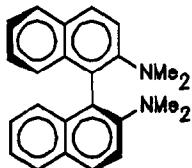


STEREOCHEMISTRY ABSTRACTS

C.Rosini, L.Franzini, A.Iuliano, D.Pini, P.Salvadori

Tetrahedron: Asymmetry 1991, 2, 363



(S)-1

$[\alpha]_D^{25} = +20$ ($c=0.06$, C_6H_6); m.p. 245-248°C
e.e.>95% [by HPLC on Chiralpack OT and PMR analysis in the presence of (R)-mandelic acid].

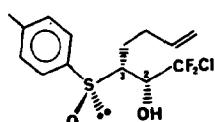
S configuration assigned because 1 has been prepared by Eschweiler-Clarke reaction on (S)-2,2'-diamino-1,1'-binaphthyl.

$^1\text{H-NMR}$: $\delta = 2.45$ (s, 12H, N- CH_2), 7.1-7.3 (2m, 6H, aromatic), 7.5 (d, 2H, aromatic), 7.8-7.9 (2d, 4H, peri protons).

(S)-N,N,N',N'-tetramethyl-2,2'-diamino-1,1'-binaphthyl

A. Arnone, P. Bravo, F. Viani, G. Cavicchio

Tetrahedron: Asymmetry 1991, 2, 399



$C_{14}\text{H}_{17}\text{ClF}_2\text{O}_2\text{S}$
(2R,3R,R_s)-1-chloro-1,1-difluoro-3-[(4-methylphenyl)sulphiny]hept-6-en-2-ol

$[\alpha]_D^{25} = +148.7$ ($c 0.8$, CHCl_3)

Source of chirality: (-)-(1*R*)-Menthyl (S)-toluene-4-sulfinate

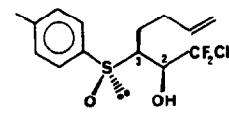
Absolute configuration: 2*R*,3*R*,*R_s*

$^1\text{H NMR}$ (δ_{H} , ppm): 4.46 (H-2) and 2.86 (H-3); $^3J_{2,3} = 1.3$ Hz

$^{19}\text{F NMR}$ (δ_{F} , ppm): -64.03 (Fa) and -64.55 (Fb)

A. Arnone, P. Bravo, F. Viani, G. Cavicchio

Tetrahedron: Asymmetry 1991, 2, 399



$C_{14}\text{H}_{17}\text{ClF}_2\text{O}_2\text{S}$
(2S,3S,R_s)-1-chloro-1,1-difluoro-3-[(4-methylphenyl)sulphiny]hept-6-en-2-ol

$[\alpha]_D^{25} = +74.6$ ($c 1.0$, CHCl_3)

Source of chirality: (-)-(1*R*)-Menthyl (S)-toluene-4-sulfinate

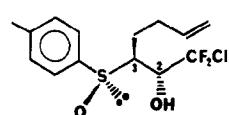
Absolute configuration: 2*S*,3*S*,*R_s*

$^1\text{H NMR}$ (δ_{H} , ppm): 4.75 (H-2) and 3.15 (H-3); $^3J_{2,3} = 1.4$ Hz

$^{19}\text{F NMR}$ (δ_{F} , ppm): -64.00 (Fa) and -64.78 (Fb)

A. Arnone, P. Bravo, F. Viani, G. Cavicchio

Tetrahedron: Asymmetry 1991, 2, 399



$C_{14}\text{H}_{17}\text{ClF}_2\text{O}_2\text{S}$
(2R,3S,R_s)-1-chloro-1,1-difluoro-3-[(4-methylphenyl)sulphiny]hept-6-en-2-ol

$[\alpha]_D^{25} = +109.6$ ($c 1.3$, CHCl_3)

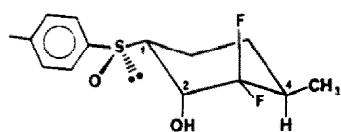
Source of chirality: (-)-(1*R*)-Menthyl (S)-toluene-4-sulfinate

