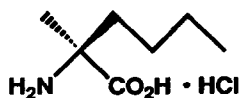


STEREOCHEMISTRY ABSTRACTS

M. Yokoyama, T. Sugai, and H. Ohta

Tetrahedron: Asymmetry 1993, 4, 1081



(*S*)- α -Methylnorleucine hydrochloride

E.e. = >99% (by chiral HPLC of *N*-Cbz-*O*-Me deriv.)

$[\alpha]_D^{23} +10$ (c 2.0, 5*N* HCl)

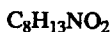
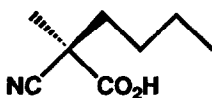
Source of chirality: Methyl (*R*)-2-carbamoyl-2-methylhexanoate

Absolute configuration: 2*S*

(assigned by optical rotatory dispersion)

M. Yokoyama, T. Sugai, and H. Ohta

Tetrahedron: Asymmetry 1993, 4, 1081



(*R*)-2-Cyano-2-methylhexanoic acid

E.e. = 96% (by chiral HPLC of β -naphthyl ester)

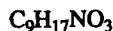
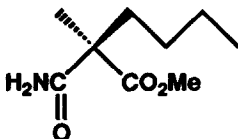
$[\alpha]_D^{19} +8.6$ (c 2.0, MeOH)

Source of chirality: Methyl (*R*)-2-carbamoyl-2-methylhexanoate

Absolute configuration: 2*R*

M. Yokoyama, T. Sugai, and H. Ohta

Tetrahedron: Asymmetry 1993, 4, 1081



Methyl (*R*)-2-carbamoyl-2-methylhexanoate

E.e. = 96%

$[\alpha]_D^{20} -15.6$ (c 1.0, $CHCl_3$)

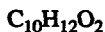
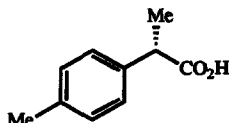
Source of chirality: enzymatic hydrolysis of prochiral dinitrile

Absolute configuration: 2*R*

(assigned *via* chemical correlation)

T. Beard, M.A. Cohen, J.S. Parratt, N.J. Turner,
J. Crosby, and J. Moilliet

Tetrahedron: Asymmetry 1993, 4, 1085



(*S*)-2-(4'-methylphenyl)-propionic acid

E.e. = >95%

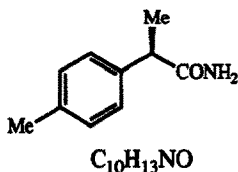
$[\alpha]_D^{25} = +57.0$ (c = 1.0, $CHCl_3$)

Source of chirality: enzyme nitrile hydrolysis

Absolute configuration: 2*S*

T. Beard, M.A. Cohen, J.S. Parratt, N.J. Turner,
J. Crosby, and J. Moilliet

Tetrahedron: Asymmetry 1993, 4, 1085



E.e. = >95%

$[\alpha]_D^{25} = -49.7$ (c = 1.14, $CHCl_3$)

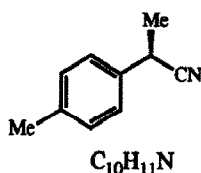
Source of chirality: enzyme nitrile hydrolysis

Absolute configuration: 2*R*

(*R*)-2-(4'-methylphenyl)-propionamide

T. Beard, M.A. Cohen, J.S. Parratt, N.J. Turner,
J. Crosby, and J. Moilliet

Tetrahedron: Asymmetry 1993, 4, 1085



E.e. = >95%

$[\alpha]_D^{25} = +13.1$ (c = 1.1, $CHCl_3$)

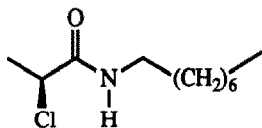
Source of chirality: enzyme nitrile hydrolysis

Absolute configuration: 2*R*

(*R*)-2-(4'-methylphenyl)-propionitrile

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



E.e. 70% [by 1H -NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

$[\alpha]_D^{25} = -10.0$ (c 0.97, $CHCl_3$)

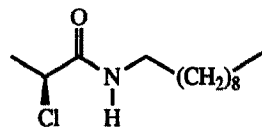
Source of chirality: Enzymatic aminolysis

Absolute configuration: S

(*S*)-2-Chloro-*N*-octylpropanamide

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



E.e. 92% [by 1H -NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

$[\alpha]_D^{25} = -9.9$ (c 1.02, $CHCl_3$)

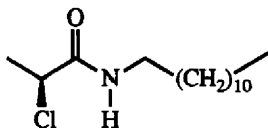
Source of chirality: Enzymatic aminolysis

Absolute configuration: S

(*S*)-2-Chloro-*N*-decylpropanamide

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



C₁₅H₃₀ClNO

(S)-2-Chloro-N-dodecylpropanamide

E.e. 51% [by ¹H-NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

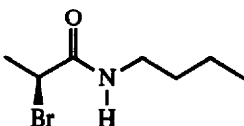
[α]_D²⁵ = -5.7 (c 1.02, CHCl₃)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



C₇H₁₄BrNO

(S)-2-Bromo-N-butylpropanamide

E.e. 90% [by ¹H-NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

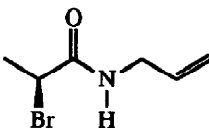
[α]_D²⁵ = -10.2 (c 0.80, CHCl₃)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



C₆H₁₀BrNO

(S)-N-Allyl-2-bromopropanamide

E.e. 50% [by ¹H-NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

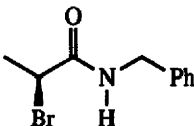
[α]_D²⁵ = -3.8 (c 0.82, CHCl₃)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



C₁₀H₁₂BrNO

(S)-N-Benzyl-2-bromopropanamide

E.e. <5% [by ¹H-NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

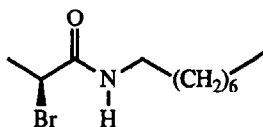
[α]_D²⁵ = -0.5 (c 0.70, CHCl₃)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{11}H_{22}BrNO$

(*S*)-2-Bromo-*N*-octylpropanamide

E.e. 61% [by 1H -NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

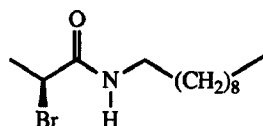
$[\alpha]_D^{25} = -6.0$ (c 0.72, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{13}H_{26}BrNO$

(*S*)-2-Bromo-*N*-decylpropanamide

E.e. 64% [by 1H -NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

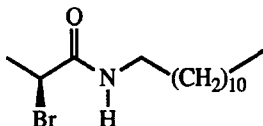
$[\alpha]_D^{25} = -6.5$ (c 0.65, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{15}H_{30}BrNO$

(*S*)-2-Bromo-*N*-dodecylpropanamide

E.e. 64% [by 1H -NMR spectroscopy using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium (III).]

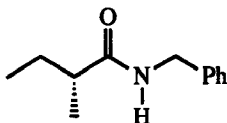
$[\alpha]_D^{25} = -3.6$ (c 0.60, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: S

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{12}H_{17}NO$

(*R*)-*N*-Benzyl-2-methylbutanamide

E.e. 78% [by comparison with an authentic sample obtained from (*S*)-(+)-2-methylbutyric anhydride]

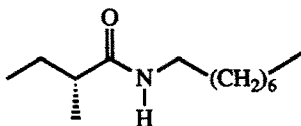
$[\alpha]_D^{25} = -6.8$ (c 1.05, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: R

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{13}H_{27}NO$

(*R*)-2-Methyl-*N*-octylbutanamide

E.e. 50% [by comparison with an authentic sample obtained from (*S*)-(+)-2-methylbutyric anhydride]

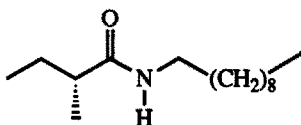
$[\alpha]_D^{25} = -6.0$ (c 0.99, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: R

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{15}H_{31}NO$

(*R*)-*N*-Decyl-2-methylbutanamide

E.e. 50% [by comparison with an authentic sample obtained from (*S*)-(+)-2-methylbutyric anhydride]

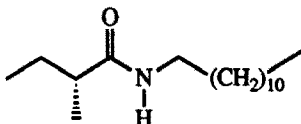
$[\alpha]_D^{25} = -3.7$ (c 0.96, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: R

M. Quirós, V. M. Sánchez, R. Brieva, F. Rebolledo and V. Gotor

Tetrahedron: Asymmetry 1993, 4, 1105



$C_{17}H_{35}NO$

(*R*)-*N*-Dodecyl-2-methylbutanamide

E.e. 48% [by comparison with an authentic sample obtained from (*S*)-(+)-2-methylbutyric anhydride]

