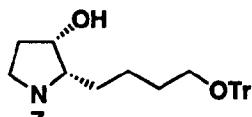


**STEREOCHEMISTRY ABSTRACTS**

**H. Takahata, Y. Banba, and T. Momose**

*Tetrahedron: Asymmetry* 1992, 3, 999



E.e=92% [by nmr with MTPA ester of a precursor]

$[\alpha]^{25}_D +25.6$  (*c* 1.46, CHCl<sub>3</sub>)

Source of chirality: Katsuki-Sharpless kinetic resolution

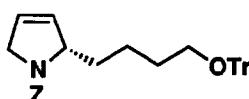
Absolute configuration: 2*S*,3*S*



(2*S*,3*S*)-1-(Benzylloxycarbonyl)-2-[4-(triphenylmethoxy)butyl]-3-hydroxypyrrolidine

**H. Takahata, Y. Banba, and T. Momose**

*Tetrahedron: Asymmetry* 1992, 3, 999



E.e=92% [by nmr with MTPA ester of a precursor]

$[\alpha]^{24}_D +82.2$  (*c* 0.46, CHCl<sub>3</sub>)

Source of chirality: Katsuki-Sharpless kinetic resolution

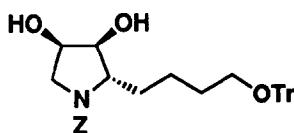
Absolute configuration: *S*



(*S*)-1-(Benzylloxycarbonyl)-2-[4-(triphenylmethoxy)butyl]-3-pyrrolidine

**H. Takahata, Y. Banba, and T. Momose**

*Tetrahedron: Asymmetry* 1992, 3, 999



E.e=92% [by nmr with MTPA ester of a precursor]

$[\alpha]^{25}_D +14.5$  (*c* 0.52, CHCl<sub>3</sub>)

Source of chirality: Katsuki-Sharpless kinetic resolution

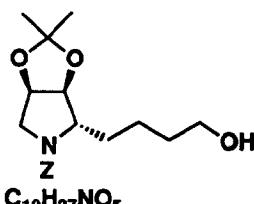
Absolute configuration: 2*S*,3*S*,4*R*



(2*S*,3*S*,4*R*)-1-(Benzylloxycarbonyl)-2-[4-(triphenylmethoxy)butyl]-3,4-dihydroxypyrrolidine

**H. Takahata, Y. Banba, and T. Momose**

*Tetrahedron: Asymmetry* 1992, 3, 999



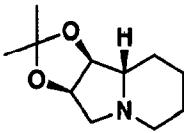
E.e=92% [by nmr with MTPA ester of a precursor]

$[\alpha]^{24}_D +30.65$  (*c* 1.55, CHCl<sub>3</sub>)

Source of chirality: Katsuki-Sharpless kinetic resolution

Absolute configuration: 2*S*,3*S*,4*R*

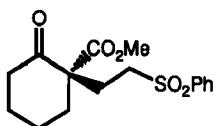
(2*S*,3*S*,4*R*)-1-(Benzylloxycarbonyl)-2-(4-hydroxybutyl)-3,4-(isopropylidenedioxy)pyrrolidine

 $C_{11}H_{19}NO_2$ (1*S*,2*R*,8*a**S*)-1,2-(isopropylidenedioxy)indolizidine

E.e=92% [by nmr with MTPA ester of a precursor]

 $[\alpha]_D^{25} -48.3$  (*c* 0.32,  $CHCl_3$ )

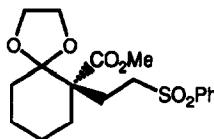
Source of chirality: Katsuki-Sharpless kinetic resolution

Absolute configuration: 1*S*,2*R*,8*a**S*ee 94% ( by  $^1H$  NMR with  $Eu(hfc)_3$  ) $[\alpha]_D^{25} -50.6$  (*c*=8, MeOH)

Source of chirality : asymm. Michael addition

Absolute configuration : *S* (assigned by chemical correlation)

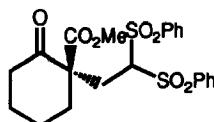
2-oxo-1-(2-phenylsulfonylethyl)-cyclohexane carboxylic acid, methyl ester

ee 94% ( by  $^1H$  NMR with  $Eu(hfc)_3$  ) $[\alpha]_D^{25} -9.6$  (*c*=5.6, MeOH)

Source of chirality : asymm. Michael addition

Absolute configuration : *S* (assigned by chemical correlation)