Absolute configuration: 2*R*,3*S*,*R_s*

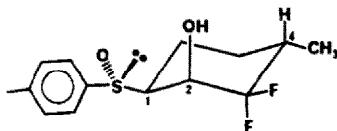
$^1\text{H NMR}$ (δ_{H} , ppm): 4.32 (H-2) and 2.96 (H-3); $^3J_{2,3} = 5.1$ Hz

$^{19}\text{F NMR}$ (δ_{F} , ppm): -61.34 (Fa) and -63.25 (Fb)

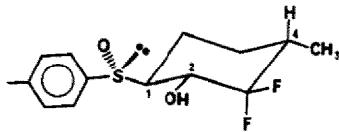
A. Arnone, P. Bravo, F. Viani, G. Cavicchio

 $[\alpha]_D^{25} = +245.1$ (*c* 1.0, CHCl_3)Source of chirality: (-)-(1*R*)-Menthyl (*S*)-toluene-4-sulfinateAbsolute configuration: 1*R*,2*S*,4*R*,*R*_S¹H NMR (δ_H , ppm): 4.33 (H-2), 2.58 (H-1), and 2.35 (H-4)¹⁹F NMR (δ_F , ppm): -113.6 (F_{eq}) and -125.4 (F_{ax}) $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}_2\text{S}$ (1*R*,2*S*,4*R*,*R*_S)-3,3-difluoro-2-hydroxy-4-methyl-1-[(4-methylphenyl)sulphinyl]cyclohexane

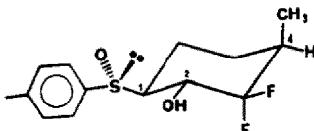
A. Arnone, P. Bravo, F. Viani, G. Cavicchio

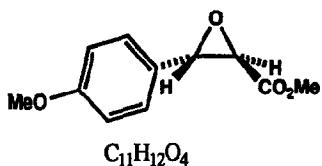
 $[\alpha]_D^{25} = +133.7$ (*c* 1.0, CHCl_3)Source of chirality: (-)-(1*R*)-Menthyl (*S*)-toluene-4-sulfinateAbsolute configuration: 1*S*,2*R*,4*S*,*R*_S¹H NMR (δ_H , ppm): 4.10 (H-2), 2.68 (H-1), and 2.29 (H-4)¹⁹F NMR (δ_F , ppm): -113.08 (F_{eq}) and -125.01 (F_{ax}) $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}_2\text{S}$ (1*S*,2*R*,4*S*,*R*_S)-3,3-difluoro-2-hydroxy-4-methyl-1-[(4-methylphenyl)sulphinyl]cyclohexane

A. Arnone, P. Bravo, F. Viani, G. Cavicchio

 $[\alpha]_D^{25} = +217.3$ (*c* 1.1, CHCl_3)Source of chirality: (-)-(1*R*)-Menthyl (*S*)-toluene-4-sulfinateAbsolute configuration: 1*S*,2*S*,4*S*,*R*_S¹H NMR (δ_H , ppm): 4.10 (H-2), 2.72 (H-1), and 1.80 (H-4)¹⁹F NMR (δ_F , ppm): -113.94 (F_{eq}) and -135.77 (F_{ax}) $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}_2\text{S}$ (1*S*,2*S*,4*S*,*R*_S)-3,3-difluoro-2-hydroxy-4-methyl-1-[(4-methylphenyl)sulphinyl]cyclohexane

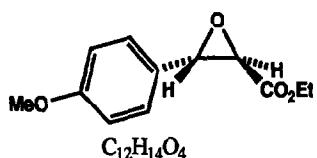
A. Arnone, P. Bravo, F. Viani, G. Cavicchio

 $[\alpha]_D^{25} = +190.5$ (*c* 0.7, CHCl_3)Source of chirality: (-)-(1*R*)-Menthyl (*S*)-toluene-4-sulfinateAbsolute configuration: 1*S*,2*S*,4*R*,*R*_S¹H NMR (δ_H , ppm): 4.21 (H-2), 2.75 (H-1), and 2.34 (H-4)¹⁹F NMR (δ_F , ppm): -113.24 (F_{eq}) and -116.22 (F_{ax}) $\text{C}_{14}\text{H}_{18}\text{F}_2\text{O}_2\text{S}$ (1*S*,2*S*,4*R*,*R*_S)-3,3-difluoro-2-hydroxy-4-methyl-1-[(4-methylphenyl)sulphinyl]cyclohexane