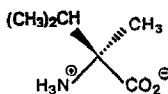
$[\alpha]_D^{25} = -4.6$ (c 0.70, $CHCl_3$)

Source of chirality: Enzymatic aminolysis

Absolute configuration: R

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters, H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



$C_6H_{13}NO_2$

2-Amino-2,3-dimethylbutanoic acid

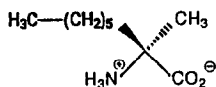
E.e. >98% [by NMR using *S*-2-chloropropionyl chloride]

$[\alpha]_D^{20} = -4.0$ (c 1.3, H_2O) HCl-salt, *S*-enantiomer

Source of chirality: enzymatic resolution

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



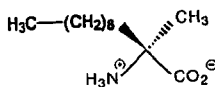
E.e. >99% [by HPLC]
[α]_D²⁰ = +13.3 (c1, 1N HCl), S-enantiomer
Source of chirality: enzymatic resolution

C₉H₁₉NO₂

2-Amino-2-methyloctanoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



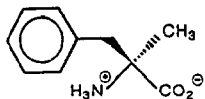
E.e. >99% [by HPLC]
[α]_D²⁰ = +16.4 (c0.5, MeOH) HCl-salt, S-enantiomer
Source of chirality: enzymatic resolution

C₁₂H₂₅NO₂

2-Amino-2-methylundecanoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



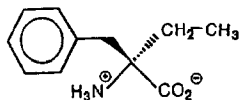
E.e. >99% [by HPLC]
[α]_D²⁰ = -22.0 (c1, H₂O), HCl-salt, S-enantiomer
Source of chirality: enzymatic resolution

C₁₀H₁₃NO₂

2-Amino-2-methyl-3-phenylpropanoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



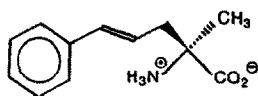
E.e. >96% [by HPLC]
[α]_D²⁰ = -22.8 (c1, H₂O), HCl-salt, S-enantiomer
Source of chirality: enzymatic resolution

C₁₁H₁₅NO₂

2-Amino-2-ethyl-3-phenylpropanoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



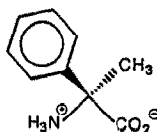
E.e. >98% [by HPLC]
[α]_D²⁵ = -1.8 (c1, 1N HCl), S-enantiomer
Source of chirality: enzymatic resolution

C₁₂H₁₅NO₂

2-Amino-2-methyl-5-phenylpent-4-enoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



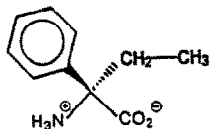
E.e. = 95% [by HPLC]
[α]_D²⁰ = +86.0 (c1, 1N HCl), S-enantiomer
Source of chirality: enzymatic resolution

C₉H₁₁NO₂

2-Amino-2-methylphenylacetic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



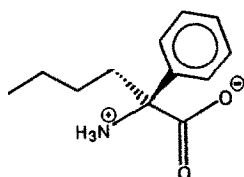
E.e. = 94% [by HPLC]
[α]_D²⁰ = +37.6 (c1, 1N HCl), S-enantiomer
Source of chirality: enzymatic resolution

C₁₀H₁₃NO₂

2-Amino-2-ethylphenylacetic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



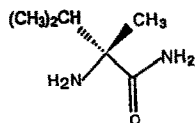
E.e. = 93% [by HPLC]
[α]_D²⁰ = +25.3 (c1, 1N HCl) S(?)-enantiomer
Source of chirality: enzymatic resolution

C₁₂H₁₇NO₂

2-Amino-2-phenylhexanoic acid

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



E.e. >98% [by NMR using S-2-chloropropionyl chloride]

$[\alpha]_D^{20} = +27.5$ (c1, H₂O) R-enantiomer

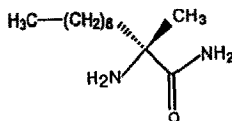
Source of chirality: enzymatic resolution

C₆H₁₃N₂O

2-Amino-2,3-dimethylbutanoic acid amide

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



E.e. =99% [by HPLC]

$[\alpha]_D^{20} = -12.6$ (c1, 1N HCl), R-enantiomer

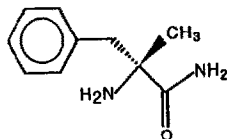
Source of chirality: enzymatic resolution

C₁₂H₂₅N₂O

2-Amino-2-methylundecanoic acid amide

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



E.e. =99% [by HPLC]

$[\alpha]_D^{20} = +42.0$ (c1, MeOH), R-enantiomer

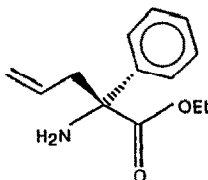
Source of chirality: enzymatic resolution

C₁₀H₁₃N₂O

2-Amino-2-methyl-3-phenylpropanoic acid amide

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



E.e. =95% [by HPLC]

$[\alpha]_D^{20} = -7.8$ (c1, 1N HCl), R-enantiomer

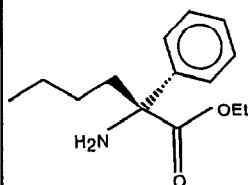
Source of chirality: enzymatic resolution

C₁₃H₁₇NO₂

Ethyl 2-amino-2-phenylpent-4-enoate

B. Kaptein, W.H.J. Boesten, Q.B. Broxterman, P.J.H. Peters,
H.E. Schoemaker and J. Kamphuis.

Tetrahedron: Asymmetry 1993, 4, 1113



$C_{14}H_{21}NO_2$

Ethyl 2-amino-2-phenylhexanoate

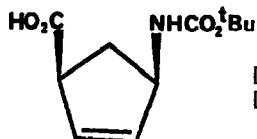
E.e.=97% [by HPLC]

$[\alpha]_D^{20} = -7.7$ (c1, 1N HCl), R(?)-enantiomer

Source of chirality: enzymatic resolution

Tetrahedron: Asymmetry 1993, 4, 1117

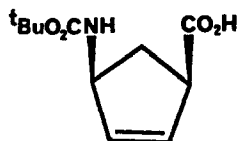
S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



[1(R), 4(S)]-N-(*tert*-Butoxycarbonyl)-4-amino-2-cyclopentene-1-carboxylic acid
 $[\alpha]_D^{25} + 40.3$ (c = 2.1, CH_2Cl_2)

Tetrahedron: Asymmetry 1993, 4, 1117

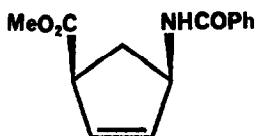
S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



[1(S), 4(R)]-N-(*tert*-Butoxycarbonyl)-4-amino-2-cyclopentene-1-carboxylic acid
 $[\alpha]_D^{25} - 40.3$ (c = 2.1, CH_2Cl_2)

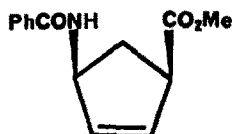
Tetrahedron: Asymmetry 1993, 4, 1117

S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



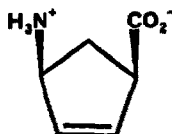
[1(R), 4(S)]-4-benzoylamino-2-cyclopentene-1-carboxylic acid, methyl ester
m.p. 80.5-82°C
 $[\alpha]_D^{25} - 33.6$ (c = 2.2, CH_2Cl_2)

S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



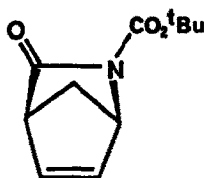
[1(S), 4(R)]-4-benzoylamino-2-cyclopentene-1-carboxylic acid, methyl ester
m.p. 80.5-82°C
 $[\alpha]_D^{25} + 33.6$ (c = 2.2, CH₂Cl₂)

S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



[1(R), 4(S)]-4-Amino-2-cyclopentene-1-carboxylic acid
 $[\alpha]_D + 242$ (c = 2, H₂O)

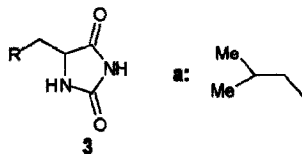
S. J. C. Taylor, R. McCague, R. Wisdom, C. Lee, K. Dickson, G. Rucroft, F. O'Brien,
J. Littlechild, J. Bevan, S. M. Roberts and C. T. Evans



[1(R), 4(S)]-N-(*tert*-Butoxycarbonyl)-2-azabicyclo[2.2.1]hept-5-en-3-one
 $[\alpha]_D - 189$ (c = 0.89, CH₂Cl₂)

