

Antonio García Martínez,* Enrique Teso Vilar,* Amelia García Fraile,	Tetrahedron: Asymmetry 13 (2002) 1457
Santiago de la Moya Cerero and Paloma Martínez-Ruiz	

 $[\alpha]_{D}^{20} = +22.2$ (*c* 0.46, MeOH) Source of chirality: natural (1*R*)-Camphor Absolute configuration: 1*R*,2*R*

PhCH_HN $C_{16}H_{23}NO$

2-Benzylamino-3,3-dimethylnorbornan-1-ol

Antonio García Martínez,* Enrique Teso Vilar,* Amelia García Fraile, Santiago de la Moya Cerero and Paloma Martínez-Ruiz $[\alpha]_D^{20} = -1.2 \ (c \ 0.80, \ MeOH)$ Source of chirality: natural (1*R*)-Camphor Absolute configuration: 1*R*,2*R* $C_{\rm u}H_{\rm N}NO$

 $C_{11}H_{21}NO$ 2-Dimethylamino-3,3-dimethylnorbornan-1-ol

Antonio García Martínez,* Enrique Teso Vilar,* Amelia García Fraile, Santiago de la Moya Cerero and Paloma Martínez-Ruiz

> $[\alpha]_{D}^{20} = -26.5$ (*c* 0.85, MeOH) Source of chirality: natural (1*R*)-Camphor Absolute configuration: 1*R*,2*R*

 $C_{11}H_{21}NO$ 1-Dimethylamino-3,3-dimethylnorbornan-2-ol

Tetrahedron: Asymmetry 13 (2002) 1457 Antonio García Martínez,* Enrique Teso Vilar,* Amelia García Fraile, Santiago de la Moya Cerero and Paloma Martínez-Ruiz $[\alpha]_{D}^{20} = +27.1$ (c 0.84, MeOH) Source of chirality: natural (1R)-Camphor Absolute configuration: 1R,2R C₁₃H₂₅NO 1-Diethylamino-3,3-dimethylnorbornan-2-ol Tetrahedron: Asymmetry 13 (2002) 1457 Antonio García Martínez,* Enrique Teso Vilar,* Amelia García Fraile, Santiago de la Moya Cerero and Paloma Martínez-Ruiz $[\alpha]_{D}^{20} = -25.8$ (c 0.88, MeOH) Source of chirality: natural (1R)-Camphor Absolute configuration: 1R,2R C₁₈H₂₇NO 1-[Benzyl(ethyl)amino]-3,3-dimethylnorbornan-2-ol Tetrahedron: Asymmetry 13 (2002) 1461 Anju Chadha* and Baburaj Baskar E.e. >99% $[\alpha]_{D}^{25} = +143 \ (c \ 1, \ CH_{3}OH)$ Source of chirality: biocatalytic deracemisation Absolute configuration: S OOMe $C_9H_{10}O_3$ Methyl (S)-(+)-mandelate Tetrahedron: Asymmetry 13 (2002) 1461 Anju Chadha* and Baburaj Baskar E.e. >99% $[\alpha]_{D}^{25} = +7.5$ (*c* 1, EtOH) Source of chirality: biocatalytic deracemisation HO Absolute configuration: S COOEt

 $C_{12}H_{16}O_{3} \label{eq:c12}$ Ethyl (S)-(+)-2-hydroxy-4-phenylbutanoate

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Isidoro Izquierdo,* María T. Plaza and Francisco Franco $(\alpha |_{D} -27 \ (c \ 1, \ chloroform)$ Source of chirality: D-fructose Absolute configuration: 2*R*,3*S*,4*R*,5*R* (assigned by NMR spectroscopy)

 $C_{36}H_{41}N_3O_5Si$ 5-Azido-3,4-di- ${\it O}$ -benzyl-1- ${\it O}$ -tert-butyldiphenylsilyl-5-deoxy- β -D-fructopyranose















 $[\alpha]_{D}^{30} = -3.2$ (*c* 0.5, CHCl₃) Source of chirality: asymmetric synthesis Absolute configuration: (1R, 2R, 5R, 6R, 7S)

C₁₅H₁₆O₂ (1*R*,2*R*,5*R*,6*R*,7*S*)-6-Benzyloxytricyclo[3.2.1.0^{2,7}]octan-3-one

