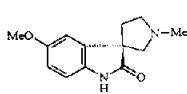


# STEREOCHEMISTRY ABSTRACTS

G.Palmisano\* R. Annunziata, G. Papeo and M.Sisti.

*Tetrahedron: Asymmetry* **1996**, 7, 1

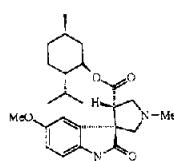


$C_{13}H_{16}N_2O_2$   
 $[\alpha]_D -7.0$  ( $c$  0.55,  $CHCl_3$ )  
 Source of chirality: (1R,2S,5R)-menthol  
 Absolute configuration: (3R)  
 Assignment based on the reaction mechanism and  $^1H$ -NMR

(-)-HORSFILINE  $\equiv$  (3R)-5-METHOXY-1'-METHYL-SPIRO[3H-INDOLE-3,3'-PYRROLIDIN]-2(1H)ONE

G.Palmisano\*, R. Annunziata, G. Papeo and M.Sisti.

*Tetrahedron: Asymmetry* **1996**, 7, 1

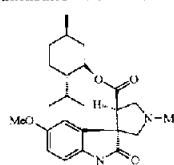


$C_{24}H_{24}N_2O_4$   
 $[\alpha]_D -25.7$  ( $c$  0.50,  $CHCl_3$ )  
 Source of chirality: (1R,2S,5R)-menthol  
 Absolute configuration: (3R,4'S)  
 Assignment based on the reaction mechanism and  $^1H$ -NMR

(3R,4'S)-1,2-DIHYDRO-5-METHOXY-1'-METHYL-2-OXOSPIRO[3H-INDOLE-3,3'-PYRROLIDINE]-4'-CARBOXYLIC ACID, (5R)-MENTHYL ESTER

G.Palmisano\* R. Annunziata, G. Papeo and M Sisti.

*Tetrahedron: Asymmetry* **1996**, 7, 1

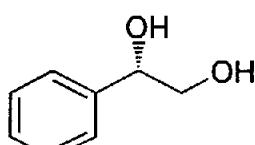


$C_{24}H_{24}N_2O_4$   
 $[\alpha]_D -184.7$  ( $c$  0.50,  $CHCl_3$ )  
 Source of chirality: (1R,2S,5R)-menthol  
 Absolute configuration: (3S,4'R)  
 Assignment based on the reaction mechanism and  $^1H$ -NMR

(3S,4'R)-1,2-DIHYDRO-5-METHOXY-1'-METHYL-2-OXOSPIRO[3H-INDOLE-3,3'-PYRROLIDINE]-4'-CARBOXYLIC ACID, (5R)-MENTHYL ESTER

Christian Wiesauer and Walter Weissensteiner\*

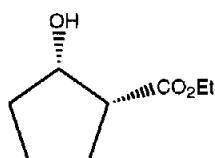
*Tetrahedron: Asymmetry* **1996**, 7, 5



$C_8H_{10}O_2$   
 1-Phenyl-1,2-ethanediol

E.e. = 79 % [ by chiral HPLC, Chiracel OB ]  
 $[\alpha]_D^{20} = + 30.5$  ( $c$  = 3.2,  $EtOH$ )

Source of chirality : asymm. synth  
 Absolute configuration 1S



E.e. 95% by chiral GC as iPr-carbamate (Chirasil-Val)

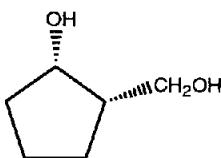
$$[\alpha]_D^{20} = +25 \text{ (c 1.3, MeOH)}$$

Source of chirality: microbial reduction

 $C_8H_{14}O_3$ 

Ethyl 2-hydroxy-cyclopentane carboxylate

Absolute configuration: 1R,2S



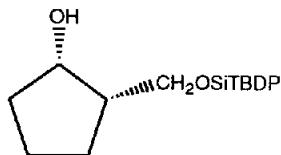
$$[\alpha]_D^{20} = +40 \text{ (c 1, MeOH)}$$

Source of chirality: microbial reduction

 $C_6H_{12}O_2$ 

2-hydroxymethyl cyclopentanol

Absolute configuration: 1S,2S



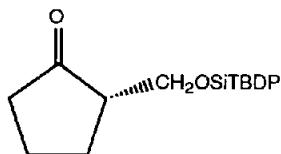
$$[\alpha]_D^{20} = +6 \text{ (c 1, MeOH)}$$

Source of chirality: microbial reduction

 $C_{22}H_{30}O_2Si$ 

2-hydroxymethyl cyclopentanol ter-butylidiphenylsilyl ether

Absolute configuration: 1S,2S



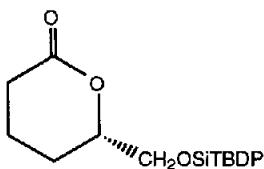
$$[\alpha]_D^{20} = -70 \text{ (c 1.5, CHCl}_3\text{)}$$

Source of chirality: microbial reduction

 $C_{22}H_{28}O_2Si$ 

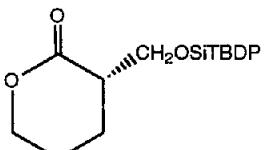
Absolute configuration: 2S

2-hydroxymethyl cyclopentanone ter-butylidiphenylsilyl ether

 $C_{22}H_{28}O_3Si$  $[\alpha]_D^{20} = +10; [\alpha]_{365}^{20} = +34 (c\ 0.7, \text{CHCl}_3)$ 

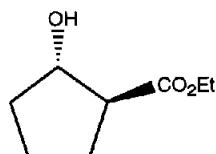
Source of chirality: microbial reduction

Absolute configuration: 6S

6-hydroxymethyl tetrahydro(2*H*)-pyran-2-one *ter*-butyldiphenylsilyl ether $C_{22}H_{28}O_3Si$  $[\alpha]_D^{20} = -18; [\alpha]_{365}^{20} = -63 (c\ 0.5, \text{CHCl}_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 3S

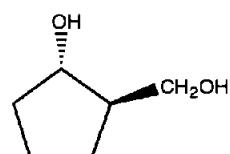
3-hydroxymethyl tetrahydro(2*H*)-pyran-2-one *ter*-butyldiphenylsilyl etherE.e. 99% by chiral GC as *i*Pr-carbamate (Chirasil-Val) $C_8H_{14}O_3$ 

Ethyl 2-hydroxy-cyclopentane carboxylate

 $[\alpha]_D^{20} = +52 (c\ 0.9, \text{Et}_2\text{O}); +66 (c\ 1, \text{MeOH})$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,2S

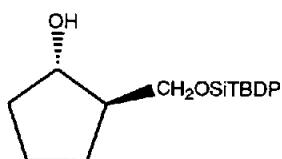
 $[\alpha]_D^{20} = +40 (c\ 3, \text{MeOH})$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,2R

 $C_6H_{12}O_2$ 

2-hydroxymethyl cyclopentanol

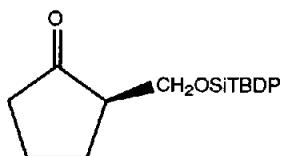

 $[\alpha]_D^{20} = +18 \text{ (c 1, MeOH)}$ 

Source of chirality: microbial reduction

C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>Si

Absolute configuration: 1S,2R

2-hydroxymethyl cyclopentanol *ter*-butyldiphenylsilyl ether

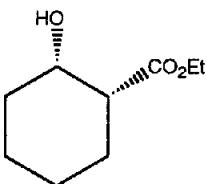

 $[\alpha]_D^{20} = +64 \text{ (c 0.9, CHCl}_3\text{)}$ 

Source of chirality: microbial reduction

C<sub>22</sub>H<sub>28</sub>O<sub>2</sub>Si

Absolute configuration: 2R

2-hydroxymethyl cyclopentanone *ter*-butyldiphenylsilyl ether



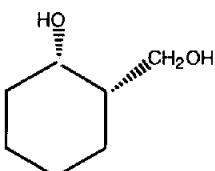
E.e. 99% by chiral GC as iPr-carbamate (Chirasil-Val)

 $[\alpha]_D^{20} = +20 \text{ (c 0.7, CHCl}_3\text{); } +36 \text{ (c 0.9, MeOH)}$ 

Source of chirality: microbial reduction

C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>  
Ethyl 2-hydroxy-cyclohexane carboxylate

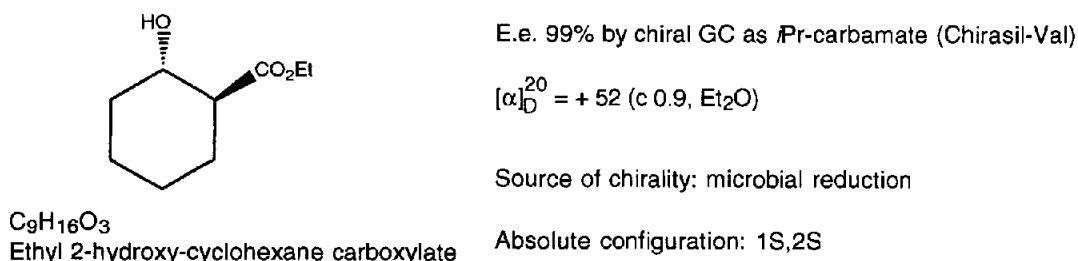
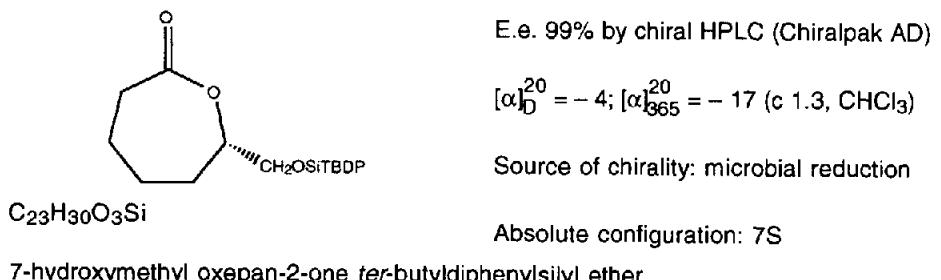
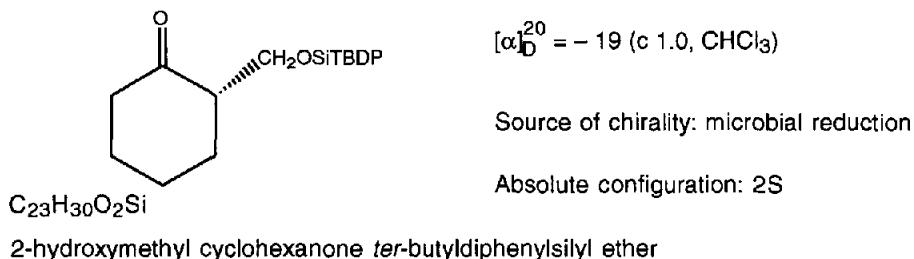
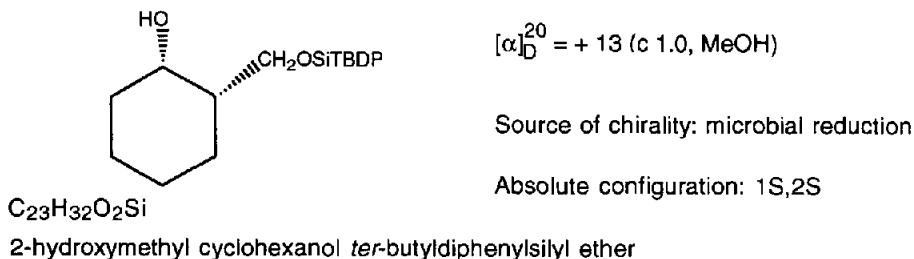
Absolute configuration: 1R,2S

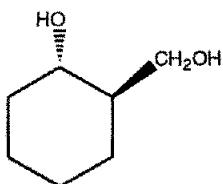

 $[\alpha]_D^{20} = +36 \text{ (c 1.0, MeOH)}$ 

Source of chirality: microbial reduction

C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>  
2-hydroxymethyl cyclohexanol

Absolute configuration: 1S,2S



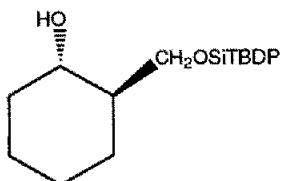


C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>  
2-hydroxymethyl cyclohexanol

[α]<sub>D</sub><sup>20</sup> = + 47 (c 1, MeOH)

Source of chirality: microbial reduction

Absolute configuration: 1S,2R



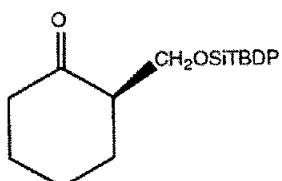
C<sub>23</sub>H<sub>32</sub>O<sub>2</sub>Si

2-hydroxymethyl cyclohexanol *ter*-butyldiphenylsilyl ether

[α]<sub>D</sub><sup>20</sup> = + 18 (c 1.4, MeOH)

Source of chirality: microbial reduction

Absolute configuration: 1S,2R



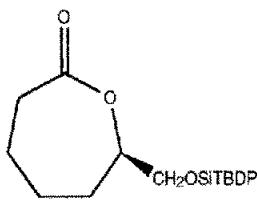
C<sub>23</sub>H<sub>30</sub>O<sub>2</sub>Si

2-hydroxymethyl cyclohexanone *ter*-butyldiphenylsilyl ether

[α]<sub>D</sub><sup>20</sup> = + 22 (c 1.2, CHCl<sub>3</sub>)

Source of chirality: microbial reduction

Absolute configuration: 2R



C<sub>23</sub>H<sub>30</sub>O<sub>3</sub>Si

7-hydroxymethyl oxepan-2-one *ter*-butyldiphenylsilyl ether

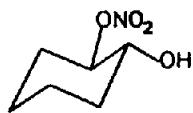
E.e. 99% by chiral HPLC (Chiraldak AD)

[α]<sub>D</sub><sup>20</sup> = + 4; [α]<sub>365</sub><sup>20</sup> = + 18 (c 1.3, CHCl<sub>3</sub>)

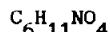
Source of chirality: microbial reduction

Absolute configuration: 7R

K. Muthukumaran

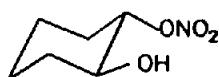


ee = >99% [by HPLC analysis of its 2-methoxybenzoate derivative using CHIRALCEL OD column]  
 $[\alpha]_D^{22} -71.5$  (c 1.17,  $\text{CH}_2\text{Cl}_2$ )  
 Source of chirality : Pig liver acetone powder  
 Absolute configuration : 1R,2R [assigned by conversion to (1R,2R)-cyclohexane-1,2-diol]

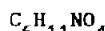


(1R,2R)-2-Nitroxycyclohexan-1-ol

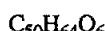
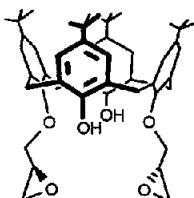
K. Muthukumaran



ee = >99% [by HPLC analysis of its 2-methoxybenzoate derivative using CHIRALCEL OD column]  
 $[\alpha]_D^{22} +71.8$  (c 0.43,  $\text{CH}_2\text{Cl}_2$ )  
 Source of chirality : Pig liver acetone powder  
 Absolute configuration : 1S,2S (based on the sign of optical rotation in comparison with that of (1R,2R)-isomer)



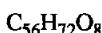
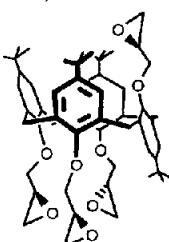
(1S,2S)-2-Nitroxycyclohexan-1-ol

 $[\alpha]_D^{25} = +4.9$  (c 6.6,  $\text{CHCl}_3$ )

Source of Chirality: (S)-glycidyl 3-nitrobenzensulfonate

Absolute configuration: S,S

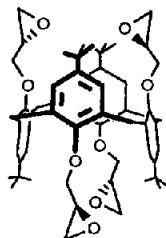
5,11,17,23-Tetra-tert-butyl-25,27-bis(2,3-epoxypropoxy)calix[4]arene-26,28-diol