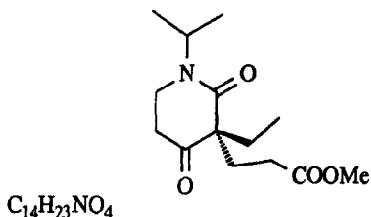
E.e. = 99.1% (by HPLC on a CHIRALCEL OD column)
 $[\alpha]_D^{23} -160$ (c 0.892, $CHCl_3$)
 Source of Chirality : resolution
 Absolute configuration 2*R*,3*S*; $[\alpha]_D$ of lit.

(2*R*,3*S*)-methyl 3-(4-methoxyphenyl)glycidate



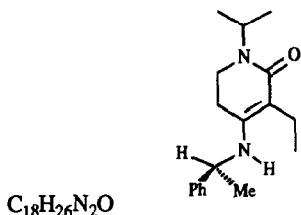
E.e. = 97.7% (by HPLC on a CHIRALCEL OD column)
 $[\alpha]_D^{23} -152$ (c 1.10, $CHCl_3$)
 Source of Chirality : resolution
 Absolute configuration 2*R*,3*S*; $[\alpha]_D$ of lit.

(2*R*,3*S*)-ethyl 3-(4-methoxyphenyl)glycidate



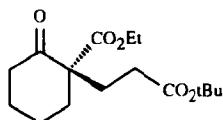
ee 88 %
 $[\alpha]_D^{20} + 5.9$ (c = 4.8, MeOH)
 source of chirality : (S)-(-)-1-phenylethylamine (93 % ee)
 absolute configuration : 3*R*

3-Ethyl-3-(2-methoxycarbonylethyl)-N-isopropyl piperidine-2,4-dione



ee 93 %
 $[\alpha]_D^{20} = -7.0$ (c 3.8 MeOH)
 source of chirality : (S)-(-)-1-phenylethylamine (93 % ee)
 absolute configuration : S

3-Ethyl-1-isopropyl-4-[(1'-phenylethyl)amino]-1,2,5,6-tetrahydropyridin-2-one

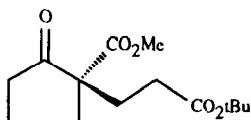
 $C_{16}H_{26}O_5$ (−)-2-(2 carbo-*tert*-butoxyethyl)-2-(carboethoxy)cyclohexanone

E.e. = 90 % [by optical rotation]

 $[\alpha]_D = -71.6$ (c 1.3, $CHCl_3$)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

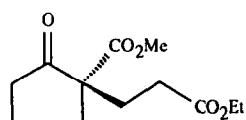
 $C_{14}H_{22}O_5$ (+)-2-(2-carbo-*tert*-butoxyethyl)-2-(carbomethoxy)cyclopentanone

E.e. = 85 % [by G.C on a chiral capillary column]

 $[\alpha]_D = +18.5$ (c 2.4, EtOH)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

 $C_{12}H_{18}O_5$

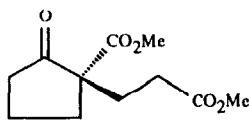
(+)-2-(2-carboethoxyethyl)-2-(carbomethoxy)cyclopentanone

E.e. = 65 % [by G.C on a chiral capillary column]

 $[\alpha]_D = +10.2$ (c 1.8, $CHCl_3$)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

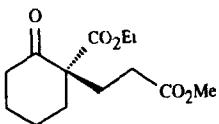
 $C_{11}H_{16}O_5$

(+)-2 carbomethoxyethyl)-2-(carbomethoxy)cyclopentanone

E.e. = 70 % [by nmr with $Eu(tfc)_3$] $[\alpha]_D = +12.6$ (c 2.8, CCl_4)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

 $C_{13}H_{20}O_5$

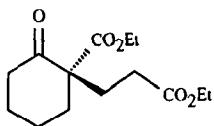
(-)-2-(2 carbomethoxyethyl)-2-(carboethoxy)cyclohexanone

E.e. = 80 % [by optical rotation]

 $[\alpha]_D = -78.3$ (c 1.5, $CHCl_3$)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