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

H. Lickefett¹, K. Krohn², W.A. König³, B. Gehrcke³ and C. Sydtk¹



C₃H₃N₂O₂

5-Isobutyl-imidazolidin-2,4-dione

E. e > 98 %

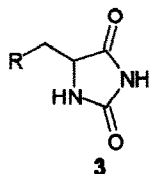
Source of chirality : Chemical synthesis from the
corresponding D- or L-α- amino acid

Absolute configuration : R or S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

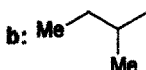
H. Lickefett*¹, K. Krohn², W.A. König³, B. Gehrcke³ and C. Syldatk¹

Tetrahedron: Asymmetry 1993, 4, 1129



C₃H₃N₂O₂

5-(1)-Methyl-propyl-imidazolidin-2,4-dione



E. e > 98 %

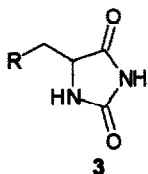
Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : 2R, 3R or 2S, 3S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

H. Lickefett*¹, K. Krohn², W.A. König³, B. Gehrcke³ and C. Syldatk¹

Tetrahedron: Asymmetry 1993, 4, 1129



C₃H₃N₂O₂

5-methyl-imidazolidin-2,4-dione



E. e > 98 %

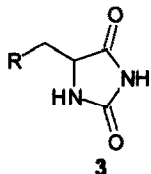
Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : R or S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

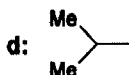
H. Lickefett*¹, K. Krohn², W.A. König³, B. Gehrcke³ and C. Syldatk¹

Tetrahedron: Asymmetry 1993, 4, 1129



C₃H₃N₂O₂

5-Isopropyl-imidazolidin-2,4-dione



E. e > 98 %

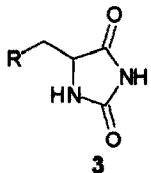
Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : R or S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

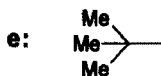
H. Lickefett*¹, K. Krohn², W.A. König³, B. Gehrcke³ and C. Syldatk¹

Tetrahedron: Asymmetry 1993, 4, 1129



C₃H₃N₂O₂

5-tert-butyl-imidazolidin-2,4-dione



E. e > 98 %

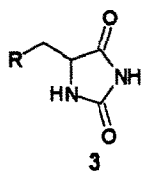
$[\alpha]_D^{20} +63.9$ (c = 0.27, ethanol)

Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : R or S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

H. Lickefett^{*1}, K. Krohn², W.A. König³, B. Gehrcke³ and C. Sydtk¹



$C_7H_{11}N_2O_2$

5-Cyclohexyl-methyl-imidazolidin-2,4-dione

f:



Tetrahedron: Asymmetry 1993, 4, 1129

E. e > 98 %

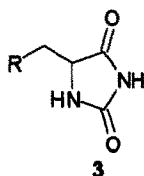
$[\alpha]_D^{20} +62.4$ (c = 1.27, ethanol)

Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : R or S

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

H. Lickefett^{*1}, K. Krohn², W.A. König³, B. Gehrcke³ and C. Sydtk¹



$C_7H_7N_2O_2$

5-Phenyl-imidazolidin-2,4-dione

g:



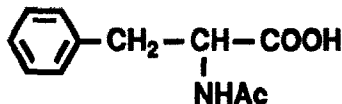
Tetrahedron: Asymmetry 1993, 4, 1129

E. e > 98 %

Source of chirality : Chemical synthesis from the corresponding D- or L- α - amino acid

Absolute configuration : R or S

R. Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$C_{11}H_{13}NO_3$

N-acetyl-phenylalanine

E.e. > 95% (¹H NMR of (S)-naphthylethylamide)

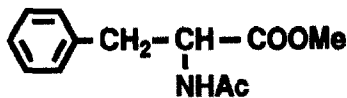
$[\alpha]_D^{23} = -51.0$ (c 4, EtOH)

Source of chirality : enzymatic hydrolysis

Absolute configuration : D

Tetrahedron: Asymmetry 1993, 4, 1137

R. Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$C_{12}H_{15}NO_3$

Methyl N-acetyl-phenylalaninate

E.e > 95% (optical rotation)

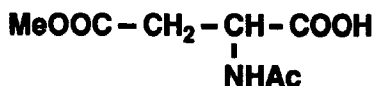
$[\alpha]_D^{23} = +19.3$ (c 3, MeOH)

Source of chirality : enzymatic hydrolysis

Absolute configuration : L

Tetrahedron: Asymmetry 1993, 4, 1137

R. Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$\text{C}_7\text{H}_{11}\text{NO}_5$

B-methyl N-acetyl-aspartate

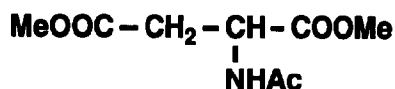
E.e > 95% (^1H NMR of (S)-1-naphthylethylamide)

$[\alpha]_{\text{D}}^{23} = -8.3$ (c 3, EtOH)

Source of chirality : enzymatic hydrolysis

Absolute configuration : D

R.Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$\text{C}_7\text{H}_{11}\text{NO}_5$

Dimethyl N-acetyl-aspartate

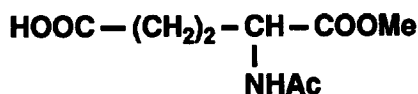
E.e > 95% (optical rotation)

$[\alpha]_{\text{D}}^{23} = -21.0$ (c 1, CHCl_3)

Source of chirality : enzymatic hydrolysis

Absolute configuration : L

R. Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$\text{C}_8\text{H}_{13}\text{NO}_5$

α -methyl N-acetyl-glutamate

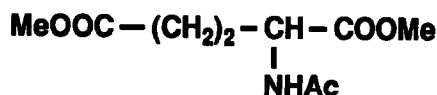
E.e > 95% (^1H NMR of (S)-1-naphthylethylamide)

$[\alpha]_{\text{D}}^{23} = +23.0$ (c 4, MeOH)

Source of chirality : enzymatic hydrolysis

Absolute configuration : D

R. Chênevert, R. BelRhliid, M. Létourneau, R. Gagnon, L. D'Astous.



$\text{C}_9\text{H}_{15}\text{NO}_5$

Dimethyl N-acetyl-glutamate

E.e > 95% (optical rotation)

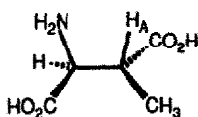
$[\alpha]_{\text{D}}^{23} = +12.2$ (c 3, MeOH)

Source of chirality : enzymatic hydrolysis

Absolute configuration : L

Catherine H. Archer, Neil R. Thomas and David Gani

Tetrahedron: Asymmetry 1993, 4, 1141



3-Methylaspartic acid

D.e. 95% (asymmetric alkylation) or
98% (enzymic amination then resolution)
100% (2S)-configuration

$H_A = H$; $[\alpha]_D +36.3$ (c 1.0, 5M HCl)

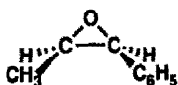
$H_A = ^2H$; $[\alpha]_D +30.5$ (c 1.0, 5 M HCl)

Source of chirality: asymm. synth. or enzyme

Absolute configuration 2S,3R

G. Bellucci, C. Chiappe, A. Cordoni and F. Marioni

Tetrahedron: Asymmetry 1993, 4, 1153



cis-1-Phenylpropene oxide

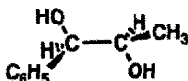
E.e. >98% [by glc: Chiraldex G-TA]

Source of chirality: enzymatic hydrolysis of the racemate

Absolute configuration (1S,2R)

G. Bellucci, C. Chiappe, A. Cordoni and F. Marioni

Tetrahedron: Asymmetry 1993, 4, 1153



threo-1-Phenylpropane-1,2-diol

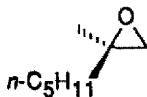
E.e. >98% [by glc: Chiraldex G-TA]

Source of chirality: enzymatic hydrolysis of (*±*)-*cis*-1-phenylpropene oxide

Absolute configuration (1R,2R)

P. Hechtberger, G. Wirsberger, M. Mischitz, N. Klempier, K. Faber*

Tetrahedron: Asymmetry 1993, 4, 1161



$C_8H_{16}O$
2-Methyl-2-pentylloxiran

E.e. = 72% [by chiral GC]

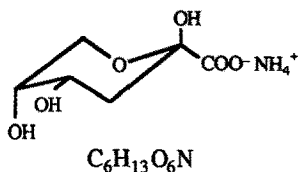
$[\alpha]_D^{20} = -6.82$ (c 3.43, $CHCl_3$)

Source of chirality: enzymatic resolution.