 $[\alpha]_D^{25} = +4.7$  (c 0.95,  $\text{CHCl}_3$ )

Source of Chirality: (S)-glycidyl tosylate

Absolute configuration: S,S,S,S

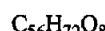
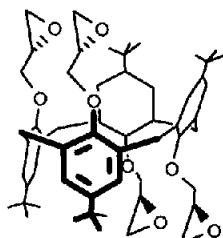
Partial-cone-5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(2,3-epoxypropoxy)calix[4]arene

 $[\alpha]^{25}_D = +9.2 (c\ 0.48, \text{CHCl}_3)$ 

Source of Chirality: (S)-glycidyl tosylate

Absolute configuration: S,S,S,S

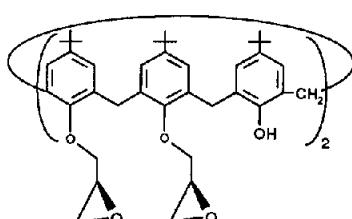
1,3-Alternate-5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(2,3-epoxypropoxy)calix[4]arene

 $[\alpha]^{25}_D = -28.1 (c\ 0.84, \text{CHCl}_3)$ 

Source of Chirality: (S)-glycidyl tosylate

Absolute configuration: S,S,S,S

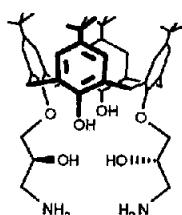
1,2-Alternate-5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(2,3-epoxypropoxy)calix[4]arene

 $[\alpha]^{25}_D = -8.4 (c\ 0.98, \text{CHCl}_3)$ 

Source of Chirality: (S)-glycidyl tosylate

Absolute configuration: S,S,S,S

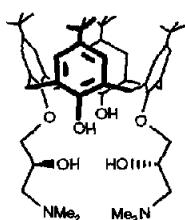
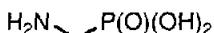
5,11,17,23,29,35-Hexa-tert-butyl-37,38,40,41-tetrakis(2,3-epoxypropoxy)calix[6]arene-39,42-diol

 $[\alpha]^{25}_D = -2.2 (c\ 0.85, \text{CHCl}_3)$ 

Source of Chirality: (S)-glycidyl 3-nitrobenzensulfonate

Absolute configuration: S,S

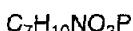
5,11,17,23-Tetra-tert-butyl-25,27-bis(3-amino-2-hydroxypropoxy)calix[4]arene-26,28-diol

 $[\alpha]_D^{25} = +12.2$  (*c* 1.03, CHCl<sub>3</sub>)Source of Chirality: (*S*)-glycidyl 3-nitrobenzenesulfonateAbsolute configuration: *S,S*5,11,17,23-Tetra-*tert*-butyl-25,27-bis(3-dimethylamino-2-hydroxypropoxy)calix[4]arene-26,28-diolE.e. >99% [by <sup>1</sup>H- and <sup>19</sup>F-NMR of the (R)-(+)-MTPA amide derivative] $[\alpha]_D^{25} = -17.8$  (*c* 1.0, 1N NaOH)

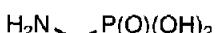
source of chirality: asymmetric synthesis

Absolute configuration: S

mp = 280-282 °C



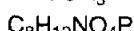
α-Amino-phenyl-methylphosphonic acid

E.e. >99% [by <sup>1</sup>H- and <sup>19</sup>F-NMR of the (R)-(+)-MTPA amide derivative] $[\alpha]_D^{25} = -25.8$  (*c* 0.58, 1N NaOH)

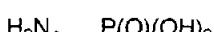
source of chirality: asymmetric synthesis

Absolute configuration: S

mp = 310-312 °C



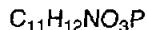
α-Amino-(p-methoxy)-phenyl-methylphosphonic acid

E.e. >99% [by <sup>1</sup>H- and <sup>19</sup>F-NMR of the (R)-(+)-MTPA amide derivative] $[\alpha]_D^{25} = 30.4$  (*c* 0.9, 1N NaOH)

source of chirality: asymmetric synthesis

Absolute configuration: S

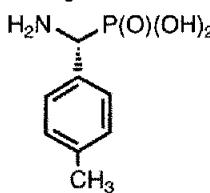
mp = 287-289 °C



α-Amino-(1-naphthyl)-methylphosphonic acid

S. K. Chung and D. H. Kang

Tetrahedron: Asymmetry 1996, 7, 21



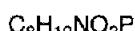
E.e. >99% [ by  $^1\text{H}$ -and  $^{19}\text{F}$ NMR of the (R)-(+)- MTPA amide derivative ]

$[\alpha]_D^{25} = -28.2$  (c 1.0, 1N NaOH)

source of chirality: asymmetric synthesis

Absolute configuration: S

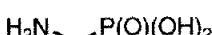
mp =280-283 °C



$\alpha$ -Amino-(p-methyl)-phenyl-methylphosphonic acid

S. K. Chung and D. H. Kang

Tetrahedron: Asymmetry 1996, 7, 21



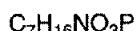
E.e. = 56% [by  $^1\text{H}$ -and  $^{19}\text{F}$ -NMR of the (R)-(+)- MTPA amide derivative]

$[\alpha]_D^{25} = -20.3$  (c 0.5, 1N NaOH)

source of chirality: asymmetric synthesis

Absolute configuration: unknown

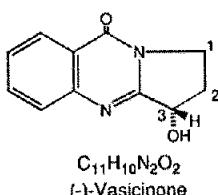
mp =267-269 °C



$\alpha$ -Amino-cyclohexyl-methylphosphonic acid

B. S. Joshi, M. G. Newton, D. Lee, A. D. Barber and S. W. Pelletier

Tetrahedron: Asymmetry 1996, 7, 25



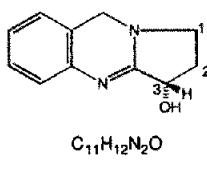
$[\alpha]_D^{20} = -122$  (C = 1,  $\text{CHCl}_3$ )

Source of chirality: *Adhatoda vasica*, Nees Leaves

Absolute configuration 3S

B. S. Joshi, M. G. Newton, D. Lee, A. D. Barber and S. W. Pelletier

Tetrahedron: Asymmetry 1996, 7, 25

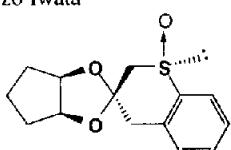


$[\alpha]_D^{20} = -210$  (C = 2,  $\text{CHCl}_3$ )

Source of chirality: *Adhatoda vasica*, Nees Leaves

Absolute configuration 3S

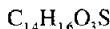
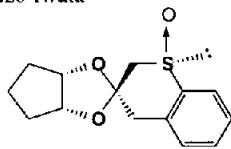
Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yûki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



(*Rs*)-*endo*-Thiochroman-1-oxide-3-spiro-3'-2', 4'-dioxabicyclo[3.3.0]octane

E.e. = 100% [by HPLC on chiral column]  
 $[\alpha]_D^{27} -49.01$  ( $c = 0.5100$ ,  $CHCl_3$ )  
 Source of chirality: *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine  
 Absolute configuration: *R*

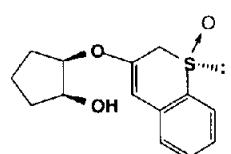
Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yûki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



(*Rs*)-*exo*-Thiochroman-1-oxide-3-spiro-3'-2', 4'-dioxabicyclo[3.3.0]octane

E.e. = 100% [by HPLC on chiral column]  
 $[\alpha]_D^{25} -159.3$  ( $c = 1.225$ ,  $CHCl_3$ )  
 Source of chirality: *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine  
 Absolute configuration: *R*

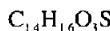
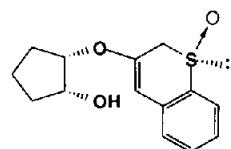
Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yûki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



(*Rs*)-3-[(1*R*, 2*S*)-2-Hydroxycyclopentyloxy]thiochroman-3-ene-1-oxide

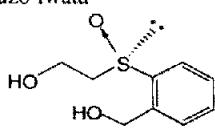
$[\alpha]_D^{20} -228.9$  ( $c = 1.745$ ,  $CHCl_3$ )  
 Source of chirality: *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine  
 Absolute configuration: 1*R*, 2*S*, *Rs*

Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yûki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



(*Rs*)-3-[(1*S*, 2*R*)-2-Hydroxycyclopentyloxy]thiochroman-3-ene-1-oxide

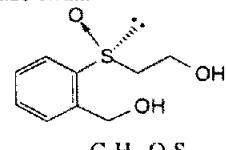
Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yuki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



$C_9H_{12}O_3S$   
(*R*)-2-Hydroxyethyl (*o*-hydroxymethyl)phenyl sulfoxide

$[\alpha]_D^{12} +161.5$  (*c* = 0.2400, MeOH)  
Source of chirality: *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine  
Absolute configuration: *R*

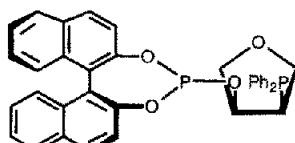
Naoyoshi Maezaki, Motohiro Soejima, Atsunobu Sakamoto, Ikuyo Sakamoto, Yuki Matsumori, Tetsuaki Tanaka, Toshimasa Ishida, Yasuko In, and Chuzo Iwata



$C_9H_{12}O_3S$   
(*S*)-2-Hydroxyethyl (*o*-hydroxymethyl)phenyl sulfoxide

$[\alpha]_D^{29} -179.8$  (*c* = 0.7800, MeOH)  
Source of chirality: *N*-(phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine  
Absolute configuration: *S*

A. Kless, J. Holz, D. Heller, R. Kadyrov, R. Selke, Ch. Fischer, A. Börner



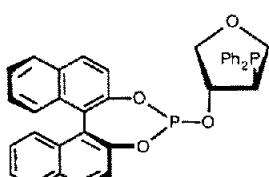
$C_{36}H_{28}O_4P_2$

(*3R,4S*)-4-[(*S*)-Bis(naphthoxy)phosphinoxy]-3-diphenylphosphinotetrahydrofuran

$[\alpha]_D^{24} = +265.7$  (*c* 1, CHCl<sub>3</sub>)

Source of chirality: L-ascorbic acid  
Absolute configuration: *S,3R,4S*

A. Kless, J. Holz, D. Heller, R. Kadyrov, R. Selke, Ch. Fischer, A. Börner

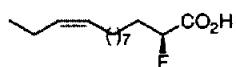


$C_{36}H_{28}O_4P_2$

(*3R,4R*)-4-[(*S*)-Bis(naphthoxy)phosphinoxy]-3-diphenylphosphinotetrahydrofuran

$[\alpha]_D^{32} = +214.1$  (*c* 1, CHCl<sub>3</sub>)

Source of chirality: D-isoascorbic acid  
Absolute configuration: *S,3R,4R*



C<sub>14</sub>H<sub>25</sub>FO<sub>2</sub>  
2-Fluoro-(Z)-11-tetradecenoic acid

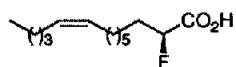
E.e. = 94 % [GC of (S)- $\alpha$ -methylbenzylamide]

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -6.5 (c 0.56 CHCl<sub>3</sub>)

Source of chirality: asymmetric synthesis

Absolute configuration S

(assigned by correlation with homologous acid)



C<sub>14</sub>H<sub>25</sub>FO<sub>2</sub>  
2-Fluoro-(Z)-9-tetradecenoic acid

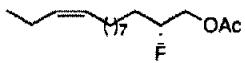
E.e. = 94 % [GC of (S)- $\alpha$ -methylbenzylamide]

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -6.6 (c 1.15 CHCl<sub>3</sub>)

Source of chirality: asymmetric synthesis

Absolute configuration S

(assigned by correlation with homologous acid)



C<sub>16</sub>H<sub>29</sub>FO<sub>2</sub>  
2-Fluoro-(Z)-11-tetradecen-1-ol acetate

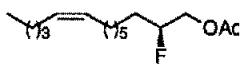
E.e. = 92 % (GC Mosher ester of interm. alkyne)

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = -4.6 (c 0.94 CHCl<sub>3</sub>)

Source of chirality: 2-fluoro carboxylic acid

Absolute configuration R

(assigned by chemical correlation)



C<sub>16</sub>H<sub>29</sub>FO<sub>2</sub>  
2-Fluoro-(Z)-9-tetradecen-1-ol acetate

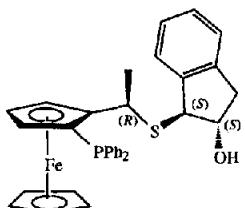
E.e. = 92 % (GC Mosher ester of interm. alkyne)

[ $\alpha$ ]<sub>D</sub><sup>25</sup> = +4.4 (c 1.01 CHCl<sub>3</sub>)

Source of chirality: 2-fluoro carboxylic acid

Absolute configuration S

(assigned by chemical correlation)



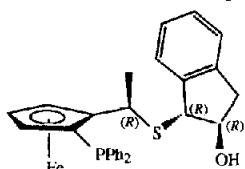
*trans*-1-{(R)-1'-(S)-(diphenylphosphino)ferrocenyl}ethyl thiolato-2-indanol

D.e. = 100 % (by <sup>1</sup>H and <sup>31</sup>P NMR).

[α]<sub>D</sub>=-387 (c=0.38, CHCl<sub>3</sub>).

Source of chirality: Synthesis  
employing enantiomerically pure ferrocenylthiol.

Absolute configuration: (R,S,S)-(S)  
(X-ray of P-oxide determined)



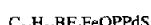
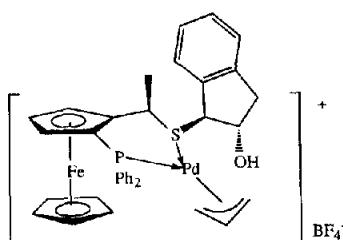
*trans*-1-{(R)-1'-(S)-(diphenylphosphino)ferrocenyl}ethyl thiolato-2-indanol

D.e. = 100 % (by <sup>1</sup>H and <sup>31</sup>P NMR).

[α]<sub>D</sub>=-328 (c=0.29, CHCl<sub>3</sub>).

Source of chirality: Synthesis  
employing enantiomerically pure ferrocenylthiol.

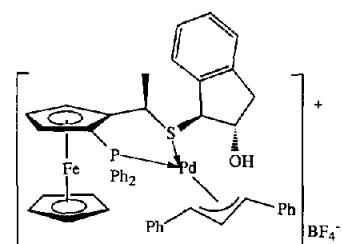
Absolute configuration: (R,S,R)-(R)  
(by comparison with other diastereomer)



[α]<sub>D</sub>=-131 (c=0.16, CH<sub>2</sub>Cl<sub>2</sub>)

Source of chirality: synthesis using  
enantiomerically pure P,S,O ligand

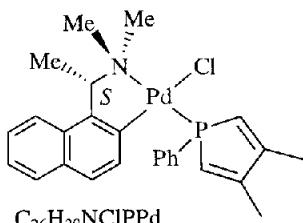
Absolute configuration: (R,S,S)-(S)  
(X-ray determined)



[α]<sub>D</sub>=-133 (c=0.11, CH<sub>2</sub>Cl<sub>2</sub>)

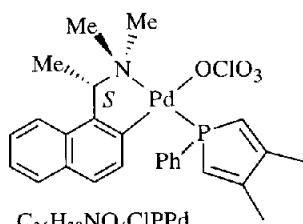
Source of chirality: synthesis using  
enantiomerically pure P,S,O ligand

Absolute configuration: (R,S,S)-(S)  
(Abs. config. of ligand determined  
by X-ray)



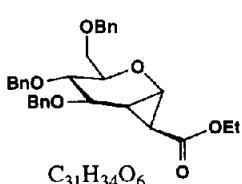
E. e. = > 99% (by nmr)  
 $[\alpha]_D = +334.9$  (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>)

Source of chirality: asymm. synth.

