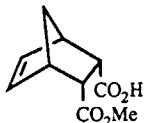


STEREOCHEMISTRY ABSTRACTS

R. A. Aitken and J. Gopal

Tetrahedron: Asymmetry 1990, 1, 517



C₁₀H₁₂O₄

(-) -*endo*-bicyclo[2.2.1]hept-5-ene 2,3-dicarboxylic acid monomethyl ester

E.e.=88% [by nmr with (+)- α -phenylethylamine]

$[\alpha]_D^{25} = -1.11$ (c 4.2, CHCl₃)

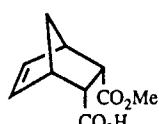
Source of chirality : quinine

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

(assigned by correlation to X-ray structure)

R. A. Aitken and J. Gopal

Tetrahedron: Asymmetry 1990, 1, 517



C₁₀H₁₂O₄

(+)-*endo*-bicyclo[2.2.1]hept-5-ene 2,3-dicarboxylic acid monomethyl ester

E.e.=93% [by nmr with (+)- α -phenylethylamine]

$[\alpha]_D^{25} = +1.18$ (c 4.2, CHCl₃)

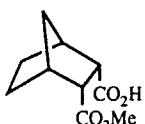
Source of chirality : quinidine

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

(assigned by correlation to X-ray structure)

R. A. Aitken and J. Gopal

Tetrahedron: Asymmetry 1990, 1, 517



C₁₀H₁₄O₄

(-) -*endo*-bicyclo[2.2.1]heptane 2,3-dicarboxylic acid monomethyl ester

E.e.=35% [by nmr with (+)- α -phenylethylamine]

$[\alpha]_D^{25} = -4.6$ (c 3, CHCl₃)

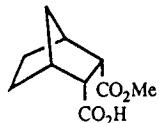
Source of chirality : quinine

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

(assigned by correlation to X-ray structure)

R. A. Aitken and J. Gopal

Tetrahedron: Asymmetry 1990, 1, 517



C₁₀H₁₄O₄

(+)-*endo*-bicyclo[2.2.1]heptane 2,3-dicarboxylic acid monomethyl ester

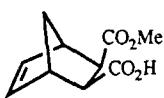
E.e.=44% [by nmr with (+)- α -phenylethylamine]

$[\alpha]_D^{25} = +5.8$ (c 3, CHCl₃)

Source of chirality : quinidine

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

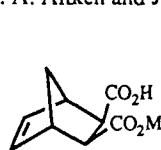
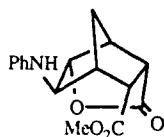
(assigned by correlation to X-ray structure)

 $C_{10}H_{12}O_4$ (-)-*exo*-bicyclo[2.2.1]hept-5-ene 2,3-dicarboxylic acid monomethyl esterE.e.=58% [by nmr with (+)- α -phenylethylamine] $[\alpha]_D^{25} = -3.0$ (c 3.8, $CHCl_3$)

Source of chirality : quinine

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

(assigned by reduction to known lactone)

 $C_{10}H_{12}O_4$ (+)-*exo*-bicyclo[2.2.1]hept-5-ene 2,3-dicarboxylic acid monomethyl ester $C_{16}H_{17}NO_4$

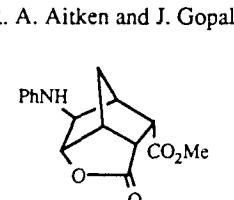
(-)-9-methoxycarbonyl-8-phenylamino-2-oxatricyclo[3.3.0.1^4.7]nonan-3-one

E.e.=65% [by nmr with $Eu(hfc)_3$] $[\alpha]_D^{20} = -56.0$ (c 0.54, acetone)

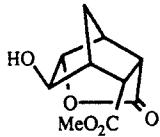
Source of chirality : quinine

Absolute configuration : 1R,4S,5S,7R,8R,9R

(assigned by correlation to X-ray structure)

 $C_{16}H_{17}NO_4$

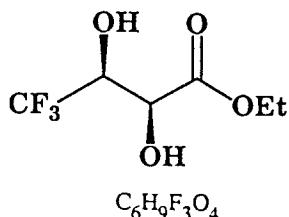
(+)-9-methoxycarbonyl-8-phenylamino-2-oxatricyclo[3.3.0.1^4.7]nonan-3-one