Absolute configuration: (*R*) by comparison with independently synthesized material.

Claudine Augé and Véronique Delest

Tetrahedron: Asymmetry 1993, 4, 1165



D.e. = 92% (by 1H and ^{13}C NMR)

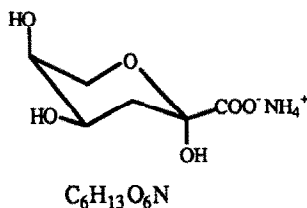
$[\alpha]_D^{20} = -26$ (c, 2, water)

Source of chirality: microbiological aldolisation

Absolute configuration 4S, 5R

Claudine Augé and Véronique Delest

Tetrahedron: Asymmetry 1993, 4, 1165



Diastereomeric mixture (by 1H and ^{13}C NMR):

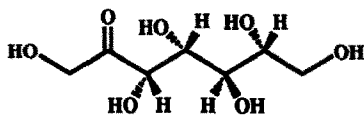
60:40 4R, 5S:4S, 5S

$[\alpha]_D^{20} = +7.9$ (c, 1.25, water)

Source of chirality: microbiological aldolisation

V. Dalmas and C. Demuynck

Tetrahedron: Asymmetry 1993, 4, 1169



D-Sedoheptulose (D-*altro*-heptulose)

$[\alpha]_D^{25} = +8$ (c = 0.03, H_2O)

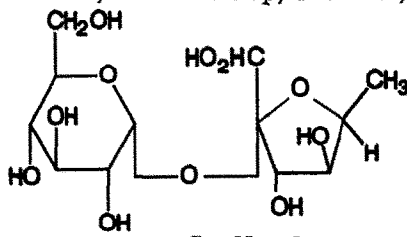
Source of chirality : Transketolase

Absolute configuration : 3S, 4R, 5R, 6R

(assigned on the basis of $[\alpha]_D^{25}$)

J. Peters, H.P. Brockamp, T. Minuth, M. Grothus, A. Steigel, M.R. Kula, L. Elling

Tetrahedron: Asymmetry 1993, 4, 1173

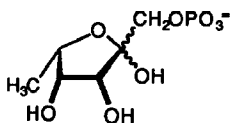


20-6-deoxy- α -L-sorbofuranosyl-D-glucose

Source of chirality: natural and enzymatic synthesis

W.-D. Fessner,* A. Schneider, O. Eyrisch, G. Sinerius, and J. Badia

Tetrahedron: Asymmetry 1993, 4, 1183



E.e. = 100%
 $[\alpha]_D^{18} = +0.5$ (c 2, H₂O)

Source of chirality: natural (from L-fucose) and enzymatic synthesis (aldol addition)

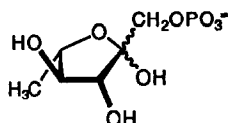
C₆H₁₁O₈P x 2 (C₆H₁₄N)

6-Deoxy-L-lyxo-hexulose 1-phosphate, bis(cyclohexylammonium) salt

Absolute configuration 3R,4R,5S
by relation to natural L-fucose

W.-D. Fessner,* A. Schneider, O. Eyrisch, G. Sinerius, and J. Badia

Tetrahedron: Asymmetry 1993, 4, 1183



E.e. = 100%
 $[\alpha]_D^{18} = +2$ (c 1, H₂O)

Source of chirality: natural (from L-rhamnose) and enzymatic synthesis (aldol addition)

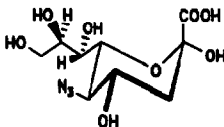
C₆H₁₁O₈P x 2 (C₆H₁₄N)

6-Deoxy-L-arabino-hexulose 1-phosphate, bis(cyclohexylammonium) salt

Absolute configuration 3R,4S,5S
by relation to natural L-rhamnose

U. Kragl, A. Gödde, C. Wandrey, W. Kinzy, J.J. Cappon, J. Lugtenburg

Tetrahedron: Asymmetry 1993, 4, 1193



$[\alpha]_D^{20} = -62.2$ (c = 0.66, H₂O)

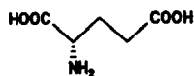
Source of chirality: natural and enzymatic asymmetric aldol condensation

C₉H₁₅N₃O₈

5-Azido-3,5-dideoxy-D-glycero-D-galacto-nonulosonic acid
5-Azido-neuraminic acid

U. Kragl, A. Gödde, C. Wandrey, W. Kinzy, J.J. Cappon, J. Lugtenburg

Tetrahedron: Asymmetry 1993, 4, 1193



E.e. > 99.5 % [by HPLC]

Source of chirality: enzymatic asymmetric reduction (reductive amination)

C₅H₉NO₄

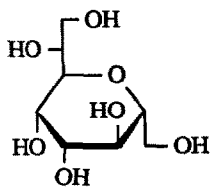
¹⁵N-L-Glutamic acid

Absolute configuration: 2S

¹⁵N content 98 %

F. Nicotra, L. Panza, G. Russo and A. Verani

Tetrahedron: Asymmetry 1993, 4, 1203



L-allo-D-erythro-3,7-anhydro-octitol

e.d. = about 100%

$[\alpha]_D = +6.6$ (c 1, MeOH)

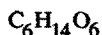
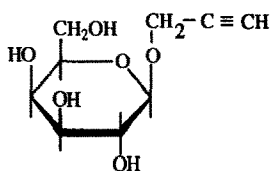
Source of chirality: D-ribose 5-phosphate

Absolute configuration: *2R,3S,4S,5S,6R,7R*

(assigned by 1H NMR and reaction mechanism)

Alexander M. Blinkovsky and Jonathan S. Dordick

Tetrahedron: Asymmetry 1993, 4, 1221



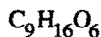
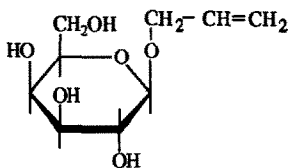
Propargyl- β -D-Galactopyranoside

$[\alpha]_D^{25} = -39.8$ (c1.8, H₂O)

Source of chirality: enzymatic synthesis from lactose

Alexander M. Blinkovsky and Jonathan S. Dordick

Tetrahedron: Asymmetry 1993, 4, 1221



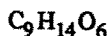
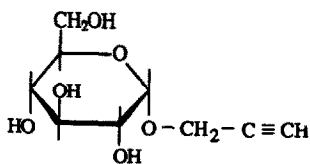
Allyl- β -D-Galactopyranoside

$[\alpha]_D^{25} = -11.2$ (c2, H₂O)

Source of chirality: enzymatic synthesis from lactose

Alexander M. Blinkovsky and Jonathan S. Dordick

Tetrahedron: Asymmetry 1993, 4, 1221



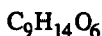
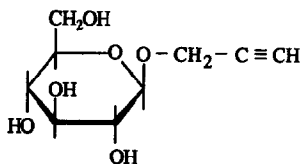
Propargyl- α -D-glucopyranoside

$[\alpha]_D^{25} = +95.9$ (c1.8, H₂O)

Source of chirality: enzymatic synthesis from maltose

Alexander M. BLinkovsky and Jonathan S. Dordick

Tetrahedron: Asymmetry 1993, 4, 1221



$[\alpha]_D^{25} = -54.5$ (c1.8, H_2O)

Source of chirality: enzymatic synthesis from cellobiose

Propargyl- β -D-Glucopyranoside

M. Hamdani, B. De Jeso, H. Deleuze,

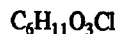
Tetrahedron: Asymmetry 1993, 4, 1233

A. Saux and B. Maillard.

Sources of chirality :



- Reduction of the corresponding ketoester by baker's yeast
d.e. = 96% (2R,3S) e.e. = 96%



- D-Threonine

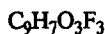
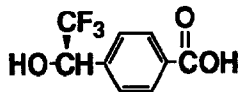
d.e. > 98% (2R,3S) e.e. > 96%

Ethyl 2-chloro-3-hydroxybutanoate

$[\alpha]_D^{25} = +12.4$ (c = 1, $CHCl_3$)

T. Fujisawa,* K. Ichikawa, and M. Shimizu

Tetrahedron: Asymmetry 1993, 4, 1237



ee = >99% (after recrystallization from toluene) [determined by GLC analysis of the corresponding MTPA ester]

$[\alpha]_D^{23} -28.1$ (c 0.08, MeOH)

