,2*R*)-(+)-2-Methylamino-1-phenyl-1-propanol hydrochloride

C₁₀H₁₅NO · HCl

MW: 201.69

[24221-86-1]

[α]_D²⁰: +34.3°, c = 5 in water



857335-1G	1 g	\$18.80
857335-25G	25 g	\$43.80

(1*R*,2*R*)-(-)-Pseudoephedrine, 98%

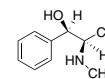
(1*R*,2*R*)-(-)-2-(Methylamino)-1-phenylpropanol

C₁₀H₁₅NO

MW: 165.23

[321-97-1]

[α]_D²⁰: -51°, c = 0.6 in C₂H₅OH



287644-25G	25 g	\$72.10
287644-100G	100 g	\$238.00

(1*S*,2*S*)-(+)-Pseudoephedrine, 98%

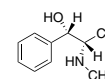
(1*S*,2*S*)-(+)-2-Methylamino-1-phenyl-1-propanol

C₁₀H₁₅NO

MW: 165.23

[90-82-4]

[α]_D²⁰: +52°, c = 0.6 in C₂H₅OH



287636-5G	5 g	\$29.10
287636-25G	25 g	\$69.00
287636-100G	100 g	\$175.50

(1*R*,2*S*)-(-)-Norephedrine, 99%

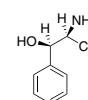
(1*R*,2*S*)-(-)-2-Amino-1-phenyl-1-propanol

C₉H₁₃NO

MW: 151.21

[492-41-1]

[α]_D²⁰: -41°, c = 7 in 1 N HCl



282553-10G	10 g	\$75.40
282553-50G	50 g	\$177.00



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(1S,2R)-(+)-Norephedrine, 98%

(1S,2R)-(+)-2-Amino-1-phenyl-1-propanol

C₉H₁₃NO

MW: 151.21

[37577-28-9]

[α]_D²⁰: +40°, c = 7 in 1 N HCl

317500-10G	10 g	\$71.60
317500-50G	50 g	\$168.50

**(1S,2R)-(-)-2-(Dibutylamino)-1-phenyl-1-propanol, 95%***N,N*-Dibutyl-D-(-)-norephedrine

(-)-DBNE

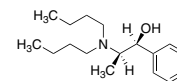
C₁₇H₂₉NO

MW: 263.42

[114389-70-7]

[α]_D²⁰: -21°, c = 2 in CHCl₃

400092-1G	1 g	\$39.80
400092-5G	5 g	\$133.50

**(1R,2S)-(+)-2-(Dibutylamino)-1-phenyl-1-propanol, 97%***N,N*-Dibutyl-L-(+)-norephedrine

(+)DBNE

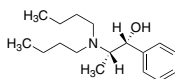
C₁₇H₂₉NO

MW: 263.42

[115651-77-9]

[α]_D²⁰: +21°, c = 2 in CHCl₃

407135-1G	1 g	\$39.80
407135-5G	5 g	\$133.50



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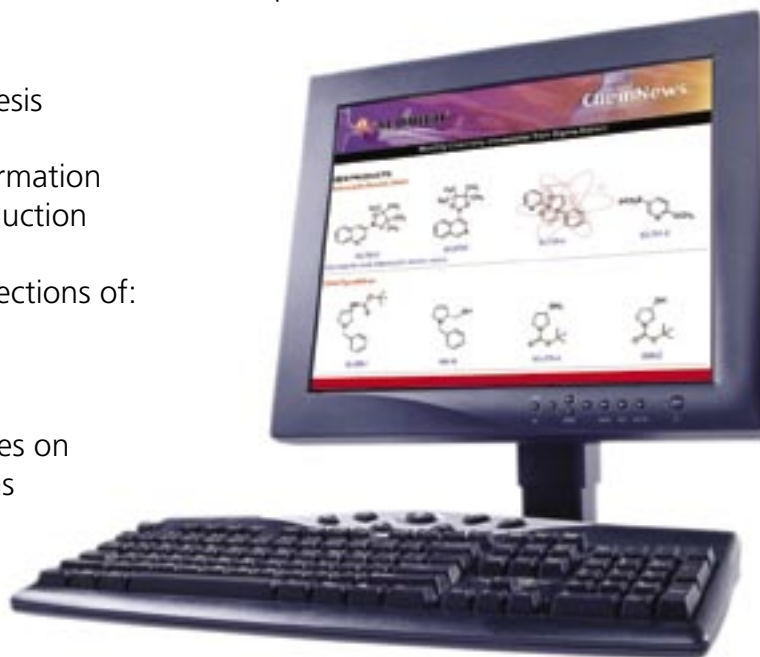
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- C-C/C-X Bond Formation
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4. Building Blocks

