

STEREOCHEMISTRY ABSTRACTS

K.-H. Engel

Tetrahedron: Asymmetry 1991, 2, 165

E.e=97% [by GC of (S)-2-octyl ester]

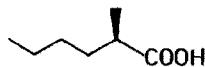
$[\alpha]_D^{20} = -20.2$ (c 5.3, Et₂O)

Source of chirality: lipase-catalyzed esterification

C₇H₁₄O₂

2-Methylhexanoic acid

Absolute configuration: R



K.-H. Engel

Tetrahedron: Asymmetry 1991, 2, 165

E.e=98% [by GC of (S)-2-octyl ester]

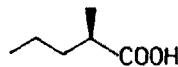
$[\alpha]_D^{20} = -20.1$ (c 5.5, Et₂O)

Source of chirality: lipase-catalyzed esterification

C₆H₁₂O₂

2-Methylpentanoic acid

Absolute configuration: R



K.-H. Engel

Tetrahedron: Asymmetry 1991, 2, 165

E.e=80% [by alkaline hydrolysis and GC of (S)-2-octyl ester]

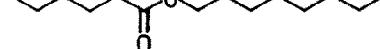
$[\alpha]_D^{20} = +11.3$ (c 5.4, Et₂O)

Source of chirality: lipase-catalyzed esterification

C₁₅H₃₀O₂

Octyl 2-methylhexanoate

Absolute configuration: S



K.-H. Engel

Tetrahedron: Asymmetry 1991, 2, 165

E.e=93% [by alkaline hydrolysis and GC of (S)-2-octylester]

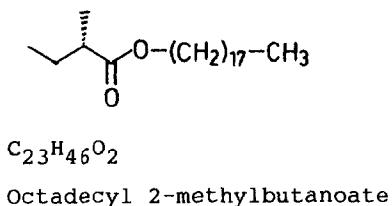
$[\alpha]_D^{20} = +11.4$ (c 5.5, Et₂O)

Source of chirality: lipase-catalyzed esterification

C₁₄H₂₈O₂

Octyl 2-methylpentanoate

Absolute configuration: S

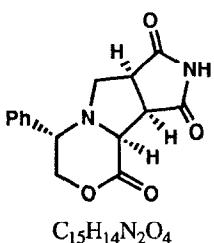


E.e=51% [by alkaline hydrolysis and GC of (R)-1-phenylethylamide]

$[\alpha]_D^{20}=+4.2$ (c 5.5, Et_2O)

Source of chirality: lipase-catalyzed esterification

Absolute configuration:S

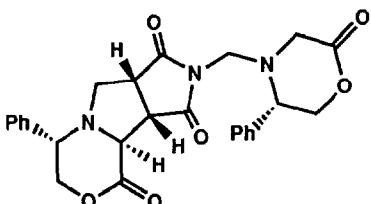


$[\alpha]_D^{20}=+45.3$ (c 1.0, CHCl_3)

Source of chirality (R)-2-phenylglycinol

Absolute configuration : 2(R), 6(S), 7(R), 8(R)

2(R),6(S),7(R),8(R) 1-aza-4-oxa[4.3.0^{1,6}]bicyclonanon-5-one-7,8-dicarboximide

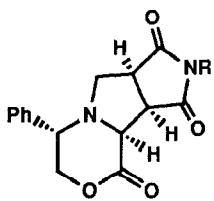


$[\alpha]_D^{20}=+13.0$ (c 1.0, CHCl_3)

Source of chirality (R)-2-phenylglycinol

Absolute configuration : 2(R), 6(S), 7(S), 8(S), 5'(R)

N -(5'(R)-phenylmorpholin-2-onyl)methyl 2(R),6(S),7(R),8(R)
1-aza-4-oxa[4.3.0^{1,6}]bicyclonanon-5-one-7,8-dicarboximide



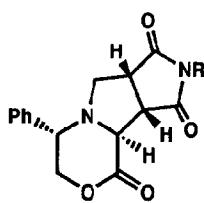
R = Me : $C_{16}H_{16}N_2O_4$ $[\alpha]_D^{20}=+45.0$ (c 1.0, CHCl_3)

R = Ph : $C_{21}H_{18}N_2O_4$ $[\alpha]_D^{20}=-42.3$ (c 0.6, CHCl_3)

Source of chirality (R)-2-phenylglycinol

Absolute configuration : 2(R), 6(S), 7(R), 8(R)