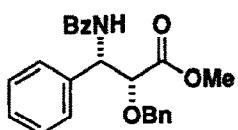
2-oxo-1-(2-phenylsulfonylethyl)-cyclohexane carboxylic acid, methyl ester

ee 50% ( by  $^1H$  NMR with  $Eu(hfc)_3$  ) $[\alpha]_D^{25} +27.8$  (*c*=5.7, acetone)

Source of chirality : asymm. Michael addition

Absolute configuration : *R* (assigned by chemical correlation)

2-oxo-1-(2,2-bis(phenylsulfonyl)ethyl)-cyclohexane carboxylic acid, methyl ester

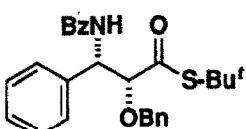
E.e. = >98% [by  $^1\text{H}$  NMR analysis] $[\alpha]^{22}_{\text{D}} -5.3$  (*c*, 0.41,  $\text{CHCl}_3$ )mp 103 - 105°C ( $\text{CHCl}_3$  - isopropyl ether)

Source of Chirality : asymm. synth. (aldol) of optically active chromium(0)-complexed aldehyde

Absolute configuration : 2R, 3S (assigned by conversion into known compound)

C<sub>24</sub>H<sub>23</sub>NO<sub>4</sub>

Methyl 3-N-Benzoyl-2-benzyloxy-3-phenylpropanoate

E.e. = >98% [by  $^1\text{H}$  NMR analysis] $[\alpha]^{23}_{\text{D}} + 58.5$  (*c*, 0.41,  $\text{CHCl}_3$ )

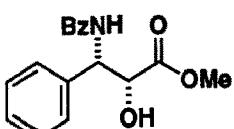
mp 138 - 139°C (hexane - acetone)

Source of Chirality : asymm. synth. (aldol) of optically active chromium(0)-complexed aldehyde

Absolute configuration : 2R, 3S (assigned by conversion into known compound)

C<sub>27</sub>H<sub>29</sub>NO<sub>3</sub>S

S-t-Butyl 3-N-Benzoyl-2-benzyloxy-3-phenylpropanethioate

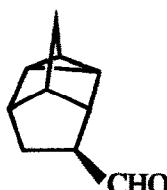
E.e. = >98% [by  $^1\text{H}$  NMR analysis] $[\alpha]^{20}_{\text{D}} - 48.1$  (*c*, 0.28, MeOH)mp 180 - 182°C ( $\text{CHCl}_3$ -isopropyl ether)

Source of Chirality : asymm. synth. (aldol) of optically active chromium(0)-complexed aldehyde

Absolute configuration : 2R, 3S (known compound)

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

Methyl 3-N-Benzoyl-2-hydroxy-3-phenylpropanoate

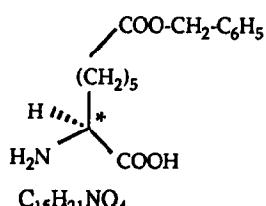
C<sub>10</sub>H<sub>12</sub>O

(S)-4-exo-formyl-tetracyclo[4.3.0.0^2,9,0^3,7]nonane

e.e.= 22% (determined by  $^1\text{H}$ NMR using chiral shift reagents /Eu(tfc)<sub>3</sub> and Eu(dcm)<sub>3</sub>/) $[\alpha]_{546}^{20} = -8.7$  (*c* 8.3, toluene)

Source of chirality: asymmetric synthesis

(enantioselective hydroformylation)

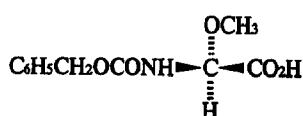
L- $\alpha$ -amino suberic acid- $\omega$ -benzyl ester

E.e. = &gt;99% (det. by chiral tlc)

 $[\alpha]_D^{25} = +18.5$  ( $c=0.5$  g/100ml in HCOOH)

Source of chirality: enzymatic resolution

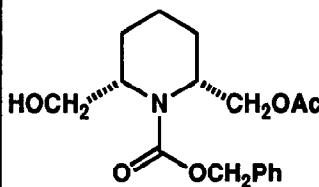
Absolute configuration: S

N-Carbobenzoxy-L- $\alpha$ -methoxyglycine  
[ Cbz-L-Gly(OMe)-OH ] $[\alpha]_D^{20} -20.1$  ( $c=0.5$ , MeOH); e.e.>99.5%. Mp. 91–92°C.