Chiral Alcohols

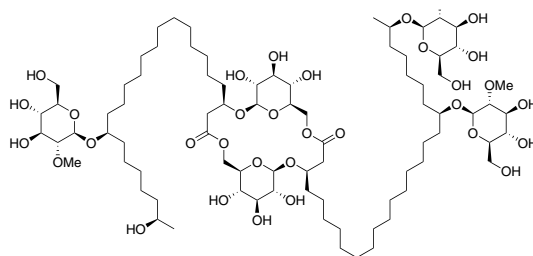
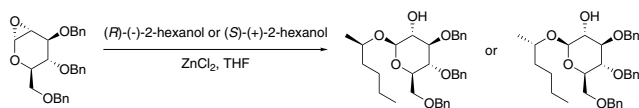
Sigma-Aldrich offers a wide range of chiral alcohols to meet their ever-growing demand. These useful reagents may serve both as starting materials in the synthesis of single-stereoisomer drugs or intermediates, or as powerful resolving agents.

2-Hexanol

(*R*)-(-)-2-Hexanol and (*S*)-(+)-2-hexanol were used in the preparation of some key intermediates for model studies in the total synthesis of antivirally active glycolipid cycloviracin B₁ (**Scheme 22**). By comparing the NMR chemical shifts of the synthesized model compounds with the ones of the isolated natural product, configurations of four previously unassigned stereocenters of cycloviracin B₁ could be elucidated.²⁷

2-Heptanol

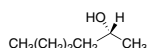
The (*R*)-enantiomer of 2-heptanol was used by Kondo et al. in resolving the diastereomeric mixture of a key intermediate in the synthesis of 1-(2-chloro-4-pyrrolidin-1-ylbenzoyl)-2,3,4,5-tetrahydro-1*H*-1-benzodiazepine, known to be a strong vasopressin V₂ receptor agonist, which helps to maintain normal plasma osmolality, blood volume, and blood pressure (**Scheme 23**).²⁸ A nonpeptidic V₂ agonist may find use in the treatment of diabetes insipidus and nocturnal enuresis.



Scheme 22

(*R*)-(-)-2-Hexanol, 99%

C₆H₁₄O
MW: 102.17
[26549-24-6]
[α]_D²⁰: -11 °, neat

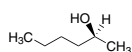


340308-1G	1 g	\$33.00
340308-5G	5 g	\$97.90

(*S*)-(+)-2-Hexanol, puriss., ≥98.5% (sum of enantiomers, GC)

NEW

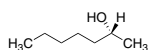
C₆H₁₄O
MW: 102.17
[52019-78-0]
[α]_D²⁰: +10.5 ± 0.5 °, neat



52847-1G	1 g	\$27.70
52847-5G	5 g	\$76.60

(*R*)-(-)-2-Heptanol, purum, ≥98.0% (sum of enantiomers, GC)

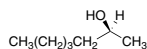
C₇H₁₆O
MW: 116.2
[6033-24-5]
[α]_D²⁰: -9.5 ± 0.5 °, neat (lit.)
enantiomeric ratio: >99:1 (GC)



07225-1ML	1 mL	\$228.10
-----------	------	----------

(*S*)-(+)-2-Heptanol, 99%

C₇H₁₆O
MW: 116.2
[6033-23-4]
[α]_D²⁰: +10 °, neat



340332-250MG	250 mg	\$18.40
340332-1G	1 g	\$50.80

Other Chiral Alcohols

(*R*)-(+)-1-Phenylethanol, puriss., ≥98.5% (sum of enantiomers, GC)

NEW

(*R*)-(+)-α-Methylbenzyl alcohol

C₈H₁₀O
MW: 122.16
[1517-69-7]

[α]_D²⁰: +45 ± 2 °, c = 5 in methanol
enantiomeric ratio: ≥97:3 (GC)



07366-5G	5 g	\$89.20
----------	-----	---------

(*S*)-(-)-1-Phenylethanol, puriss., ≥98.5% (sum of enantiomers, GC)

NEW

(*S*)-(-)-α-Methylbenzyl alcohol

C₈H₁₀O
MW: 122.16
[1445-91-6]

[α]_D²⁰: -45 ± 2 °, c = 5 in methanol
enantiomeric ratio: ≥97:3 (GC)

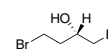


05512-5G	5 g	\$48.30
05512-25G	25 g	\$189.40

(*S*)-1,4-Dibromo-2-butanol, purum, ≥95.0% (sum of enantiomers, GC)

NEW

C₄H₈Br₂O
MW: 231.91
[64028-90-6]



