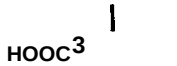
L. DUHAMEL, A. RAVARD, J. C. PLAQUEVENT

Tetrahedron: Asymmetry **1990, I,** 341



$C_{12}H_{20}O_2$

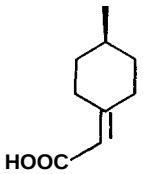
4-tert-Butylcyclohexylideneacetic acid

E.e.= 82 %, $[\alpha]_{546}^{25}$ = +77.3 (1. EtOH)

Source of chiraiity : enantioselective dehydrochlorination by means of **chiral** lithium amide
Absolute configuration : S
(assigned by the comparison of the sign of the specific rotation)

L. DUHAMEL, A. RAVARD, J.C. PLAQUEVENT

Tetrahedron: Asymmetry **1990,** *1*, 347



$C_9H_{14}O_2$

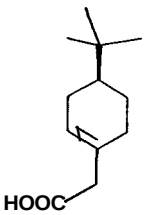
4-Methylcyclohexylideneacetic acid

E.e. = 80 %, $[\alpha]_{546}^{25}$ = +76.8 (0.9, EtOH)

Source of chirality : enantioseiective dehydrochtorinatlon by means of chlral lithium amide
Absolute conflguration : S
(assigned by the comparison of the sign of the specific rotation)

L. DUHAMEL, A. RAVARD, J. C. PLAQUEVENT

Tetrahedron: Asymmetry **1990, I,** 347



$C_{12}H_{20}O_2$

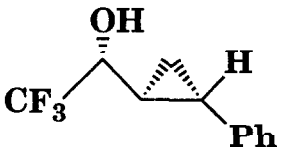
4-tert-Butyl-1-cyclohexeneacetic acid

E.e = 52 %, $[\alpha]_{546}^{25}$ = - 57.4 (0.7, EtOH)

Source of chirality : enantioselective deconjugation of the **isomeric (S) 4-tert-butylcyclohexylideneacetic** acid under basic treatment.
Absolute configuration : S
(assigned by mechanistic considerations)

T. **Yamazaki,** J-T. Lin, M. Takeda and T. Kitazume

Tetrahedron: Asymmetry **1990,** *1*, 35 1



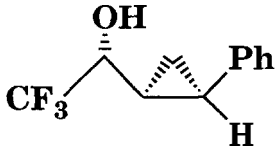
$C_{10}H_{11}F_3O$

1-Trifluoromethyl-3-phenyl-(2,3)-cyclopropyl-1-propanol

E.e = >95% [by GLC with (-)-MTPA ester]
$[\alpha]_D^{21}$ = +57.9 (c = 1.04 , MeOH)
Source of chirality: sammarium-based carbenoids
Absolute configuration 1R
Relative configuration (E)-syn

T. **Yamazaki,** J-T. Lin, M. Takeda and T. Kitazume

Tetrahedron: Asymmetry **1990,** *1*, 351



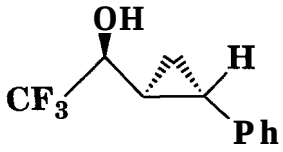
$C_{10}H_{11}F_3O$

E.e = >95% [by GLC with (-)-MTPA ester]
$[\alpha]_D^{21}$ = +124.7 (c = 1.01, MeOH)
Source of chirality: sammarium-based carbenoids
Absolute configuration 1R
Relative configuration (Z)-syn

1-Trifluoromethyl-3-phenyl-(2,3)-cyclopropyl-1-propanol

T. Yamazaki, J-T. Lin, M. Takeda and T. Kitazume

Tetrahedron: Asymmetry **1990,** *1*, 351



$C_{10}H_{11}F_3O$

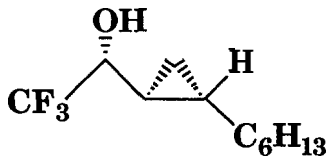
E.e = >95% [by GLC with (-)-MTPA ester]
$[\alpha]_D^{21}$ = +13.4 (c = 1.03 , MeOH)
Source of chirality: sammarium-based carbenoids
Absolute configuration 1S
Relative configuration (E)-anti