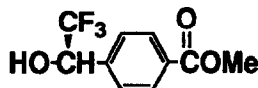
Source of chirality: Bakers' yeast reduction

Absolute configuration: R (assigned by comparison with the authentic sample prepared from the known (R)-p-(2,2,2-trifluoro-1-hydroxyethyl)bromobenzene)

(R)-p-(2,2,2-Trifluoro-1-hydroxyethyl)benzoic Acid

T. Fujisawa,* K. Ichikawa, and M. Shimizu

Tetrahedron: Asymmetry 1993, 4, 1237



ee = >99% (after recrystallization from n-hexane) [determined by GLC analysis of the corresponding MTPA ester]

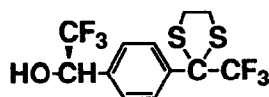
$[\alpha]_D^{23} -28.3$ (c 0.12, MeOH)

Source of chirality: Bakers' yeast reduction

Absolute configuration: R (assigned by comparison with the authentic sample prepared from the known (R)-p-(2,2,2-trifluoro-1-hydroxyethyl)bromobenzene)

Methyl (R)-p-(2,2,2-Trifluoro-1-hydroxyethyl)benzoate

T. Fujisawa,* K. Ichikawa, and M. Shimizu



$C_{12}H_{10}OS_2F_6$

(*R*)-4-(2,2,2-Trifluoro-1-hydroxyethyl)-1-(2-trifluoromethyl-1,3-dithiolan-2-yl)benzene

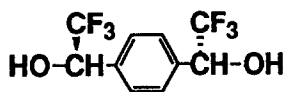
ee = >99% (after recrystallization from toluene) [determined by HPLC analysis of the corresponding MTPA ester]

$[\alpha]_D^{23} -21.0$ (c 0.20, MeOH)

Source of chirality: Bakers' yeast reduction

Absolute configuration: *R* (assigned by comparison with the authentic sample prepared from the known (*R*)-*p*-(2,2,2-trifluoro-1-hydroxyethyl)bromobenzene)

T. Fujisawa,* K. Ichikawa, and M. Shimizu



$C_{10}H_8O_2F_6$

(*R,R*)-*p*-Bis(2,2,2-trifluoro-1-hydroxyethyl)benzene

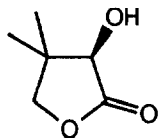
ee = >99% (after recrystallization from carbon tetrachloride) [determined by GLC analysis of the corresponding MTPA ester]

$[\alpha]_D^{23} -48.0$ (c 0.10, MeOH)

Source of chirality: Bakers' yeast reduction

Absolute configuration: *R,R* (assigned by comparison with the authentic sample prepared from the known (*R*)-*p*-(2,2,2-trifluoro-1-hydroxyethyl)bromobenzene)

K. Nakamura, S. Kondo, Y. Kawai, and A. Ohno



$C_6H_{10}O_3$

(*R*)-(-)-Pantolactone

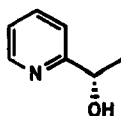
(*R*)-Dihydro-3-hydroxy-4,4-dimethyl-2(3*H*)-furanone

E.e. = 93% [by chiral HPLC analysis of corresponding 3,5-dinitrobenzoyl ester]

Source of chirality : Microbial reduction

Absolute configuration : *R*

D. Bailey, D. O'Hagan, U. Dyer and R. B. Lamont



C_7H_9NO

2- α -ethanolpyridine

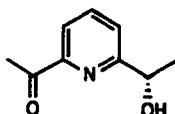
E.e. = >95 [by n m r of acetate with $Eu(hfc)_3$]
 $[\alpha]_D^{20} = -29.14$ (c4.94, $CHCl_3$)

Source of chirality: Bakers' yeast reduction

Absolute configuration (*S*)

D. Bailey, D. O'Hagan, U. Dyer and R. B. Lamont

Tetrahedron: Asymmetry 1993, 4, 1255



E.e. = 99.8 [chiral HPLC analysis]
[α]_D²⁰ = -7.5 (c1.5, CHCl₃)

Source of chirality: Bakers' yeast reduction

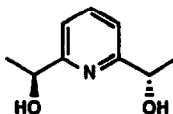
Absolute configuration (S)

C₉H₁₁NO₂

2-Acetyl-6- α -ethanolpyridine

D. Bailey, D. O'Hagan, U. Dyer and R. B. Lamont

Tetrahedron: Asymmetry 1993, 4, 1255



E.e. = 99.97 [chiral HPLC analysis]
[α]_D²⁰ = -26.84 (c2.98, CHCl₃)

Source of chirality: Bakers' yeast reduction

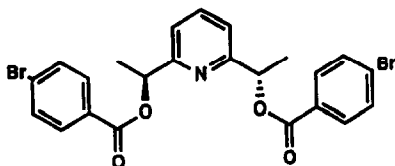
Absolute configuration (S,S)
(assigned by X-ray of di-*p*-bromobenzoate)

C₉H₁₃NO₂

2,6-di- α -ethanolpyridine

D. Bailey, D. O'Hagan, U. Dyer and R. B. Lamont

Tetrahedron: Asymmetry 1993, 4, 1255



E.e. = 99.97 [chiral HPLC analysis]
[α]_D²⁰ = +70.18 (c1.71, CHCl₃)
mp 154-154.5°C

Source of chirality: Bakers' yeast reduction

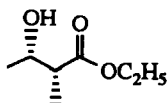
Absolute configuration (S,S)
(assigned by X-ray analysis)

C₂₃H₁₉Br₂NO₄

2,6-diethylpyridine di- $\alpha,\alpha,-p$ -bromobenzoate

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry 1993, 4, 1259



C₇H₁₄O₃

Ethyl 2-methyl-3-hydroxybutanoate

D.e. = 82% [by GC]

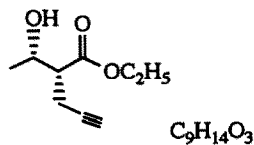
E.e. = 98% [by HPLC analysis of the Mosher's ester]
[α]_D²³ = +6.15 (c 2.42, CHCl₃)

Source of chirality: yeast reduction

Absolute configuration: 2R,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry 1993, 4, 1259



Ethyl 2-propargyl-3-hydroxybutanoate

D.e. = 52% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

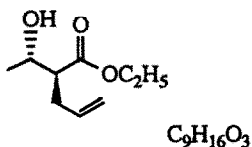
$[\alpha]_D^{23} = +23.13$ (c 2.35, CHCl₃)

Source of chirality: yeast reduction

Absolute configuration: 2R,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry 1993, 4, 1259



Ethyl 2-allyl-3-hydroxybutanoate

D.e. = 54% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

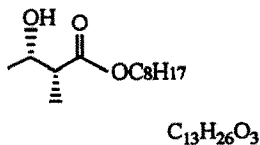
$[\alpha]_D^{23} = +12.61$ (c 1.83, CHCl₃)

Source of chirality: yeast reduction

Absolute configuration: 2S,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry 1993, 4, 1259



Octyl 2-methyl-3-hydroxybutanoate

D.e. = 92% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

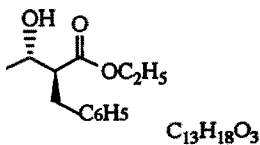
$[\alpha]_D^{23} = +3.30$ (c 3.18, CHCl₃)

Source of chirality: yeast reduction

Absolute configuration: 2R,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry 1993, 4, 1259



Ethyl 2-benzyl-3-hydroxybutanoate

D.e. = 40% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

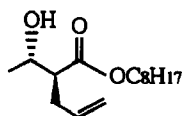
$[\alpha]_D^{23} = -9.03$ (c 2.9, CHCl₃)

Source of chirality: yeast reduction

Absolute configuration: 2S,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry **1993**, *4*, 1259



$C_{15}H_{28}O_3$

Octyl 2-allyl-3-hydroxybutanoate

D.e. = 20% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

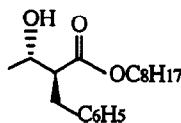
$[\alpha]_D^{23} = +5.10$ (c 1.88, $CHCl_3$)

Source of chirality: yeast reduction

Absolute configuration: 2S,3S

W.-R. Shieh and C. J. Sih*

Tetrahedron: Asymmetry **1993**, *4*, 1259



$C_{19}H_{30}O_3$

Octyl 2-benzyl-3-hydroxybutanoate

D.e. = 88% [by GC]

E.e. = 98% [by HPLC analysis of the Mosher's ester]