 $C_{10}H_{12}O_5$ (-)-9-methoxycarbonyl-2-oxatricyclo[3.3.0.1^{4.7}]nonan-8-ol-3-oneE.e.>99% [by nmr with Eu(hfc)₃] $[\alpha]_D^{25} = -36.55$ (c 1.0, CHCl₃)

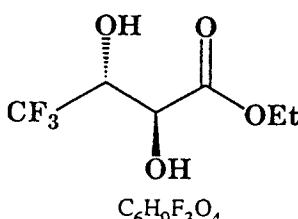
Source of chirality : quinine

Absolute configuration : 1R,4S,5S,7R,8R,9R

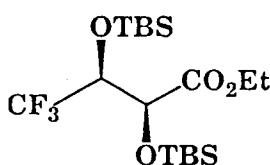
(assigned by X-ray structure of (+)-MTPA ester)

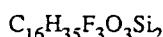
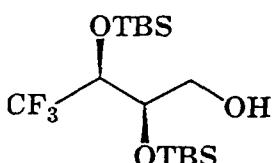


Ethyl 2,3-dihydroxy-4,4,4-trifluorobutyrate

E.e. = 98% [by ¹H NMR analysis of MTPA ester after derived into 2,3-bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutan-1-ol]
 $[\alpha]_D^{22} +13.30$ (c 1.36, MeOH)Absolute configuration : 2*S*,3*S* [chemical correlation of optically active trifluorinated threonine into this compound]Relative configuration : *syn* [estimated from its reaction mechanism]

Ethyl 2,3-dihydroxy-4,4,4-trifluorobutyrate

E.e. = >95% [by ¹H NMR analysis of MTPA ester after derived into 2,3-bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutan-1-ol]
 $[\alpha]_D^{19} +4.53$ (c 1.09, MeOH)Absolute configuration : 2*S*,3*R* [by chemical correlation to the known compound for 3-position]Relative configuration : *anti* [estimated from its reaction mechanism] $C_{18}H_{37}F_3O_4Si_2$ Ethyl 2,3-bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutyrateE.e. = 98% (by ¹H NMR analysis of MTPA ester after derived into 2,3-bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutan-1-ol)
 $[\alpha]_D^{18} +14.63$ (c 1.57, MeOH)Absolute configuration : 2*S*,3*S*Relative configuration : *syn*

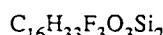
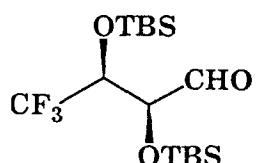


2,3-Bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutan-1-ol

E.e. = 98% [by ^1H NMR after derivatization into its MTPA ester]
 $[\alpha]_D^{16} -4.40$ (*c* 1.26, MeOH)

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

Relative configuration : *syn*



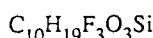
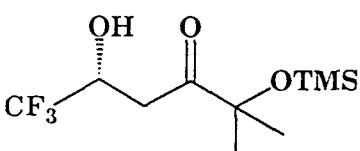
2,3-Bis[(*t*-butyldimethylsilyl)oxy]-4,4,4-trifluorobutan-1-al

E.e. = 98% [estimated from the ee value of its starting material and the observation of no epimerization at α -position]

$[\alpha]_D^{16} +11.55$ (*c* 1.46, MeOH)

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

Relative configuration : *syn*

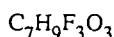
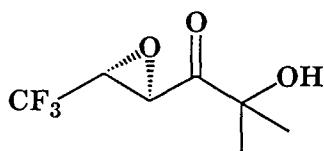


2-Hydroxy-5-methyl-1,1,1-trifluoro-5-[(trimethylsilyl)oxy]hexan-4-one

E.e. = >95% (by ^1H NMR for the corresponding MTPA ester)
 $[\alpha]_D^{17} +5.11$ (*c* 1.36, MeOH)

Source of chirality : Lipase-catalyzed asymmetric hydrolysis

Absolute configuration : *R*

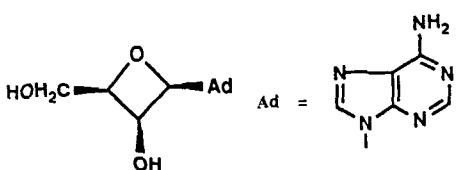


2,3-Epoxy-5-hydroxy-5-methyl-1,1,1-trifluorohexan-4-one

E.e. = >95% (estimated from the ee value for its starting material)
 $[\alpha]_D^{15} -16.5$ (*c* 1.57, MeOH)