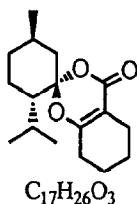
Source of chirality:

Resolution with (+)-(1S,2S)-2-amino-1-phenyl-1,3-propanediol or (S)-2-amino-1-phenylpropanol.

(+)-D-Enantiomer,  $[\alpha]_D^{20} +20.0$ , e.e.>99.5%, was also obtained using (R)-2-amino-3-phenyl-1-propanol.



N-benzyloxycarbonyl-cis-2-acetoxymethyl-6-hydroxymethyl piperidine



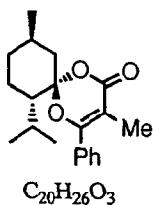
(2S,2'S,5'R)-5,6,7,8-Tetrahydro-4-oxo-1,3-benzodioxane-2-spiro(2'-isopropyl-5'-methyl)cyclohexane

D.e.= 100% (by NMR analysis)

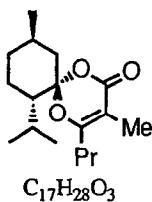
 $[\alpha]_D^{24} = +32.8$  ( $c 1.20$ ,  $CHCl_3$ )

Source of chirality: chromatographic separation of the (S)- and (R)-isomers

Absolute configuration: 2S,2'S,5'R ( $^1H$ -NMR analysis)



D.e.= 100% (by NMR analysis)

 $[\alpha]_D^{20}= +124.0$  (*c* 1.06,  $CHCl_3$ )Source of chirality: chromatographic separation of the (*S*)- and (*R*)-isomersAbsolute configuration: 6*S*,7*S*,10*R* ( $^1H$ -NMR analysis)(6*S*,7*S*,10*R*)-7-Isopropyl-3,10-dimethyl-4-oxo-2-phenyl-1,5-dioxa-spiro[5.5]undec-2-ene

D.e.= 100% (by NMR analysis)

 $[\alpha]_D^{24}= +10.2$  (*c* 1.00,  $CHCl_3$ )Source of chirality: chromatographic separation of the (*S*)- and (*R*)-isomersAbsolute configuration: 6*S*,7*S*,10*R* ( $^1H$ -NMR analysis)(6*S*,7*S*,10*R*)-7-Isopropyl-3,10-dimethyl-4-oxo-2-propyl-1,5-dioxa-spiro[5.5]undec-2-ene

E.e.=&gt;98% (by NMR analysis of MTPA ester of the corresponding hydroxy-methyl derivative)

 $[\alpha]_D^{21}= +107.8$  (*c* 1.00,  $CHCl_3$ )

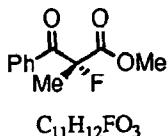
Source of chirality: resolution of synth. intermed.

Absolute configuration: *R* (assigned from convex  $F_2$  addition to the (*S*)-spirocyclic dioxinone derived from 2-oxocyclohexanecarboxylic acid and *l*-menthone)Methyl (*R*)-1-Fluoro-2-oxocyclohexanecarboxylate

E.e.=&gt;98% (by comparison of specific rotation)

 $[\alpha]_D^{22}= -85.0$  (*c* 1.00,  $MeOH$ )

Source of chirality: resolution of synth. intermed.

Absolute configuration: *R* (assigned by conversion to the known ethyl ester)Methyl (*R*)-2-Benzoyl-2-fluoropropionate



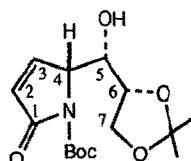
E.e. = 73% (by comparison of specific rotation)

 $[\alpha]_D^{23} = -28.8$  (*c* 2.39, MeOH)

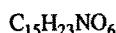
Source of chirality: resolution of synth. intermed.

Absolute configuration: *R* (assigned by conversion to the known ethyl ester)Methyl (*R*)-2-Fluoro-2-methyl-3-oxohexanoate

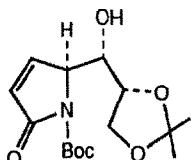
Gloria Russu,\* Giovanni Casiraghi, Pietro Spanu, Luigi Pinna, Giovanna Gasparri Fava, Marisa Belicchi Ferrari, and Giorgio Pelosi



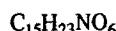
E.e. = ca. 100%

 $[\alpha]_D^{25} = +197.6$  (*c* 0.83, CHCl<sub>3</sub>); m.p. 138-140 °CSource of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesisAbsolute configuration: 4*R*, 5*S*, 6*R*; by X-ray analysis*N*-tert-Butoxycarbonyl-6,7-*O*-isopropylidene-2,3-dideoxy-hept-2-enono-1,4-lactam