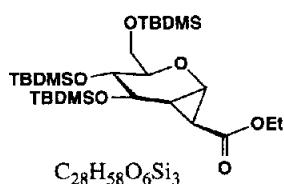


E. e. = > 99% (by nmr)  
 $[\alpha]_D = +285.0$  (*c* 0.2, CH<sub>2</sub>Cl<sub>2</sub>)

Source of chirality: asymm. synth.



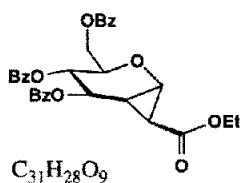
D.e. > 97% (by 300 MHz <sup>1</sup>H NMR spectroscopy)  
 $[\alpha]_D^{20} = +21.6$  (*c* 1.0, CHCl<sub>3</sub>)  
 Source of chirality: D-glucal  
 Absolute configuration: 1S, 2S, 3R, 4S, 5R, 7S  
 1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbethoxymethylene)-  
 3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucitol



D.e. > 97% (by 300 MHz <sup>1</sup>H NMR spectroscopy)  
 $[\alpha]_D^{20} = +17.4$  (*c* 1.0, CHCl<sub>3</sub>)  
 Source of chirality: D-glucal  
 Absolute configuration: 1S, 2S, 3R, 4S, 5R, 7S  
 1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbethoxymethylene)-  
 3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)- $\alpha$ -D-glucitol

C.M. Timmers, M.A. Leeuwenburgh, J.C. Verheijen,  
G.A. van der Marel and J.H. van Boom

Tetrahedron: Asymmetry 1996, 7, 49



D.e. > 97% (by 300 MHz  $^1\text{H}$  NMR spectroscopy)

$$[\alpha]_D^{20} = -4.4 \text{ (c 1.0, CHCl<sub>3</sub>)}$$

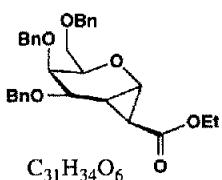
Source of chirality: D-glucal

Absolute configuration: 1S, 2S, 3R, 4S, 5R, 7S

1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbethoxymethylene)-3,4,6-tri-*O*-benzoyl- $\alpha$ -D-glucitol

C.M. Timmers, M.A. Leeuwenburgh, J.C. Verheijen,  
G.A. van der Marel and J.H. van Boom

Tetrahedron: Asymmetry 1996, 7, 49



D.e. > 97% (by 300 MHz  $^1\text{H}$  NMR spectroscopy)

$$[\alpha]_D^{20} = -19.2 \text{ (c 1.0, CHCl}_3\text{)}$$

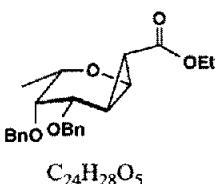
Source of chirality: D-galactose

Absolute configuration: 1S, 2S, 3R, 4R, 5R, 7S

1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbethoxymethylene)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-galactitol

C.M. Timmers, M.A. Leeuwenburgh, J.C. Verheijen,  
G.A. van der Marel and J.H. van Boom

Tetrahedron: Asymmetry 1996, 7, 49



D.e. = 47% (by 300 MHz  $^1\text{H}$  NMR spectroscopy)

$$[\alpha]_D^{20} = -9.0 \text{ (c 1.0, CHCl}_3\text{)}$$

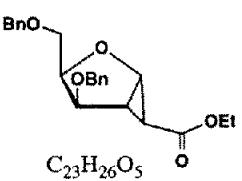
#### Source of chirality: L-fucal

Absolute configuration: 1R, 2R, 3S, 4R, 5S, 7R

1,5-anhydro-2-deoxy-3,4-di-O-benzyl-1,2-C-(*exo*-carbethoxymethylene)- $\alpha$ -L-fucitol

C.M. Timmers, M.A. Leeuwenburgh, J.C. Verheijen,  
G.A. van der Marel and J.H. van Boom

Tetrahedron: Asymmetry 1996, 7, 49



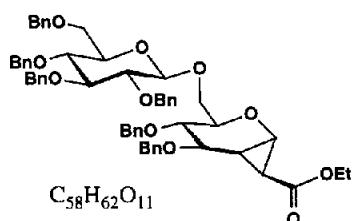
D.e. = 61% (by 300 MHz  $^1\text{H}$  NMR spectroscopy)

$$[\alpha]_D^{20} = -21.8 \text{ (c 1.0, CHCl}_3\text{)}$$

Source of chirality: D-xylal

Absolute configuration: 1S, 2S, 3R, 4R, 6S

1,4-anhydro-2-deoxy-3,5-di-O-benzyl-1,2-C-(*exo*-carbethoxymethylene)- $\alpha$ -D-xylitol



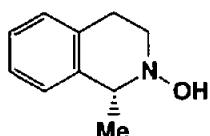
D.e. > 97% (by 300 MHz  $^1H$  NMR spectroscopy)

$[\alpha]_D^{20} = -7.0$  (c 1.0, CHCl<sub>3</sub>)

Source of chirality: D-glucal

Absolute configuration: 1S, 2S, 3R, 4S, 5R, 7S

1,5-anhydro-3,4-di-O-benzyl-2-deoxy-1,2-C-(exo-carbethoxy-methylene)-6-O-(2,3,4,6-tetra-O-benzyl-beta-D-glucopyranosyl)-alpha-D-glucitol



Ee = 47% (by HPLC on Chiralcel OD-H)

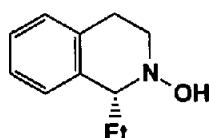
$[\alpha]_D^{25} +34$  (c 1.00, MeOH)

Source of chirality: asymm. synth.

Absolute configuration R

(assigned by chemical correlation)

2-Hydroxy-1-methyl-1,2,3,4-tetrahydroisoquinoline



Ee = 48% (by HPLC on Chiralcel OD-H)

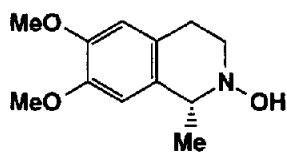
$[\alpha]_D^{25} +27$  (c 1.00, MeOH)

Source of chirality: asymm. synth.

Absolute configuration R

(tentatively assigned by specific rotation compared to 2-hydroxy-1-methyl-1,2,3,4-tetrahydroisoquinoline)

1-Ethyl-2-hydroxy-1,2,3,4-tetrahydroisoquinoline



Ee = 34% (by HPLC on Chiralcel OD-H)

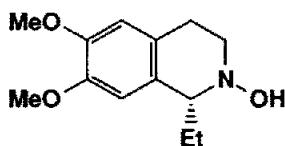
$[\alpha]_D^{25} +15$  (c 0.30, MeOH)

Source of chirality: asymm. synth.

Absolute configuration R

(assigned by chemical correlation)

2-Hydroxy-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline

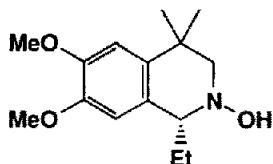
 $C_{15}H_{19}NO_3$ 

1-Ethyl-2-hydroxy-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline

Ee = 65% (by HPLC on Chiralcel OD-H)

 $[\alpha]_D^{25} +33$  (c 1.00, MeOH)

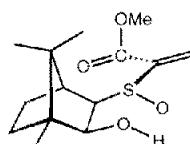
Source of chirality: asymm. synth.

Absolute configuration R  
(tentatively assigned by specific rotation compared to 2-hydroxy-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline) $C_{15}H_{23}NO_3$ 

1-Ethyl-2-hydroxy-6,7-dimethoxy-4,4-dimethyl-1,2,3,4-tetrahydroisoquinoline

Ee = 76% (by conversion to MTPA ester and  $^1H$  NMR analysis) $[\alpha]_D^{25} +41$  (c 0.92, MeOH)

Source of chirality: asymm. synth.

Absolute configuration R  
(tentatively assigned by specific rotation compared to 2-hydroxy-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline) $C_{14}H_{23}O_4S$ 

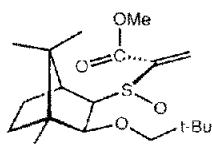
(1'-methoxycarbonylethylene)-(SR)-sulfinyl-2S-hydroxy-1R,7,7-trimethylbicyclo[2.2.1]heptane 5a

 $[\alpha]_D^{20} 12.9$  (c 1.4,  $CHCl_3$ )

E.e. = &gt;98% (by HPLC analysis)

Source of chirality: Asymmetric synthesis

Absolute configuration: 1R, 2S, 3R, SR

 $[\alpha]_D^{20} 19.5$  (c 1.0,  $CHCl_3$ )

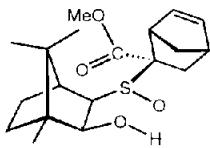
E.e. = &gt;98% (by HPLC analysis)

Source of chirality: Asymmetric synthesis

Absolute configuration: 1R, 2S, 3R, SR

 $C_{19}H_{32}O_4S$ 

(1'-methoxycarbonylethylene)-(SR)-sulfinyl-2S-neopentoxy-1R,7,7-trimethylbicyclo[2.2.1]heptane 5b



$[\alpha]_D^{20} 32.9$  (c 2.4,  $\text{CHCl}_3$ ).

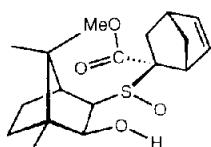
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1*R*, 2*S*, 3*R*, *SR*, 1*S*

$\text{C}_{19}\text{H}_{28}\text{O}_4\text{S}$

3*R*-{((1*S*, 2*R*, 4*S*)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(*SR*)-sulfinyl)-2*S*-hydroxy-1*R*,7,7-trimethylbicyclo[2.2.1]heptane Endo-(*Re*)- 6a



$[\alpha]_D^{20} 180.4$  (c 3.2,  $\text{CHCl}_3$ ).

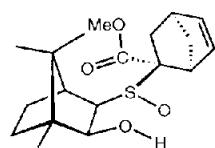
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1*R*, 2*S*, 3*R*, *SR*, 1*R*

$\text{C}_{19}\text{H}_{29}\text{NO}_2\text{S}$

3*R*-{((1*R*, 2*S*, 4*R*)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(*SR*)-sulfinyl)-2*S*-hydroxy-1*R*,7,7-trimethylbicyclo[2.2.1]heptane Endo-(*Si*)- 7a



$[\alpha]_D^{20} 28.9$  (c 2.0,  $\text{CHCl}_3$ ).

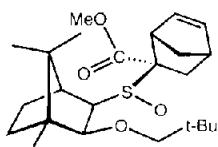
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1*R*, 2*S*, 3*R*, *SR*, 1*S*

$\text{C}_{20}\text{H}_{31}\text{NO}_2\text{S}$

3*R*-{((1*R*, 2*R*, 4*R*)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(*SR*)-sulfinyl)-2*S*-hydroxy-1*R*,7,7-trimethylbicyclo[2.2.1]heptane Exo-(*Re*)- 9a



$[\alpha]_D^{20} -6.1$  (c 1.9,  $\text{CHCl}_3$ ).

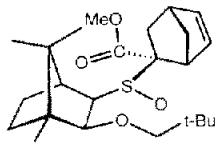
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1*R*, 2*S*, 3*R*, *SR*, 1*S*

$\text{C}_{24}\text{H}_{38}\text{O}_4\text{S}$

3*R*-{((1*S*, 2*R*, 4*S*)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(*SR*)-sulfinyl)-2*S*-neopentoxy-1*R*,7,7-trimethylbicyclo[2.2.1]heptane Endo-(*Re*)- 6b



$[\alpha]_D^{20}$  113.6 (c 2.1, CHCl<sub>3</sub>).

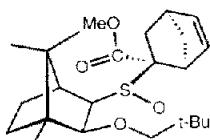
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1'R, 2S, 3R, SR, 1'R

C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>S

3R-{(1'R, 2'S, 4'R)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(SR)-sulfinyl}-2S-neopentoxy-1R,7,7-trimethylbicyclo[2.2.1]heptane Endo-(*Si*)- 7b



$[\alpha]_D^{20}$  -15.6 (c 1.5, CHCl<sub>3</sub>).

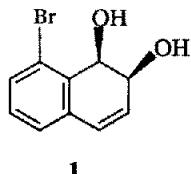
E.e. = >98% (by HPLC analysis)

Source of chirality: Asymmetric cycloaddition

Absolute configuration: 1R, 2S, 3R, SR, 1'S

C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>S

3R-{(1'R, 2'R, 4'R)-2-methoxycarbonylbicyclo[2.2.1]hept-5'-en-2'-yl-(SR)-sulfinyl}-2S-neopentoxy-1R,7,7-trimethylbicyclo[2.2.1]heptane Exo-(*R*e)- 9b



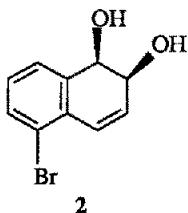
E.e. > 98%

$[\alpha]_D^{25}$  +28 (c=0.44 CHCl<sub>3</sub>)

Source of chirality: Enzymatic dihydroxylation

Absolute configuration 1R, 2S

C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>Br  
1,2-dihydroxy-1,2-dihydro-8-bromonaphthalene



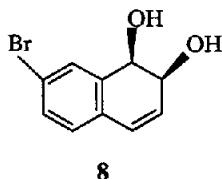
E.e. > 98%

$[\alpha]_D^{25}$  +84.4 (c=0.5 MeOH)

Source of chirality: Enzymatic dihydroxylation

Absolute configuration 1R, 2S

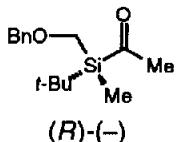
C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>Br  
1,2-dihydroxy-1,2-dihydro-5-bromonaphthalene



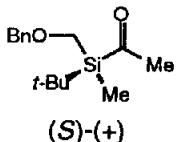
E.e. > 98%  
 $[\alpha]_D^{25} +255$  ( $c=1.0$  MeOH)

Source of chirality: Enzymatic dihydroxylation  
 Absolute configuration 1*R*, 2*S*

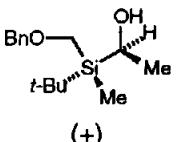
$C_{10}H_9O_2Br$   
 1,2-dihydroxy-1,2-dihydro-7-bromonaphthalene



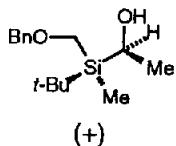
**(*R*)-(-)-[(Benzoyloxymethyl)(*tert*-butyl)methylsilyl] Methyl Ketone** [(-)-3]. ( $C_{15}H_{24}O_2Si$ );  $[\alpha]_D^{23}=9.9\pm2$  ( $c = 0.8$ , THF). Enantiomeric purity >95% ee (determined with the precursor and verified by reduction and application of the Mosher method). Absolute configuration from NOE studies of a derivative of the precursor.



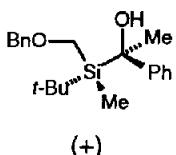
**(*S*)-(+)-[(Benzoyloxymethyl)(*tert*-butyl)methylsilyl] Methyl Ketone** [(+)-3]. ( $C_{15}H_{24}O_2Si$ );  $[\alpha]_D^{23}=12\pm2$  ( $c = 1.6$ , THF). Enantiomeric purity >95% ee (determined with the precursor and verified by reduction and application of the Mosher method). Absolute configuration from NOE studies of a derivative of the precursor.



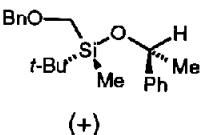
**(Si*R*,1*R*)-(+)-1-[(Benzoyloxy)methyl](*tert*-butyl)methylsilyl-ethanol** [(+)-4]. ( $C_{15}H_{26}O_2Si$ );  $[\alpha]_D^{23}=16\pm2$  ( $c = 0.8$ , THF). Enantiomeric purity >96% ee (determined by the Mosher method). Absolute configurations from the Mosher method and from NOE studies of a derivative.