N -methyl (or phenyl) 2(R),6(S),7(R),8(R) 1-aza-4-oxa[4.3.0^{1,6}]bicyclonanon-5-one-7,8-dicarboximide



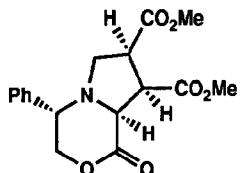
R = Me : C₁₆H₁₆N₂O₄ [α]_D²⁰ = +30.9 (c 1.0, CHCl₃)

R = Ph : C₂₁H₁₈N₂O₄ [α]_D²⁰ = +88.0 (c 0.25, CHCl₃)

Source of chirality (*R*)-2-phenylglycinol

Absolute configuration : 2(*R*), 6(*S*), 7(*S*), 8(*S*)

N-methyl (or phenyl) 2(*R*),6(*S*),7(*S*),8(*S*) 1-aza-4-oxa[4.3.0^{1,6}]bicyclonan-5-one-7,8-dicarboximide



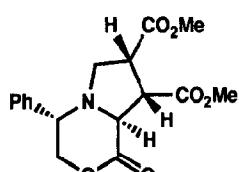
[α]_D²⁰ = +6.0 (c 0.73, CHCl₃)

Source of chirality (*R*)-2-phenylglycinol

Absolute configuration : 2(*R*), 6(*S*), 7(*R*), 8(*R*)

C₁₇H₁₉NO₆

2(*R*),6(*S*),7(*R*),8(*R*) dimethyl 1-aza-4-oxa[4.3.0^{1,6}]bicyclonan-5-one-7,8-dicarboxylate



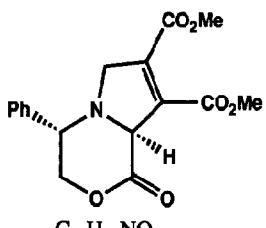
[α]_D²⁰ = -14.7 (c 0.87, CHCl₃)

Source of chirality (*R*)-2-phenylglycinol

Absolute configuration : 2(*R*), 6(*S*), 7(*S*), 8(*S*)

C₁₇H₁₉NO₆

2(*R*),6(*S*),7(*S*),8(*S*) dimethyl 1-aza-4-oxa[4.3.0^{1,6}]bicyclonan-5-one-7,8-dicarboxylate



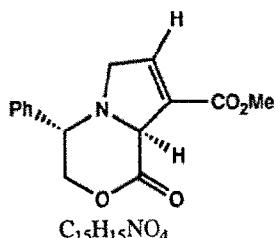
[α]_D²⁰ = -76.0 (c 0.82, CHCl₃)

Source of chirality (*R*)-2-phenylglycinol

Absolute configuration : 2(*R*), 6(*S*)

C₁₇H₁₇NO₆

2(*R*),6(*S*) dimethyl 1-aza-4-oxa[4.3.0^{1,6}]bicyclonan-7-en-5-one-7,8-dicarboxylate

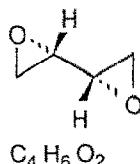


$[\alpha]_D^{20} = -32.8$ (c 0.83, CHCl₃)

Source of chirality (*R*)-2-phenylglycinol

Absolute configuration : 2(*R*), 6(*S*)

2(*R*), 6(*S*) methyl 1-aza-4-oxa[4.3.0]^{1,6}bicyclonan-7-en-5-one-7-carboxylate

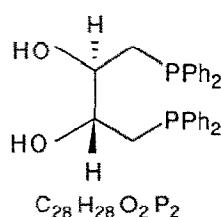


(S,S)-1,2:3,4-diepoxy-butane

E.e. = 100 %

$[\alpha]_D^{22} = -24$ (c, 4.5 in CCl₄)

Source of chirality: (*R,R*)-tartaric acid

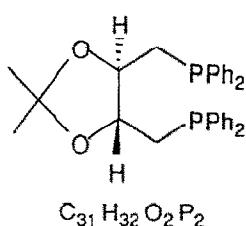


(2*R*,3*R*)-1,4-bis(diphenylphosphino)-2,3-butanediol

E.e. = 100 %

$[\alpha]_D^{22} = -34.2$ (c, 0.76 in CHCl₃)

Source of chirality: (*R,R*)-tartaric acid

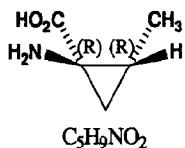


(2*R*,3*R*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane (DIOP)

E.e. = 100 %

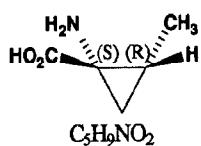
$[\alpha]_D^{22} = -12.5$ (c, 4.19 in benzene)