77082-1G	1 g	\$36.50
77082-5G	5 g	\$146.00

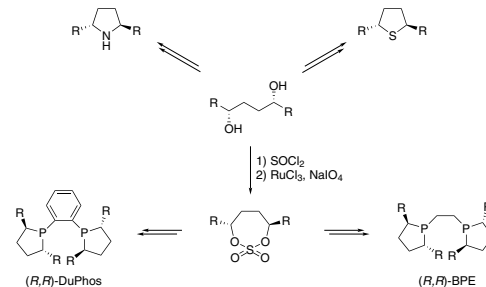


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Chiral Diols

2,5-Hexanediol and 3,6-Octanediol

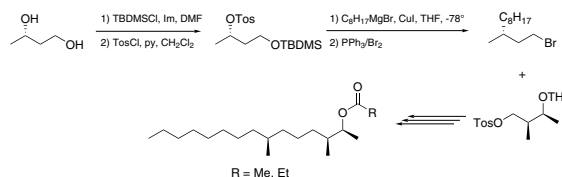
Enantiomerically pure C_2 -symmetrical alkanediols such as (2*S*,5*S*)-, and (2*R*,5*R*)-hexanediol are valuable building blocks for the synthesis of chiral ligands such as (2*S*,5*S*)-dimethylpyrrolidine or (2*S*,5*S*)-dimethylthiolane (**Scheme 24**, R = Me). (3*R*,6*R*)-Octanediol was used as a convenient starting material for the preparation of enantiomerically pure bis(phospholano)ethane ligands (**Scheme 24**, R = Et). Their use in Rh-catalyzed highly enantioselective hydrogenation reactions was described by Burk et al.²⁹



Scheme 24

2-Methyl-1,4-butanediol

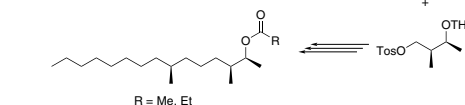
Huang et al. reported a concise asymmetric total synthesis of (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-yl acetate and propionate, the sex pheromones of the pine sawflies.³⁰ Starting from (*S*)-2-Methyl-1,4-butanediol, these pheromones are synthesized efficiently as depicted in **Scheme 25**.



Scheme 25

cis-4-Cyclopentene-1,3-diol 1-acetate

(1*R*,3*S*)-(+)-*cis*-4-Cyclopentene-1,3-diol 1-acetate has proven to be a valuable precursor for the synthesis of carbocyclic nucleosides and prostaglandins (**Scheme 26**).³¹



Scheme 26

(2*R*,5*R*)-(-)-2,5-Hexanediol, puriss., ≥99.0% (sum of enantiomers, GC)

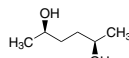
$C_6H_{14}O_2$

MW: 118.17

[17299-07-9]

$[\alpha]_D^{20}$: $-35 \pm 2^\circ$, $c = 9$ in $CHCl_3$

enantiomeric ratio: ≥99.5:0.5 (GC)



52792-250MG	250 mg	\$34.20
52792-1G	1 g	\$103.70

(2*S*,5*S*)-2,5-Hexanediol, 99%

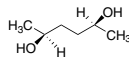
$C_6H_{14}O_2$

MW: 118.17

[34338-96-0]

$[\alpha]_D^{20}$: $+34.5^\circ$, $c = 9$ in $CHCl_3$

ee: 99% (GLC)



396729-250MG	250 mg	\$44.00
396729-1G	1 g	\$122.50

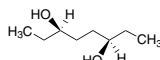
(3*R*,6*R*)-3,6-Octanediol, purum, ≥98.0% (sum of enantiomers, GC)

$C_8H_{18}O_2$

MW: 146.23

[129619-37-0]

enantiomeric ratio: ≥99:1



18717-250MG	250 mg	\$111.30
18717-1G	1 g	\$356.20

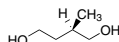
(*R*)-2-Methyl-1,4-butanediol, purum, ≥98.0% (sum of enantiomers, GC)

$C_5H_{12}O_2$

MW: 104.15

[22644-28-6]

04964-1ML	1 mL	\$161.50
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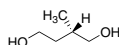
(*S*)-2-Methyl-1,4-butanediol, purum, ≥98.0% (sum of enantiomers, GC)

$C_5H_{12}O_2$

MW: 104.15

[70423-38-0]

53586-1ML	1 mL	\$124.70
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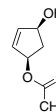
(1*R*,3*S*)-(+)-*cis*-4-Cyclopentene-1,3-diol 1-acetate, ≥99%

$C_7H_{10}O_3$

MW: 142.15

[60410-16-4]

$[\alpha]_D^{20}$: $+68^\circ$, $c = 2.3$ in $CHCl_3$



446041-50MG	50 mg	\$15.50
446041-250MG	250 mg	\$51.90
446041-1G	1 g	\$143.00

Other Chiral Diols

(3*S*,6*S*)-2,7-Dimethyl-3,6-octanediol

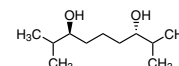
NEW

$C_{10}H_{22}O_2$

MW: 174.28

[129705-30-2]

enantiomeric ratio: ≥99:1 (GC)



≥99.0% (sum of enantiomers, GC)

50407-250MG	250 mg	\$39.70
50407-1G	1 g	\$142.10

puriss., ≥99.0% (sum of enantiomers, GC)

39277-250MG	250 mg	\$39.70
39277-1G	1 g	\$142.10

Chiral Amines

Chiral amines have found widespread application in asymmetric synthesis serving, for instance, as chiral bases in enantioselective deprotonation reactions³² or being valuable substances for resolving racemic mixtures of acids. Additionally, chiral amines are prevalent, essential parts of many drugs and drug candidates.