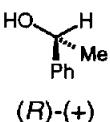
**(SiS,1R)-(+)-1-[(Benzylxy)methyl](tert-butyl)methylsilyl}-ethanol [(+)-5]. ( $C_{15}H_{26}O_2Si$ );  $[\alpha]_D^{23}= 12\pm 2$  ( $c = 1.9$ , THF). Enantiomeric purity  $>96\%$  ee (determined by the Mosher method). Absolute configurations from the Mosher method and from NOE studies of a derivative.**



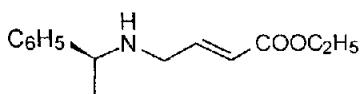
**(SiR,1R)-(+)-1-[(Benzylxy)methyl](tert-butyl)methylsilyl]-1-phenylethanol [(+)-10]. ( $C_{21}H_{30}O_2Si$ );  $[\alpha]_D^{23}= 20\pm 2$  ( $c = 0.8$ , THF). Enantiomeric purity  $92\pm 2\%$  ee (determined by the Mosher method of a precursor). Absolute configurations deduced from the stereochemical course of the reactions to (+)-12 and the configurations of the precursor molecule (-)-3 and the final product (+)-12.**



**(+)-{-(R)-[(Benzylxy)methyl](tert-butyl)methylsilyl}-(R)-1-Phenylethyl Ether [(+)-11]. ( $C_{21}H_{30}O_2Si$ );  $[\alpha]_D^{23}= 47\pm 2$  ( $c = 0.7$ , THF). Enantiomeric purity  $92\pm 2\%$  ee (determined by the Mosher method of a precursor). Absolute configurations deduced from the stereochemical course of the reactions to (+)-12 and the configurations of the precursor molecule (-)-3 and the final product (+)-12.**

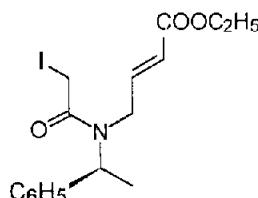


**(R)-(+)-1-Phenylethanol [(+)-12]. ( $C_8H_{10}O$ );  $[\alpha]_D^{23}= 40\pm 2$  ( $c = 0.7$ , THF). Enantiomeric purity  $88\pm 2\%$  (determined by the Mosher method). Commercially available (e.g., Fluka):  $[\alpha]_D^{20}= 45\pm 1$  ( $c = 5$ , MeOH).**



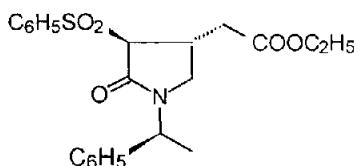
E.e. > 98%  
 $[\alpha]_D -32.6$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: (*S*)-phenylethylamine  
 Absolute configuration: *S*

(*S*)-*N*-[3-Ethoxycarbonyl-2(*E*)-propen-1-yl]-*N*-(1-phenyleth-1-yl)-amine



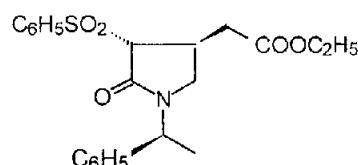
D.e. > 98%  
 $[\alpha]_D -87.2$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: (*S*)-phenylethylamine  
 Absolute configuration: *S*

(*S*)-*N*-[3-Ethoxycarbonyl-2(*E*)-propen-1-yl]-*N*-(1-phenyleth-1-yl)iodoacetamide



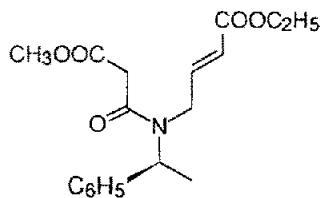
D.e. > 98%  
 $[\alpha]_D -130.8$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3*S*,4*R*,1'*S*

Ethyl (3*S*,4*R*,1'*S*)-[3-benzensulphonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



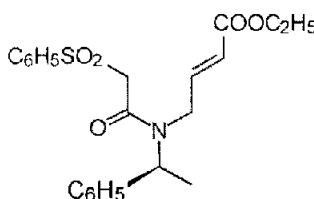
D.e. > 98%  
 $[\alpha]_D -69.7$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3*R*,4*S*,1'*S*

Ethyl (3*R*,4*S*,1'*S*)-[3-benzensulphonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



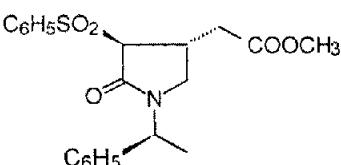
E.e. > 98%  
 $[\alpha]_D -83.2$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: (S)-phenylethylamine  
 Absolute configuration: S

(S)-N-[3-Ethoxycarbonyl-2(E)-propen-1-yl]-N-(1-phenyleth-1-yl)methoxycarbonylacetamide



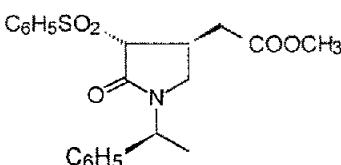
E.e. > 98%  
 $[\alpha]_D -116.1$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: (S)-phenylethylamine  
 Absolute configuration: S

(S)-N-[3-Ethoxycarbonyl-2(E)-propen-1-yl]-N-(1-phenyleth-1-yl)benzenesulphonylacetamide



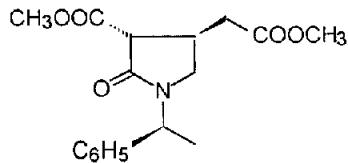
D.e. > 98%  
 $[\alpha]_D -160.7$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3S,4R,1'S

Methyl (3S,4R,1'S)-[3-benzensulphonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



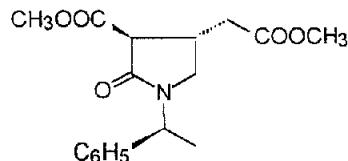
D.e. > 98%  
 $[\alpha]_D -89.3$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3R,4S,1'S

Methyl (3R,4S,1'S)-[3-benzensulphonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



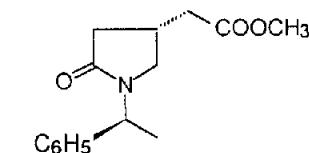
D.e. > 98%  
 $[\alpha]_D -157.2$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3*R*,4*R*,1'*S*

Methyl (3*R*,4*R*,1'*S*)-[3-methoxycarbonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



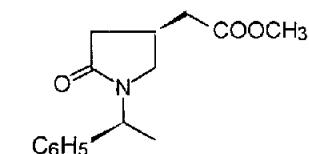
D.e. > 98%  
 $[\alpha]_D -250.1$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 3*S*,4*S*,1'*S*

Methyl (3*S*,4*S*,1'*S*)-[3-methoxycarbonyl-2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



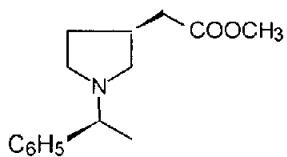
D.e. > 98%  
 $[\alpha]_D -103.8$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 4*R*,1'*S*

Methyl (4*R*,1'S)-[2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



D.e. > 98%  
 $[\alpha]_D -98.6$  (c 1, CHCl<sub>3</sub>)  
 Source of chirality: asymmetric synthesis  
 Absolute configuration: 4*S*,1'*S*

Methyl (4*S*,1'S)-[2-oxo-1-(1'-phenyleth-1'-yl)pyrrolidin-4-yl]acetate



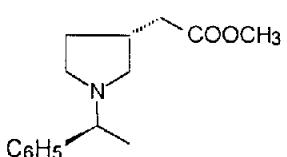
D.e. &gt; 98%

 $[\alpha]_D^{20} -34.2$  (c 1, CH<sub>3</sub>OH)

Source of chirality: asymmetric synthesis

Absolute configuration: 3S,1'S

Methyl (3S,1'S)-[1-(1'-phenyleth-1'-yl)pyrrolidin-3-yl]acetate



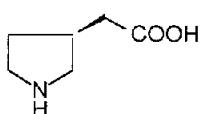
D.e. &gt; 98%

 $[\alpha]_D^{20} -55.3$  (c 1, CHCl<sub>3</sub>)

Source of chirality: asymmetric synthesis

Absolute configuration: 3R,1'S

Methyl (3R,1'S)-[1-(1'-phenyleth-1'-yl)pyrrolidin-3-yl]acetate



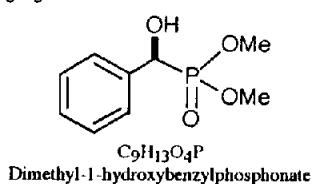
E.e. &gt; 98%

 $[\alpha]_D^{20} 9.2$  (c 1, H<sub>2</sub>O)

Source of chirality: asymmetric synthesis

Absolute configuration: S

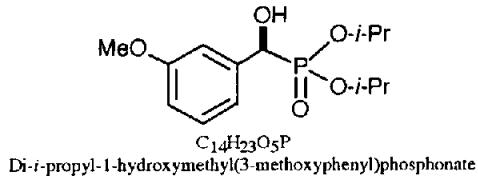
(S)-3-Pyrrolidineacetic acid

E.e. = 34% [by <sup>31</sup>P NMR of the (1S)-(-)-camphanic acid ester] $[\alpha]_D^{20} = -15.7$  (c = 0.8, CHCl<sub>3</sub>)Source of chirality: (-)-Ipc<sub>2</sub>B-Cl

Absolute configuration: S

Chris Meier and Wolfgang H. G. Laux

Tetrahedron: Asymmetry 1996, 7, 89

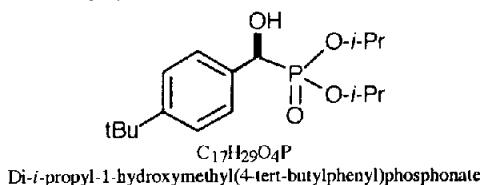


E.e. = 52% [by <sup>31</sup>P NMR of the R-(+)-Mosher ester]  
[α]<sub>D</sub><sup>20</sup> = -9.0 (c = 1.0, CHCl<sub>3</sub>)

Source of chirality: (-)-Ipc<sub>2</sub>B-Cl  
Absolute configuration: S

Chris Meier and Wolfgang H. G. Laux

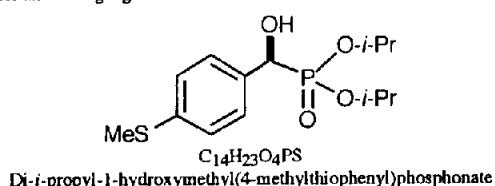
Tetrahedron: Asymmetry 1996, 7, 89



E.e. = 52% [by <sup>31</sup>P NMR of the (1S)-(-)-camphanic acid ester]  
[α]<sub>D</sub><sup>20</sup> = -15.6 (c = 1.0, CHCl<sub>3</sub>)  
Source of chirality: (-)-Ipc<sub>2</sub>B-Cl  
Absolute configuration: S

Chris Meier and Wolfgang H. G. Laux

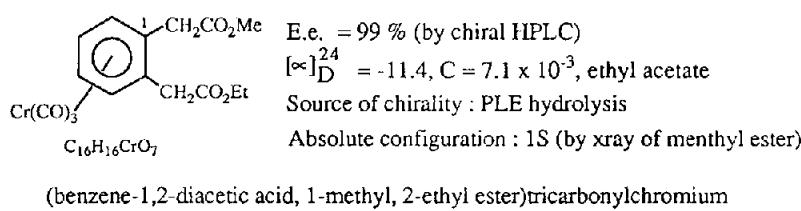
Tetrahedron: Asymmetry 1996, 7, 89

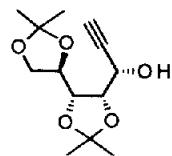


E.e. = 63% [by <sup>31</sup>P NMR of the (1S)-(-)-camphanic acid ester]  
[α]<sub>D</sub><sup>20</sup> = -18.8 (c = 1.1, CHCl<sub>3</sub>)  
Source of chirality: (-)-Ipc<sub>2</sub>B-Cl  
Absolute configuration: S

James A.S. Howell, Michael G. Palin, Gérard Jaouen, Bernard Malezieux, Siden Top, Jean Michel Cense, Jacques Salaün, Patrick McArdle, Desmond Cunningham, Margaret O'Gara.

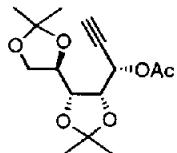
Tetrahedron: Asymmetry 1996, 7, 95



 $[\alpha]_D^{25} -1.7$  (c 1.52, CHCl<sub>3</sub>)

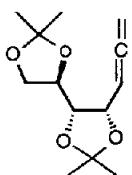
Source of chirality: natural

Absol. configuration: 3S, 4S, 5R, 6R

C<sub>13</sub>H<sub>20</sub>O<sub>5</sub>1, 2-Dideoxy-4,5:6,7-di-*O*-isopropylidene-D-allo-hept-1-yntol. $[\alpha]_D^{25} -5.7$  (c 1.81, CHCl<sub>3</sub>)

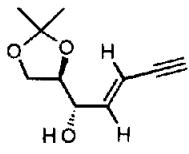
Source of chirality: natural

Absol. configuration: 3S, 4R, 5R, 6R

C<sub>15</sub>H<sub>22</sub>O<sub>6</sub>3-*O*-Acetyl-1, 2-dideoxy-4,5:6,7-di-*O*-isopropylidene-D-allo-hept-1-yntol. $[\alpha]_D^{25} -3.7$  (c 0.2, CHCl<sub>3</sub>)

Source of chirality: natural

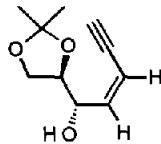
Absol. configuration: 2R, 3S, 4S

C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>(2R, 3S)-1,2:3,4-di-*O*-Isopropylidendioxy-hept-5,6-diene $[\alpha]_D^{25} -8.7$  (c 0.4, CHCl<sub>3</sub>)

Source of chirality: natural

Absol. configuration: 2R, 3S

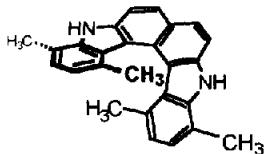
C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>(E) (2R, 3S)-3-Hydroxy-1,2-*O*-isopropylidendioxy-hept-4-en-6-yne



$[\alpha]_D^{25} -10$  (c 0.6, CHCl<sub>3</sub>)  
Source of chirality: natural  
Absol. configuration: 2*R*, 3*S*

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>

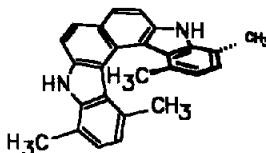
(Z) (2*R*, 3*S*)-3-Hydroxy-1,2-*O*-isopropylidenedioxy-hept-4-en-6-yne



$[\alpha]_{578}^{20} = +588$  (c=0.02, CHCl<sub>3</sub>)  
CD:  $[\Delta\epsilon]_{189} +80$ ,  $[\Delta\epsilon]_{201} 0$ ,  $[\Delta\epsilon]_{215} -159$ ,  $[\Delta\epsilon]_{238} 0$ ,  
 $[\Delta\epsilon]_{246} +25$ ,  $[\Delta\epsilon]_{320} +69$ ,  $[\Delta\epsilon]_{363} 0$ ,  $[\Delta\epsilon]_{373} -8$  (hexane).  
Source of chirality: separation of enantiomers by HPLC  
using a chiral stationary phase (CDMPC)  
Absolute Configuration was assigned by CD calculation

C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>

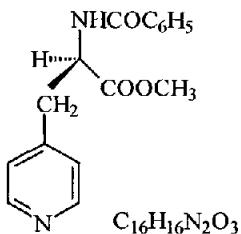
(P)-1,4,11,14-Tetramethyl-5,10-dihydro-carbazolo[3.4-c]carbazole



CD:  $[\Delta\epsilon]_{190} -82$ ,  $[\Delta\epsilon]_{201} 0$ ,  $[\Delta\epsilon]_{213} +160$ ,  $[\Delta\epsilon]_{238} 0$ ,  
 $[\Delta\epsilon]_{246} -32$ ,  $[\Delta\epsilon]_{322} -72$ ,  $[\Delta\epsilon]_{363} 0$ ,  $[\Delta\epsilon]_{370} +10$  (hexane).  
Source of chirality: separation of enantiomers by HPLC  
using a chiral stationary phase (CDMPC)  
Absolute Configuration was assigned by CD calculation