 $C_{14}H_{22}O_5$

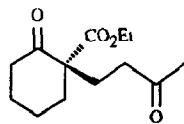
(-)-2-(2 carboethoxyethyl)-2-(carboethoxy)cyclohexanone

E.e. = 79 % [by GC on a chiral capillary column]

 $[\alpha]_D = -79.2$ (c 1.4, $CHCl_3$)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

 $C_{13}H_{20}O_4$

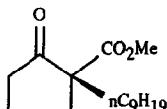
(-)-2-(3-oxobutyl)-2-(carboethoxy)cyclohexanone

E.e. = 79 % [by G.C on a chiral capillary column]

 $[\alpha]_{578}^{20} = -76.2$ (c 2.2, CCl_4)

source of chirality : asymm. synthesis (Michael reaction)

absolute configuration 2S

 $C_{16}H_{28}O_3$

(+)-2-nonyl-2-(carbomethoxy)cyclopentanone

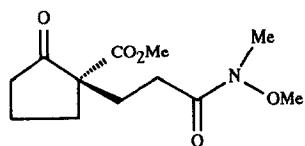
E.e. > 95 % [by nmr with $Eu(hfc)_3$] $[\alpha]_D = +21.4$ (c 1.2, $CHCl_3$)

source of chirality : asymm. synthesis

absolute configuration 2R

A. Guingant

Tetrahedron: Asymmetry 1991, 2, 415



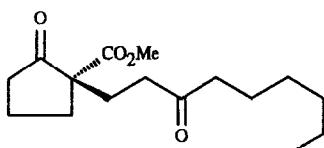
C₁₂H₂₂NO₄

(+)-2-(3-N-methoxy-N-methylamino-3-oxopropyl)-2-(carbomethoxy)cyclopentanone

E.e. > 95 % (by optical rotation)
[α]_D = +19.6 (c 6, EtOH)
source of chirality : asymm. synthesis
absolute configuration 2S

A. Guingant

Tetrahedron: Asymmetry 1991, 2, 415



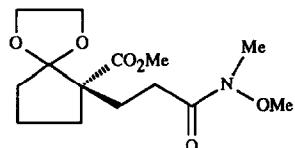
C₁₆H₂₆O₄

(+)-2-(3-oxononyl)-2-(carbomethoxy)cyclopentanone

E.e. > 95 % [by nmr with Eu(hfc)₃]
[α]_D = +16.5 (c 2.8, EtOH)
source of chirality : asymm. synthesis
absolute configuration 2S

A. Guingant

Tetrahedron: Asymmetry 1991, 2, 415



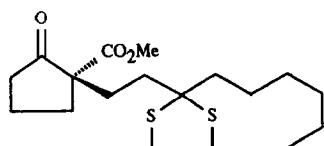
C₁₄H₂₃NO₆

(+)-1,1-ethylenedioxy-2-(3-N-methoxy-N-methylamino-3-oxopropyl)-2-(carbomethoxy)cyclopentane

E.e. > 95 % (estimated from the ee value of its precursor)
[α]_D = +10.3 (c 2.2, EtOH)
source of chirality : asymm. synthesis
absolute configuration 2S

A. Guingant

Tetrahedron: Asymmetry 1991, 2, 415



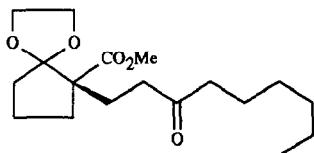
C₁₈H₃₀O₃S₂

(+)-2-(3,3-ethylenedithiononyl)-2-(carbomethoxy)cyclopentanone

E.e. > 95 % [by nmr of a precursor]
[α]_D = +27.4 (c 1.5, EtOH)
source of chirality : asymm. synthesis
absolute configuration 2S

A. Guingant

Tetrahedron: Asymmetry 1991, 2, 415



C₁₈H₃₀O₅

(+)-1,1-ethylenedioxy-2-(3-oxononyl)-2-(carbomethoxy)cyclopentane

E.e. > 95 % (estimated from the ee value of its precursor)