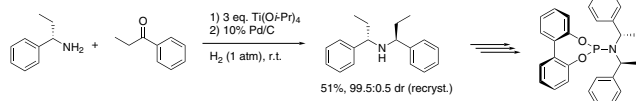
α -Ethylbenzylamine

Alexakis has recently reported on a practical solvent-free reductive amination reaction. In a one-pot synthesis, C₂-symmetrical secondary amines could be obtained in high diastereoselectivities starting from (*R*)- α -ethylbenzylamine or (*S*)- α -ethylbenzylamine, respectively (**Scheme 27**).

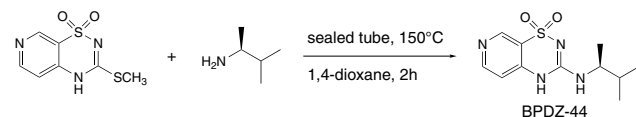
These secondary amines also serve as valuable chiral building blocks for the synthesis of atropisomeric phosphoramidites used in highly enantioselective copper-catalyzed conjugate additions³³ or in iridium-catalyzed allylic substitutions.³⁴

2-Amino-3-methylbutane

Diazoxide BPDZ-44 was found to be a tissue selective ATP-sensitive potassium channel opener, resulting in inhibition of important physiological processes such as insulin release or muscle tone and contractility. The straightforward synthesis of BPDZ-44 used (*S*)-2-amino-3-methylbutane as a chiral building block in a key step (**Scheme 28**).³⁵



Scheme 27



Scheme 28

(*R*)-(+)- α -Ethylbenzylamine

NEW

(*R*)-(+)-1-Phenylpropylamine
C₉H₁₃N
MW: 135.21
[3082-64-2]
[α]_D²⁰: +20 ± 2°, neat
enantiomeric ratio: ≥99.0:1.0 (GC)



purum, ≥95.0% (GC)

50282-5G	5 g	\$46.40
50282-25G	25 g	\$175.00

≥95.0% (GC)

65988-5G	5 g	\$49.60
65988-25G	25 g	\$187.30

(*S*)-(–)- α -Ethylbenzylamine

NEW

(*S*)-(–)-1-Phenylpropylamine
C₉H₁₃N
MW: 135.21
[3789-59-1]
[α]_D²⁰: –20 ± 2°, neat
enantiomeric ratio: ≥99.0:1.0 (GC)



purum, ≥95.0% (GC)

51432-5G	5 g	\$85.70
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≥95.0% (GC)

49847-5G	5 g	\$91.70
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(*R*)-(+)-2-Amino-3-methylbutane, purum, ≥97.0% (GC)

NEW

(*R*)-(+)-3-Methyl-2-butylamine
C₅H₁₃N
MW: 87.16
[34701-33-2]
[α]_D: –5.5 ± 1, neat



18241-1G	1 g	\$24.30
18241-5G	5 g	\$79.00

(*S*)-(–)-2-Amino-3-methylbutane

NEW

(*S*)-(–)-3-Methyl-2-butylamine
C₅H₁₃N
MW: 87.16
[22526-46-1]
[α]_D²⁰: +5.3 ± 0.5°, neat



≥98.0% (GC)

03198-1G	1 g	\$19.30
03198-5G	5 g	\$86.40

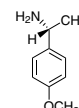
purum, ≥98.0% (GC)

91936-1G	1 g	\$20.70
91936-5G	5 g	\$92.90

(*R*)-(+)-4-Methoxy- α -methylbenzylamine, purum, ≥95.0% (GC)

NEW

(*R*)-(+)-1-(4-Methoxyphenyl)ethylamine
C₉H₁₃NO
MW: 151.21
[22038-86-4]
[α]_D²⁰: +32 ± 2°, neat
enantiomeric ratio: ≥99.0:1.0 (GC)

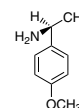


18159-5G	5 g	\$52.00
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(*S*)-(–)-4-Methoxy- α -methylbenzylamine

NEW

(*S*)-(–)-1-(4-Methoxyphenyl)ethylamine
C₉H₁₃NO
MW: 151.21
[41851-59-6]
[α]_D²⁰: –32 ± 2°, neat
enantiomeric ratio: ≥99.0:1.0 (GC)



purum, ≥95.0% (GC)

95889-5G	5 g	\$43.80
95889-25G	25 g	\$175.00

≥95.0% (GC)

18305-5G	5 g	\$43.80
18305-25G	25 g	\$175.00



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Chiral Pyrrolidines

Chiral pyrrolidines are playing an important role both as chiral building blocks for auxiliaries as well as key structures relevant to biologically active substances. Sigma-Aldrich has a large selection of pyrrolidines and other heterocyclic building blocks for organic synthesis and medicinal chemistry, the majority of which are available in both enantiomeric forms. Listed below are selected new chiral pyrrolidines.