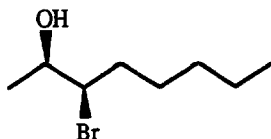
$[\alpha]_D^{23} = -24.31$ (c 0.54, $CHCl_3$)

Source of chirality: yeast reduction

Absolute configuration: 2S,3S

P. Besse and H. Veschambre

Tetrahedron: Asymmetry **1993**, *4*, 1271



$C_8H_{17}BrO$
(2R,3R)-3-bromo-2-octanol

E.e. > 98 % (by GC analysis of esters obtained with
(+)-(S)-O-acetylactic acid chloride)

$[\alpha]_D^{25} = +38$ (c = 0.02, $CHCl_3$)

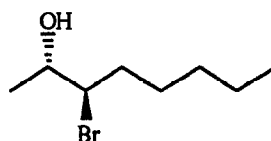
Source of chirality : Microbiological reduction

Absolute configuration : 2R, 3R

(assigned by chemical correlation)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry **1993**, *4*, 1271



$C_8H_{17}BrO$
(2S,3R)-3-bromo-2-octanol

E.e. > 98 % (by GC analysis of esters obtained with
(+)-(S)-O-acetylactic acid chloride)

$[\alpha]_D^{25} = +40$ (c = 0.02, $CHCl_3$)

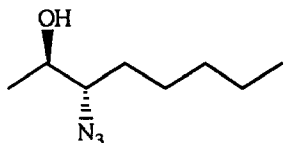
Source of chirality : Microbiological reduction

Absolute configuration : 2S, 3R

(assigned by chemical correlation)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry 1993, 4, 1271



$C_8H_{17}N_3O$
(2R,3S)-3-azido-2-octanol

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = -8$ (c = 0.01, $CHCl_3$)

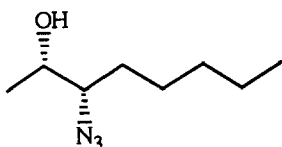
Source of chirality : Microbiological reduction

Absolute configuration : 2R, 3S

(assigned by chemical correlation)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry 1993, 4, 1271



$C_8H_{17}N_3O$
(2S,3S)-3-azido-2-octanol

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = +21$ (c = 0.03, $CHCl_3$)

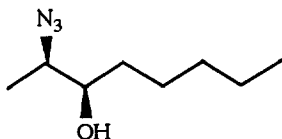
Source of chirality : Microbiological reduction

Absolute configuration : 2S, 3S

(assigned by chemical correlation)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry 1993, 4, 1271



$C_8H_{17}N_3O$
(2R,3R)-2-azido-3-octanol

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = -50$ (c = 0.03, $CHCl_3$)

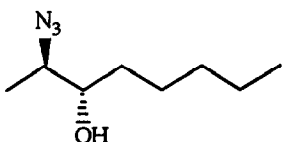
Source of chirality : from a precursor obtained by
microbiological reduction

Absolute configuration : 2R, 3R

(assigned based on the reaction mechanism)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry 1993, 4, 1271



$C_8H_{17}N_3O$
(2R,3S)-2-azido-3-octanol

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = -51$ (c = 0.02, $CHCl_3$)

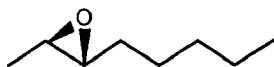
Source of chirality : from a precursor obtained by
microbiological reduction

Absolute configuration : 2R, 3S

(assigned based on the reaction mechanism)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry **1993**, *4*, 1271



$C_8H_{16}O$
(2R,3S)-2,3-epoxyoctane

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = -8$ (c = 0.04, Pentane)

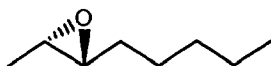
Source of chirality : from a precursor obtained by
microbiological reduction

Absolute configuration : 2R, 3S

(assigned based on the reaction mechanism)

P. Besse and H. Veschambre

Tetrahedron: Asymmetry **1993**, *4*, 1271



$C_8H_{16}O$
(2S,3S)-2,3-epoxyoctane

E.e. > 98 % (by GC analysis with chiral column : Lipodex E)

$[\alpha]_D^{25} = +5$ (c = 0.03, Pentane)

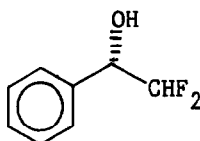
Source of chirality : from a precursor obtained by
microbiological reduction

Absolute configuration : 2S, 3S

(assigned based on the reaction mechanism)

Y. Yamazaki and H. Kobayashi

Tetrahedron: Asymmetry **1993**, *4*, 1287



$C_8H_8F_2O$

α -(Difluoromethyl)benzyl alcohol

E.e. = 97 % (by HPLC)

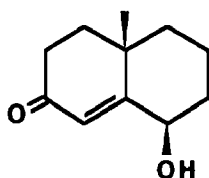
$[\alpha]_D^{27} = +19$ (c = 2.8, CH_2Cl_2)

Source of chirality : enzymic reduction

Absolute configuration: S

A.Hammoui, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry **1993**, *4*, 1295



$C_{11}H_{16}O_2$
4a-methyl-8-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3H)-naphthalenone

E.e. \geq 95% (from e.e. of the precursor)

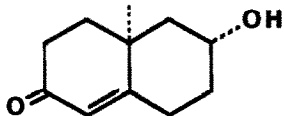
$[\alpha]_D^{21} = +96.5$ (c 1.025, $CHCl_3$)

Source of chirality: microbial hydroxylation of the
corresponding (S)-naphthalenone

Absolute configuration: 4aS,8R (relative configuration
assigned by NMR)

A.Hammoumi, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295



$C_{10}H_{15}O_2$
4a-methyl-6-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3*H*)-naphthalenone

E.e. \geq 95% (from e.e. of the precursor)

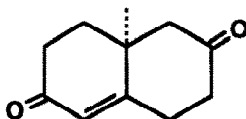
$[\alpha]_D^{21} = -210$ (c 1.025, $CHCl_3$)

Source of chirality: microbial hydroxylation of the
corresponding (R)-naphthalenone

Absolute configuration: 4a*S*,6*R* (relative configuration
assigned by NMR)

A.Hammoumi, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295



$C_{11}H_{14}O_2$
4a-methyl-4,4a,7,8-tetrahydro-
naphthalene-2(3*H*), 6(5*H*)-dione

E.e. \geq 95% (from e.e. of the precursor)

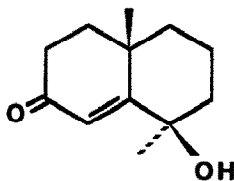
$[\alpha]_D^{21} = -115$ (c 0.3, $CHCl_3$)

Source of chirality: microbial hydroxylation of the
corresponding (R)-naphthalenone

Absolute configuration: 4a*S*

A.Hammoumi, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295



$C_{12}H_{18}O_2$
4a,8-dimethyl-8-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3*H*)-naphthalenone

E.e. \geq 95% (from e.e. of the precursor)

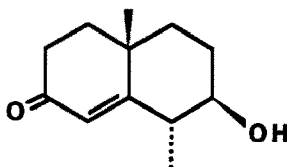
$[\alpha]_D^{21} = +71$ (c 0.21, $CHCl_3$)

Source of chirality: microbial hydroxylation of the
corresponding (4a*S*,8*S*)-naphthalenone

Absolute configuration: 4a*S*,8*R* (relative configuration
assigned by NMR)

A.Hammoumi, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295



$C_{12}H_{18}O_2$
4a,8-dimethyl-7-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3*H*)-naphthalenone

E.e. \geq 95% (from e.e. of the precursor)

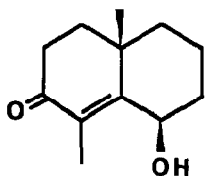
$[\alpha]_D^{21} = +62$ (c 0.47, $CHCl_3$)

Source of chirality: microbial hydroxylation of the
corresponding (4a*S*,8*S*)-naphthalenone

Absolute configuration: 4a*S*,7*R* (relative configuration
assigned by NMR)

A.Hammoui, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295

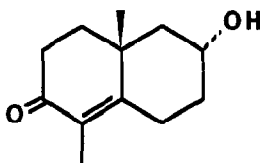


$C_{12}H_{18}O_2$
1,4a-dimethyl-8-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3H)-naphthalenone

E.e. \geq 90% (from e.e. of the precursor)
 $[\alpha]_D^{21} = +40$ (c 3.7, $CHCl_3$)
Source of chirality: microbial hydroxylation of the
corresponding (S)-naphthalenone
Absolute configuration: 4aS,8R (relative configuration
assigned by NMR)