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

Relative configuration : *anti*

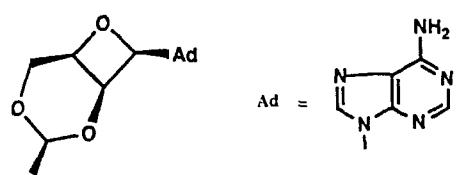


E.e. = 100%

$[\alpha]_D^{20} = -12.8$ (c, 0.12 in DMF)

Source of chirality: D-lyxonolactone as starting material

$C_{9}H_{11}N_5O_3$ norepoxetanocin
9-(β -D-threooxetanosyl)adenine



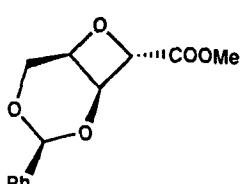
E.e. = 100%

$[\alpha]_D^{20} = +96.2$ (c, 0.26 in methanol)

Source of chirality: D-lyxonolactone as starting material

$C_{16}H_{15}N_5O_3$

9-(2',4'-O-benzylidene- β -D-threooxetanosyl)adenine



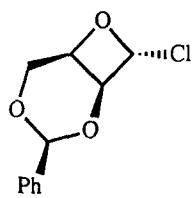
E.e. = 100%

$[\alpha]_D^{20} = -28.2$ (c, 1.0 in chloroform)

Source of chirality: D-lyxonolactone as starting material

$C_{13}H_{14}O_5$

methyl 2,4-anhydro-3,5-O-benzylidene-D-lyxonate



E.e. = 100%

$[\alpha]_D^{20} = +40.8$ (c, 0.73 in chloroform)

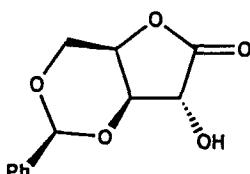
Source of chirality: D-lyxonolactone as starting material

$C_{11}H_{11}ClO_3$

2,4-O-benzylidene- α -D-threo-octanoyl chloride

Y.Wang, G.W.J.Fleet, R.Storer, P.L.Myers, C.J.Wallis, O.Doherty,
D.J.Watkin, K.Vogt, D.R.Witty, F.X.Wilson, J.M.Peach

Tetrahedron: Asymmetry 1990, 1, 525



E.e. = 100%

$[\alpha]_D^{20} = +63.3$ (c, 1.0 in acetone)

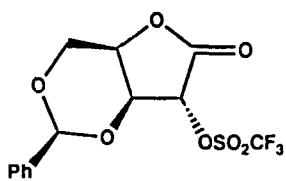
Source of chirality: D-lyxonolactone as starting material

C₁₂H₁₂O₅

3,5-O-benzylidene-D-xylonolactone

Y.Wang, G.W.J.Fleet, R.Storer, P.L.Myers, C.J.Wallis, O.Doherty,
D.J.Watkin, K.Vogt, D.R.Witty, F.X.Wilson, J.M.Peach

Tetrahedron: Asymmetry 1990, 1, 525



E.e. = 100%

$[\alpha]_D^{20} = +63.6$ (c, 1.0 in acetone)

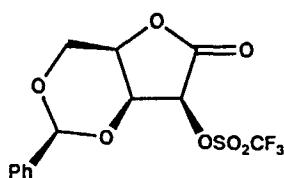
Source of chirality: D-lyxonolactone as starting material

C₁₃H₁₁F₃O₇S

3,5-O-benzylidene-2-O-trifluoromethanesulphonyl-D-xylonolactone

Y.Wang, G.W.J.Fleet, R.Storer, P.L.Myers, C.J.Wallis, O.Doherty,
D.J.Watkin, K.Vogt, D.R.Witty, F.X.Wilson, J.M.Peach

Tetrahedron: Asymmetry 1990, 1, 525



E.e. = 100%

$[\alpha]_D^{20} = +60.5$ (c, 1.0 in acetone)

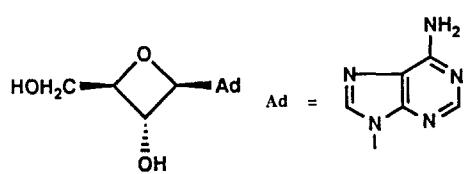
Source of chirality: D-lyxonolactone as starting material