1-Trifluoromethyl-3-phenyl-(2,3)-cyclopropyl-1-propanol

1

T. Yamazaki, J-T. Lin, M. Takeda and T. Kitazume

Tetrahedron: Asymmetry **1990,** *1*, 351



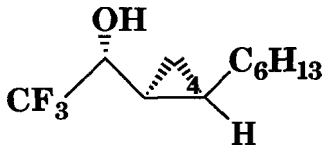
$C_{11}H_{19}F_3O$

E.e = >93% [by GLC with (-)-MTPA ester]
$[\alpha]_D^{21}$ = +12.2 (c = 1.13, MeOH)
source of chirality: sammarium-based carbenoids
Absolute configuration 1R
Relative configuration (E)-syn

1-Trifluoromethyl-3-hexyl-(2,3)-cyclopropyl-1-propanol

T. Yamazaki, J-T. Lin, M. Takeda and T. Kitazume

Tetrahedron: Asymmetry **1990,** *1*, 351



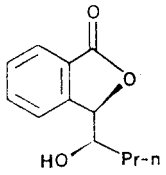
$C_{11}H_{19}F_3O$

E.e = >93% [by GLC with (-)-MTPA ester]
$[\alpha]_D^{21}$ = +2.90 (c = 1.14, MeOH)
Source of chirality: sammarium-based carbenoids
Absolute configuration 1R
Relative configuration (Z)-syn

1-Trifluoromethyl-3-hexyl-(2,3)-cyclopropyl-1-propanol

R. Annunziata, M. Cinquini, F. Cozzi, P. Giaroni

Tetrahedron: Asymmetry **1990, I,** 355



$C_{12}H_{14}O_3$

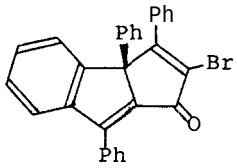
3-(1-Hydroxybutyl)-1(3H)-isobenzofuranone

D.e. ⩾96% bynmr
E.e. ⩾96% by LSR/nmr
m.p. 106-107°C
$[\alpha]_D^{22}$ -40.0 (c 0.5 , $CHCl_3$)

Source of chirality: asymmetric synthesis
Absolute configuration: R,R assigned by chemical **correlation**

F. Toda and K. Tanaka

Tetrahedron: Asymmetry **1990,** *1*, 359



$C_{30}H_{19}OBr$

Name: 7-Bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]-octa-2,4,7-trien-6-one
E.e.=100%[by HPLC of YMC A-KO3]
$[\alpha]_D^{20}$ +480 and -480 (*c* 0.41, $CHCl_3$)
Source of chirality: prepared by preferential crystallization as an inclusion complex with solvent

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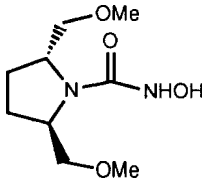
V. Gouverneur and L. Ghosez

Tetrahedron: Asymmetry **1990,** *1*, 363

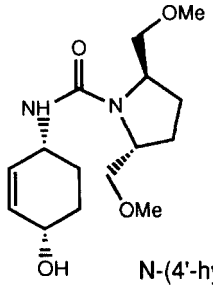


$C_9H_{18}N_2O_4$
N-(hydroxycarbamoyl)-2,5-bismethoxymethylpyrrolidine

Homochiral
[a] $^{25}_D$=+1 11.6 (c 0.62 , MeOH)
Source of chirality : 2,5-(R,R)-pyrrolidine
Absolute configuration : 2R,5R

V. Gouverneur and L. Ghosez

Tetrahedron: ***Asymmetry*** **1990,** *1*, 363



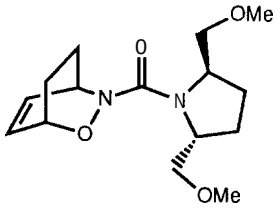
$C_{15}H_{26}N_2O_4$

N-(4'-hydroxycyclohex-2'-en)-2,5-bis(methoxymethyl)-pyrrolidinocarboxamide

Homochiral
[a] $^{25}_D$=+151.73 (c 0.66 , MeOH)
Source of chirality : reduction of the corresponding cycloadduct
Absolute configuration : 2R,5R,1'R,4'S (assigned by the X-Ray diffraction analysis by reference to the known configuration of the asymmetric carbon atoms of the pyrrolidine ring)