Source of chirality: (*R,R*)-tartaric acid



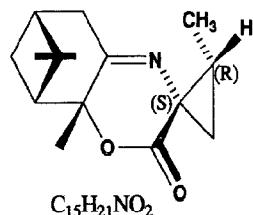
ee \Rightarrow 99%
 $[\alpha]_D^{20} -45$ ($c = 0.4$, H₂O)
 Absolute configuration : 1R,2R
 Source of chirality : asymmetric synthesis

2-Methyl-1-aminocyclopropane-1-carboxylic acid



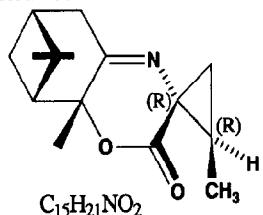
ee \Rightarrow 99%
 $[\alpha]_D^{20} -75$ ($c = 0.3$, H₂O)
 Absolute configuration : 1S,2R
 Source of chirality : asymmetric synthesis

2-Methyl-1-aminocyclopropane-1-carboxylic acid



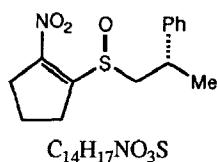
ee \Rightarrow 99%
 $[\alpha]_D^{20} -272$ ($c = 5$, CH₂Cl₂)
 Absolute configuration : 3S,5aR,6aR,6bR,8R
 Source of chirality : Asymmetric synthesis

3-(Pinano[2,3-b]4,5-dehydro-morpholine-2-one]-spiro-1'-(2'-methyl cyclopropane)



ee \Rightarrow 99%
 $[\alpha]_D^{20} -192$ ($c = 5$, CH₂Cl₂)
 Absolute configuration : 3R,5aR,6aR,6bR,8R
 Source of chirality : Asymmetric synthesis

3-(Pinano[2,3-b]4,5-dehydro-morpholine-2-one]-spiro-1'-(2'-methyl cyclopropane)



E.e. = 100%

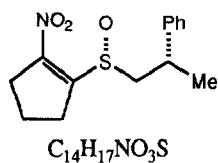
 $[\alpha]_D^{20} = -72.9$ ($c = 1.68, CHCl_3$)

Source of chirality: (S)-Phenylpropionic acid

Absolute configuration: SS, 2S

Use: Chiral dienophile for asymmetric Diels -Alder reaction

(SS,2S)-1-(2-phenylpropylsulfinyl)-2-nitrocyclopentene



E.e. = 100%

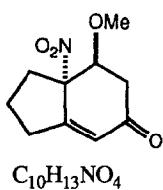
 $[\alpha]_D^{20} = +388.3$ ($c = 0.84, CHCl_3$)

Source of chirality: (S)-Phenylpropionic acid

Absolute configuration: SR, 2S

Use: Chiral dienophile for asymmetric Diels -Alder reaction

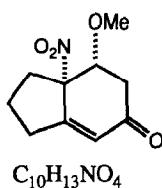
(SR,2S)-1-(2-phenylpropylsulfinyl)-2-nitrocyclopentene

E.e. = >95% [1H -NMR with Eu(hfc)₃] $[\alpha]_D^{22} = +87.1$ ($c = 1.00, CHCl_3$)

Source of chirality: Asymmetric Diels-Alder reaction with chiral sulfoxide

Absolute configuration: 1S, 2S

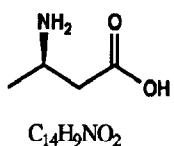
(1S,2S)-Bicyclo[4.3.0]-1-nitro-2-methoxy-5-nonene-4-one

E.e. = >95% [1H -NMR with Eu(hfc)₃] $[\alpha]_D^{22} = +302.5$ ($c = 1.62, CHCl_3$)

Source of chirality: Asymmetric Diels-Alder reaction with chiral sulfoxide

Absolute configuration: 1S, 2R

(1S,2R)-Bicyclo[4.3.0]-1-nitro-2-methoxy-5-nonene-4-one



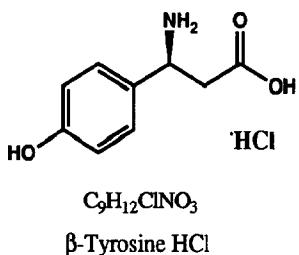
3-Amino butanoic acid

E.e. = 100%

 $[\alpha]_D^{19} -39.8$ ($c = 0.47, \text{H}_2\text{O}$)

Source of chirality: asymmetric synthesis

Absolute configuration: R.