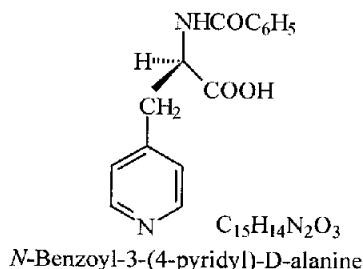
C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>

(M)-1,4,11,14-Tetramethyl-5,10-dihydro-carbazolo[3.4-c]carbazole

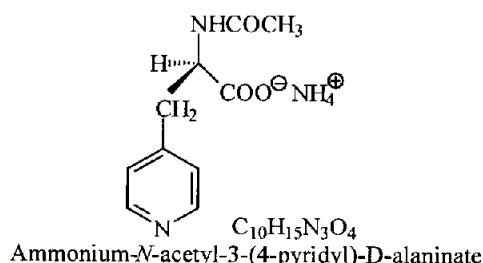


Methyl N-benzoyl-3-(4-pyridyl)-D-alaninate

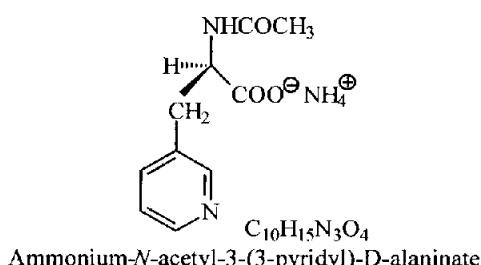
86 % ee (by GLC)  
 $[\alpha]_D^{25} -84.3$  (c 1.0 ,CHCl<sub>3</sub>)  
Source of chirality : enantioselective  
hydrogenation of a precursor.  
Absolute configuration : *R*  
(assigned by catalyst configuration)



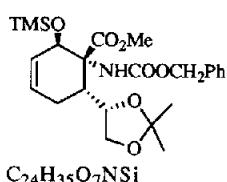
84 % ee (by GLC)  
 $[\alpha]_D^{25}$  98.6 (c 1.0, 1*n* HCl)  
 Source of chirality : enantioselective hydrogenation of a precursor.  
 Absolute configuration : *R*  
 (assigned by catalyst configuration)



> 99 % ee (by GLC)  
 $[\alpha]_D^{25}$  -92.4 (c 1.0, EtOH)  
 Source of chirality : enantioselective hydrogenation of a precursor.  
 Absolute configuration : *R*  
 (assigned by catalyst configuration)

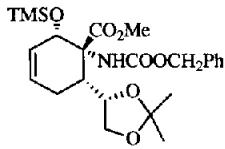


92 % ee (by GLC)  
 $[\alpha]_D^{25}$  -87.1 (c 1.0, EtOH)  
 Source of chirality : enantioselective hydrogenation of a precursor.  
 Absolute configuration : *R*  
 (assigned by catalyst configuration)



$[\alpha]_D = -134.9$  (c = 2.43, CHCl<sub>3</sub>)  
 Source of chirality: D-Mannitol.  
 Absolute configuration 1*S*, 2*R*, 6*R*

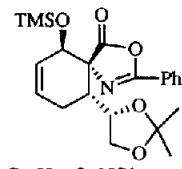
Methyl-1-benzyloxycarbonylamino-6-[(4*S*)-4-(2,2-dimethyl-1,3-dioxolo)-2-trimethylsilyloxy-3-cyclohexen-1-carboxylate.



$[\alpha]_D = -44.3$  ( $c = 1.31$ ,  $\text{CHCl}_3$ )  
Source of chirality: D-Mannitol.  
Absolute configuration 1S, 2S, 6R

C<sub>24</sub>H<sub>35</sub>O<sub>7</sub>NSi

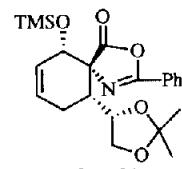
Methyl-1-benzyloxycarbonylamino-6-[(4S)-4-(2,2-dimethyl-1,3-dioxolo)]-2-trimethylsilyloxy-3-cyclohexen-1-carboxylate.



$[\alpha]_D = -120.6$  ( $c = 0.68$ ,  $\text{CHCl}_3$ )  
Source of chirality: D-Mannitol.  
Absolute configuration 1R, 2S, 3R

C<sub>22</sub>H<sub>29</sub>O<sub>5</sub>NSi

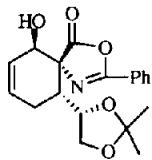
3-[(4S)-4-(2,2-dimethyl-1,3-dioxolo)]-2-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-1-trimethylsilyloxy-5-cyclohexene.



$[\alpha]_D = +153.4$  ( $c = 1.63$ ,  $\text{CHCl}_3$ )  
Source of chirality: D-Mannitol.  
Absolute configuration 1S, 2S, 3R

C<sub>22</sub>H<sub>29</sub>O<sub>5</sub>NSi

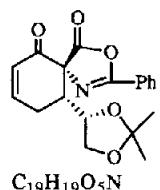
3-[(4S)-4-(2,2-dimethyl-1,3-dioxolo)]-2-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-1-trimethylsilyloxy-5-cyclohexene.



$[\alpha]_D = +194.8$  ( $c = 2.32$ ,  $\text{CHCl}_3$ )  
Source of chirality: D-Mannitol.  
Absolute configuration 1R, 2S, 3R

C<sub>19</sub>H<sub>21</sub>O<sub>5</sub>N

3-[(4S)-4-(2,2-dimethyl-1,3-dioxolo)]-2-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-5-cyclohexen-1-ol.

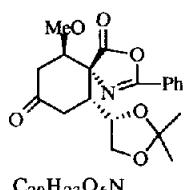


$[\alpha]_D = +228.1$  ( $c = 0.57$ ,  $\text{CHCl}_3$ )

Source of chirality: D-Mannitol.

Absolute configuration 2*S*, 3*R*

3-[(4*S*)-4-(2,2-dimethyl-1,3-dioxolo)]-2-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-5-cyclohexen-1-one.

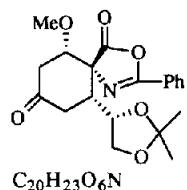


$[\alpha]_D = -46.6$  ( $c = 3.97$ ,  $\text{CHCl}_3$ )

Source of chirality: D-Mannitol.

Absolute configuration 3*R*, 4*S*, 5*R*

5-[(4*S*)-4-(2,2-dimethyl-1,3-dioxolo)]-4-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-3-methoxy-cyclohexen-1-one.

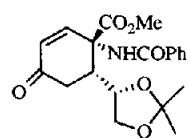


$[\alpha]_D = +78.5$  ( $c = 0.56$ ,  $\text{CHCl}_3$ )

Source of chirality: D-Mannitol.

Absolute configuration 3*R*, 4*S*, 5*R*

5-[(4*S*)-4-(2,2-dimethyl-1,3-dioxolo)]-4-spiro{4'[2'-phenyl-5'(4')-oxazolone]}-3-methoxy-cyclohexen-1-one.



$[\alpha]_D = +74.4$  ( $c = 0.86$ ,  $\text{CHCl}_3$ )

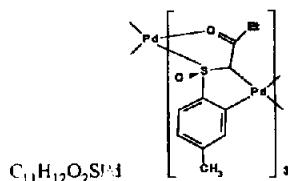
Source of chirality: D-Mannitol.

Absolute configuration 1*S*, 6*R*

Methyl-1-benzamido-6-[(4*S*)-4-(2,2-dimethyl-1,3-dioxolo)]-4-oxo-2-cyclohexen-1-carboxylate.

José L. García Ruano,\* Ana M. González, Ana I. Bárcena, María J. Camazón, Carmen Navarro-Ramínger.\*

Tetrahedron: Asymmetry 1996, 7, 139



D.e.> 98%

$[\alpha]_D = -375.5$  ( $c = 0.098, CHCl_3$ )

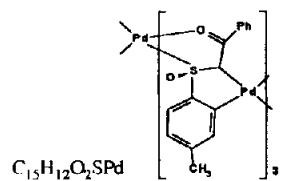
Source of chirality: (-)(S)-menthyl sulfinate

Absolute configuration: (R,R)

(Assigned by chemical and X-ray diffraction evidences)

José L. García Ruano,\* Ana M. González, Ana I. Bárcena, María J. Camazón, Carmen Navarro-Ramínger.\*

Tetrahedron: Asymmetry 1996, 7, 139



D.e.> 98%

$[\alpha]_D = +130.3$  ( $c = 0.112, CHCl_3$ )

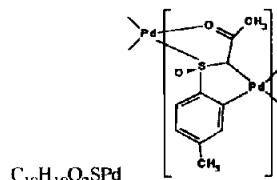
Source of chirality: (-)(S)-menthyl sulfinate

Absolute configuration: (R,R)

(Assigned by chemical and X-ray diffraction evidences)

José L. García Ruano,\* Ana M. González, Ana I. Bárcena, María J. Camazón, Carmen Navarro-Ramínger.\*

Tetrahedron: Asymmetry 1996, 7, 139



D.e.> 98%

$[\alpha]_D = -486.5$  ( $c = 0.2, CHCl_3$ )

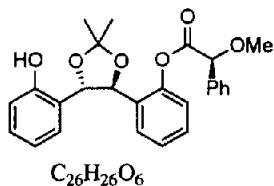
Source of chirality: (-)(S)-menthyl sulfinate

Absolute configuration: (R,R)

(Assigned by chemical and X-ray diffraction evidences)

H. Yamamoto, S. Kobayashi, and S. Kanemasa

Tetrahedron: Asymmetry 1996, 7, 149



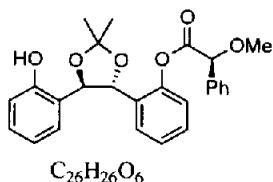
E.e.> 99%

$[\alpha]_D^{24} = 71.2$  ( $c 0.70, CHCl_3$ )

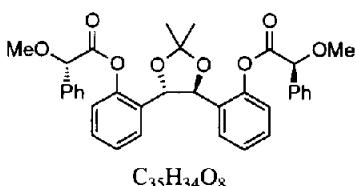
Source of chirality: esterification with (S)-*O*-methylmandelic acid

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

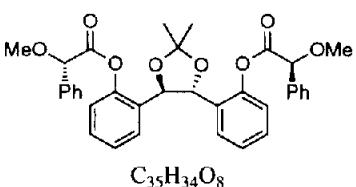
2-[(4*S*,5*S*)-4-(2-Hydroxyphenyl)-2,2-dimethyl-1,3-dioxolan-5-yl]phenyl (*S*)-1-methoxy-1-phenylacetate



E.e. &gt; 99%

 $[\alpha]_D^{24} = 66.3 (c 1.03, CHCl_3)$ Source of chirality: esterification with (*S*)-*O*-methylmandelic acidAbsolute configuration: 4*R*,5*R*,*S*2-[(4*R*,5*R*)-4-(2-Hydroxyphenyl)-2,2-dimethyl-1,3-dioxolan-5-yl]phenyl (*S*)-1-methoxy-1-phenylacetate

E.e. &gt; 99%

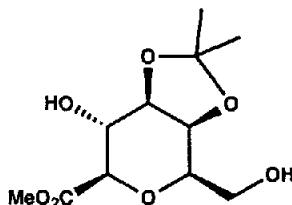
 $[\alpha]_D^{24} = 148.7 (c 0.73, CHCl_3)$ Source of chirality: esterification with (*S*)-*O*-methylmandelic acidAbsolute configuration: 4*S*,5*S*,*S*,*S*2,2'-(4*S*,5*S*)-2,2-dimethyl-1,3-dioxolan-4,5-diyl]phenyl bis[(*S*)-1-methoxy-1-phenylacetate]

E.e. &gt; 99%

 $[\alpha]_D^{24} = 77.3 (c 0.78, CHCl_3)$ Source of chirality: esterification with (*S*)-*O*-methylmandelic acidAbsolute configuration: 4*R*,5*R*,*S*,*S*2,2'-(4*R*,5*R*)-2,2-dimethyl-1,3-dioxolan-4,5-diyl]phenyl bis[(*S*)-1-methoxy-1-phenylacetate]

E.e. &gt; 99%

 $[\alpha]_D^{24} = 37.6 (c 0.29, CHCl_3)$ Source of chirality: resolution using (*S*)-*O*-methylmandelic acidAbsolute configuration: 4*R*,5*R*[(4*S*,4*S*)-isomer is also available](4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane



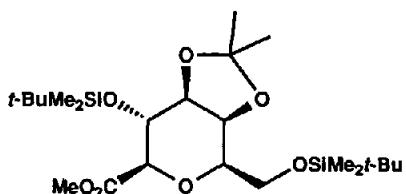
E.e. = 100%

$[\alpha]_D^{25} = +32.4$  (*c*, 1.0 in acetone)

methyl 2,6-anhydro-4,5-O-isopropylidene-D-glycero-L-manno-heptonate

C<sub>9</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>

Source of chirality: D-galactose as starting material



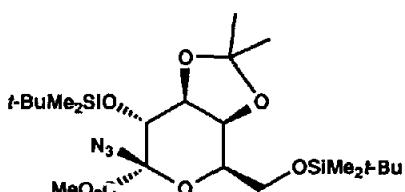
E.e. = 100%

$[\alpha]_D^{22} = +13.8$  (*c*, 1.0 in CHCl<sub>3</sub>)

methyl 2,6-anhydro-3,7-di-O-tert-butyldimethylsilyl-4,5-O-isopropylidene-D-glycero-L-manno-heptonate

C<sub>23</sub>H<sub>46</sub>O<sub>7</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material



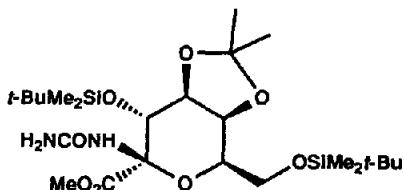
E.e. = 100%

$[\alpha]_D^{22} = +3.6$  (*c*, 1.0 in CHCl<sub>3</sub>)

methyl 2-azido-3,7-di-O-tert-butyldimethylsilyl-2-deoxy-4,5-O-isopropylidene-beta-D-galacto-2-heptulopyranonate

C<sub>23</sub>H<sub>45</sub>N<sub>3</sub>O<sub>7</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material



E.e. = 100%

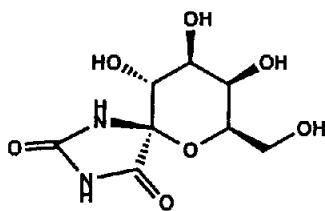
$[\alpha]_D^{22} = -46.9$  (*c*, 1.0 in MeOH)

methyl 3,7-di-O-tert-butyldimethylsilyl-2-deoxy-4,5-O-isopropylidene-2-ureido-beta-D-galacto-2-heptulopyranonate

C<sub>24</sub>H<sub>48</sub>N<sub>2</sub>O<sub>8</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%



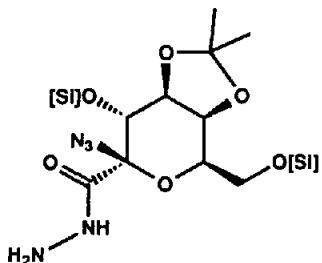
$[\alpha]_D^{22} = +84.4$  (*c*, 1.0 in MeOH)

(*2R,3R,4S,5R,6S*) 3,4,5-trihydroxy-2-hydroxymethyl-7,9-diaza-oxaspiro-[4.5]decane-8,10-dione

C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>7</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%



$[\alpha]_D^{22} = -27.3$  (*c*, 1.0 in CHCl<sub>3</sub>)

2-azido-3,7-di-O-*tert*-butyldimethylsilyl-2-deoxy-4,5-O-isopropylidene- $\beta$ -D-galacto-2-heptulopyranosonic hydrazide

C<sub>22</sub>H<sub>45</sub>N<sub>5</sub>O<sub>6</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%

$[\alpha]_D^{25} = +31.7$  (*c*, 1.0 in CHCl<sub>3</sub>)

2-(1-Azido-2,6-di-O-*tert*-butyldimethylsilyl)-3,4-O-isopropylidene- $\alpha$ -D-galactopyranosyl)-4,5-dihydro-1,3,4-oxadiazol-5-one