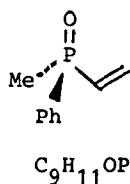
[α]_D = +14.0 (c 4.5 EtOH)

source of chirality : asymm. synthesis

absolute configuration 2S

K. M. Pietrusiewicz, M. Zabłocka, W. Wieczorek and
A. Brandi

Tetrahedron: Asymmetry 1991, 2, 419



Methylphenylvinylphosphine oxide

E.e. = 100%

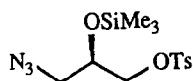
[α]_D = -80 (c 2.6, CHCl₃)

Source of chirality: synthetic

Absolute configuration: S_P

K. I. Sutowardoyo and D. Sinou

Tetrahedron: Asymmetry 1991, 2, 437



C₁₃H₂₁N₃O₄SSi

E.e. = 93 % (by ¹H NMR of Mosher's ester)

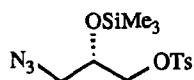
[α]_D²⁵ = + 10.4 (c 1.5, CHCl₃)

Source of chirality: (R)-glycidyl tosylate (e.e. 93 %)

(R)-1-Azido-2-trimethylsilyloxy-3-tosyloxyp propane

K. I. Sutowardoyo and D. Sinou

Tetrahedron: Asymmetry 1991, 2, 437



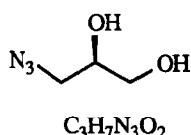
C₁₃H₂₁N₃O₄SSi

E.e. = 93 % (by ¹H NMR of Mosher's ester)

[α]_D²⁵ = - 10.4 (c 1.5, CHCl₃)

Source of chirality: (S)-glycidyl tosylate (e.e. 95 %)

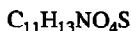
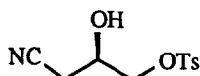
(S)-1-Azido-2-trimethylsilyloxy-3-tosyloxyp propane



(R)-1-Azido-2,3-dihydroxypropane

E.e. = 90 % (by ^1H NMR of bis-Mosher's ester) $[\alpha]_D^{25} = +0.7$ (c 1, CHCl_3)

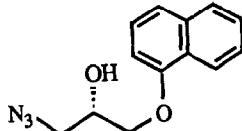
Source of chirality: (R)-glycidol (e.e. 91 %)



(R)-1-Cyano-2-hydroxy-3-tosyloxypropane

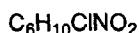
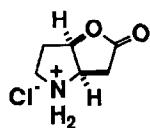
E.e. = 90 % (by ^1H NMR of Mosher's ester) $[\alpha]_D^{25} = +2.7$ (c 1, CHCl_3)

Source of chirality: (R)-glycidyl tosylate (e.e. 93 %)

E.e. = 94 % (by ^1H NMR of Mosher's ester) $[\alpha]_D^{25} = -12.4$ (c 1, CHCl_3)

Source of chirality: (S)-glycidyl tosylate (e.e. 95 %)

(S)-1-Azido-3-naphthyoxy-2-hydroxypropane

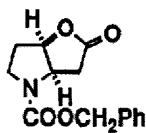
(1*R*,5*R*)-2-oxa-6-azabicyclo[3.3.0]octan-3-one hydrochloride

E.e.= >92%

 $[\alpha]_D^{23} +45.8$ (c 0.56, MeOH)

Source of chirality: Katsuki-Sharpless kinetic resolution

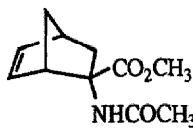
Absolute configuration: 1*R*,5*R*



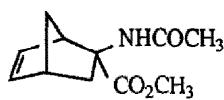
E.e = >92%

[α]_D²⁰ -122.3 (c 4.7, CHCl₃)

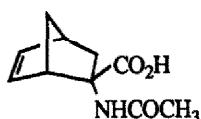
Source of chirality: Katsuki-Sharpless kinetic resolution

Absolute configuration: 1*R*,5*R*C₁₄H₁₅NO₄(1*R*,5*R*)-benzyl 3-oxo-2-oxa-6-azabicyclo[3.3.0]octane-6-carboxylateAbsolute configuration: 1*S*,2*S*,4*S*

(assigned by comparing with the corresponding hydrogenated amino acid)