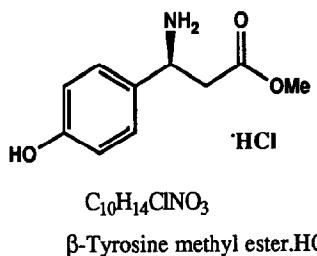


E.e. = >99%

 $[\alpha]_D^{25} +3.55$ ($c = 1.38, \text{H}_2\text{O}$)

Source of chirality: asymmetric synthesis

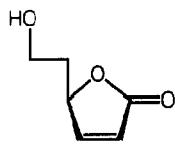
Absolute configuration: S



E.e. = >99%

(by ^1H nmr with S-2,2,2-trifluoro-1-(9-anthryl)ethanol) $[\alpha]_D^{20} +10.55$ ($c = 1.9, \text{H}_2\text{O}$)

Source of chirality: asymmetric synthesis

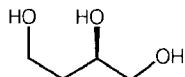
Absolute configuration: S established by correlation with S- β -tyrosine.HCl

(R)-5-(2-Hydroxyethyl)-2(5H)-furanone

 $[\alpha]_D^{25} = -48.2$ ($c 2.2, \text{CHCl}_3$)

Source of chirality: synthesis from (R)-malic acid

B. Herradon

Tetrahedron: Asymmetry 1991, 2, 191

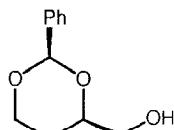
$$[\alpha]_D^{25} = +27.5 \text{ (c 1.1, MeOH)}$$

 $C_4H_{10}O_3$

Source of chirality: synthesis from (R)-malic acid

(R)-1,2,4-Butanetriol

B. Herradon

Tetrahedron: Asymmetry 1991, 2, 191

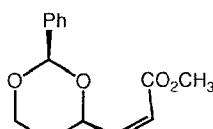
$$[\alpha]_D^{25} = -9.4 \text{ (c 1.2, CHCl}_3\text{)}$$

Source of chirality: synthesis from (R)-malic acid

 $C_{11}H_{14}O_3$

(R,R)-4-Hydroxymethyl-2-phenyl-1,3-dioxane

B. Herradon

Tetrahedron: Asymmetry 1991, 2, 191

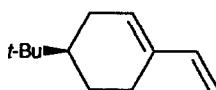
$$[\alpha]_D^{25} = -63.2 \text{ (c 1.2, CHCl}_3\text{)}$$

Source of chirality: synthesis from (R)-malic

 $C_{14}H_{16}O_4$

Methyl (Z)-3-[(R,R)-2-phenyl-1,3-dioxan-4-yl]propenoate

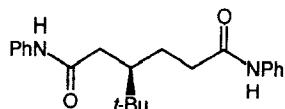
T. Hayashi, K. Kishi, and Y. Uozumi

Tetrahedron: Asymmetry 1991, 2, 195 $C_{12}H_{20}$
4-tert-butyl-1-vinylcyclohexene

E.e. = 21% [by converting into

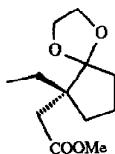
and HPLC with chiral stationary phase column, Sumipax OA-3100]

$$[\alpha]_D^{21} -23.4 \text{ (c 1.0, chloroform)}$$

Source of chirality: catalytic asymmetric elimination of 4-tert-butyl-1-vinylcyclohexyl acetate
Absolute configuration: R (oxidized into (R)-3-tert-butylhexanedioic acid)

J. d'Angelo, G. Revial, P.R.R. Costa, R.N. Castro, O.A.C. Antunes

Tetrahedron: Asymmetry 1991, 2, 199



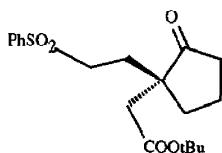
ee 86% (by ^1H NMR)
 $[\alpha]^{20}_D = -1.9^\circ$ (c 10.5 MeOH)
source of chirality : asymm. Michael
absolute configuration : 6 R

$\text{C}_{12}\text{H}_{20}\text{O}_4$

2,5-dioxaspiro[4,4]decane-6-ethyl-6-acetic acid, methyl ester

J. d'Angelo, G. Revial, P.R.R. Costa, R.N. Castro, O.A.C. Antunes

Tetrahedron: Asymmetry 1991, 2, 199



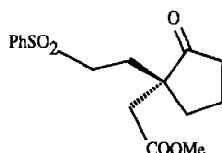
ee 86% (by ^1H NMR)
 $[\alpha]^{20}_D = -0.6^\circ$ (c 5, MeOH)
source of chirality : asymm. Michael
absolute configuration : 1 S