C<sub>22</sub>H<sub>45</sub>N<sub>5</sub>O<sub>6</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%

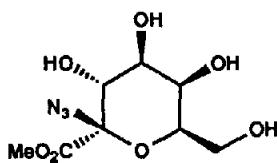
$[\alpha]_D^{26} = +98.2$  (*c*, 1.0 in MeOH)

2-(1-Azido- $\alpha$ -D-galactopyranosyl)-4,5-dihydro-1,3,4-oxadiazol-5-one

C<sub>8</sub>H<sub>11</sub>N<sub>5</sub>O<sub>7</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%



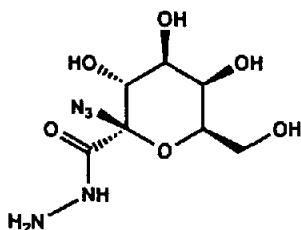
$[\alpha]_D^{24} = +75.7$  (*c*, 1.0 in MeOH)

methyl 2-azido-2-deoxy- $\beta$ -D-galacto-2-heptulopyranosonate

C<sub>8</sub>H<sub>13</sub>N<sub>3</sub>O<sub>7</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%



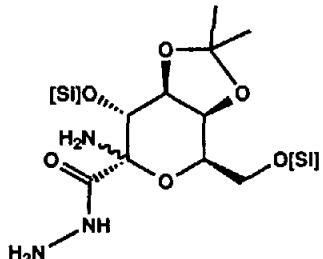
$[\alpha]_D^{24} = +70.0$  (*c*, 1.0 in MeOH)

2-amido-2-deoxy- $\beta$ -D-galacto-2-heptulopyranosonic hydrazide

C<sub>7</sub>H<sub>13</sub>N<sub>5</sub>O<sub>6</sub>

Source of chirality: D-galactose as starting material

E.e. = 100%



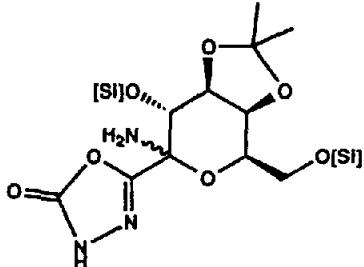
$[\alpha]_D^{22} = -45.6$  (*c*, 1.0 in CHCl<sub>3</sub>)

2-amino-3,7-di-O-tert-butyldimethylsilyl-2-deoxy-4,5-O-isopropylidene-D-galacto-2-heptulopyranosonic hydrazide

C<sub>22</sub>H<sub>47</sub>N<sub>3</sub>O<sub>6</sub>Si<sub>2</sub>

Source of chirality: D-galactose as starting material

E.e. ≈ 100%

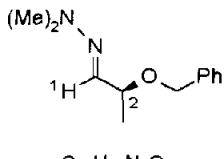


$[\alpha]_D^{22} = +31.5$  (*c*, 1.0 in CHCl<sub>3</sub>)

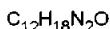
2-(1-Amino-2,6-di-O-tert-butyldimethylsilyl-3,4-O-isopropylidene-alpha-D-galactopyranosyl)-4,5-dihydro-1,3,4-oxadiazol-5-one

C<sub>23</sub>H<sub>45</sub>N<sub>3</sub>O<sub>7</sub>Si<sub>2</sub>

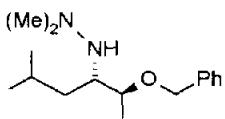
Source of chirality: D-galactose as starting material



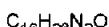
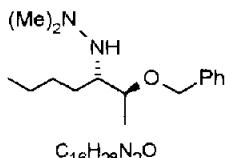
From S-Ethyl lactate

*E*-configuration from *n*Oe diff. experiment $J(H1-H2) = 7$  Hz $[\alpha]_D^{25} = -89$  ( $c = 2.17$ ,  $CCl_4$ )

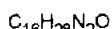
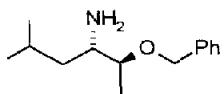
S-2-Benzyl-1-(dimethylaminomethyl)-2-propanol



From S-Ethyl lactate and NOESY of the corresponding oxazolidone

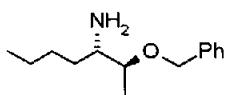
 $[\alpha]_D^{25} = -51$  ( $c = 2.17$ ,  $CHCl_3$ )1*S*,2*S*-N,N-dimethyl-N-[1-isobutyl-2-benzyl] propylhydrazine

From S-Ethyl lactate and NOESY of the corresponding oxazolidone

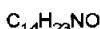
 $[\alpha]_D^{25} = +5$  ( $c = 2.1$ ,  $CHCl_3$ )1*S*,2*S*-N,N-dimethyl-N-[1-butyl-2-benzyl] propylhydrazine

From S-Ethyl lactate and NOESY of the corresponding oxazolidone

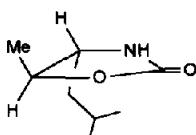
 $[\alpha]_D^{25} = +17$  ( $c = 2.16$ ,  $CHCl_3$ )1*S*,2*S*-1-isobutyl-2-benzyl-1-propylamine



From S-Ethyl lactate and NOESY of the corresponding oxazolidone  
 $[\alpha]_D^{25} = +26$  ( $c = 2.08$ ,  $\text{CHCl}_3$ )



1S,2S-1-butyl-2-benzyloxy propylamine

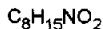


From S-Ethyl lactate

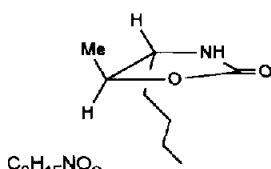
Trans from NOESY

$J(H4-H5) = 6$  Hz

$[\alpha]_D^{25} = -30$  ( $c = 1.34$ ,  $\text{CHCl}_3$ )



4S,5S-4-isobutyl-5-methyl-oxazolidin-2-one

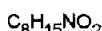


From S-Ethyl lactate

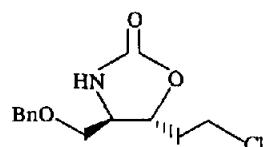
Trans from NOESY

$J(H4-H5) = 6$  Hz

$[\alpha]_D^{25} \approx -28$  ( $c = 1.52$ ,  $\text{CHCl}_3$ )



4S,5S-4-butyl-5-methyl-oxazolidin-2-one



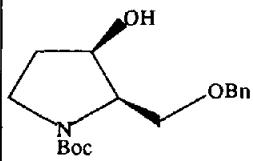
$[\alpha]_D^{25} + 67.5$  ( $c = 0.25$ ,  $\text{CHCl}_3$ )

Source of chirality : L - serine

Absolute configuration : 4R,5R



(4R,5R)-4-(Benzyl)oxy-5-(2-chloroethyl)-2-methyl-oxazolidin-2-one



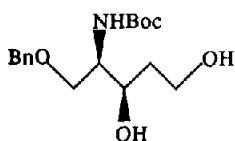
$[\alpha]_D^{25} - 20.0$  (c 1.88 MeOH)

Source of chirality : L - serine

Absolute configuration : 2R,3R

C<sub>17</sub>H<sub>25</sub>NO<sub>4</sub>

(2R,3R)-1-(tert-Butoxycarbonyl)-2-(benzyloxymethyl)-3-hydroxy-pyrrolidine



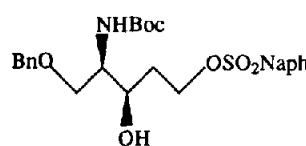
$[\alpha]_D^{25} + 27.8$  (c 0.13 MeOH)

Source of chirality : L - serine

Absolute configuration : 2R,3R

C<sub>17</sub>H<sub>25</sub>NO<sub>5</sub>

(2R,3R)-1-Benzyl-2-(tert-butoxycarbonyl)amino-3,5-pentandiol



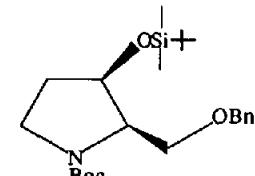
$[\alpha]_D^{25} + 14.4$  (c 0.16 MeOH)

Source of chirality : L - serine

Absolute configuration : 2R,3R

C<sub>17</sub>H<sub>25</sub>NO<sub>5</sub>

(2R,3R)-1-Benzyl-2-(tert-butoxycarbonyl)amino-5-((beta-naphthyl)sulphonyloxy)-3-pentanol



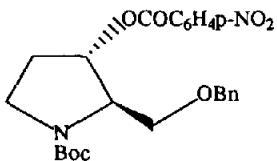
$[\alpha]_D^{25} - 20.0$  (c 0.28 CHCl<sub>3</sub>)

Source of chirality : L - serine

Absolute configuration : 2R,3R

C<sub>23</sub>H<sub>39</sub>SiNO<sub>4</sub>

(2R,3R)-1-(tert-Butoxycarbonyl)-2-(benzyloxymethyl)-3-(tert-butyldimethylsilyloxy)-pyrrolidine



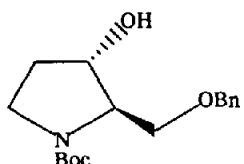
$[\alpha]_D^{25} + 13.52$  (c 0.15 CHCl<sub>3</sub>)

Source of chirality : L - serine

Absolute configuration : 2R,3S

C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>

(2R,3S)-1-(tert-Butoxycarbonyl)-2-(benzyloxymethyl)-3-(4-nitrobenzoyloxy)-pyrrolidine



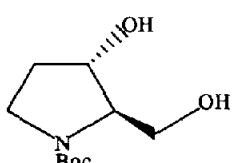
$[\alpha]_D^{25} - 33.4$  (c 0.18 MeOH)

Source of chirality : L - serine

Absolute configuration : 2R,3S

C<sub>17</sub>H<sub>25</sub>NO<sub>4</sub>

(2R,3S)-1-(tert-Butoxycarbonyl)-2-(benzyloxymethyl)-3-hydroxy-pyrrolidine



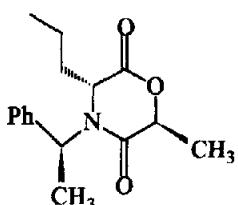
$[\alpha]_D^{25} - 21.5$  (c 0.66 MeOH)

Source of chirality : L - serine

Absolute configuration : 2R,3S

C<sub>10</sub>H<sub>19</sub>NO<sub>4</sub>

(2R,3S)-1-(tert-Butoxycarbonyl)-2-hydroxymethyl-3-hydroxy-pyrrolidine



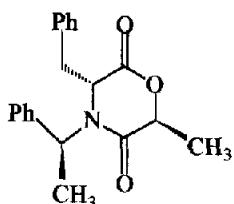
$[\alpha]_D^{25} = -254.7$  (c=0.55, chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3R,6S assigned by <sup>1</sup>H-NMR

C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>

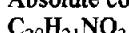
(3R,6S)-4-N-((S)-1-phenethyl)-3-propyl-6-methyl-1,4-morpholin-2,5-dione



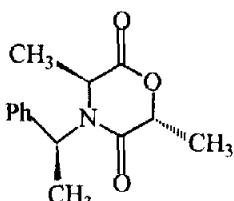
$[\alpha]_D^{25} = -19.6$  ( $c=2.13$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3R,6S assigned by  $^1\text{H-NMR}$



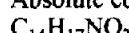
(3R,6S)-4-N-((S)-1-phenethyl)-3-benzyl-6-methyl-1,4-morpholin-2,5-dione



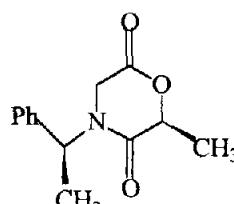
$[\alpha]_D^{25} = 42.2$  ( $c=0.64$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3S,6R assigned by  $^1\text{H-NMR}$



(3S,6R)-4-N-((S)-1-phenethyl)-3,6-dimethyl-1,4-morpholin-2,5-dione

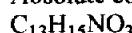


mp 118-9°C

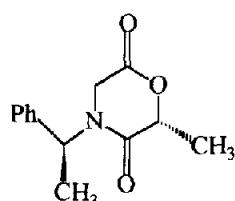
$[\alpha]_D^{25} = -199.4$  ( $c=2.05$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 6S assigned by  $^1\text{H-NMR}$



(6S)-4-N-((S)-1-phenethyl)-6-methyl-1,4-morpholin-2,5-dione

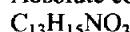


mp 98-9°C

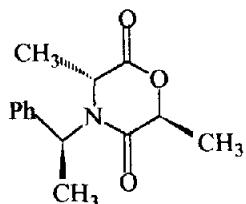
$[\alpha]_D^{25} = -106.8$  ( $c=2.25$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 6S assigned by  $^1\text{H-NMR}$



(6R)-4-N-((S)-1-phenethyl)-6-methyl-1,4-morpholin-2,5-dione



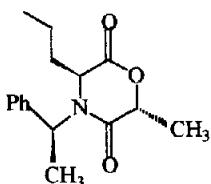
$[\alpha]_D^{25} = -290.7$  ( $c=1.08$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3R,6S assigned by  $^1\text{H-NMR}$

$\text{C}_{14}\text{H}_{17}\text{NO}_3$

(3R,6S)-4-N-((S)-1-phenethyl)-3,6-dimethyl-1,4-morpholin-2,5-dione



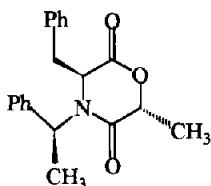
$[\alpha]_D^{25} = 49.4$  ( $c=0.84$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3S,6R assigned by  $^1\text{H-NMR}$

$\text{C}_{16}\text{H}_{21}\text{NO}_3$

(3S,6R)-4-N-((S)-1-phenethyl)-3-propyl-6-methyl-1,4-morpholin-2,5-dione



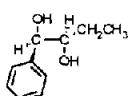
$[\alpha]_D^{25} = 54.1$  ( $c=2.27$ , chloroform)

Source of chirality : from (S)-phenethylamine

Absolute configuration : 3S,6R assigned by  $^1\text{H-NMR}$

$\text{C}_{20}\text{H}_{21}\text{NO}_3$

(3S,6R)-4-N-((S)-1-phenethyl)-3-benzyl-6-methyl-1,4-morpholin-2,5-dione



$\text{C}_{10}\text{H}_{14}\text{O}_2$   
threo-1-Phenyl-1,2-butanediol

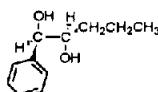
E.e. > 90% (by HPLC on bis(MTPA) derivative)

$[\alpha]_D = -28.5$  ( $c = 0.01$ ,  $\text{CHCl}_3$ )

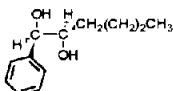
Source of chirality: enzymatic resolution

Absolute Configuration : 1R,2R (assigned by comparison of  $[\alpha]_D$  with the literature value.)

G. Bellucci, C. Chiappe, A. Cordoni

E.e. > 90% (by HPLC on bis(MTPA) derivative)  
[ $\alpha$ ]D = -23.5 (c = 0.01, CHCl3)C11H16O2  
*threo*-1-Phenyl-1,2-pentanediolSource of chirality: enzymatic resolution  
Absolute Configuration : 1R,2R (assigned by CD correlation)

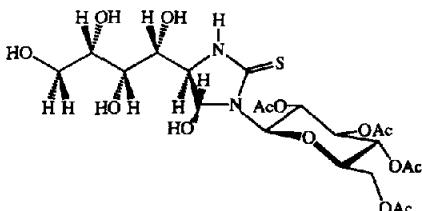
G. Bellucci, C. Chiappe, A. Cordoni

E.e. > 90% (by HPLC on bis(MTPA) derivative)  
[ $\alpha$ ]D = -21.5 (c = 0.01, CHCl3)C12H18O2  
*threo*-1-Phenyl-1,2-hexanediolSource of chirality: enzymatic resolution  
Absolute Configuration : 1R,2R (assigned by CD correlation)

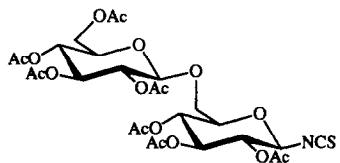
G. Bellucci, C. Chiappe, A. Cordoni

E.e. > 90% (by HPLC on bis(MTPA) derivative)  
[ $\alpha$ ]D = -14.7 (c = 0.01, CHCl3)C14H22O2  
*threo*-1-Phenyl-1,2-octanediolSource of chirality: enzymatic resolution  
Absolute Configuration : 1R,2R (assigned by CD correlation)

José Fuentes, José L. Molina, David Olano, and M. Angeles Pradera

E. e = 100%  
[ $\alpha$ ]D<sup>22</sup> = +60 (c 1.0, dichloromethane)  
Source of chirality: D-glucosamine and 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate as starting materials.