2-(Diphenylmethyl)pyrrolidine

Recently, Aggarwal et al. used protonated (*S*)-(-)-2-(diphenylmethyl)-pyrrolidine as catalyst in a novel process for enantioselective epoxidation of alkenes without the use of a transition metal catalyst (**Scheme 29**).

However, best results were obtained with the chiral pyrrolidine derivative bearing 1-naphthyl groups.³⁶

Furthermore, both enantiomers of 2-(diphenylmethyl)pyrrolidine have found use as excellent chiral solvating agents to determine the enantiomeric composition of chiral carboxylic acids directly by NMR analysis. Optimal chemical shift non-equivalence between the diastereoisomeric salts is established when a 1:1 salt complex is formed in solution.³⁷

N-*tert*-Butoxycarbonyl-3-pyrrolidinol

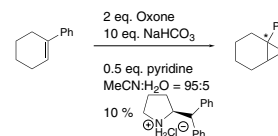
In search of novel compounds for the treatment of acute and chronic pain, pyridyl ethers, were developed by Lee et al. as ligands for the nicotinic acetylcholine receptor as shown in **Scheme 30**.³⁸ The most potent molecule turned out to be the one bearing the piperidyl ring moiety, which was synthesized from *N*-Boc-(*R*)-(+)-3-pyrrolidinol.

1-Benzyl-3,4-pyrrolidinediol

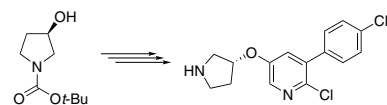
Enantiomerically pure 3,4-pyrrolidinediols have been extensively studied because of their well-known pharmacological properties as well as serving as powerful chiral building blocks in asymmetric synthesis. (3*R*,4*R*)-(-)-1-Benzyl-3,4-pyrrolidinediol served as starting material for the total synthesis of the antibiotic (-)-anisomycin, which exhibits strong and selective activity against pathogenic protozoa and fungi (**Scheme 31**).³⁹

1-Boc-pyrrolidinecarbonitrile

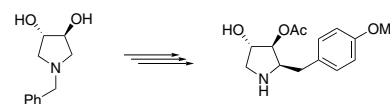
Prolyl oligopeptidase inhibitors (**Figure 1**) might be beneficial in the treatment of patients with cognitive disturbances, as promising experiments with rats and monkeys have shown. Wallen et al. recently presented the synthesis of a very potent inhibitor, which was synthesized using (*S*)-(-)-1-Boc-pyrrolidinecarbonitrile.⁴⁰



Scheme 29



Scheme 30



Scheme 31

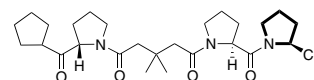


Figure 1

(*R*)-(+)-2-(Diphenylmethyl)pyrrolidine, 97% NEW

C₁₇H₁₉N
MW: 237.34
[22348-31-8]



552542-1G	1 g	\$88.10
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(*S*)-(-)-2-(Diphenylmethyl)pyrrolidine, 97%

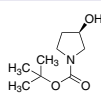
C₁₇H₁₉N
MW: 237.34
[119237-64-8]



552534-500MG	500 mg	\$94.90
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N-*tert*-Butoxycarbonyl-(*R*)-(-)-3-pyrrolidinol, 98%

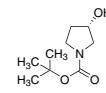
C₉H₁₇NO₃
MW: 187.24
[109431-87-0]
[α]_D²⁰: -7°, c = 1 in CH₃OH



532169-1G	1 g	\$65.00
532169-5G	5 g	\$185.50

N-*tert*-Butoxycarbonyl-(*S*)-(+)-3-pyrrolidinol, 97% NEW

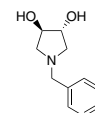
C₉H₁₇NO₃
MW: 187.24
[101469-92-5]



634786-1G	1 g	\$50.40
634786-5G	5 g	\$149.50

(3*R*,4*R*)-(-)-1-Benzyl-3,4-pyrrolidinediol, purum, ≥97.0% (sum of enantiomers, HPLC)

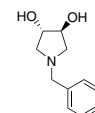
C₁₁H₁₅NO₂
MW: 193.24
[163439-82-5]
[α]_D²⁰: -33.6 ± 3°, c = 1.05 in methanol



37034-500MG	500 mg	\$75.80
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(3*S*,4*S*)-(+)-1-Benzyl-3,4-pyrrolidinediol, purum, ≥97.0% (sum of enantiomers, HPLC)

C₁₁H₁₅NO₂
MW: 193.24
[90365-74-5]
[α]_D²⁰: +33.6 ± 3°, c = 1.05 in methanol

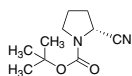


52057-500MG	500 mg	\$75.80
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(R)-(+)-1-Boc-2-pyrrolidinecarbonitrile, 97%