$\text{C}_{19}\text{H}_{26}\text{O}_5\text{S}$

2-oxo-1(2-phenylsulfonylethyl)-cyclopentylacetic acid, r-butyl ester

J. d'Angelo, G. Revial, P.R.R. Costa, R.N. Castro, O.A.C. Antunes

Tetrahedron: Asymmetry 1991, 2, 199



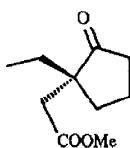
ee 86% (by ^1H NMR)
 $[\alpha]^{20}_D = -1.0^\circ$ (c 5.0, MeOH)
source of chirality : asymm. Michael
absolute configuration : 1 S

$\text{C}_{16}\text{H}_{20}\text{O}_5\text{S}$

2-oxo-1(2-phenylsulfonylethyl)-cyclopentylacetic acid, methyl ester

J. d'Angelo, G. Revial, P.R.R. Costa, R.N. Castro, O.A.C. Antunes

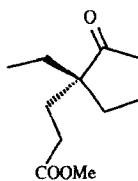
Tetrahedron: Asymmetry 1991, 2, 199



ee 86% (by capillary VPC)
 $[\alpha]^{20}_D = -2.3^\circ$ (c 6.2, CCl_4)
source of chirality : asymm. Michael
absolute configuration : 1 R

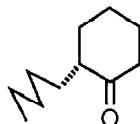
$\text{C}_{10}\text{H}_{16}\text{O}_3$

1-ethyl-2-oxo-cyclopentylacetic acid, methyl ester

 $C_{11}H_{18}O_3$

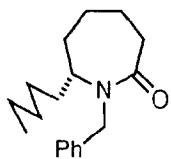
3-(1-ethyl-2-oxo-cyclopentyl)-propionic acid, methyl ester

ee 90 % (by capillary VPC)
 $[\alpha]^{20}_D = -8.4^\circ$ (c 3, EtOH)
 source of chirality : asymm. Michael
 absolute configuration : 1 R

 $C_{11}H_{20}O$

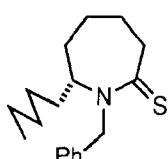
2-Pentylcyclohexanone

E.e. = 78% [by Wynberg's method]
 $[\alpha]^{25}_D = -17.8$ (c=5, MeOH)
 Source of chirality: asymmetric synthesis
 Absolute configuration: R (assigned by analogy
 to J. Amer. Chem. Soc., 1976, **98**, 3032)



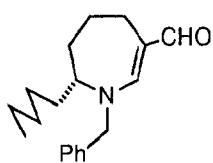
$C_{18}H_{27}NO$
 N-Benzyl-7-pentylhexahydroazepin-2-one

E.e. = 74% [by nmr with Eu(hfc)₃]
 $[\alpha]^{25}_D = +13.0$ (c=6, MeOH)
 Source of chirality: asymmetric synthesis
 Absolute configuration: R



$C_{18}H_{27}NS$
 N-Benzyl-7-pentylhexahydroazepin-2-thione

E.e. = >95% [by nmr of a derivative with Eu(hfc)₃]
 $[\alpha]^{25}_D = +65.8$ (c=5, MeOH)
 Source of chirality: asymmetric synthesis
 Absolute configuration: R

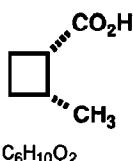
E.e. = >95% [by nmr with Eu(hfc)₃][α]_D²⁵ = +164 (c=5, MeOH)

Source of chirality: asymmetric synthesis

Absolute configuration: R

 $C_{19}H_{27}NO$

N-Benzyl-7-pentyl-[1H]-4,5,6,7-tetrahydroazepine-3-carbaldehyde



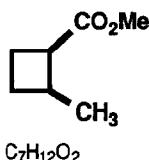
E.e. = >97% (by NMR with (+)-1-methylbenzylamine)

[α]_D²⁵ = +6.8 (c 16.2, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1S,2R

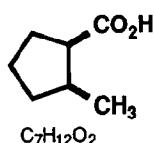
(+)-(1S,2R)-1-carboxy-2-methylcyclobutane

E.e. = >97% (by NMR with Eu(hfc)₃)[α]_D²⁵ = -19.4 (c 5.0, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1R,2S