(4R, 5R)-5-Hydroxy-1-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)-4-(D-arabinotetitol-1-yl)-imidazolidine-2-thione

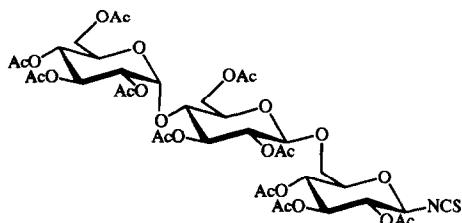


E. e = 100%

 $[\alpha]_D^{24} = +3$  (c 1.0, dichloromethane)

Source of chirality: D-glucose as starting materials.

2,3,4-Tri-O-acetyl-6-O-(2',3',4',6'-tetra-O-acetyl-beta-D-glucopyranosyl)-beta-D-glucopyranosyl isothiocyanate

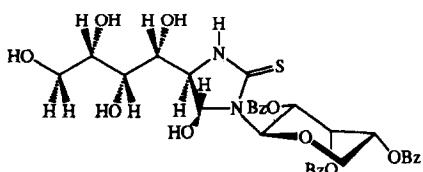


E. e = 100%

 $[\alpha]_D^{25} = +62$  (c 0.17, dichloromethane)

Source of chirality: D-glucose and maltose as starting materials.

2,3,4-Tri-O-acetyl-6-O-[2',3',6'-tri-O-acetyl-4'-O-(2'',3'',4'',6''-tetra-O-acetyl-alpha-D-glucopyranosyl)-beta-D-glucopyranosyl]-beta-D-glucopyranosyl isothiocyanate

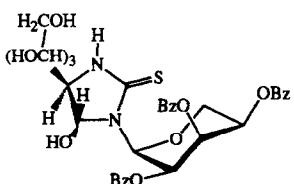


E. e = 100%

 $[\alpha]_D^{22} = +6$  (c 1.0, dichloromethane)

Source of chirality: D-glucosamine and 2,3,4-tri-O-benzoyl-beta-D-ribopyranosyl isothiocyanate as starting materials.

(4R, 5R)-5-Hydroxy-4-(D-arabinotetitol-1-yl)-1-(2',3',4"-tri-O-benzoyl-beta-D-ribopyranosyl) imidazolidine-2-thione

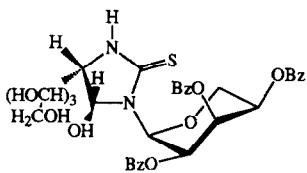


E. e = 100%

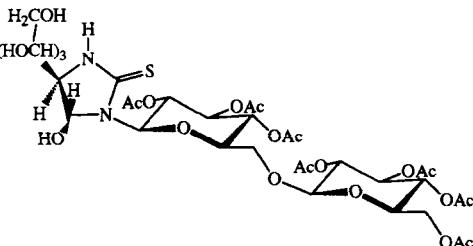
 $[\alpha]_D^{24} = -49$  (c 0.55, dichloromethane)

Source of chirality: D-glucosamine and 2,3,4-tri-O-benzoyl-alpha-D-ribopyranosyl isothiocyanate as starting materials.

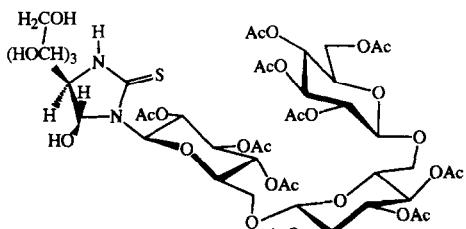
(4R, 5R)-5-Hydroxy-4-(D-arabinotetitol-1-yl)-1-(2',3',4"-tri-O-benzoyl-alpha-D-ribopyranosyl) imidazolidine-2-thione



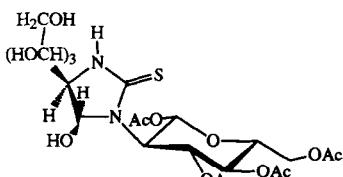
E. e = 100%  
 $[\alpha]_D^{24} = -54$  (*c* 0.7, dichloromethane)  
 Source of chirality: D-glucosamine and 2,3,4-tri-*O*-benzoyl- $\alpha$ -D-ribopyranosyl isothiocyanate as starting materials.

(4*R*, 5*S*)-5-Hydroxy-4-(D-arabinotetritol-1-yl)-1-(2',3',4"-tri-*O*-benzoyl- $\alpha$ -D-ribopyranosyl) imidazolidine-2-thione

E. e = 100%  
 $[\alpha]_D^{26} +19$  (*c* 1.0, dichloromethane)  
 Source of chirality: D-glucosamine and 2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6"-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl isothiocyanate as starting materials.

(4*R*, 5*R*)-5-Hydroxy-1-[2',3',4'-tri-*O*-acetyl-6-*O*-(2",3",4",6"-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl]-4-(D-arabinotetritol-1-yl) imidazolidine-2-thione

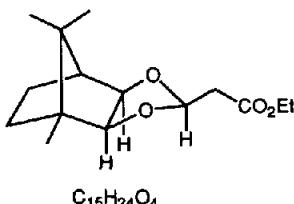
E. e = 100%  
 $[\alpha]_D^{25} +158$  (*c* 0.24, dichloromethane)  
 Source of chirality: D-glucosamine and 2,3,4-tri-*O*-acetyl-6-*O*-(2',3',6"-tri-*O*-acetyl-4'-*O*-(2",3",4",6"-tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl isothiocyanate as starting materials.

(4*R*, 5*R*)-5-Hydroxy-1-[2',3',4'-tri-*O*-acetyl-6-*O*-(2",3",4",6"-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl]-4-(D-arabinotetritol-1-yl) imidazolidine-2-thione

D. e = 66%  
 $[\alpha]_D^{25} = +35$  (*c* 1.2, dichloromethane)  
 Source of chirality: D-glucosamine and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-isothiocyanato- $\beta$ -D-glucopyranose as starting materials.

(4*R*, 5*R* and 5*S*)-5-Hydroxy-1-(1',3',4',6"-tetra-*O*-acetyl-2-deoxy- $\beta$ -D-glucopyranos-2-yl)-4-(D-arabinotetritol-1-yl) imidazolidine-2-thione

Mercedes Caballero, María García-Valverde, Rafael Pedrosa and Martina Vicente



B.p. 173°C/ 0.9 mmHg

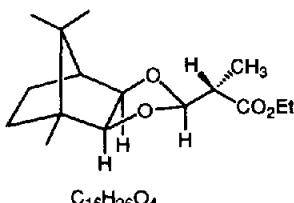
D.e. >96% (by  $^1H$ -NMR) $[\alpha]_D^{23} = -13.3$  ( $c = 1, CHCl_3$ )

Source of chirality: (-)-(1R,2S,3S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-diol

Absolute configuration: 1R, 2S, 4R, 6S, 7S

(1R, 2S, 4R, 6S, 7S)-4-(1'-Ethoxycarbonylmethylen)-1,10,10-trimethyl-3,5-dioxa-tricyclo[3.2.1.0^2.6]decane

Mercedes Caballero, María García-Valverde, Rafael Pedrosa and Martina Vicente



B.p. 183°C/ 0.9 mmHg

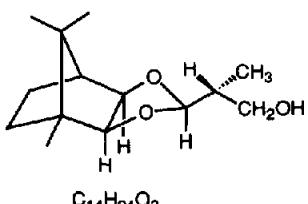
D.e. 31% (by G.C. and  $^1H$ -NMR) $[\alpha]_D^{23} = -0.4$  ( $c = 5.8, CHCl_3$ )

Source of chirality: Asymmetric synthesis

Absolute configuration: 1R, 1'S, 2S, 4R, 6S, 7S

(1R, 1'S, 2S, 4R, 6S, 7S)-4-(1'-Ethoxycarbonylethyl)-1,10,10-trimethyl-3,5-dioxa-tricyclo[3.2.1.0^2.6]decane

Mercedes Caballero, María García-Valverde, Rafael Pedrosa and Martina Vicente



B.p. 173°C/ 0.9 mmHg

D.e. 31 %

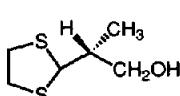
 $[\alpha]_D^{23} = -13.3$  ( $c = 1, CHCl_3$ )

Source of chirality: Asymmetric synthesis

Absolute configuration: 1R, 1'R, 2S, 4R, 6S, 7S

(1R, 1'R, 2S, 4R, 6S, 7S)-4-(2'-Hydroxy-1'-methylethylen)-1,10,10-trimethyl-3,5-dioxa-tricyclo[3.2.1.0^2.6]decane

Mercedes Caballero, María García-Valverde, Rafael Pedrosa and Martina Vicente

 $C_6H_{12}OS_2$ 

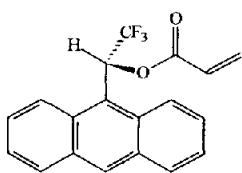
E.e. 31%

 $[\alpha]_D^{23} = -5.2$  ( $c = 1, EtOH$ )

Source of chirality: Asymmetric synthesis

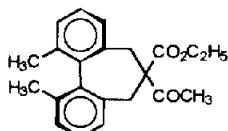
Absolute configuration: 1'R

(1'R)-2-(2'-Hydroxy-1'-methylethylen)-1,3-ditiolane



$[\alpha]^{25}_D = +18.7$  ( $c = 0.75$ ,  $\text{CHCl}_3$ ).  
Source of chirality: (R)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol  
Absolute configuration: *IR*

$\text{C}_{19}\text{H}_{13}\text{F}_3\text{O}_2$   
[1-(9-anthryl)-2,2,2-trifluoroethoxy]acrylate



$\text{C}_{22}\text{H}_{24}\text{O}_3$   
(R)-6-Acetyl-1,11-dimethyl-6-ethoxycarbonyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene

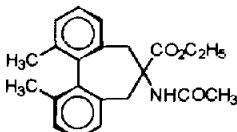
M.p. 79-81°C (hexane)

E.e. ~100%

$[\alpha]_D^{20} = +87.6$  ( $c 0.5$ , acetone)

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound)



$\text{C}_{22}\text{H}_{25}\text{NO}_3$   
(R)-6-Acetylamino-1,11-dimethyl-6-ethoxycarbonyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene

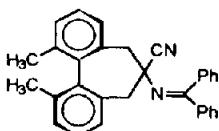
M.p. 194-196°C (toluene)

E.e. ~100%

$[\alpha]_D^{20} = +165.4$  ( $c 0.5$ , acetone)

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound)



$\text{C}_{34}\text{H}_{26}\text{N}_2$   
(R)-6-(N-Diphenylmethylene)amino-6-cyano-1,11-dimethyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene

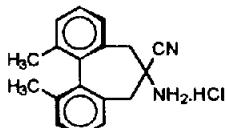
M.p. 161-164°C (EtOH)

E.e. ~100%

$[\alpha]_D^{20} = +101.7$  ( $c 0.5$ ,  $\text{CHCl}_3$ )

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound)

 $C_{18}H_{19}CN_2$ 

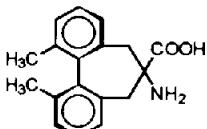
(R)-6-Amino-6-cyano-1,11-dimethyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene hydrochloride

M.p. 173-175°C (aq. EtOH)

E.e.~100%

 $[\alpha]D^{20} = +41.4$  (c 0.5, CHCl<sub>3</sub>)

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound) $C_{18}H_{19}NO_2$ 

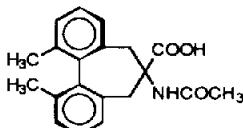
(R)-6-Amino-1,11-dimethyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene-6-carboxylic acid

M.p. 225-227°C /dec. / (aq. EtOH)

E.e.~100%

 $[\alpha]D^{20} = -23.3$ ,  $[\alpha]578 = -23.7$ ,  $[\alpha]546 = -22.9$ ,  $[\alpha]436 = +8.1$ ,  
 $[\alpha]365 = +147.0$  (c 0.5, MeOH)CD:  $\Delta\varepsilon 195 = -85.3$ ,  $\Delta\varepsilon 205 = -57.2$ ,  $\Delta\varepsilon 221 = +23.5$ ,  $\Delta\varepsilon 243 = +25.5$ ,  
 $\Delta\varepsilon 271 = -2.2$  (c 0.004, MeOH).

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

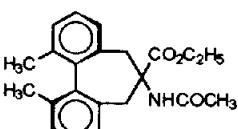
Absolute configuration: R  
(assigned by synthesis from known compound) $C_{20}H_{21}NO_3$ 

(R)-6-N-Acetyl-amino-1,11-dimethyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene-6-carboxylic acid

M.p. 241-243°C

E.e.~100%

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound) $C_{22}H_{24}O_3$ 

(R)-6-Acetyl-amino-1,11-dimethyl-6-ethoxycarbonyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene

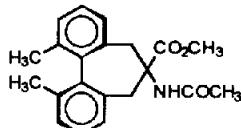
M.p. 194-196°C (toluene)

E.e.~100% (by HPLC)

 $[\alpha]D^{20} = +165.4$  (c 0.5, acetone)

Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound)

 $C_{22}H_{26}NO_3$ 

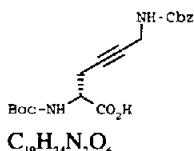
(R)-6-Acetylaminol-1,11-dimethyl-6-methoxycarbonyl-6,7-dihydro-5H-dibenzo[a,c]cycloheptene

M.p. 202-204°C

E.e.~100% (by HPLC)

[ $\alpha$ ]D<sup>20</sup> = +168.7 (c 0.5, acetone)

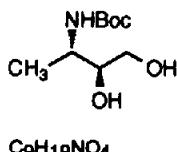
Source of chirality: (R)-2,2'-bis(bromomethyl)-6,6'-dimethylbiphenyl

Absolute configuration: R  
(assigned by synthesis from known compound) $C_{16}H_{24}N_2O_6$ 

(2R)-6-Benzylloxycarbonylamino-2-tert-butoxycarbonyl-amino-6-ynoic acid

E.e. >97% [by reverse phase HPLC of the 2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl thiourea derivative after hydrolysis of the protecting groups][ $\alpha$ ]D<sup>25</sup> = -15.0 (c 0.3, MeOH)

Source of chirality: induction from natural asymmetric center.