NEW

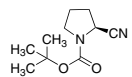
C₁₀H₁₆N₂O₂
MW: 196.25
[α]_D²⁰: +105.5°, c = 1 in CHCl₃



647233-1G	1 g	\$88.00
647233-5G	5 g	\$425.00

(S)-(-)-1-Boc-2-pyrrolidinecarbonitrile, 97%

C₁₀H₁₆N₂O₂
MW: 196.25
[228244-04-0]
[α]_D²⁰: -105.5°, c = 1 in CHCl₃

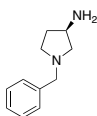


542091-500MG	500 mg	\$83.50
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Other Pyrrolidines**(R)-(-)-1-Benzyl-3-aminopyrrolidine, 95%**

NEW

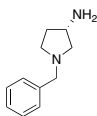
C₁₁H₁₆N₂
MW: 176.26
[114715-39-8]
[α]_D²⁰: -1.99°, c = neat



536601-1G	1 g	\$72.40
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(S)-(+)-1-Benzyl-3-aminopyrrolidine, 97%

C₁₁H₁₆N₂
MW: 176.26
[114715-38-7]
[α]_D²⁰: +1.99°, c = neat



536598-1G	1 g	\$73.30
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(R)-(+)-4-Hydroxy-2-pyrrolidone, purum, ≥97.0% (sum of enantiomers, GC)

(R)-(+)-β-Hydroxy-γ-butyrolactam
C₄H₇NO₂
MW: 101.1
[22677-21-0]
[α]_D²⁰: +41 ±3°, c = 1 in EtOH



56439-1G	1 g	\$42.00
56439-5G	5 g	\$165.70

(S)-(-)-4-Hydroxy-2-pyrrolidone, purum, ≥97.0% (sum of enantiomers, GC)

NEW

(S)-(-)-β-Hydroxy-γ-butyrolactam
C₄H₇NO₂
MW: 101.1
[68108-18-9]
[α]_D²⁰: -41 ±3°, c = 1 in EtOH



76557-1G	1 g	\$152.90
76557-5G	5 g	\$581.00

(R)-(-)-1-Methyl-3-pyrrolidinol

NEW

(R)-(-)-3-Hydroxy-N-methylpyrrolidine
C₅H₁₁NO
MW: 101.15
[104641-60-3]



647241-1G	1 g	\$70.00
647241-5G	5 g	\$278.00

(S)-(+)-1-Methyl-3-pyrrolidinol, 95%

(S)-(+)-3-Hydroxy-N-methylpyrrolidine
C₅H₁₁NO
MW: 101.15
[104641-59-0]
[α]_D²⁰: +6°, c = 1 in CHCl₃

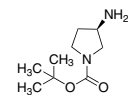


573337-1G	1 g	\$87.70
573337-5G	5 g	\$292.00

(R)-(+)-N-Boc-3-aminopyrrolidine, 97%

NEW

C₉H₁₈N₂O₂
MW: 186.25
[147081-49-0]

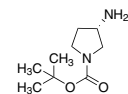


644064-1G	1 g	\$95.00
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(S)-(-)-1-Boc-3-aminopyrrolidine, 95%

NEW

C₉H₁₈N₂O₂
MW: 186.25
[147081-44-5]

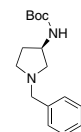


634794-1G	1 g	\$72.40
634794-5G	5 g	\$328.00

(R)-(+)-1-Benzyl-3-(Boc-amino)pyrrolidine, 97%

NEW

(R)-(+)-1-Benzyl-3-(tert-butoxycarbonylamino)pyrrolidine
C₁₆H₂₄N₂O₂
MW: 276.37
[131878-23-4]
[α]_D²⁰: +6°, c = 1 in CHCl₃

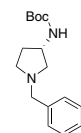


649961-1G	1 g	\$40.00
649961-5G	5 g	\$175.00

(S)-(-)-1-Benzyl-3-(Boc-amino)pyrrolidine, 97%

NEW

(S)-(-)-1-Benzyl-3-(tert-butoxycarbonylamino)pyrrolidine
C₁₆H₂₄N₂O₂
MW: 276.37
[α]_D²⁰: -6°, c = 1 in CHCl₃

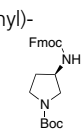


649988-1G	1 g	\$48.00
649988-5G	5 g	\$220.00

(R)-(-)-N-Boc-3-N-Fmoc-aminopyrrolidine, 97%

NEW

(R)-(-)-1-(tert-Butoxycarbonyl)-3-N-(9-fluorenylmethoxycarbonyl)-aminopyrrolidine
C₂₄H₂₈N₂O₄
MW: 408.49
[352530-40-6]

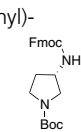


650919-1G	1 g	\$150.00
650919-5G	5 g	\$525.00

(S)-(+)-N-Boc-3-N-Fmoc-aminopyrrolidine, 97%

NEW

(S)-(+)-1-(tert-Butoxycarbonyl)-3-N-(9-fluorenylmethoxycarbonyl)-aminopyrrolidine
C₂₄H₂₈N₂O₄
MW: 408.49
[307531-88-0]
[α]_D²⁰: +6.0 ±3°, c = 1 in CHCl₃