(-)-(1R,2S)-1-carbomethoxy-2-methylcyclobutane



E.e. = 22 % (by NMR with (+)-1-methylbenzylamine)

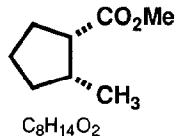
[α]_D²⁵ = +2.4 (c 24.9, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1R,2S

(+)-(1R,2S)-1-carboxy-2-methylcyclopentane

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E.e. = 17% (by NMR with Eu(hfc)₃)

(+)-(1S,2R)-1-carbomethoxy-2-methylcyclopentane

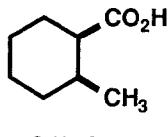
 $[\alpha]_D^{25} = +5.6$ (c 14.8, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

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

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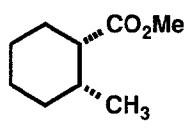
E.e. = >97% (by NMR with (+)-1-methylbenzylamine)

(+)-(1*R*,2*S*)-1-carboxy-2-methylcyclohexane $[\alpha]_D^{25} = +7.4$ (c 37.2, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

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

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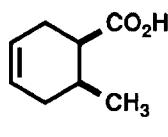
E.e. = >97% (by NMR with Eu(hfc)₃)(-)-(1*S*,2*R*)-1-carbomethoxy-2-methylcyclohexane $[\alpha]_D^{25} = -0.41$ (c 32.4, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

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

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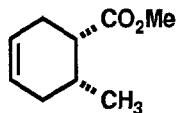
E.e. =>97 % (by NMR with (+)-1-methylbenzylamine)

(-)-(1*R*,2*S*)-1-carboxy-2-methyl-4-cyclohexene $[\alpha]_D^{25} = -26.9$ (c 26, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

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

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(±)-(1S,2R)-1-carbomethoxy-2-methyl-4-cyclohexene

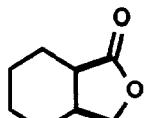
E.e. = >97% (by NMR with Eu(hfc)₃)

[α]_D²⁵ = +18.1 (c 34, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1S,2R

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(-)-(1R,6S)-11

98%, ≥97% ee



(-)-(1R,6S)-8-oxabicyclo[4.3.0]nonan-9-one

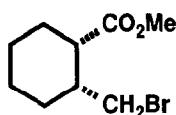
E.e. = >97% (by NMR with Eu(hfc)₃)

[α]_D²⁵ = -38.0 (c 2.37, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1R,6S

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(+)-(1S,2R)-1-carbomethoxy-2-bromomethylcyclohexane

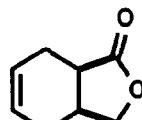
E.e. = >97% (by NMR with Eu(hfc)₃)

[α]_D²⁵ = +11.3 (c 41.0, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1S,2R

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(+)-(1R,6S)-8-oxabicyclo[4.3.0]non-3-ene-9-one

E.e. = >97 % (by NMR with Eu(hfc)₃)

[α]_D²⁵ = +50.9 (c 18.1, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1R,6S

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C₉H₁₃O₂Br

(+)-(1S,2R)-1-carbomethoxy-2-bromomethyl-4-cyclohexene

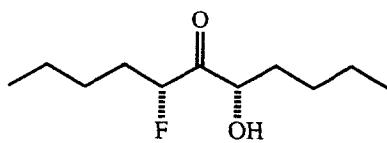
E.e. = >97% (by NMR with Eu(hfc)₃)

[α]_D²⁵ = +29.0 (c 31, CHCl₃)

Source of chirality: Enantioselective enzymic hydrolysis

Absolute configuration: 1S,2R

C. Gosmini, T. Dubuffet, R. Sauvêtre, J.-F. Normant.



7-fluoro undecan-5-ol-6-one

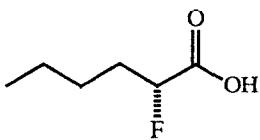
E.e. > 95% [NMR]

[α]_D²⁴ = + 128.84 (c = 6.9, CHCl₃)

Source of chirality : asymmetric epoxidation of fluorinated allylic alcohols

Absolute configuration : 5S, 7R.

C. Gosmini, T. Dubuffet, R. Sauvêtre, J.-F. Normant.



2-fluorohexanoic acid

E.e. > 95% [NMR]

[α]_D²⁵ = + 14.06 (c = 1.7, CHCl₃)

Source of chirality : asymmetric epoxidation of fluorinated allylic alcohols

Absolute configuration : R