A.Hammoui, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295

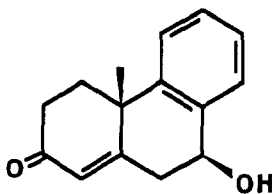


$C_{12}H_{18}O_2$
1,4a-dimethyl-6-hydroxy-4,4a,5,6,7,8-
hexahydro-2(3H)-naphthalenone

E.e. \geq 90% (from e.e. of the precursor)
 $[\alpha]_D^{21} = +164$ (c 1.34, $CHCl_3$)
Source of chirality: microbial hydroxylation of the
corresponding (S)-naphthalenone
Absolute configuration: 4aR,6R (relative configuration assigned
by NMR)

A.Hammoui, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295

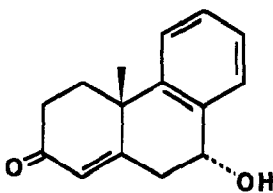


$C_{15}H_{16}O_2$
4a-methyl-9-hydroxy-4,4a,9,10-
tetrahydro-2(3H)-phenanthrenone

E.e. \geq 90% (from e.e. of the precursor)
 $[\alpha]_D^{21} = +208$ (c 1.85, $CHCl_3$)
Source of chirality: microbial hydroxylation of the
corresponding (S)-phenanthrenone
Absolute configuration: 4aS,6S (relative configuration
assigned by NMR)

A.Hammoui, J.-P.Girault, R. Azerad, G.Revial and J. d'Angelo

Tetrahedron: Asymmetry 1993, 4, 1295

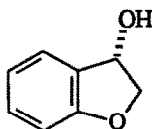


$C_{15}H_{16}O_2$
4a-methyl-9-hydroxy-4,4a,9,10-
tetrahydro-2(3H)-phenanthrenone

E.e. \geq 90% (from e.e. of the precursor)
 $[\alpha]_D^{21} = +105$ (c 0.6, $CHCl_3$)
Source of chirality: microbial hydroxylation of the
corresponding (S)-phenanthrenone
Absolute configuration: 4aS,6R (relative configuration
assigned by NMR)

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima,and H.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



$C_8H_8O_2$

3-Hydroxy-2,3-dihydrobenzofuran

E.e. = >98% [by CSP-HPLC analysis]

$[\alpha]_D = +67$ (c 0.63 , $CHCl_3$)

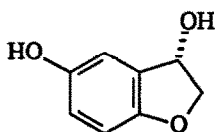
Source of chirality : Resolution of the camphanate esters .

Absolute configuration : 3S

(Assigned by X-ray structure analysis of the camphanate ester)

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima andH.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



$C_8H_8O_3$

3,5-Dihydroxy-2,3-dihydrobenzofuran

E.e. = > 98% [by CSP-HPLC analysis and by 1H -NMR analysis of di-MTPA esters].

$[\alpha]_D = +22.5$, (c 0.67 , MeOH)

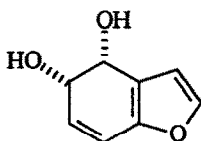
Source of chirality : Biotransformation of enantiopure (+)-3-hydroxy-2,3-dihydrobenzofuran.

Absolute configuration : 3S

[Derived from (3S)-3-hydroxy-2,3-dihydrobenzofuran].

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima andH.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



$C_8H_8O_3$

cis-4,5-Dihydroxy-4,5-dihydrobenzofuran

E.e. = >98% [by 1H -NMR analysis of di-MTPA esters].

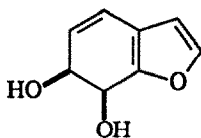
Source of chirality : Biotransformation of enantiopure (+)-3-hydroxy-2,3-dihydrobenzofuran.

Absolute configuration : 4R,5S

[Assigned by stereochemical correlation]

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima andH.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



$C_8H_8O_3$

cis-6,7-Dihydroxy-6,7-dihydrobenzofuran

E.e. = >98% [by 1H -NMR analysis of di-MTPA esters].

$[\alpha]_D = -35$ (c 0.96, MeOH).

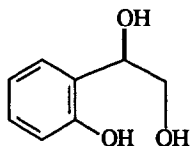
Source of chirality : Biotransformation of benzofuran

Absolute configuration : 6S,7S

[Assigned by stereochemical correlation]

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima,H.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



1,2-Dihydroxy-1-(2'-hydroxyphenyl)ethane

E.e.= 51% (by $[\alpha]_D$ comparison)

$[\alpha]_D = -24$ (c 0.76, MeOH)

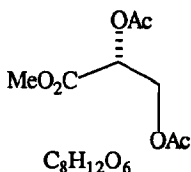
Source of chirality : Biotransformation of benzofuran.

Absolute configuration : 1R

[Assigned by stereochemical correlation with (2R)-methyl (2,3-diacetoxy)propanoate].

D.R.Boyd,N.D.Sharma,R.Boyle,J.F.Malone,J.Chima,H.Dalton.

Tetrahedron: Asymmetry 1993, 4, 1307



Methyl (2,3-diacetoxy)propanoate

E.e. = >98% (by synthesis from enantiopure (R)-glyceric acid.

$[\alpha]_D = +15.8$ (c 2.0, $CHCl_3$)

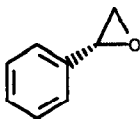
Source of chirality : Synthesis from enantiopure (R)- glyceric acid.

Absolute configuration : 2R

[Assigned by stereochemical correlation with (R)-glyceric acid].

S.Colonna, N.Gaggero, L.Casella, G.Carrea, P.Pasta

Tetrahedron: Asymmetry 1993, 4, 1325



Styrene oxide

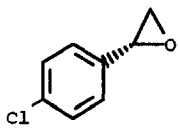
E.e.=49% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R

S.Colonna, N.Gaggero, L.Casella, G.Carrea, P.Pasta

Tetrahedron: Asymmetry 1993, 4, 1325



4-Chlorostyrene oxide

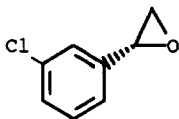
E.e.=66% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R

S.Colonna, N.Gaggero, L.Casella, G.Carrea, P.Pasta

Tetrahedron: Asymmetry 1993, 4, 1325



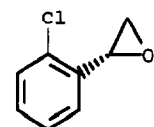
C_8H_7ClO

3-Chlorostyrene oxide

E.e.=62% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R



C_8H_7ClO

2-Chlorostyrene oxide

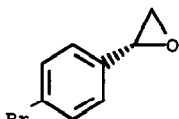
E.e.=64% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R

S.Colonna, N.Gaggero, L.Casella, G.Carrea, P.Pasta

Tetrahedron: Asymmetry 1993, 4, 1325



C_8H_7BrO

4-Bromostyrene oxide

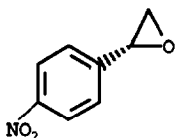
E.e.=68% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R

S.Colonna, N.Gaggero, L.Casella, G.Carrea, P.Pasta

Tetrahedron: Asymmetry 1993, 4, 1325



$C_8H_7NO_3$

4-Nitrostyrene oxide

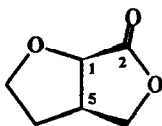
E.e.=28% (by chiral HPLC with Chiralcel OB column)

Source of chirality: Chloroperoxidase

Absolute configuration: R

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



3,8-dioxabicyclo[3.3.0]octan-2-one.

E.e. > 98 % (by chiral GC)

$[\alpha]_D^{25} - 103.2$ ($c = 0.5$, $CHCl_3$)

Source of chirality : enzymatic

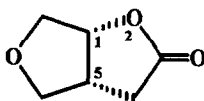
Baeyer-Villiger oxidation .

Absolute configuration : 1R,5S

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,7-dioxabicyclo[3.3.0]octan-3-one.

E.e. 97 % (by chiral GC)

$[\alpha]_D^{25} - 37$ ($c = 0.5$, $CHCl_3$)

Source of chirality : enzymatic

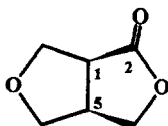
Baeyer-Villiger oxidation

Absolute configuration : 1R,5R

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



3,7-dioxabicyclo[3.3.0]octan-2-one.

E.e. > 98 % (by chiral GC)

$[\alpha]_D^{25} - 101.2$ ($c = 0.5$, $CHCl_3$)

Source of chirality : enzymatic

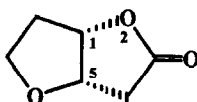
Baeyer-Villiger oxidation .

Absolute configuration : 1S,5R

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,6-dioxabicyclo[3.3.0]octan-3-one.