C₁₃H₁₁F₃O₇S

3,5-O-benzylidene-2-O-trifluoromethanesulphonyl-D-lyxonolactone

F.X.Wilson, G.W.J.Fleet, K.Vogt, D.R.Witty, Y.Wang, R.Storer,
P.L.Myers, C.J.Wallis

Tetrahedron: Asymmetry 1990, 1, 527



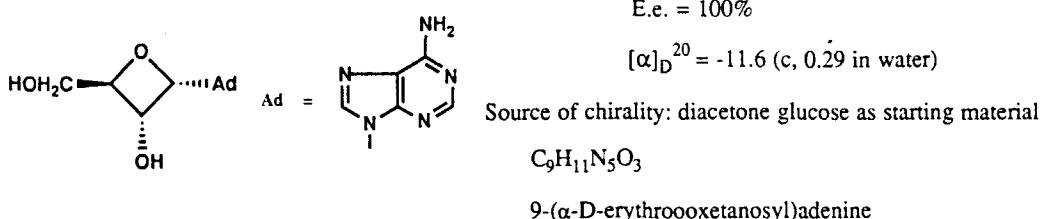
E.e. = 100%

$[\alpha]_D^{20} = -11.25$ (c, 0.24 in water)

Source of chirality: diacetone glucose as starting material

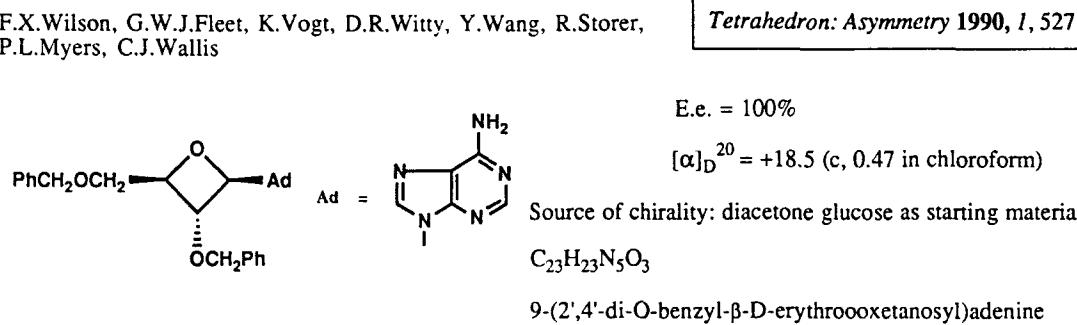
C₉H₁₁N₅O₃ noroxetanocin

9-(β-D-erythroooxetanosyl)adenine



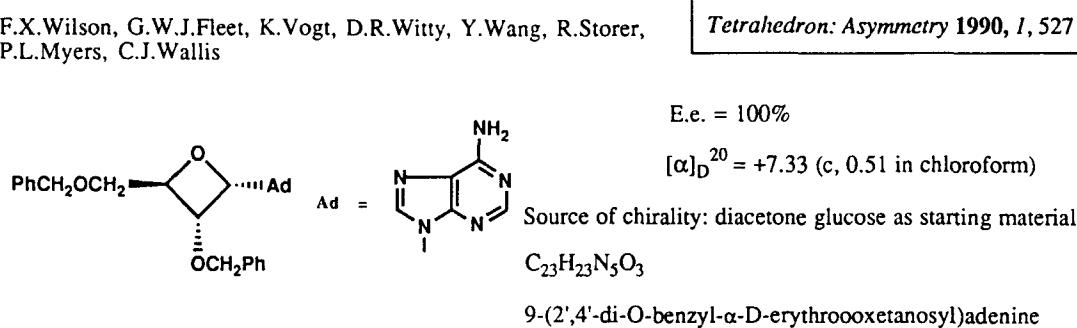
E.e. = 100%

$[\alpha]_D^{20} = -11.6$ (c, 0.29 in water)