OBn

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama*

Ee = 95%[α]_D²² = -80.4 (*c* 1.00, CHCl₃) Source of chirality: asymmetric synthesis Absolute configuration: (1*R*,2*R*,5*S*,6*S*,7*S*)

O OBn

C₁₅H₁₄O₃ (1*R*,2*R*,5*S*,6*S*,7*S*)-6-Benzyloxytricyclo[3.2.1.0^{2,7}]octane-3,4-dione

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama*

Tetrahedron: Asymmetry 13 (2002) 1519

Ee = 95%[\$\alpha]_D^{26} = -11.7 (c 1.04, CHCl_3)
Source of chirality: asymmetric synthesis
Absolute configuration: (1*S*,2*S*,3*S*,5*R*,6*R*)

MeO₂C

C₁₇H₂₀O₅ Dimethyl (1*S*,2*S*,3*S*,5*R*,6*R*)-2-benzyloxybicyclo[3.1.0]hexane-3,6-dicarboxylate

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama*

OTBS

TMSO

Tetrahedron: Asymmetry 13 (2002) 1519

Ee = 86% $[\alpha]_D^{26} = +59.6 (c 1.16, CHCl_3)$ Source of chirality: asymmetric synthesis Absolute configuration: not determined

 $\label{eq:C16} C_{16}H_{32}O_2Si_2 \\ (1R^*,5S^*,6S^*)-6-(tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-2-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-3-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxy)bicyclo[3.1.0]hex-3-ene (tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(trimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethyl)-3-(tert-Butyldimethylsilyloxymethylbyldimethylsilyloxymethylbyldimethylsilyloxymethylbyldimethylsilyloxymethylbyldimethylsilyloxymethylbyldimethylby$



 $(1R^*, 2R^*, 5R^*, 6S^*)$ -6-(tert-Butyldimethylsilyloxymethyl)-2-hydroxybicyclo[3.1.0]hexan-3-one

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama*

Tetrahedron: Asymmetry 13 (2002) 1519

Ee = 77% $[\alpha]_D^{26} = -57.8$ (*c* 0.92, CHCl₃) Source of chirality: asymmetric synthesis Absolute configuration: (1*R*,5*S*,6*S*)

Ee = 77%

 $[\alpha]_{D}^{22} = -110.8$ (c 1.27, CHCl₃)

Source of chirality: asymmetric synthesis

Absolute configuration: (1S,5S,6S)

H C₂₄H₂₇F₃O₄SSi (1*R*,5*S*,6*S*)-6-(*tert*-Butyldiphenylsilyloxymethyl)bicyclo[3.1.0]hex-2-ene-3-yl triflate

Tetrahedron: Asymmetry 13 (2002) 1519

OTBDPS MeO₂

 $C_{25}H_{30}O_{3}Si$ Methyl (1*S*,5*S*,6*S*)-6-(*tert*-butyldiphenylsilyloxymethyl)bicyclo[3.1.0]hex-2-ene-3-carboxylate

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama* $Ee = 77\% [x]_{D}^{18} = -109.3 (c 1.50, CHCl_3)$ Source of chirality: asymmetric synthesis Absolute configuration: (1*S*,5*S*,6*S*) (1*S*,5*S*,6*S*)-6-(*tert*-Butyldiphenylsilyloxymethyl)-3-(hydroxymethyl)bicyclo[3.1.0]hex-2-ene Hitoshi Aba * Takanagi Taujing, Kanta Araki, Yagua Takaughi

Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi and Takashi Harayama* Ee=82% $[\alpha]_{D}^{18} = -60.5 \ (c \ 1.20, \ CHCl_{3})$ Source of chirality: asymmetric synthesis TBDPSC OTBDPS Absolute configuration: (1S,5S,6S) C40H48O2Si2 (1S,5S,6S)-3,6-Bis(tert-butyldiphenylsilyloxymethyl)bicyclo[3.1.0]hex-2-ene

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(1*R*,5*S*,6*S*)-6-(*tert*-Butyldiphenylsilyloxymethyl)bicyclo[3.1.0]hex-2-ene-3-yl triflate Hitoshi Abe,* Takenori Tsujino, Kenta Araki, Yasuo Takeuchi

and Takashi Harayama*

TfC

OTBDPS



Tetrahedron: Asymmetry 13 (2002) 1535

 $[\alpha]_D^{22} = +8.9$ (*c* 1.0, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $3R_2S_1'S_2'S_3'R$