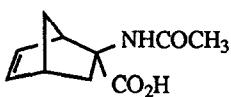
¹H-NMR [Eu(tfc)₃ / S molar relationship = 0.85, CD₃CN] :NHCOCH₃ : 5.05 ppm ; CO₂CH₃ : 4.75 ppm[α]_D²⁴ (c = 17.9 x 10⁻¹, MeOH) : - 97.3 ± 0.5C₁₁H₁₅NO₃Methyl (1*S*, 2*S*, 4*S*)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylateAbsolute configuration: 1*R*,2*S*,4*R*

(assigned by comparing with the corresponding hydrogenated amino acid)

¹H-NMR [Eu(tfc)₃ / S molar relationship = 0.85, CD₃CN] :NHCOCH₃ : 5.295 ppm ; CO₂CH₃ : 5.07 ppm[α]_D²⁴ (c = 12.75 x 10⁻¹, MeOH) : +72.5 ± 0.5C₁₁H₁₅NO₃Methyl (1*R*, 2*S*, 4*R*)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylateAbsolute configuration: 1*S*,2*S*,4*S*

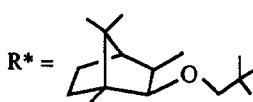
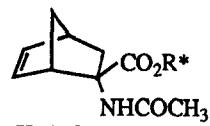
(assigned by comparing with the corresponding methyl ester)

[α]_D²⁴ (c = 12 x 10⁻¹, MeOH) : - 106.2 ± 0.5C₁₀H₁₃NO₃(1*S*, 2*S*, 4*S*)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylic acid

 $C_{10}H_{13}NO_3$

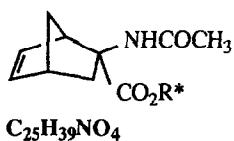
(1R, 2S, 4R)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylic acid

Absolute configuration: 1R,2S,4R
 (assigned by comparing with the corresponding methyl ester)
 $[\alpha]_D^{24}$ ($c = 11.4 \times 10^{-1}$, MeOH) : +156.0 ± 0.5

 $C_{25}H_{39}NO_4$

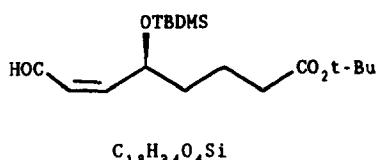
(1S, 2S, 4S)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylate of (-)-cis-3-hydroxy isobornyl neopentyl ether

Absolute configuration: 1S,2S,4S
 (assigned by comparing with the corresponding methyl ester)
 $[\alpha]_D^{24}$ ($c = 7.9 \times 10^{-1}$, MeOH) : - 61.4 ± 0.5

 $C_{25}H_{39}NO_4$

(1R, 2S, 4R)-2-acetamidobicyclo[2.2.1]hept-5-ene-2-carboxylate of (-)-cis-3-hydroxy isobornyl neopentyl ether

Absolute configuration: 1R,2S,4R
 (assigned by comparing with the corresponding methyl ester)
 $[\alpha]_D^{24}$ ($c = 6.4 \times 10^{-1}$, MeOH) : +32.8 ± 0.5

 $C_{18}H_{34}O_4Si$

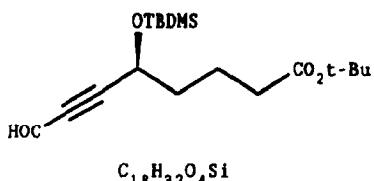
(5S,6Z)-t-butyl 5-t-butyldimethylsilyloxy-7-formyl-6-hexenoate

e.e. = 92%

 $[\alpha]_D = + 26$ ($c=1, CHCl_3$)Source of chirality: asymmetric reduction of the β -ketosulfoxide

Absolute configuration: S

(assigned from the reduction mechanism)



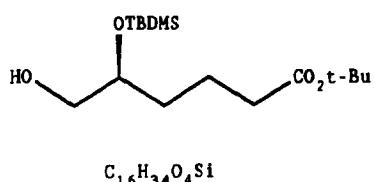
e.e = 92%

 $[\alpha]_D = -28$ ($c=1, CHCl_3$)Source of chirality: asymmetric reduction of the β -ketosulfoxide

Absolute configuration: S

(assigned from the reduction mechanism)