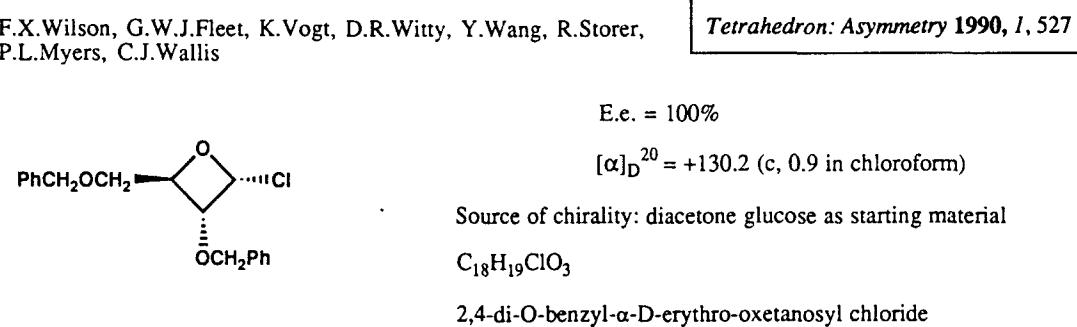
E.e. = 100%

$[\alpha]_D^{20} = +18.5$ (c, 0.47 in chloroform)



E.e. = 100%

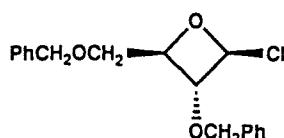
$[\alpha]_D^{20} = +7.33$ (c, 0.51 in chloroform)



E.e. = 100%

$[\alpha]_D^{20} = +130.2$ (c, 0.9 in chloroform)

A69



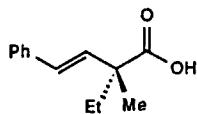
E.e. = 100%

$[\alpha]_D^{20} = -3.2$ (c, 1.4 in chloroform)

Source of chirality: diacetone glucose as starting material

C₁₈H₁₉ClO₃

2,4-di-O-benzyl-beta-D-erythro-oxetanoyl chloride



E.e. = 96% [by ¹H n.m.r. of amide formed with (S)-(-)-alpha-methylbenzylamine]

$[\alpha]_{546}^{25} = +8.8$ (c = 1.7 g/100 ml, CHCl₃)

(*Nouv. J. Chim.*, 1977, 1, 243)

Source of chirality: (S)-(-)-alpha-methylbenzylamine

Absolute configuration: R

Trans-2-methyl-2-ethyl-4-phenylbut-3-enoic acid

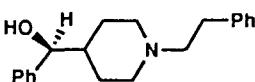
E.e. ≥ 97% (¹⁹F NMR of alpha-methoxy-alpha-trifluoromethylphenyl acetate ester)

$[\alpha]_D^{20} = -29.9$ (c = 1.0, CHCl₃)

Source of chirality: enzymatic resolution

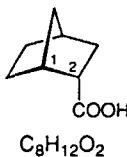
Absolute configuration: S (¹H NMR of O-methylmandelate ester)

m.p. = 123–125°C



C₂₀H₂₅NO

S-(-)-alpha-phenyl-1-(2-phenethyl)-4-piperidinemethanol



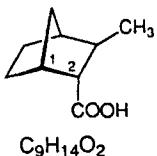
ee = >99 % (by HPLC analysis of a precursor)

$|\alpha|_{D}^{22} = -31.5$ (c = 1.06, 95 % ethanol)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1R, 2S

(1R,2S)-2-Bicyclo[2.2.1]heptane-2-carboxylic acid



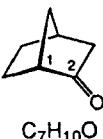
(1R,2R,3R)-3-Methyl-bicyclo[2.2.1]heptane-2-carboxylic acid

ee = >99 % (by HPLC analysis of a precursor)

|α|²²_D - 45.9 (c = 5.63, 95 % ethanol)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1R, 2R, 3R



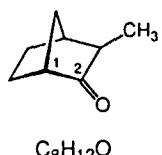
(1R)-2-Bicyclo[2.2.1] heptanone

ee = >99 % (by HPLC analysis of a precursor)

|α|²⁵_D - 29.6 (c = 2.2, chloroform)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1R



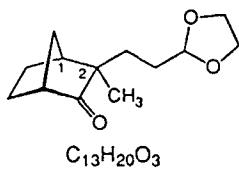
(1R,3R)-3-Methyl-bicyclo[2.2.1]heptan-2-one

ee = >99 % (by HPLC analysis of a precursor)

|α|¹⁹_D - 51.5 (c = 1.35, chloroform)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1R, 3R