 $C_{18}H_{32}N_2O_5$ 2,5-Diethoxy-3,6-dihydro-3-(1-hydroxy-2,3-isopropylidenedioxybutyl)-6-isopropylpyrazine







 $[\alpha]_{D}^{22} = -13.3$ (c 0.7, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $3R_{0}S_{1}I'S_{2}I'S_{3}I'R$



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 $[\alpha]_{D}^{23} = +26.1$ (c 1.0, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $3R_{0}6S_{0}1'R_{0}2'S_{0}3'R$

 $C_{25}H_{38}N_2O_5$ 3-(1-Benzyloxy-2,3-isopropylidenedioxybutyl)-2,5-diethoxy-3,6-dihydro-6-isopropylpyrazine



 $[\alpha]_{D}^{22} = -65.2$ (c 1.5, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $3R_{0}S_{1}I'R_{2}I'S_{3}I'R_{fl}I$

 $C_{25}H_{38}N_2O_5$ 3-(1-Benzyloxy-2,3-isopropylidenedioxybutyl)-2,5-diethoxy-3,6-dihydro-6-isopropylpyrazine

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Source Absolu

C₁₂H₂₃NO₅ Ethyl 2-amino-4,5-isopropylidenedioxy-3-methoxyhexanoate

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 $[\alpha]_{D}^{22} = -15.0$ (c 1.9, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: 2R,3R,4S,5R

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CO₂Et

C₁₈H₂₇NO₅ Ethyl 2-amino-3-benzyloxy-4,5-isopropylidenedioxyhexanoate

 $[\alpha]_D^{22} = -13.3$ (c 1.0, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: 2*R*,3*S*,4*S*,5*R*

Tetrahedron: Asymmetry 13 (2002) 1535

 $[\alpha]_{D}^{26} = -4.0$ (c 1.1, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $2S_{3}R_{4}S_{5}R$



Ethyl 2-amino-3-benzyloxy-4,5-isopropylidenedioxyhexanoate





María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{21} = -5.4 \ (c \ 0.5, \ CH_2Cl_2) \\ Source of chirality: asymmetric aldol reaction \\ Absolute configuration: 2R,3S,4S,5R \end{bmatrix}$

C₂₆H₃₃NO₇ Ethyl 3-benzyloxy-2-[*N*-(benzyloxycarbonyl)amino]-4,5-isopropylidenedioxyhexanoate

Tetrahedron: Asymmetry 13 (2002) 1535

 $[\alpha]_{D}^{21} = -1.4$ (*c* 1.2, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $2S_{3}R_{4}S_{5}R$



C₂₆H₃₃NO₇ Ethyl 3-benzyloxy-2-[N-(benzyloxycarbonyl)amino]-4,5-isopropylidenedioxyhexanoate





María Ruiz,* Vicente Ojea and José M. Quintela $\begin{array}{c} Tetrahedron: Asymmetry 13 (2002) 1535 \\ \hline \\ (\alpha]_{D}^{24} = +77.1 \ (c \ 1.9, \ CH_2Cl_2) \\ Source of chirality: asymmetric aldol reaction \\ Absolute configuration: 2R,3R,4S,5R \end{array}$

Ethyl 3-benzyloxy-4,5-isopropylidenedioxy-2-[N-methyl-N-(diphenylmethyl)amino]hexanoate

María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{20} = -2i$ Source of Absolute $C_{15}H_{19}NO_{6}$ 3-[N-(Benzyloxycarbonyl)amino]-5-(1-hydroxyethyl)-4-methoxytetrahydrofuran-2-one

Tetrahedron: Asymmetry 13 (2002) 1535

 $[\alpha]_{D}^{20} = -28.2$ (c 1.7, CH₂Cl₂) Source of chirality: asymmetric aldol reaction Absolute configuration: $3R_{4}R_{5}S_{7}I'R$



María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{21} = +4.3 \ (c \ 1.4, \ CH_2Cl_2) \\ Source of chirality: asymmetric aldol reaction \\ Absolute configuration: 3S,4R,5S,1'R \\ \hline H_{23}NO_6 \\ 4-Benzyloxy-3-[N-(benzyloxycarbonyl)amino]-5-(1-hydroxyethyl)tetrahydrofuran-2-one \\ \end{bmatrix}$

María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{24} = -23.6 \ (c \ 1.0, \ CH_2Cl_2) \\ Source of chirality: asymmetric aldol reaction \\ Absolute configuration: 3R,4R,5S,1'R \\ \end{bmatrix}$