V.Gouverneur and L.Ghosez

Tetrahedron: Asymmetry **1990,** *1,363*

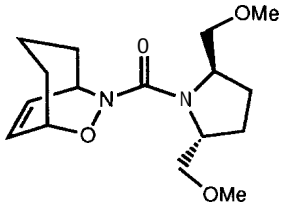


Homochiral
[a] $^{25}_{D}$=+106.8 (c 1.24 , MeOH)
Source of chirality : asymmetric cycloaddition of chiral carbamoylnitroso compound
Absolute configuration : 2'R,5'R,1S,4R (by reference to the known configuration of the reduced product)

$C_{15}H_{24}N_2O_4$
3-(2',5'-bis(methoxymethyl)-pyrrolidinocarbonyl)-2-oxa-3-aza-bicyclo[2,2,2]oct-5-ene

V.Gouverneur and L.Ghosez

Tetrahedron: Asymmetry **1990,** *1*, 363

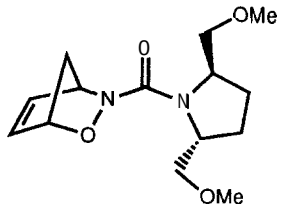


Homochiral
[a] $^{25}_{D}$=+94.9 (c 0.69, MeOH)
Source of chirality : asymmetric cycloaddition of chiral carbamoylnitroso compound
Absolute configuration : 2'R,5R',1S,4R (by analogy with the cyclohexadiene adduct)

$C_{16}H_{26}N_2O_4$
3- (2',5'-bis(methoxymethyl)-pyrrolidinocarbonyl)-2-oxa-3-aza-bicyclo[3,2,2]non-5-ene

V.Gouverneur and L.Ghosez

Tetrahedron: Asymmetry **1990,** I, *363*

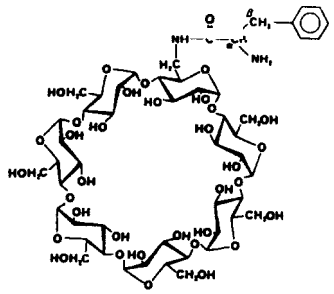


Homochiral
[a] $^{25}_{D}$=+149.5 (c 0.19 , MeOH)
Source of chirality : asymmetric cycloaddition of chiral carbamoylnitroso compound
Absolute configuration : 2'R,5'R,1S,4R (by analogy with the cyclohexadiene adduct)

$C_{14}H_{22}N_2O_4$
3-(2',5'-bis(methoxymethyl)-pyrrolidinocarbonyl)-2-oxa-3-aza-bicyclo[2,2,1]hept-5-ene

H. Parrot-Lopez, H. Galons, A.W. Coleman, F. **Djedaïni,** N. Keller and B. Perly

Tetrahedron: Asymmetry **1990,** *1,367*



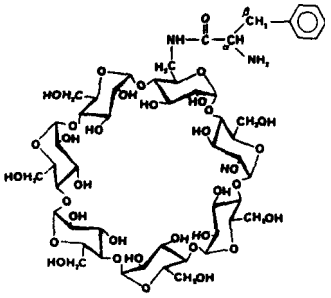
Mono **6-L-phenylanylamino-6-deoxy β-cyclodextrin**

Absolute configuration : **S** at **Cα**

Source of Chirality : Optically **pure** amino-acid and racemization-free coupling.

H. Parrot-Lopez, H. Galons, A.W. Coleman, F. Djedaïni, N. Keller and B. Perly

Tetrahedron: Asymmetry **1990,** *1*, 367



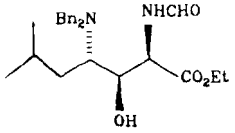
Mono **6-D-phenylanylamino-6-deoxy β-cyclodextrin**

Absolute configuration : R at **Cα**

Source of Chirality : Optically pure amino-acid and racemization-free coupling.