651559-1G	1 g	\$150.00
651559-5G	5 g	\$525.00



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(S)-(+)-3-Fluoropyrrolidine hydrochloride, 97%

NEW

 $C_4H_8FN \cdot HCl$

MW: 125.57

[136725-53-6]

[α]_D²⁰: +8°, c = 1 in methanol

637513-1G	1 g	\$82.40
637513-5G	5 g	\$356.00

(S)-(-)-2-Aminomethyl-1-ethylpyrrolidine, 96%

NEW

 $C_7H_{16}N_2$

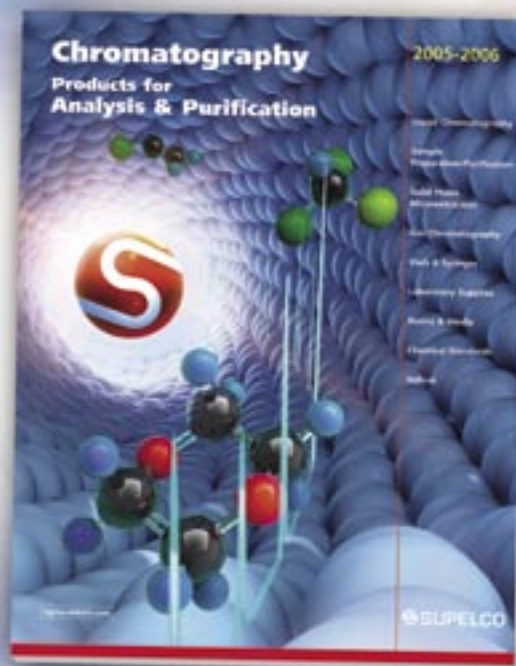
MW: 128.22

[022795-99-9]

[α]_D²⁰: -100°, c = 1 in methanol

647446-1G	1 g	\$41.50
647446-5G	5 g	\$98.70

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HKR Epoxides

One of the most effective and recent methods for obtaining several classes of chiral building blocks is Jacobsen's hydrolytic kinetic resolution technique (HKR). The method provides general access to many chiral epoxides and 1,2-diols that are otherwise difficult to obtain, in high conversions and enantiopurities, from inexpensive racemic starting materials. Sigma-Aldrich is the exclusive distributor of chiral compounds manufactured by Rhodia Pharma Solutions, under license, using Jacobsen HKR technology.

Styrene oxide

Starting from (*R*)-(+)-styrene oxide, Bassingdale and co-workers were able to synthesize a family of chiral ligands which were subsequently employed in a Mg-mediated enantioselective deprotonation process showing high general selectivity (**Scheme 32**).⁴¹

Kang and Chang used (*R*)-styrene oxide as a starting material, while also employing HKR techniques to produce a homologated epoxide as part of their synthetic approach to (+)-allosedamine (**Scheme 33**).⁴²

Epichlorohydrin

(*S*)-Epichlorohydrin was recently employed by Moriarty and co-workers as a building block for the synthesis of a key intermediate in the synthesis of stable PGI₂ analogue UT-15, an effective candidate for the treatment of pulmonary hypertension (**Scheme 34**).⁴³

The (*R*)-enantiomer was used by Munkata and co-workers to make a few key (*E*)-iodoalkene intermediates used in the total syntheses of Macquarimicins (**Scheme 35**), which have demonstrated cytotoxicity against the P388 leukemia cell line and anti-inflammatory activity.⁴⁴

Burova and McDonald have also recently used (*R*)-epichlorohydrin to synthesize the C10–C16 module in their total synthesis of the macrolide RK-397 (**Scheme 36**).⁴⁵

Glycidyl tosylate

Both glycidyl tosylate isomers were used in the first enantioselective syntheses of (*R*)- and (*S*)-4-acetyl-3-(hydroxymethyl)-3,4-dihydro-2*H*-pyrido[3,2-*b*]oxazines (**Scheme 37**).⁴⁶

Ghosh and Liu employed (2*S*)-glycidyl tosylate in the synthesis of a vinyl ether fragment in their enantioselective total synthesis of (+)-amphidinolide T1 (**Scheme 38**).⁴⁷

(*R*)-(+)-Styrene oxide, 97%

(*R*)-(+)-Phenylloxirane

C₈H₈O

MW: 120.15

[20780-53-4]

[α]_D²⁰: +33 °, neat

ee: 97% (GLC)

540099-5G	5 g	\$137.00
540099-25G	25 g	\$358.00

(*S*)-(–)-Styrene oxide, 98%

(*S*)-(–)-Phenylloxirane

C₈H₈O

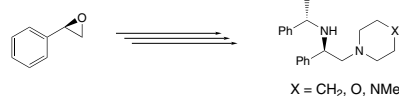
MW: 120.15

[20780-54-5]