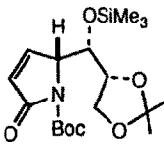
Gloria Russu,\* Giovanni Casiraghi, Pietro Spanu, Luigi Pinna, Giovanna Gasparri Fava, Marisa Belicchi Ferrari, and Giorgio Pelosi



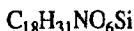
E.e. = ca. 100%

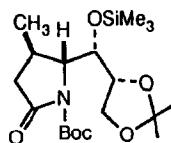
 $[\alpha]_D^{25} = -120.0$  (*c* 0.8, CHCl<sub>3</sub>); m.p. 118-120 °CSource of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesisAbsolute configuration: 4*S*, 5*S*, 6*R*; by X-ray analysis*N*-tert-Butoxycarbonyl-6,7-*O*-isopropylidene-2,3-dideoxy-hept-2-enono-1,4-lactam

Gloria Russu,\* Giovanni Casiraghi, Pietro Spanu, Luigi Pinna, Giovanna Gasparri Fava, Marisa Belicchi Ferrari, and Giorgio Pelosi



E.e. = ca. 100%

 $[\alpha]_D^{25} = +156.7$  (*c* 1.24, CHCl<sub>3</sub>); colorless oilSource of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesisAbsolute configuration: 4*R*, 5*S*, 6*R**N*-tert-Butoxycarbonyl-5-O-trimethylsilyl-6,7-*O*-isopropylidene-2,3-dideoxy-hept-2-enono-1,4-lactam



E.e. = ca. 100%

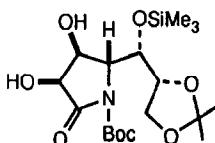
$[\alpha]_D^{25} = +33.6$  (*c* 1.28, CHCl<sub>3</sub>); colorless oil

Source of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesis

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



*N*-tert-Butoxycarbonyl-3-methyl-5-*O*-trimethylsilyl-6,7-*O*-isopropylidene-2,3-dideoxy-heptono-1,4-lactam



E.e. = ca. 100%

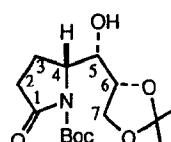
$[\alpha]_D^{25} = +3.1$  (*c* 1.9, CHCl<sub>3</sub>); colorless oil

Source of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesis

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



*N*-tert-Butoxycarbonyl-5-*O*-trimethylsilyl-6,7-*O*-isopropylidene-heptono-1,4-lactam



E.e. = ca. 100%

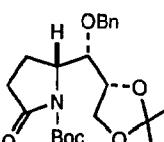
$[\alpha]_D^{25} = +59.24$  (*c* 1.26, CHCl<sub>3</sub>); m.p. 99–103 °C

Source of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesis

Absolute configuration: 4R, 5S, 6R



*N*-tert-Butoxycarbonyl-6,7-*O*-isopropylidene-2,3-dideoxy-heptono-1,4-lactam

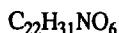


E.e. = ca. 100%

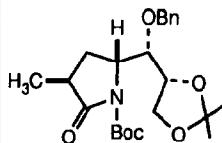
$[\alpha]_D^{25} = -18.6$  (*c* 0.7, CHCl<sub>3</sub>); colorless oil

Source of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesis

Absolute configuration: 4R, 5S, 6R



*N*-tert-Butoxycarbonyl-5-*O*-benzyl-6,7-*O*-isopropylidene-2,3-dideoxy-heptono-1,4-lactam



E.e. = ca. 100%

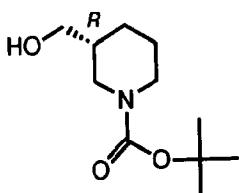
$[\alpha]_D^{25} = -75.4$  (*c* 0.35, CHCl<sub>3</sub>); colorless oil

Source of chirality: 2,3-*O*-isopropylidene-D-glyceraldehyde and asymmetric synthesis

Absolute configuration: 2S, 4R, 5S, 6R



*N*-tert-Butoxycarbonyl-2-methyl-5-*O*-benzyl-6,7-*O*-isopropylidene-2,3-dideoxy-heptono-1,4-lactam