M.T. Reetz, T. Wünsch, K. Harms

Tetrahedron: Asymmetry **1990,** *1*, 371



$C_{25}H_{34}N_2O_4$

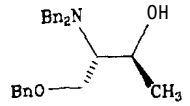
(2R,3S,4S)-2-(N-formylamino)-3-hydroxy-4-(N,N-dibenzylamino)-6-methyl heptanoic acid ethylester

Source of chirality: S-leucine
ee = > 96 %
Absolute configuration: 2R,3S,4S

3 further examples based on other S-amino acids

M.T. Reetz, M.W. Drewes, K. Lennick, A. Schmitz, X. Holdgriin

Tetrahedron: Asymmetry **1990,** *1* , 375



$C_{25}H_{29}NO_2$

4-Benzyloxy-3-(N,N-dibenzylamino)-2-butanol

Source of chirality: S-serine
ee = 99 %
Absolute configuration: 2S,3S

16 further examples of S,S configurated amino alcohols from other amino acids

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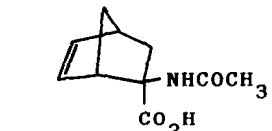
C. Cativiela. P. López, J. A. Mayoral.

Tetrahedron: Asymmetry **1990,** *1*, 379



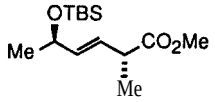
$C_{10}H_{13}NO_2$

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

Absolute configuration: 1S,2R,4S
(assigned by comparing with the corresponding hydrogenated amino acid)

T. Ibuka, H. Habashita, S. Funakoshi, N. Fujii, K. Baba, M. Kozawa, Y. Oguchi, T. Uyehara, and Y. Yamamoto

Tetrahedron: Asymmetry 1990, I, 389



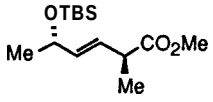
D.e = > 98 % [by ^{1}H NMR with Eu(hfc)$_3$]
$[\alpha]^{25}_D$ = - 30.9 (c = 0.687, CHCl 3)
$\Delta\varepsilon$ = - 4.65 (216) (in isooctane)
Source of Chirality: L-Threonine
Absolute Configumtion: 2*R*,5*R*

$C_{14}H_{28}O_3Si$

Methyl (*E*,2*R*,5*R*)-2-Methyl-5-(*tert*-butyldimethylsiloxy)-3-hexenoate

T. Ibuka, H. Habashita, S. Funakoshi, N. Fujii, K. Baba, M. Kozawa, Y. Oguchi, T. Uyehara, and Y. Yamamoto

Tetrahedron: Asymmetry **1990,** *1*, *389*



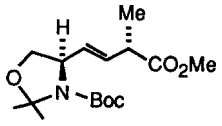
D.e = > 98 % [by ^{1}H NMR with Eu(hfc)$_3$]
$[\alpha]^{27}_D$ = + 30.8 (c = 0.761, CHC13)
A& = + 4.67 (216) (in isooctane)
Source of Chirality: D-Threonine
Absolute Configuration: 2*S*,5*S*

$C_{14}H_{28}O_3Si$

Methyl (*E*,2*S*,5*S*)-2-Methyl-5-(*tert*-butyldimethylsiloxy)-3-hexenoate

T. Ibuka, H. Habashita, S. Funakoshi. N. Fujii, K. Baba, M. Kozawa, Y. Oguchi, T. Uyehara, and Y. Yamamoto

Tetrahedron: Asymmetry **1990,** *1*, *389*



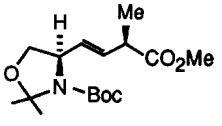
D.e = > 95 % [by ^{1}H NMR and capillary GC]
$[\alpha]^{20}_D$ = + 27.1 (c = 0.597, CHCl 3)
$\Delta\varepsilon$ = + 6.80 (216) (in isooctane)
Source of Chirality: L-Serine

$C_{16}H_{27}O_5N$

Methyl (2*S*,3*E*)-4-[(4*R*)-N-*tert*-Butoxycarbonyl-2,2-dimethyl-4-oxazolidinyl]-2-methyl-3-butenoate

T. Ibuka, H. Habashita. S. Funakoshi, N. Fujii, K. Baba, M. Kozawa, Y. Oguchi, T. Uyehara. and Y. Yamamoto

Tetrahedron: Asymmetry **1990,** *1*, *389*



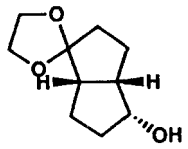
D.e = > 98 % [by ^{1}H NMR and capillary GC]
$[\alpha]^{20}_D$ = - 31.6 (c = 0.645, CHC13)
$\Delta\varepsilon$ = - 3.73 (219) (in isooctane)
Source of Chirality: L-Serine