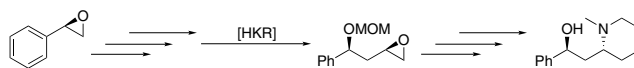
[α]_D²⁰: –33 °, neat

ee: 98% (HPLC)

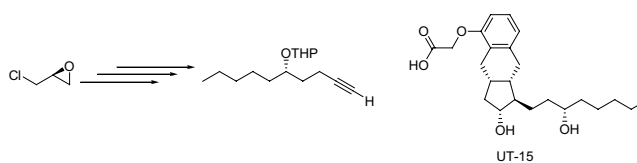
540102-5G	5 g	\$137.00
540102-25G	25 g	\$358.00



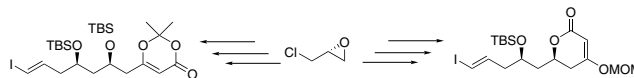
Scheme 32



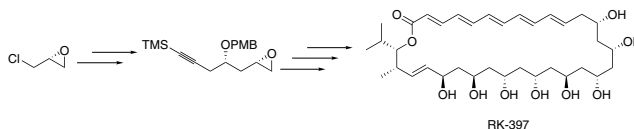
Scheme 33



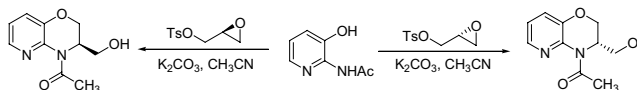
Scheme 34



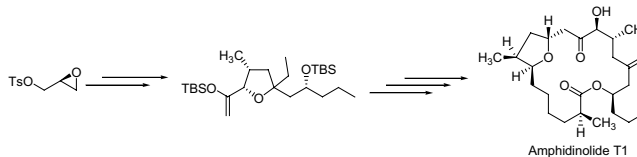
Scheme 35



Scheme 36



Scheme 37



Scheme 38



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(R)-(-)-Epichlorohydrin, 99%*(R)*-(-)-2-(Chloromethyl)oxiraneC₃H₅ClO

MW: 92.52

[51594-55-9]

[α]_D²⁰: -34 °, c = 1 in CH₃OH

ee: 98% (GLC)

540072-5G	5 g	\$144.00
540072-25G	25 g	\$292.50

**(S)-(+)-Epichlorohydrin, 98%***(S)*-(+)-2-(Chloromethyl)oxiraneC₃H₅ClO

MW: 92.52

[67843-74-7]

[α]_D²⁰: +35 °, c = 1 in CH₃OH

ee: 97% (GLC)

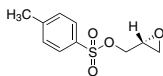
540080-5G	5 g	\$144.00
540080-25G	25 g	\$291.50

**(2R)-(-)-Glycidyl tosylate, 98%***(R)*-(-)-Oxirane-2-methanol *p*-toluenesulfonateC₁₀H₁₂O₄S

MW: 228.26

[113826-06-5]

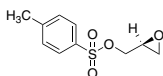
540110-5G	5 g	\$98.20
540110-25G	25 g	\$306.00

**(2S)-(+)-Glycidyl tosylate, 98%***(S)*-(+)-Oxirane-2-methanol *p*-toluenesulfonateC₁₀H₁₂O₄S

MW: 228.26

[70987-78-9]

540129-5G	5 g	\$98.20
540129-25G	25 g	\$306.00

**Other HKR Epoxides****(R)-(+)-Propylene oxide, 99%***(R)*-(+)-MethyloxiraneC₃H₆O

MW: 58.08

[15448-47-2]

[α]_D²⁰: +14.0 °, neat

540048-5G	5 g	\$143.50
540048-25G	25 g	\$292.50

**(S)-(-)-Propylene oxide, 99%***(S)*-(-)-MethyloxiraneC₃H₆O

MW: 58.08

[16088-62-3]

[α]_D²⁰: -14.0 °, neat

540021-5G	5 g	\$143.50
540021-25G	25 g	\$292.50

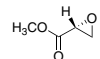
**(R)-(+)-Methyl glycidate, 97%**Methyl *(R)*-oxiranecarboxylateC₄H₆O₃

MW: 102.09

[111058-32-3]

[α]_D²⁰: +32.0 °, c = 1 in CHCl₃

469424-5G	5 g	\$172.00
469424-25G	25 g	\$451.50

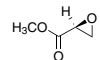
**(S)-(-)-Methyl glycidate, 98%**Methyl *(S)*-oxiranecarboxylateC₄H₆O₃

MW: 102.09

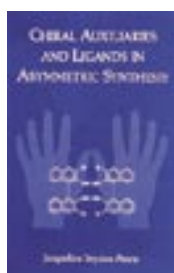
[118712-39-3]

[α]_D²⁰: -32.0 °, c = 1 in CHCl₃

469432-5G	5 g	\$172.00
469432-25G	25 g	\$451.50



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