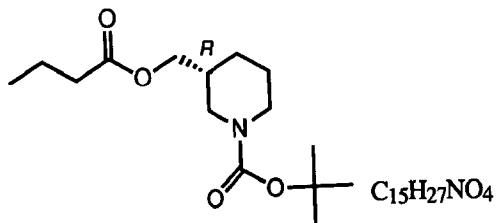
ee > 98 % (GLC of trifluoroacetate on chiral phase)

$[\alpha]_{365}^{20} = -60.7$  (*c* = 1.0, EtOH)

Source of chirality: enantioselective enzymatic hydrolysis of butyryl ester

Absolute configuration: R

tert-Butyl (R)-3-(hydroxymethyl)-1-piperidinecarboxylate



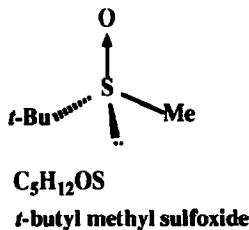
ee = 94 % (GLC of corresponding alcohol derivative on chiral phase)

$[\alpha]_{365}^{20} = -57.5$  (*c* = 1.0, CHCl<sub>3</sub>) (96 % GLC)

Source of chirality: enantioselective enzymatic hydrolysis of racemic butyryl ester

Absolute configuration: R

tert-Butyl (R)-3-[(butyryloxy)methyl]-1-piperidinecarboxylate



E.e. = 99 % by chiral GC with CP-Cyclodextrin- $\beta$ -2,3,6-M19 column

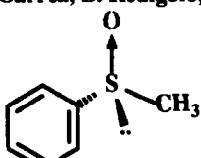
Source of chirality : Cyclohexanone monooxygenase

Absolute configuration : R



t-butyl methyl sulfoxide

G. Carrea, B. Redigolo, S. Riva, S. Colonna, N. Gaggero, E. Battistel, D. Bianchi



E.e. = 99 % by chiral HPLC with a Chiralcel OB column

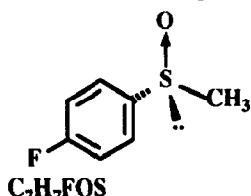
### **Source of chirality : Cyclohexanone monooxygenase**

**Absolute configuration : R**

C<sub>7</sub>H<sub>9</sub>OS

#### **methyl phenyl sulfoxide**

G. Carrea, B. Redigolo, S. Riva, S. Colonna, N. Gaggero, E. Battistel, D. Bianchi



E.e. = 92 % by chiral HPLC with a Chiralcel OB column

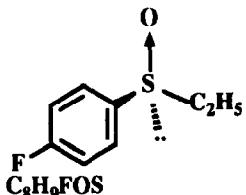
**Source of chirality : Cyclohexanone monooxygenase**

Absolute configuration : R

### **methyl-*n*-**

11. *W. E. B. DuBois*, *The Souls of Black Folk* (1903), 10.

G. Carrea, B. Redigolo, S. Riva, S. Colonna, N. Gaggero, E. Battistel, D. Bianchi

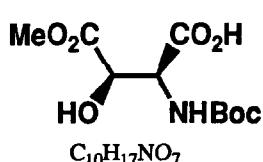


E.e. = 93 % by chiral HPLC with a Chiralcel OB column

**Source of chirality : Cyclohexanone monooxygenase**

**Absolute configuration : S**

### **ethyl-*p*-fluorophenyl sulfoxide**

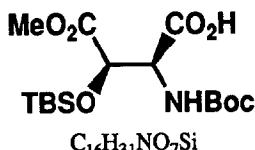


$$[\alpha]^{22}_{D} + 18.6 \text{ (c 0.90, CHCl}_3\text{)}$$

source of chirality : (2R,3R)-epoxysuccinic acid

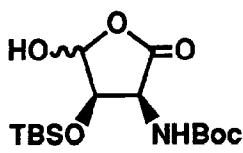
absolute configuration : 2S, 3R

## N-tert-Butoxycarbonyl-(2*S*,3*R*)-3-hydroxyaspartic acid $\beta$ -methyl ester



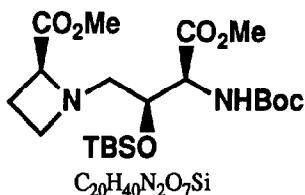
$[\alpha]_D^{22} +68.5$  (c 1.04, CHCl<sub>3</sub>)  
source of chirality : (2R,3R)-epoxysuccinic acid  
absolute configuration : 2S, 3R

N-tert-Butoxycarbonyl-(2S,3R)-3-tert-butyldimethylsiloxy-aspartic acid β-methyl ester