E.e. > 98 % (by chiral GC)

$[\alpha]_D^{25} - 67.3$ ($c = 0.639$, $CHCl_3$)

Source of chirality : enzymatic

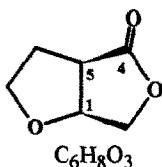
Baeyer-Villiger oxidation .

Absolute configuration : 1S,5S

(assigned by circular dichroism measurement)

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



3,8-dioxabicyclo[3.3.0]octan-4-one.

E.e. > 98 % (by chiral GC)
 $[\alpha]_D^{25} - 113.3$ ($c = 0.6$, CHCl_3)

Source of chirality : enzymatic

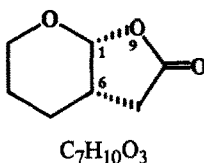
Baeyer-Villiger oxidation .

Absolute configuration : 1S,5R

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,9-dioxabicyclo[4.3.0]nonan-8-one.

E.e. 70 % (by chiral GC)
 $[\alpha]_D^{25} - 4$ ($c = 0.55$, CHCl_3)

Source of chirality : enzymatic

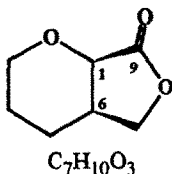
Baeyer-Villiger oxidation .

Absolute configuration : 1R,6S

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,8-dioxabicyclo[4.3.0]nonan-9-one.

E.e. > 98 % (by chiral GC)
 $[\alpha]_D^{25} - 105.1$ ($c = 0.69$, CHCl_3)

Source of chirality : enzymatic

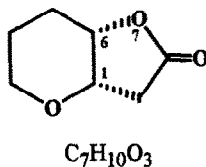
Baeyer-Villiger oxidation .

Absolute configuration : 1R,6S

(assigned by circular dichroism measurement).

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,7-dioxabicyclo[3.3.0]nonan-8-one.

E.e. 33 % (by chiral GC)
 $[\alpha]_D^{25} - 24$ ($c = 0.5$, CHCl_3)

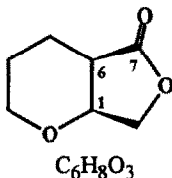
Source of chirality : enzymatic

Baeyer-Villiger oxidation .

Absolute configuration : 1S,6R

F. Petit and R. Furstoss

Tetrahedron: Asymmetry 1993, 4, 1341



2,8-dioxabicyclo[4.3.0]nonan-7-one.

E.e. > 98 % (by chiral GC)

$[\alpha]_D^{25} - 26.5$ ($c = 0.577$, CHCl_3)

Source of chirality : enzymatic

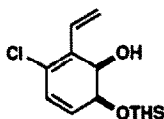
Baeyer-Villiger oxidation .

Absolute configuration : 1S,6R

(assigned by circular dichroism measurement).

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365



$[\alpha]_D = +101.1$ (c 1.12, CHCl_3)

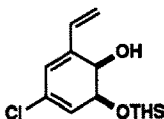
E.e. >98%

Obtained from *Pp*-39D oxidation of *o*-chlorostyrene and protection.

Absolute configuration established by convergent synthesis.

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365



$[\alpha]_D = +82.9$ (c 0.42, CHCl_3)

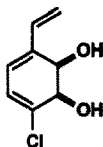
E.e. 54%

Obtained from *Pp*-39D oxidation of *m*-chlorostyrene and protection.

Absolute configuration established by convergent synthesis.

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365



$[\alpha]_D = +12.4$ (c 0.064, CHCl_3)

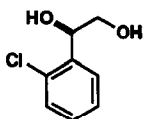
E.e. 15%

Obtained from *Pp*-39D oxidation of *p*-chlorostyrene.

Absolute configuration established by convergent synthesis.

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365

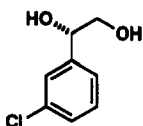


$[\alpha]_D = -47.2$ (c 1.9, EtOH)
E.e. 73%

Obtained from *Pp*-39D oxidation of *o*-chlorostyrene.
Absolute configuration established by convergent synthesis.

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365

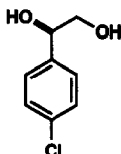


$[\alpha]_D = +24.05$ (c 1.24, EtOH)
E.e. 95%

Obtained from *Pp*-39D oxidation of *m*-chlorostyrene.
Absolute configuration established by convergent synthesis.

T. Hudlicky, E. E. Boros, C. H. Boros, Department of Chemistry
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212

Tetrahedron: Asymmetry 1993, 4, 1365

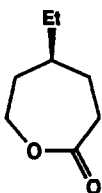


$[\alpha]_D = -27.60$ (c 0.96, EtOH)
E.e. 79%

Obtained from *Pp*-39D oxidation of *p*-chlorostyrene.
Absolute configuration established by convergent synthesis.

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387

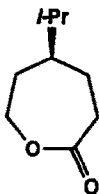


$C_8H_{14}O_2$
5-ethyl-2-oxepanone

E.e. > 98% (by 1H -NMR of a MTPA ester derivative)
 $[\alpha]_D = -38$ (c 5.55, $CHCl_3$)
Source of chirality: Enzymatic Baeyer-Villiger oxidation
Absolute Configuration: 5*S* (assignment tentative)

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387



$C_9H_{16}O_2$
5-(2-propyl)-2-oxepanone

E.e. > 98% (by 1H -NMR of a MTPA ester derivative)

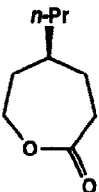
$[\alpha]_D = -40$ (c 0.44, $CHCl_3$)

Source of chirality: Enzymatic Baeyer-Villiger oxidation

Absolute Configuration: 5*S* (assignment tentative)

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387



$C_9H_{16}O_2$
5-(1-propyl)-2-oxepanone

E.e. > 98% (by 1H -NMR of a MTPA ester derivative)

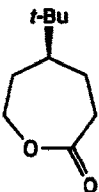
$[\alpha]_D = -38$ (c 6.41, $CHCl_3$)

Source of chirality: Enzymatic Baeyer-Villiger oxidation

Absolute Configuration: 5*S* (assignment tentative)

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387



$C_{10}H_{18}O_2$
5-*tert*-butyl-2-oxepanone

E.e. > 98% (by 1H -NMR of a MTPA ester derivative)

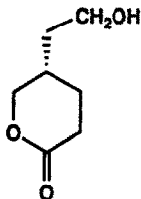
$[\alpha]_D = -34.9$ (c 0.78, $CHCl_3$)

Source of chirality: Enzymatic Baeyer-Villiger oxidation

Absolute Configuration: 5*S* (assignment via chemical correlation)

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387



$C_7H_{12}O_3$
tetrahydro-5-(2-hydroxyethyl)-2*H*-pyran-2-one

E.e. > 98% (by 1H -NMR of a MTPA ester derivative)

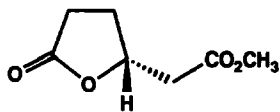
$[\alpha]_D = -6.2$ (c 5.66, $CHCl_3$)

Source of chirality: Enzymatic Baeyer-Villiger oxidation

Absolute Configuration: 5*S* (assignment tentative)

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen

Tetrahedron: Asymmetry 1993, 4, 1387



$C_7H_{10}O_4$
tetrahydro-5-oxo-2-furanacetic acid methyl ester

E.e. = 9.6% (by 1H -NMR of a MTPA ester derivative)

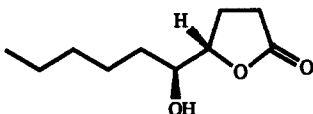
$[\alpha]_D = -3.65$ (c 0.99, EtOH)

Source of chirality: Enzymatic Baeyer-Villiger oxidation

Absolute Configuration: 2*R* (assignment via chemical correlation)

Wolfgang Albrecht and Roland Tressl

Tetrahedron: Asymmetry 1993, 4, 1391



E.e. = 92.4% [by GC after conversion into the carbamate derivative with (R)-(+)-1-Phenylethylisocyanate]

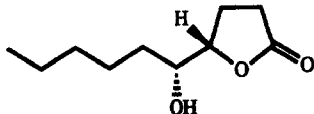
$[\alpha]_D = +26.2$ (c 1.74, $CHCl_3$)

Source of chirality: (S)-glutamic acid

Absolute configuration: 4*S*, 5*S*

Wolfgang Albrecht and Roland Tressl

Tetrahedron: Asymmetry 1993, 4, 1391



E.e. = not determined

$[\alpha]_D = +13.3$ (c 1.35, $CHCl_3$)

Source of chirality: (S)-glutamic acid

Absolute configuration: 4*S*, 5*R*