 $C_9H_{19}NO_4$ 

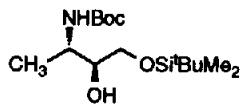
(2S, 3S)-3-tert-butoxycarbonylamino-1,2-butanediol

E. e.=90% [by Mosher diester of a precursor]

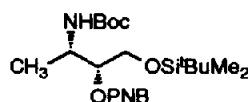
[ $\alpha$ ]D<sup>20</sup>=-5.8 (c=1, CHCl<sub>3</sub>)

Source of chirality: Sharpless asym. epoxidation

Absolute configuration: 2S, 3S

 $C_{15}H_{33}NO_4Si$ 

(2S, 3S)-1-tert-butyldimethylsilyloxy-3-tert-butoxycarbonylamino-2-butanol

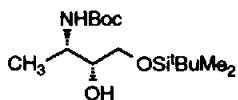


E. e.=90% [by Mosher diester of a precursor]  
 $[\alpha]_D^{20}=0.84$  (c=1.7, CHCl<sub>3</sub>)

Source of chirality: Sharpless asym. epoxidation  
 Absolute configuration: 2*R*, 3*S*

C<sub>22</sub>H<sub>36</sub>N<sub>2</sub>O<sub>7</sub>Si

(2*R*, 3*S*)-1-tert-butyldimethylsilyloxy-3-tert-butoxycarbonylamino-2-*p*-nitrophenylcarbonyloxybutane

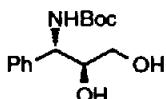


E. e.=90% [by Mosher diester of a precursor ]  
 $[\alpha]_D^{20}=-9.6$  (c=1.5, CHCl<sub>3</sub>)

Source of chirality: Sharpless asym. epoxidation  
 Absolute configuration: 2*R*, 3*S*

C<sub>15</sub>H<sub>33</sub>NO<sub>4</sub>Si

(2*R*, 3*S*)-1-tert-butyldimethylsilyloxy-3-tert-butoxycarbonylamino-2-butanol

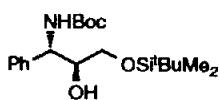


E. e.=100% [by HPLC of a precursor ]  
 $[\alpha]_D^{20}=52.7$  (c=1, CHCl<sub>3</sub>)

Source of chirality: Sharpless asym. epoxidation  
 Absolute configuration: 2*S*, 3*S*

C<sub>14</sub>H<sub>21</sub>NO<sub>4</sub>

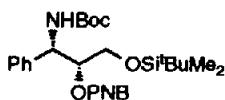
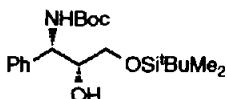
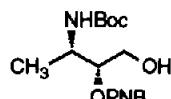
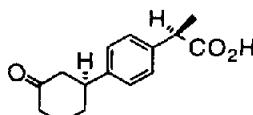
(2*S*, 3*S*)-3-tert-butoxycarbonylamino-3-phenyl-1,2-propanediol



E. e.=100% [by HPLC of a precursor ]  
 $[\alpha]_D^{20}=25.9$  (c=0.21, CHCl<sub>3</sub>)

Source of chirality: Sharpless asym. epoxidation  
 Absolute configuration: 2*S*, 3*S*

(2*S*,3*S*)-1-tert-butyldimethylsilyloxy-3-tert-butoxycarbonylamino-3-phenyl-2-propanol

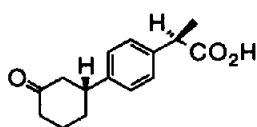
 $C_{27}H_{38}N_2O_7Si$ E. e.=100% [by HPLC of a precursor]  
 $[\alpha]_D^{20}=37.4$  ( $c=1.5$ ,  $CHCl_3$ )Source of chirality: Sharpless asym. epoxidation  
Absolute configuration: 2*R*, 3*S*(2*R*,3*S*)-1-*tert*-butylidimethylsilyloxy-3-*tert*-butoxycarbonylamino-2-*p*-nitrophenylcarbonyloxy-3-phenylpropane $C_{20}H_{35}NO_4Si$ E. e.=100% [by HPLC of a precursor]  
 $[\alpha]_D^{20}=2.65$  ( $c=1.1$ ,  $CHCl_3$ )Source of chirality: Sharpless asym. epoxidation  
Absolute configuration: 2*R*, 3*S*(2*R*,3*S*)-1-*tert*-butylidimethylsilyloxy-3-*tert*-butoxycarbonylamino-3-phenyl-2-propanol $C_{16}H_{22}N_2O_7$ E. e.=90% [by Mosher diester of a precursor]  
 $[\alpha]_D^{20}=-12.4$  ( $c=1.1$ ,  $CHCl_3$ )Source of chirality: Sharpless asym. epoxidation  
Absolute configuration: 2*R*, 3*S*(2*R*,3*S*)-3-*tert*-butoxycarbonylamino-2-*p*-nitrophenylcarbonyloxy-1-butanol $C_{15}H_{18}O_3$   
2-(4'-(3''-Oxocyclohexyl)phenyl) propanoic acid. $[\alpha]_D^{20}=-53$  ( $c=1.75$ , EtOH)

Source of chirality: asymmetric synthesis

Absolute configuration 2*R*, 1*S*

D. P. G. Harmon, P. J. Hayball, R. A. Massy-Westropp,  
J. L. Newton and J. G. Tamblyn.

Tetrahedron: Asymmetry 1996, 7, 263



$C_{15}H_{18}O_3$   
2-(4'-(3''-Oxocyclohexyl)phenyl) propanoic acid.

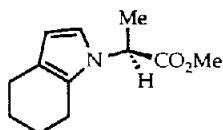
$[\alpha]_D^{20} = -48$  (c=0.51, EtOH)

Source of chirality: asymmetric synthesis

Absolute configuration 2*R*, 1''*R*

R. Grigg and G. Yoganathan

Tetrahedron: Asymmetry 1996, 7, 273



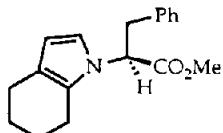
$C_{12}H_{17}O_2N$

Methyl (S)-2-(N-4,5,6,7-tetrahydroindolyl)propionate

$[\alpha]_D^{20} = -51.47$  (c 1.5, CHCl<sub>3</sub>)  
ee 92.2% (chiral HPLC)

R. Grigg and G. Yoganathan

Tetrahedron: Asymmetry 1996, 7, 273



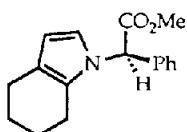
$C_{18}H_{21}O_2N$

Methyl (S)-2-(N-4,5,6,7-tetrahydroindolyl)-3-phenylpropionate

$[\alpha]_D^{20} = -61.27$  (c 1.58, CHCl<sub>3</sub>)  
ee 99% (chiral HPLC)

R. Grigg and G. Yoganathan

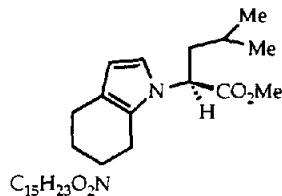
Tetrahedron: Asymmetry 1996, 7, 273



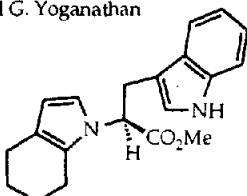
$C_{17}H_{19}O_2N$

Methyl (R)-2-(N-4,5,6,7-tetrahydroindolyl)phenylacetate

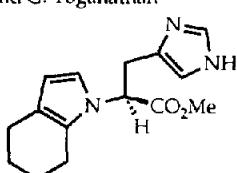
$[\alpha]_D^{20} = +71.85$  (c 1.08, CHCl<sub>3</sub>)  
ee 100% (chiral HPLC)



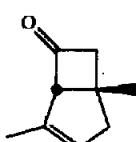
Methyl (S)-2-(N-4,5,6,7-tetrahydroindolyl)-3-i-propylpropionate

 $[\alpha]_D^{25} -39.26$  (c 1.08, CHCl<sub>3</sub>)  
ee 99.6% (chiral HPLC)


Methyl (S)-2-(N-4,5,6,7-tetrahydroindolyl)-3-(3'-indolyl)propionate

 $[\alpha]_D^{25} -49.11$  (c 1.01, CHCl<sub>3</sub>)  
ee 96.8% (chiral HPLC)


Methyl (S)-2-(N-4,5,6,7-tetrahydroindolyl)-3-(4'-imidazoyl)propionate

 $[\alpha]_D^{25} -65.97$  (c 0.77, CHCl<sub>3</sub>)  
ee 96.2% (chiral HPLC)


1,4-dimethyl-bicyclo[3.2.0]hept-3-en-6-one

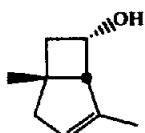
ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 828.4$  (c 0.985, CHCl<sub>3</sub>)

Source of chirality: microbial reduction

Absolute configuration: 1S,5R,6S

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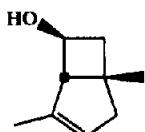
 $C_9H_{14}O$ 

ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = -104.5 (c\ 1.05, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1R,5S,6S

*endo*-1,4-dimethyl-bicyclo[3.2.0]hept-3-en-6-ol $C_9H_{14}O$ 

ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

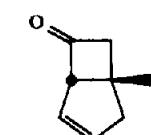
 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 2.93 (c\ 1.07, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5R,6S

*exo*-1,4-dimethyl-bicyclo[3.2.0]hept-3-en-6-ol

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 $C_8H_{10}O$ 

ee = 99% [by GLC analysis on a 25 m dimethyl-n-pentyl-

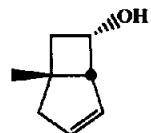
 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 449.6 (c\ 0.9, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5S

1-methyl-bicyclo[3.2.0]hept-3-en-6-one

G. Fantin, M. Fogagnolo, A. Medici, P. Pedrini, E. Marotta, M. Monti, P. Righi

 $C_8H_{12}O$ 

ee = 95% [by GLC analysis on a 25 m dimethyl-n-pentyl-

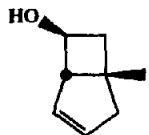
 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = -165.3 (c\ 3, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1R,5R,6S

*endo*-1-methyl-bicyclo[3.2.0]hept-3-en-6-ol

G. Fantin, M. Fogagnolo, A. Medici, P. Pedrini, E. Marotta, M. Monti, P. Righi

 $C_8H_{12}O$ *exo*-1-methyl-bicyclo[3.2.0]hept-3-en-6-ol

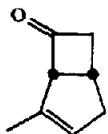
ee = 97% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 82.3 (c \ 1.2, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5S,6S

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 $C_8H_{10}O$ 

4-methyl-bicyclo[3.2.0]hept-3-en-6-one

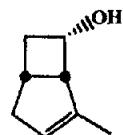
ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 797.3 (c \ 0.995, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5R

G. Fantin, M. Fogagnolo, A. Medici, P. Pedrini, E. Marotta, M. Monti, P. Righi

 $C_8H_{12}O$ *endo*-4-methyl-bicyclo[3.2.0]hept-3-en-6-ol

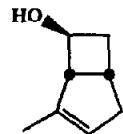
ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = -136.8 (c \ 1.065, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5R,6S

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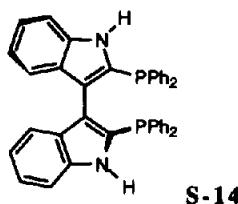
 $C_8H_{12}O$ *exo*-4-methyl-bicyclo[3.2.0]hept-3-en-6-ol

ee = 100% [by GLC analysis on a 25 m dimethyl-n-pentyl-

 $\beta$ -cyclodextrin in OV 1701] $[\alpha]_D^{25} = 12.7 (c \ 1.5, CHCl_3)$ 

Source of chirality: microbial reduction

Absolute configuration: 1S,5R,6S

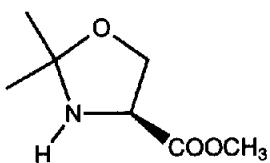
C5H9O2N(-)-(1*S*, 2*R*)-Allonorcoronamic Acid $[\alpha]_D^{20} = -74$  ( $c = 0.3, \text{H}_2\text{O}$ )Source of chirality: (*S*)-(−)-1,2-propanediolAbsolute configuration: 1*S*, 2*R*

E.e. = &gt;98%

(S)-enantiomer  $[\alpha]_D^{25} = -81.9$  ( $c = 1, \text{CH}_2\text{Cl}_2$ )Source of chirality - resolution with the palladium complex derived from (*R*) - N,N-dimethyl-1-naphthyl-1'-ethylamine.

Abs. configuration; X-ray of the resolution complex.

2,2'-bis-diphenylphosphino[3,3']biindolyl

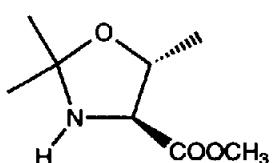
C7H13NO3

E.e. = ≥95%

b.p. 80°C/20 mBar

 $[\alpha]_D^{25} = -59.0$  ( $c 4, \text{CHCl}_3$ )Source of chirality: (*S*)-serineAbsolute configuration: 4*S*

2,2-Dimethyl-4-methoxycarbonyl-1,3-oxazolidine

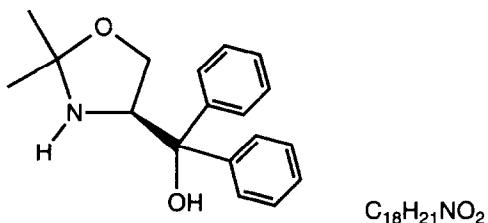
C8H15NO3

E.e. = ≥95%

b.p. 90°C/20 mBar

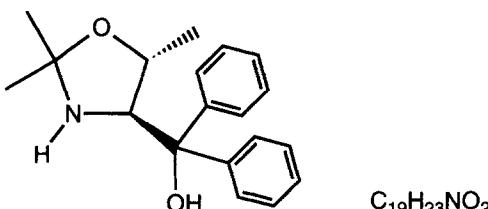
 $[\alpha]_D^{25} = -19.23$  ( $c 4, \text{CHCl}_3$ )Source of chirality: (2*S*,3*R*)-threonineAbsolute configuration: 4*S*,5*R*

2,2-Dimethyl-5-methyl-4-methoxycarbonyl-1,3-oxazolidine



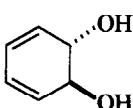
Diphenyl-(2,2-dimethyl-1,3-oxazolidin-4-yl)-methanol

E.e. =  $\geq 70\%$  [by  $^{19}F$  nmr of (+)-MTPA amide]  
 m.p. 135-140°C  
 $[\alpha]_D^{25} -51.0$  (c 3,  $CHCl_3$ )  
 Source of chirality: (S)-serine  
 Absolute configuration: 4S



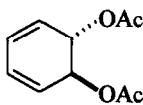
Diphenyl-(2,2-dimethyl-5-methyl-1,3-oxazolidin-4-yl)-methanol

D.e. =  $\geq 86\%$  [by nmr]  
 m.p. 90-92°C  
 $[\alpha]_D^{25} -138.0$  (c 2,  $CHCl_3$ )  
 Source of chirality: (2S,3R)-threonine  
 Absolute configuration: 4S,5R



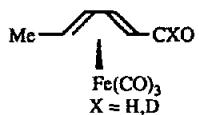
(S,S)-3,5-Cyclohexadiene-1,2-diol

$[\alpha]_D^{20} +325.0$  (c 0.75;  $CHCl_3$ )  
 CD:  $\Delta\epsilon +10.0$  (256 nm); -11.2 (204 nm) in methanol  
 UV:  $\epsilon 3630$  (260 nm) in methanol  
 Source of chirality: asymmetric synthesis

(S,S)-3,5-Cyclohexadiene-1,2-diol  
diacetate

CD:  $\Delta\epsilon +12.6$  (254 nm); +9.1 (206 nm) in methanol  
 UV:  $\epsilon 3520$  (257 nm) in methanol  
 Source of chirality: asymmetric synthesis

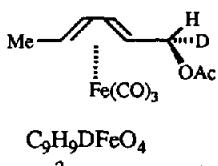
James A.S. Howell, Paula J. O'Leary, Michael G. Palin, Gérard Jaouen, Siden Top



E.e. = 100 % (by NMR)  
Source of chirality = resolution with (+)-ephedrine  
Absolute configuration = 2R  
 $[\alpha]_D^{20} -110$  (c=1, CHCl<sub>3</sub>) ([1-<sup>1</sup>H] complex)

C<sub>9</sub>H<sub>8</sub>FeO<sub>4</sub> or C<sub>9</sub>H<sub>7</sub>DFeO<sub>4</sub>  
[1-<sup>1</sup>H] or [1-<sup>2</sup>H] (2,4-hexadienyl)tricarbonyliron

James A.S. Howell, Paula J. O'Leary, Michael G. Palin, Gérard Jaouen, Siden Top



E.e. = 100 % (by NMR)  
Source of chirality = Bakers yeast reduction  
Absolute configuration = 1S, 2S  
 $[\alpha]_D^{20} -17$  (c=1, CHCl<sub>3</sub>)

C<sub>9</sub>H<sub>9</sub>DFeO<sub>4</sub>  
[1-<sup>2</sup>H] (2,4-hexadien-1-yl acetate)tricarbonyliron