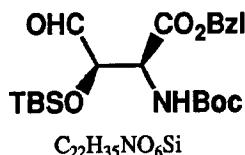
source of chirality : (2R,3R)-epoxysuccinic acid  
absolute configuration : 3S, 4R

2-tert-Butoxycarbonylamino-3-tert-butyldimethylsiloxy-4-hydroxy-D-lyxo-1,4-lactone



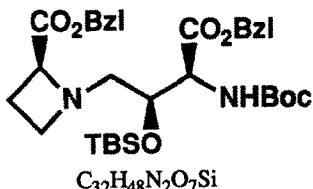
$[\alpha]_D^{23} -19.3$  (c 0.42, CHCl<sub>3</sub>)  
source of chirality : (2R,3R)-epoxysuccinic acid and  
(S)-azetidine carboxylic acid  
absolute configuration : 2S, 2'S, 3'S

Methyl N-[(2S,2'S,3'S)-3'-tert-butoxycarbonylamino-3'-methoxycarbonyl-2'-tert-butyldimethylsiloxypropyl]-2-azetidinecarboxylate



$[\alpha]_D^{22} +26.5$  (c 0.76, CHCl<sub>3</sub>)  
source of chirality : (2R,3R)-epoxysuccinic acid  
absolute configuration : 2R, 3R

Benzyl (2R,3R)-2-tert-butoxycarbonylamino-3-tert-butyldimethylsiloxy-4-oxobutylate



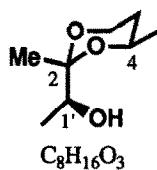
Benzyl N-[(2S,2'S,3'S)-3'-tert-butoxycarbonylamino-3'-benzyloxycarbonyl-2'-tert-butylidemethylsiloxypropyl]-2-azetidinecarboxylate

$[\alpha]_D^{23} -11.9$  ( $c = 1, \text{CH}_2\text{Cl}_2$ )

source of chirality : (2R,3R)-epoxysuccinic acid and

S-azetidine carboxylic acid

absolute configuration : 2S, 2'S, 3'S



(2R,4R,1'S)-2-(1-Hydroxyethyl)-2,4-dimethyl-1,3-dioxane

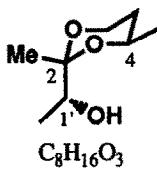
D.e.= >99% (determined by  $^1\text{H-NMR}$ )

$[\alpha]_D^{24} -11.7$  ( $c=0.24, \text{CHCl}_3$ )

Source of chirality: (R)-1,3-butanediol

Absolute configuration: 1'S

(assigned by chemical correlation)



(2R,4R,1'R)-2-(1-Hydroxyethyl)-2,4-dimethyl-1,3-dioxane

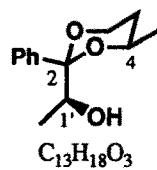
D.e.= >99% (determined by  $^1\text{H-NMR}$ )

$[\alpha]_D^{24} +13.8$  ( $c=0.10, \text{CHCl}_3$ )

Source of chirality: (R)-1,3-butanediol

Absolute configuration: 1'R

(assigned by chemical correlation)



(2R,4R,1'S)-2-(1-Hydroxyethyl)-2-methyl-4-phenyl-1,3-dioxane

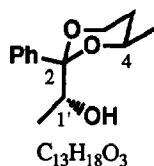
D.e.= >99% (determined by  $^1\text{H-NMR}$ )

$[\alpha]_D^{22} +21.6$  ( $c=0.11, \text{CHCl}_3$ )

Source of chirality: (R)-1,3-butanediol

Absolute configuration: 1'S

(assigned by Mosher's method)

(2*R*,4*R*,1'*R*)-2-(1-Hydroxyethyl)-2-methyl-4-phenyl-1,3-dioxane

D.e.= >99% (determined by  $^1\text{H-NMR}$ )  
 $[\alpha]_D^{22} +73.7$  ( $c=0.10$ ,  $\text{CHCl}_3$ )

Source of chirality: (*R*)-1,3-butanediol  
 Absolute configuration: 1'*R*  
 (assigned by Mosher's method)



(S)-2-Methyl-1,4-diphenylbutane-1,4-dione

E.e.= 48% (derived from precursor 14 of  
 48% d.e.)  
 $[\alpha]_D^{20} -42.7$  ( $c=2.29$ ,  $\text{CHCl}_3$ )

Source of chirality: (*R,R*)-2,4-pentanediol  
 Absolute configuration: *S*  
 (assigned by specific rotation of the authentic  
 sample)