$C_{16}H_{27}O_5N$

Methyl (2 *R*,3*E*)-4-[(4*R*)-N-*tert*-Butoxycarbonyl-2,2-dimethyl-4-oxazolidinyl]-2-methyl-3-butenoate

Z.-F. Xie, H. Suemune, and K. Sakai

Tetrahedron: Asymmetry **1990,** *1,395*



$C_{10}H_{16}O_3$

(1S,2R,5S)-2-Hydroxy-6,6-ethylenedioxybicyclo[3.3.0]octane

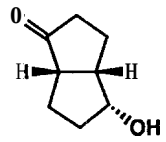
E.e.=99% [by ^{1}H NMR of its (+)-MTPA ester]

$[\alpha]_D^{21}$ +29.7 (c=1.0, $CHCl_3$)

Source of chirality; enantioselective enzymatic hydrolysis

Z.-F. Xie, H. Suemune, and K. Sakai

Tetrahedron: Asymmetry **1990,** *1*, 395



$C_8H_{12}O_2$

(1S,2R,5S)-2-Hydroxy-6-oxo-bicyclo[3.3.0]octane

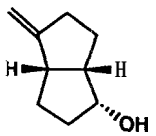
E.e.=99% [by ^{1}H NMR of its (+)-MTPA ester]

$[\alpha]_D^{20}$ +103.8 (c=1.38, $CHCl_3$)

Source of chirality; enantioselective enzymatic hydrolysis

Z.-F. Xie, H. Suemune, and K. Sakai

Tetrahedron: Asymmetry **1990,** *1*, 395



$C_9H_{14}O$

(1S,2R,5S)-2-Hydroxy-6-methylenebicyclo[3.3.0]octane

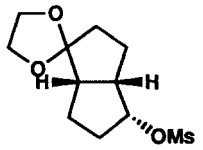
E.e.=99% [by ^{1}H NMR of its (+)-MTPA ester]

$[\alpha]_D^{25}$ +67.6 (c=0.34, $CHCl_3$)

Source of chirality; enantioselective enzymatic hydrolysis

Z.-F. Xie, H. Suemune, and K. Sakai

Tetrahedron: Asymmetry **1990,** *1*, 395



$C_{11}H_{18}O_5S$

(1S,2R,5S)-6,6-Ethylenedioxy-2-mesyloxybicyclo[3.3.0]octane

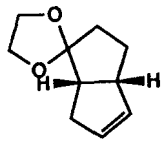
E.e.=99% [by ^{1}H NMR of a precursor]

$[\alpha]_D^{22}$ +54.7 (c=1.0, $CHCl_3$)

Source of chirality; enantioselective enzymatic hydrolysis

Z.-F. Xie, H. Suemune, and K. Sakai

Tetrahedron: Asymmetry **1990,** *1,395*



$C_{10}H_{14}O_2$

(1S,2R,5S)-6,6-Ethylenedioxy-bicyclo[3.3.0]octan-2-ene

E.e.=99% [by ^{1}H NMR of a precursor]
$[\alpha]_D^{21}$ -39.7 (c=1.27, $CHCl_3$)
Source of chirality; enantioselective enzymatic hydrolysis

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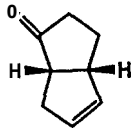
Tetrahedron: Asymmetry **1990,** *1, 395*



$C_8H_{10}O$

(1S,2R,5S)-2-Hydroxy-6-methylenebicyclo[3.3.0]octane

E.e.=99% [by ^{1}H NMR of a precursor]
$[\alpha]_D^{25}$ +259.2 (c=1.30, $CHCl_3$)
Source of chirality; enantioselective enzymatic hydrolysis

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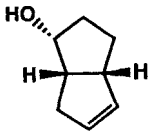
Tetrahedron: Asymmetry **1990,** *1, 395*



$C_8H_{12}O$

(1S,2R,5S)-2-Hydroxy-bicyclo[3.3.0]oct-6-ene

E.e.=99% [by ^{1}H NMR of a precursor]
$[\alpha]_D^{20}$ -67.5 (c=1.28, $CHCl_3$)
Source of chirality; enantioselective enzymatic hydrolysis