4-Benzyloxy-3-[N-(benzyloxycarbonyl)amino]-5-(1-hydroxyethyl)tetrahydrofuran-2-one









 $\label{eq:2.1} 4-Benzyloxy-5-[1-(isopropyldimethylsilanyloxy)ethyl)]-3-[N-methyl-N-(diphenylmethyl)amino]tetrahydrofuran-2-one (Marcon Marcon Marco$









2-N-[(Benzyloxycarbonyl)amino]-2,6-dideoxy-5-O-(isopropyldimethylsilyl)-3-O-methyl-D-galactofuranose

María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{20} = -54.1 \ (c \ 2.5, \ CH_2Cl_2) \\ Source of chirality: asymmetric aldol reaction \\ Absolute configuration: 2R,3R,4R,5R \\ \hline C_{26}H_{37}NO_6Si \\ 3-O-Benzyl-2-N-(benzyloxycarbonyl)amino-2,6-dideoxy-5-O-(isopropyldimethylsilyl)-D-galactofuranose \\ \end{bmatrix}$



María Ruiz,* Vicente Ojea and José M. Quintela Tetrahedron: Asymmetry 13 (2002) 1535 $[\alpha]_{D}^{22} = +92.1 (final, c 0.6, H_2O)$ Source of chirality: asymmetric aldol reaction Absolute configuration: 2R,3R,4R,5R C₇H₁₆ClNO₄ 2-Amino-2,6-dideoxy-3-*O*-methyl-D-galactose hydrochloride

María Ruiz,* Vicente Ojea and José M. Quintela $\begin{bmatrix} \alpha \end{bmatrix}_{D}^{23} = +76.1 \text{ (final, } c \ 0.6, \ H_2O) \\ \text{Source of chirality: asymmetric aldol reaction} \\ \text{Absolute configuration: } 2R, 3R, 4R, 5R \\ \text{C}_6 \text{H}_{14}\text{CINO}_4 \end{bmatrix}$

D-Fucosamine hydrochloride



Adelina Vallribera

 $[\alpha]_{D} = +116.4$ (*c* 0.55, dichloromethane) Source of chirality: (*R*)-2-(1-adamantyl)-2aminoethanol Absolute configuration: *R*,*R*

 $\label{eq:c29} C_{29}H_{44}N_2O_2Cl_2 \\ \textit{N,N'-Bis}[(1R)-(1-adamantyl)-2-chloroethyl]-2,3-dimethyl-1,3-propanodiamide$

Jaume Clariana, Josep Comelles, Marcial Moreno-Mañas* and Adelina Vallribera

OH H Me Me H OH

Tetrahedron: Asymmetry 13 (2002) 1551

 $[\alpha]_{D} = -36$ (*c* 0.55, dichloromethane) Source of chirality: (*R*)-2-(1-adamantyl)-2-aminoethanol Absolute configuration: *R*,*R*







Stephen G. Davies,* Simon W. Epstein, A. Christopher Garner, Osamu Ichihara and Andrew D. Smith $\begin{array}{c} \hline Tetrahedron: Asymmetry 13 (2002) 1555 \\ \hline D.e. >98\% (^{1}H NMR analysis) \\ [\alpha]_{D}^{22} = -48.7 (c \ 1.0, CHCl_{3}) \\ Source of chirality: \alpha-methylbenzylamine and asymmetric synthesis \\ Absolute configuration: (4E,2R,3R,\alpha R) \\ \hline (4E,2R,3R,\alpha R)-2-Hydroxy-3-(N-benzyl-N-\alpha-methylbenzylamino)hex-4-enol \\ \end{array}$







Stephen G. Davies,* Simon W. Epstein, A. Christopher Garner, Osamu Ichihara and Andrew D. Smith $\begin{array}{c} \hline \\ Ph \\ \downarrow \\ \downarrow \\ C \\ R^{H_{21}}NO \\ (2R, \alpha R)-2-(N-Benzyl-N-\alpha-methylbenzylamino)propanal \end{array}$



 $C_{23}H_{23}NO$ (2*R*, α *R*)-2-Phenyl-2-(*N*-benzyl-*N*- α -methylbenzylamino)ethanal

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N,N'-Di[(1S)-2-hydroxy-1-phenylethyl]-1,3-benzenedisulfonamide