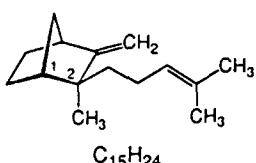
(1S,2R)-2-[{(2-Methyl-3-oxo-bicyclo[2.2.1]hept-2-yl)-2-ethenyl}-1,3-dioxolane

ee = >99 % (by HPLC analysis of a precursor)

|α|²²_D - 83.0 (c = 3.84, chloroform)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1S, 2R



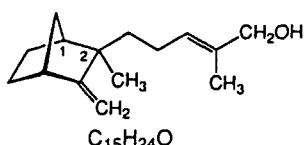
ee = >99 % (by HPLC analysis of a precursor)

$[\alpha]_D^{20} +119.8$ (c = 0.99, chloroform)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1R, 2S

(1R,2S)-2-Methyl-5-(2-methyl-3-methylidene)bicyclo[2.2.1]hept-2-yl)-2-pentene [ent- β -Santalene]



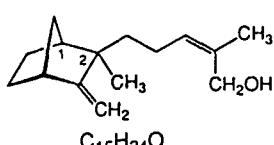
ee = >99 % (by HPLC analysis of a precursor)

$[\alpha]_D^{21} -113.7$ (c = 0.33, chloroform)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1S, 2R

(1S,2R)-(E)-2-Methyl-5-(2-methyl-3-methylidene)bicyclo[2.2.1]hept-2-yl)-2-penten-1-ol [(E)- β -Santalol]



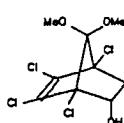
ee = >99 % (by HPLC analysis of a precursor)

$[\alpha]_D^{20} -109.4$ (c = 0.7, methanol)

Source of chirality: diastereoselective Diels-Alder reaction

Absolute configuration: 1S, 2R

(1S,2R)-(Z)-2-Methyl-5-(2-methyl-3-methylidene)bicyclo[2.2.1]hept-2-yl)-2-penten-1-ol [(Z)- β -Santalol]



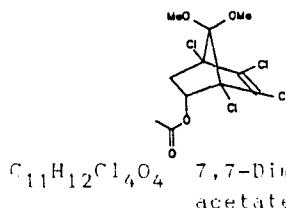
E.e.=98% (by (-)-menthyl chloroformate)

$[\alpha]_D^{20} -34.9$ (c 2.54, MeOH)

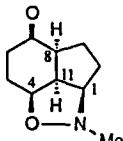
Source of chirality: enzymatic resolution

Absolute configuration 1R, 2S, 4S by chemical correlation with lit.

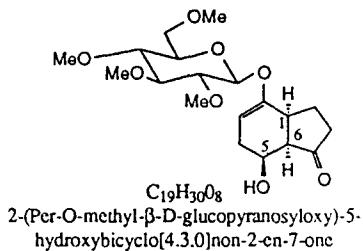
C9H10Cl4O3 7,7-Dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-en-2-ol



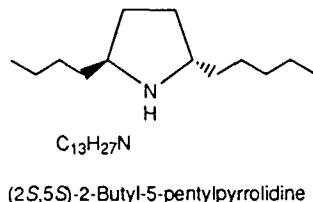
E.e. >99% (by $(-)$ -menthyl chloroformate)
 $[\alpha]_D^{20} = +47.6$ ($c = 2.85$, MeOH)
 Source of chirality: enzymatic resolution
 Absolute configuration 1S, 2R, 4R by chemical correlation with lit.



E.e. = 90 % [by nmr with Eu(fod)₃]
 $[\alpha]_D^{20} = +50.2$ ($c = 1.4$, CDCl₃)
 CD : $\Delta\epsilon = 0.7$ (R-band at 292 nm)
 Source of chirality : asymmetric synthesis
 (diastereoselective alkylation)
 Absolute configuration : 1R, 4S, 8S, 11S
 (assigned by conversion to known compound and CD).



E.e. = 92 % [by nmr with Eu(fod)₃]
 $[\alpha]_D^{20} = +60.5$ ($c = 0.4$, CDCl₃)
 Source of chirality : asymmetric synthesis
 (diastereoselective alkylation)
 Absolute configuration : 1S, 5S, 6R
 (assigned by conversion to known compound).



E.e. = 98% [by nmr with MTPA ester]

$[\alpha]_D^\infty = +8.8$ ($c = 1.05$, MeOH)

Source of chirality: (S)-(+) -2-aminohexanoic acid

Absolute configuration: 2S,5S