(S) t-butyl 5-t-butyldimethylsilyloxy-7-formyl-6-heptynoate



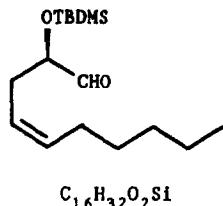
e.e = 92%

 $[\alpha]_D = +5$ ($c=1, CHCl_3$)Source of chirality: asymmetric reduction of the β -ketosulfoxide

Absolute configuration: S

(assigned from the reduction mechanism)

(S) t-butyl 6-hydroxy-5-t-butyldimethylsilyloxy hexanoate



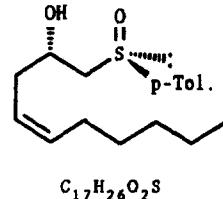
e.e > 95% (NMR)

 $[\alpha]_D = +7.9$ ($c=1, CHCl_3$)Source of chirality: asymmetric reduction of the β -ketosulfoxide

Absolute configuration: R

(assigned from the reduction mechanism)

2(R),4(Z)-2-t-butyldimethylsilyloxy-4-decenal



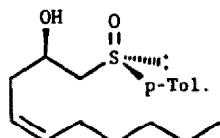
e.e > 95% (NMR)

 $[\alpha]_D = +179$ ($c=2.8, acetone$)Source of chirality: asymmetric reduction of the β -ketosulfoxide

Absolute configuration: R,S

(assigned from the reduction mechanism)

[2(S),4(Z),S(R)] 1-p-tolylsulfinyl 4-nonen-2-ol

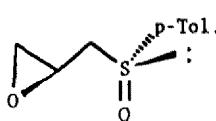
 $C_{17}H_{26}O_2S$

e.e. > 95% (NMR)

 $[\alpha]_D = + 99$ ($c=2.3$, acetone)Source of chirality: asymmetric reduction of the β -ketosulfoxideAbsolute configuration: $R_S R$

(assigned from the reduction mechanism)

[2(R),4(Z),S(R)] 1-p-tolylsulfinyl 4-decen-2-ol

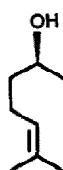
 $C_{10}H_{12}O_2S$

e.e. > 98% (NMR)

 $[\alpha]_D = + 239$ ($c=2$, acetone)Source of chirality: asymmetric reduction of the β -ketosulfoxideAbsolute configuration: $R_S S$

(assigned from the reduction mechanism)

[2(S),S(R)] 2-(p-tolylsulfinyl)methyl oxirane

 $C_8H_{16}O$

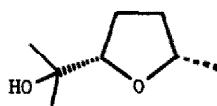
E.e. = 90% [by GC after derivatization with (R)-(+)-1-phenylethylisocyanate]

Source of chirality: Microbial conversion

Absolute configuration: 2S

 $C_8H_{16}O$

2-Methyl-2-hepten-6-ol (Sulcatol)

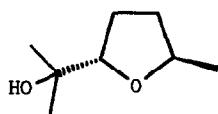
 $C_8H_{16}O_2$

2-(1-Hydroxy-1-methylethyl)-5-methyltetrahydrofuran

E.e. = 46% [by chiral GC with CP-Cyclodextrin-2,3,6-M-19]

Source of chirality: Microbial conversion

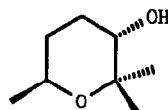
Absolute configuration: 2R,5R



E.e. - 80% [by chiral GC with CP-Cyclodextrin-
2,3,6-M-19]
Source of chirality: Microbial conversion
Absolute configuration: 2R,5S

C₈H₁₆O₂

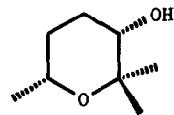
2-(1-Hydroxy-1-methylethyl)-5-methyltetrahydrofuran



E.e. - 60% [by chiral GC with CP-Cyclodextrin-
2,3,6-M-19]
Source of chirality: Microbial conversion
Absolute configuration: 3S,6S

C₈H₁₆O₂

Tetrahydro-2,2,6-trimethyl-2H-pyran-3-ol



E.e. - 56% [by chiral GC with CP-Cyclodextrin-
2,3,6-M-19]
Source of chirality: Microbial conversion
Absolute configuration: 3S,6R

C₈H₁₆O₂

Tetrahydro-2,2,6-trimethyl-2H-pyran-3-ol